4th AIR QUALITY MANAGEMENT

AQM 2012

at Urban, Regional and Global Scales

# PROCEEDINGS

**Air Quality Management at Urban, Regional and Global Scales**
**4th International Symposium**
**&**
**IUAPPA Regional Conference**

**10 – 13 September 2012**
**Istanbul Technical University, Istanbul – Turkey**

**organized by**

**Istanbul Technical University - ITU**
**Turkish National Committee for Air Pollution and Control – TUNCAP**

**Editors**
**Selahattin İNCECİK**
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## Aerosols (AER)

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**AER2.1.20. Sanja Potgieter-Vermaak, Andrew Brown, Judith Barrett, Rene Van Grieken**
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**AER4.1.37. H.-G. Mücke, S. Wagener, K.-C. Bergmann**
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**AER4.1.39. Mirjana Čačković, Krešimir Šega, Vladimira Vađic, Ivan Bešlić**
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**AER4.1.40. Gulten Gunes, Arslan Saral, Hakan Celikten, S.Levent Kuzu, Selami Demir, Nihan Uygur**
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**AER4.1.43. Deniz Derya Genç Tokgöz, Gürdal Tuncel, Güray Doğan**
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**AER4.1.44. Ilker Balcılar, Abdullah Zararsız, Yakup Kalaycı, Güray Dogan, Gürdal Tuncel**
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**AER4.1.45. P. Avino, M. Manigrasso, C. Fanizza, G. Capannesi, A. Rosada, G. Buonanno, L. Stabile, M.V. Russo**
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**AER4.1.46. Melik Kara, Yetkin Dumanoğlu, Hasan Altiok, Tolga Elbir, Mustafa Odabaşi, Abdurrahman Bayram**
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**APE3.1.2. Ö. Parlar, N. E. Machin, A. Ersöz**
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**APE3.1.3. Betül Özer, Erdem Gorgun, Selahattin İncecik**
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**APM2.1.2. Turenjai Doolgindachbaporn , Rungson Raksa, Natthida Binsomprasong, and Pairin Kok- oun**
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**APM2.1.3. Sef van den Elshout, Karine Léger, Hermann Heich**
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**APM2.1.4. Mi Sook Lee, Hyo Choi**
**Double compressions of atmospheric layer by geopontial tendency and vorticity and atmospheric boundary layer influenced upon abrupt high ($PM_1$, $PM_{2.5}$ and $PM_{10}$) concentrations at a mountainous coastal city during a yellow dust period in October**

**APM2.1.5. Fulya Evirgen, Alper Unal, Tayfun Kındap, Luca Pozolli, Ziya Bahçivan, Gökhan İnalhan, Nizamettin Mangır**
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**APM2.1.6. Roberto San José, Juan Luis Pérez, Marisol Callen, José Manuel López, Ana Mastral**
**BaP simulations including gas/particle partitioning and degradation into the WRF-CMAQ system**

**APM2.1.7. Alan W. Gertler, Danny Moshe, Yinon Rudich**
**Urban PM Source Apportionment Mapping using Microscopic Chemical Imaging**

**APM2.1.8. Le Hoang Nghiem, Do Thuy Van**
**A Model Based Study of Impact of Climate Change on Ground-Level Ozone Concentrations in Ho Chi Minh City, Viet Nam**

**APM2.1.9. Young Sunwoo, Young-Il Ma, Suhyang Kim, Areum Kim, Byung-Geun Kang, Ki-Ho Hong, Woo-Keun Lee**
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**APM2.1.10. Soo Min Choi, Hyo Choi**
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**Ambient air quality of Lahore City**

**APM3.1.13. Zuber Farooqui, Kuruvilla John**
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**APM3.1.14. V. Lemaire, I. Coll; F. Couvidat; C. Seigneur ; B. Bessagnet**
**Modelling viewpoint on oligomerization**

**APM3.1.15. Saikat Ghosh, Jhumoor Biswas, Sarath Guttikunda, Kevin Crist, S. Roychowdhury, Mugdha Nayak**
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**APM3.1.16. Hyo Choi, Mi Sook Lee**
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**APM3.1.18. Saeed Samadianfard, Habib Sayyadi, Reza Deleare-hasannia, Elena Agirre-Basurko**
**Forecasting hourly ozone levels using gene expression programming and multi-layer perceptron models in Bilbao, Spain**

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**Assessment of climatological potential of transboundary air pollution transport in Eastern Siberia and the Russian Far East**

**APM3.1.20. K.Onur Demirarslan, Şenay Çetin Doğruparmak, Aykan Karademir, Ertan Durmuşoğlu**
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**APM3.2.21. Elisa Sá, Helena Martins, Anabela Carvalho, Ana Isabel Miranda, Carlos Borrego**
**WRF-CAMx application over an urban area: parameterizations sensitivy study for air quality purposes**

**APM3.2.22. Saeed Samadianfard, Reza Deleare-hasannia, Gholamreza Rowshan**
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**APM3.2.24. Adriana Coman, Benjamin Gaubert, Gilles Foret, Matthias Beekmann, Maxim Eremenko, Gaëlle Dufour, Anthony Ung, Gilles Bergametti, Jean-Marie Flaud**
**Analysis of European ozone distribution using a joint assimilation system using ground and satellite measurements with a Regional CTM**

**APM3.2.25. Hakki Baltaci, Tayfun Kindap, Alper Unal, Seden Baltacibasi, Luca Pozzoli,Selahattin Incecik, Mehmet Karaca**
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## Air Quality Management (AQM)

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**AQM1.2.3. G L Suma Lata, D.Prasad, N Karuna**
**Urbanisation and air pollution: a case study of Hyderabad, India**

**AQM1.2.4. Devis Panont, Claudia Tarricone**
**Environmental assessment of a steel industry through chemical characterization of PM10 and bulk deposition in the urban area of Aosta (Italy)**

**AQM1.2.5. Sef van den Elshout, Rinkje Molenaar and Bart Wester**
**Adaptive traffic management in cities – comparing decision making methods**

**AQM 1.2.6. Alfred Lawrence, Nishat Fatima**
**Urban Air pollution and its assessment of Lucknow City- the Second Largest City of North India**

**AQM1.2.7. Claire C. Austin**
**Merging air pollution datasets: Pitfalls and opportunities**

**AQM1.2.8. Ivan Bešlić, Krešimir Šega, Ranka Godec, Silvije Davila**
**Comparison of equivalence tests for PM samplers**

**AQM1.2.9. Sarath Guttikunda, Kalpana Balakrishnan, Giuseppe Calori**
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**AQM1.2.10. Sule Kusdogan, Mine Sertsöz, Önder Altuntas**
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**EFCA2.2.2. J. Hjorth, F. Cavalli, E. Cuccia, P. Kalabokas, S. Nava, P. Prati, C. Schembari, K. Velchev, F. Raes, F. Dentener**
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**EFCA2.2.3. Alper Ünal, Burcu Kabataş, R. Brad Pierce, Tayfun Kındap**
**Quantification of Saharan Dust on Northwestern Anatolian Peninsula via RAQMS Modeling**

**EFCA2.2.4. Ana Alebic-Juretic**
**Air pollution in the Northern Adriatic coastal area- evidence of long-range transport**

**EFCA2.2.5. Nicola Pirrone**
**Regional and global scale transport patterns of persistent atmospheric pollutants: the need for a global observation system**

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**EMS4.1.2. Kadir Alp, Ümmügülsüm Alyüz**
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**Defining Socially Optimal Emission Standards for Thermal Power Plants in Chile**

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**EMS4.1.5. Ali Can, Aysel T. Atımtay**
**Spatial Distribution of $CO_2$ Emissions in Turkey on District and Province Basis**

**EMS4.1.6. Baptiste Perrissin Fabert, Etienne Espagne, Antonin Pottier**
**The “doomsday" effect How the window of opportunity for political action on emission reductions is closing**

**EMS4.1.7. Deniz Sarı, Abdurrahman Bayram**
**Inventory of air pollutant emissions from domestic heating in residential areas of İzmir**

**EMS4.1.8. Richa Bhattarai, Atindra Sapkota, Sandeep Shrestha, Ramesh Kumar Maskey**
**Comparative study of briquettes made from different raw materials on the basis of emission**

**EMS4.1.9. U. Im, M. Kanakidou**
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**Combining environment and health information systems for an integrated assessment on human health**

**HEF2.1.2. Jorge E. Pachon, Ted Russell, Jim Mulholland**
**Human Health Benefits of Emission Controls using Single and Multipollutant Indicators of Mobile Sources**

**HEF2.1.3. Sirajuddin M. Horaginamani, M. Ravichandran**
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**HEF2.1.4. Mihriban Yılmaz Civan, Tolga Elbir, Remzi Seyfioğlu, Öznur Oğuz Kuntasal, Abdurrahman Bayram, Güray Doğan, Sema Yurdakul, Özgün Andiç, Aysen Müezzinoğlu, Sait Sofuoğlu, Hakan Pekey, Beyhan Pekey, Ayşe Bozlaker, Mustafa Odabaşi, Gürdal Tuncel**
**Spatial Distribution of VOC Concentrations and Cancer Risk Around an Industrial Region at Western Turkey**

## Impacts of Forest and Vegetation (IFV)

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**IFV4.1.2. Doğan Kantarcı, Burcu Onat, Ülkü Alver Şahin, Serdar Aydın**
**The Effects of the Hamitabat-Lüleburgaz Power Plant NOx Emissions**

**IFV4.1.3. Chedlia Ben Ahmed, Imene Sellami, Mohamed Zouari, Ferjani Ben Abdallah**
**Responses of adult olive tree to air fluoride pollution under aride climate in the south of Tunisia: Leaf antioxidant defense system and oil quality characteristics**

**IFV4.1.4. Güray Doğan, Claire C. Austin**
**Determination of sources of particulate matter in a forestry based industry city in Canada**

**IFV4.1.5. Nesrine Rhimi, Mouhiba Nasri Ayachi, Ben Ahmed Chedlia, Ferjani BenAbdallah**
**Morphological and anatomical responses of pear and almond trees exposed to air fluoride pollution**

**IFV4.1.6. Sellami Imène, Ben Ahmed Chedlia, Ben Abdallah Ferjani**
**Effects of air pollution on fluoride accumulation pattern in *Rosa damascena* L. cultivated in the south of Tunisia**

**IFV4.1.7. En-Jang Sun, W. J. Swei, Che-Ming Chang**
**Measuring the Uptake Rates of Ethylene by 23 Plant Species in Taiwan**

**IFV4.1.8. Mohamed Zouari, Chedlia Ben Ahmed, Bechir Ben Rouina, Chiraz Jomni, Nacim Zouari, Ferjani Ben Abdullah**
**Responses of young olive tree (*Olea europaea* L. cv Chemlali) to different soil NaF levels under natural environmental conditions in the south of Tunisia**

## Indoor Air Quality (IAQ)

**IAQ2.1.1. Sanaz Lakestani, Söngül Acar Vaizoğlu, Bahar Güçiz Doğan, Çağatay Güler, Bülent Şekerel, Abbas Taner, Gülen Güllü**
**Investigation of indoor air quality in children homes at prenatal and postnatal period**

**IAQ2.1.2. Omnya A. El-Batrawy**
**Indoor Air Quality and Sick Building Syndrome**

**IAQ2.1.3. Elham Aghlarai, Sanaz Lakestani Söngül Acar Vaizoğlu, Bahar Güçiz Doğan, Çağatay Güler, Bülent Şekerel, Abbas Taner, Gülen Güllü**
**Levels of bioaerosols in indoor environments in Ankara**

**IAQ2.1.4. Bilge Karakaş, Çağatay Güler, Bahar Güçiz Doğan, Songül Acar Vaizoğlu, Abbas Taner, Bülent Enis Şekerel, Gülen Güllü**
**Indoor and outdoor concentrations of particulate matter at domectic homes**

**IAQ3.1.5. R. H. M. Godoi, Ana F. L.Godoi, M. G. Arantes, S.J. Gonçalves Junior, S. L. Paralovo, G. Borillo, R. C. Charello, D. Banhuk, N. A. Rosário Filho, M. T. Grassi, Carlos I. Yamamoto, S. Potgieter-Vermaak,G. G. Rotondo, K. De Wael, R. van Grieke**
**Healthy environment – indoor air quality of Brazilian elementary schools nearby Petrochemical Industry**

**IAQ3.1.6. Md. Hamidur Rahman and A.K.M. Sadrul Islam**
**$CO_2$ emissions from urban residential kitchen of Bangladesh- a CFD study**

**IAQ3.1.7. Sanja Potgieter-Vermaak, Anna Buczynska, Rene Van Grieken**
**Indoor Air Quality during high pollution event days in Antwerp**

**IAQ3.1.8. Dilşad Akal, Mihriban Yılmaz Civan, Sema Yurdakul, Hülya Yavuz Ersan**
**Determination and evaluation of air pollutants in indoor air at chemical engineering department of Hacettepe University**

**IAQ3.1.9. Simge Taner, Beyhan Pekey, Hakan Pekey, Demet Arslanbaş**
**Determination of Particulate Matter Concentrations in Different Microenvironments**

**IAQ3.1.10. Sushil kumar Aggarwal[*], Alfred Lawrence, Nishat Fatima, Shalima Gupta, Rajkumar**
**Ill-Effects of Indoor Air Pollution on Health of Lucknow Population**

**IAQ3.1.11. Sema Yurdakul, Gül Ayaklı, Mihriban Civan, Güray Doğan, Gürdal Tuncel**
**Vertical and Temporal Variation of the Indoor Air Quality of the Working Offices in METU in Terms of Volatile Organic Compounds**

**IAQ3.1.12. Jamson Masih, Alfred J. Lawrence, Ajay Taneja**
**Indoor/outdoor concentrations of Polycyclic Aromatic Hydrocarbons and Particulate Matter, seasonal variation in a semi arid region of rural India**

**IAQ3.1.13. Ecem Demirel, Cihan Paloluoğlu, Hanefi Bayraktar, F. Sezer Turalioğlu**
**Wet deposition of polycyclic aromatic hydrocarbons (PAHs) in Erzurum city atmosphere**

## Poster Session (POS)

**POS3.2.1. Ho-yong Shin, Shin-Do Kim, Sung-Joon Bae, In Yeong Jeong**
**A Study on the Seasonal Variation of Carbon Component in the Subway Particulate Matter(PM)**

**POS3.2.2. Füsun Uysal, Asude Hanedar**
**The Application of ISO 14064 in Turkey**

**POS3.2.3. Do Yeon Hwang, Shin Do Kim, Jai-Young Lee, Heekwan Lee, Dong Sul Kim**
**A Study on the components of Inorganic elements in the Subway's Particulate Matters**

**POS3.2.4. Eun Hee Jang, Shin Do Kim, Heekwan Lee, Gong-Unn Kang, In Yeong Jeong**
**A Study on the Ionic Components in the Subway's Particulate Matter**

**POS3.2.5. Jong-Ho Kim, Hyeok-Gyu Kim, Sang-Hyun Pang, Sung-Won Lee**
**Removal of od Particulate Matter in a Wet Scrubber using Electrospray**

**POS3.2.6. Jin-Sik Kim, Shin-Do Kim**
**An Energy Usage Analysis of the GHG Emission bySource Inventory Data in Seoul**

**POS3.2.7. Kyoung Bin Lee, Shin Do Kim, Heekwan Lee, Sung-Joon Bae, In Yeong Jeong, Jung Geun Han**
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**POS3.2.35. Fatma Yazıcı, Selahattin İncecik, Tayfun Kındap, Berna Ataksor, Nesli Albayrak, Ayhan Akkaş, Volkan Simsek**
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**POS3.2.37. Yilmaz Acar, Serpil Yağan, Mithat Ekici**
**The vertical distribution of ozone over Ankara for 2007-2011 period according to Brewer Spectrophotometer data**

**POS3.2.38. Gül Ayaklı, Gürdal Tuncel, Ali İhsan İlhan, Tülay Balta, Fatma Öztürk**

## Chemical composition of precipitation at different parts of Turkey

# SMOKE EMISSIONS FROM PRESCRIBED BURNING IN THE LAKE TAHOE BASIN

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## ABSTRACT

We characterized particulate emissions from different types of biomass burning, including prescribed fires which is an important tool to manage fuel loads in forests. Samples were analyzed for organic and elemental carbon (OC and EC); polar organic compounds; soluble potassium ($K^+$); and particle-bound mercury (PHg). OC/EC showed highest ratios during combustion of green tissues (including foliage and surface duff), which we attribute to stronger smoldering-phase combustion phases of high-moisture fuels. Of the polar organic compounds, levoglucosan, mannsan and resin acids dominated across all combustion types, but comparatively higher levels of inositols and arabitol were found when burning green manzanita leaves. A combination of PHg/TC and $K^+$/TC ratios can be utilized to differentiate between emissions from various burn types.

**Key Words:** Biomass Burning, Organic and Elemental Carbon, Polar Organic Compounds, Water-Soluble Potassium, Particle-bound Mercury

## 1. INTRODUCTION

Biomass burning contributes more than one third of primary $PM_{2.5}$ loads (i.e., particulate matter [PM] with an aerodynamic diameter less than 2.5 µm; Chen et al., 2007) in the US. PM pollution leads to reductions in atmospheric visibility (Watson, 2002), can cause acute health effects (Huttunen et al., 2012), and affect environmental quality such as water clarity (Dolislager et al., 2012). The relative importance of PM emissions from various biomass combustion types, such as from wildfires, prescribed fires, or residential wood combustion, is poorly quantified. In this study, we analyzed $PM_{2.5}$ emission patterns from various prescribed burning activities in the watershed of Lake Tahoe, a remote alpine lake known for its unique water clarify. Specifically, we collected biomass burning emission from: landscape ‘underburns’ in the field consisting of wooden tissues, foliage and branches, and surface duff; ‘pile’ burns in the field mainly consisting of wooden tissues; ‘mixed underburn/pile’ burns consisting of a mix of the two types above; controlled combustion of biomass collected from Lake Tahoe basin in a wood stove, including wooden logs, green foliage, and surface duff; and ambient air from residential neighborhoods in the basin during winter when domestic wood combustion is abundant. To characterize chemical composition of $PM_{2.5}$ emissions, we measured the following chemical constituents: Organic Carbon (OC) and Elemental Carbon (EC); water-soluble $K^+$, a common tracer for biomass burning emissions; a suite of 12 different polar organic compounds considered characteristic for different types of biomass burning (Burshtein et al., 2011; Mazzoleni et al., 2007; Medeiros and Simoneit, 2008); and particulate-bound mercury, a compound that may be used to differentiate various fuel sources because of inherently different Hg levels of different tissues (Obrist et al., 2011).

# 2. RESULTS AND DISCUSSION

## 2.1. OC/EC ratios

OC/EC ratios for samples are shown in Table 1. Of field burning emissions, OC/EC showed higher ratios in green foliage combustion both in field and under controlled conditions in the wood stove, as compared to combustion consisting of wooden types (i.e,. pile burns, and logs). Highest OC/EC ratios of all samples were observed in ambient air in winter 2010 and winter 2011. OC/EC ratios are often attributed to different fire intensity: in general, higher temperature of flaming phase burnings have been shown to lead to produce more soot (EC), and hence lower OC/EC ratios than smoldering fires (Posfai et al., 2003). Our study supports a role of fire intensity for OC/EC emission patterns as evident by generally lower OC/EC ratios when burning wooden biomass types (both in the field and in the controlled stove combustion) compared to combustion of mixed fuel types (e.g., field underburns) or controlled stove combustion of green leaves and branches. Our observations also generally indicate higher OC/EC rations during emissions from prescribed fires compared to controlled stove combustion; this likely reflects low combustion intensities during prescribed burning in the field which are only conducted when fuels are relatively moist to prevent uncontrolled spread of fires.

OC/EC ratios of ambient air were much higher than ratios observed in any biomass combustion, and were also higher than levels observed in other areas (e.g., IMPROVE sites; Zeng and Wang, 2011). It is not clear what caused these high ambient-air OC/EC ratios as sources in the basin are expected to show lower ratios as well (e.g., mobile sources and stationary sources such as gas cooking). It is possible that absorption of gas-phase volatile organic species onto the quartz fiber filter during sampling contributed to these high OC/EC ratios in ambient air samples.

### 2.2. Select polar organic compounds typical for biomass combustion

In our study, 12 polar organic compounds specific to biomass burning were selected and the sum of concentrations of these polar organics was standardized to TC (Table 1). Generally, polar organics were emitted at higher levels in filed burns than in stove burns. The organic’s level in 2010 ambient air samples was much higher than that in 2011. We attribute the higher levels in 2010 to the presence of more visitors (samples were taken between Christmas and New Year Eve) and strong influence of domestic wood combustion during this cold, snowy wintertime period. In winter 2010 samples were taken before the Christmas holidays and few tourists were present due to lack of snow and presence of very warm, sunny conditions.

Polar organics were divided into four groups (i.e. anhydrosugars, monosaccharides, resin acids, and lignin derivatives) and the fractional abundance of each group in all samples is shown in Figure 1. Emissions in all types of burning were dominated by anhydrosugars (i.e. levoglucosan and mannosan) and resin acids, followed by monosaccharides (i.e. inositols and arabitol) and lignin derivatives (i.e. 4-hydroxybenzoic acid, pyrogallol, and shikimic acid). Higher contributions of levoglucosan were observed in prescribed field burns as compared to controlled stove burning, but no clear differences were observed between different fuel types. Further, much higher levels of levoglucosan were present in ambient air in 2010 than 2011, probably due to the higher amounts of residential wood combustion activity. Inositiols and arabitol showed the highest levels in stove burns of greenleaf manzanita, a common evergreen understory shrub in the Lake Tahoe Basin. However, these two compounds were not prominent in field underburns where manzanita was also present, which we attribute to the low mass of manzanita leaves compared to other fuel material during prescribed burning in the field.

In our study, resin acids are reported as the sum of pimaric acid, abietic acid, and dehydroabietic acid. For the total resin acids, both field burns and stove burns of wooden logs showed higher levels than burns of leaves or duff (Table 1); this finding is consistent with Iimuna et al.'s (2007) conclusion that pine and pine with green needles had higher percentage of resin acids in relation to TC than savanna grass. Finally, stove combustion of leaves and duff had higher average lignin levels compared to wooden tissues, but the uncertainty is large (Table 1). Lignin derivatives such as 4-hydroxybenzoic acid, pyrogallol, and shikimic acid are generally present both in green and dry vegetation (Medeiros and Simoneit, 2008).

## 2.3. Soluble potassium ($K^+$)

In our study, the percentage of soluble $K^+$ in TC in biomass burning emission was in a quite narrow range. Only one emission source of biomass burning, field underburns, had lower $K^+$ levels compared to the other groups.

Percentage of $K^+$ in TC in ambient air samples were in the similar range as most biomass burning emissions. These high levels $K^+$ in ambient air are surprising as we consider ambient air, particularly in 2011, only minimally influenced by biomass emission sources. However, it is possible that ambient air is influenced by other sources of soluble $K^+$ such as meat cooking or soil dust

## 2.4. Particulate-bound Hg (PHg)

PHg/TC ratios of field burns and stove burns greatly overlapped. Unexpectedly, lower PHg/TC emission ratios were observed in underburns in the field compared to pile burns and mixed pile/underburns; similarly, lower PHg/TC ratios were observed for leaves and duff combusted in the wood stove as compared to wooden logs. This was surprising as green foliage and branches normally show much higher mercury levels compared to woody tissues (Obrist et al., 2011).

We observed much higher PHg/TC ratios in ambient air as compared to levels observed in biomass smoke. The main reason for this is likely that ambient air has much lower C content (for example, averaging around 18% and 22% in January and December based on IMPROVE network data from Sierra Nevada; Hand et al., 2011) as compared to biomass smoke where we expect that most aerosols are composed of carbonaceous material (> 60% of PM mass; Chen et al., 2007).

## 2.5. Combined tracers to differentiate different types of biomass burning

In this study, PHg/TC and $K^+$/TC ratios were used as tracers to differentiate biomass burning groups. Four clusters can be differentiated as shown in Figure 2. Using PHg/TC ratios, ambient air during winter with highest PHg/TC ratios was separated from other groups, while stove burning of green foliage with lowest Hg ratios was separated from other emissions well. Similarly, using $K^+$/TC ratios, prescribed underburns were separated from other groups by their lowest $K^+$ emission level.

The differentiation of biomass buring types by these tracers, however, has some limitations. Fist, the specific types of samples (i.e. ambient air during wood combustion season, prescribed burning and controlled stove burning) are regionally characteristic, and the results of this study hence may only apply to major biomass burning sources from the Lake Tahoe Basin. Second, our study is limited in number of samples, and several burn types (pile burns, mixed pile/underburns and stove burns of logs) were not separated due to a large overlap.

## 3. CONCLUSIONS

OC/EC showed higher ratios in combustion of green foliage and surface duff, indicating that potentially high fuel moisture in these samples led to combustion dominated by smoldering phase both in prescribed fires in the field and in controlled burning in a wood stove. Anhydrosugars (levoglucosan/mannosan) and resin acids were dominated among all biomass burning groups and in ambient air. Levoglucosan showed higher level in prescribed field burnings than controlled stove burning, while resin acids had higher percentage in wooden logs than green foliage. A high percent of inositols and arabitol was observed only in stove combustion of green manzanita leaves. A large variation in abundance of molecular markers for biomass combustion was present in field and controlled burns which is due to the complex nature of combustion chemistry (Zielinska and Samburova, 2011). Finally, the combination of various tracers, for example PHg/TC and $K^+$/TC ratios, might be utilized to differentiate emissions from different biomass burning sources. However, several burn types cannot be separated based on these tracers, and this application may be specific to the observed fuel types and combustion characteristics in the Lake Tahoe Basin.

## 4. ACKNOWLEDGEMENTS

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## Figures

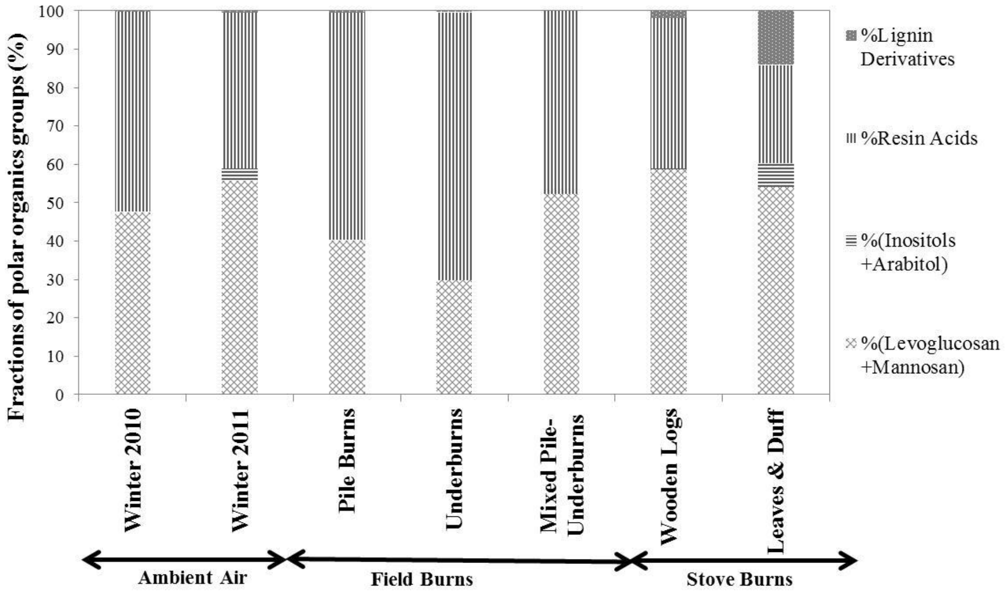

**Figure 1.** Fraction of each polar organic group.

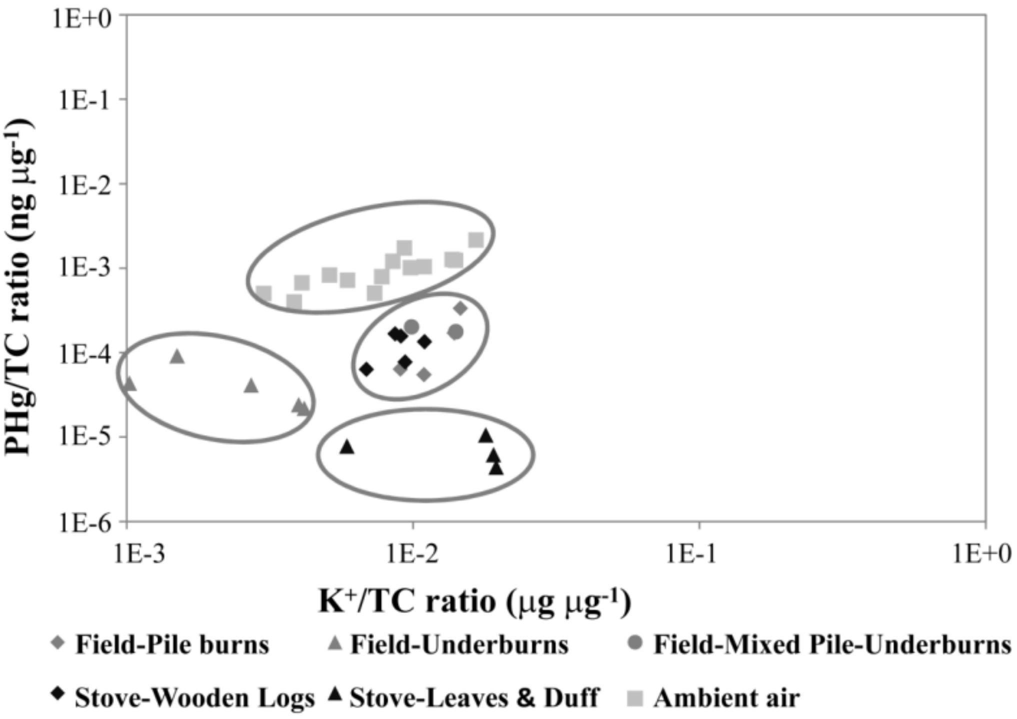

**Figure 2.** PHg/TC and $K^+$/TC ratios as combined tracers.

## Tables

Table 1. Concentrations of organic carbon, elemental carbon, water-soluble potassium, 12 polar organics and particle-bound Hg; mean ± standard errors.

| **Component** | **Units** | **Ambient air** | | **Field burns** | | | **Stove burns** | | **Data from various references** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 2010 | 2011 | Pile burns | Underburns | Mixed pile/underburns | Logs | Leaves/ duff | Ambient air | Prescribed burning | Fireplace /woodstove | Cooking |
| **Organic carbon** | mg m$^{-3}$ | 0.02±0.00 | 0.02±0.00 | 0.51±0.14 | 4.78±0.86 | 0.87±0.30 | 17.73±10.87 | 37.95±5.08 | | | | |
| **Elemental carbon** | mg m$^{-3}$ | <0.001 | <0.001 | 0.04±0.01 | 0.28±0.09 | 0.07±0.00 | 4.07±2.72 | 4.57±1.72 | | | | |
| **OC/EC** | mg mg$^{-1}$ | 26.2±10.4 | 38.4±12.0 | 13.0±0.6 | 26.2±7.1 | 12.2±4.0 | 2.8±1.3 | 12.1±3.3 | 24.0 | 15.4,25.8, 88,28.8,21 | 26.1,42,7.5,3.1,7.3,119. | 23.9 |
| **K$^+$/TC** | % | 0.8±0.1 | 0.9±0.2 | 1.2±0.1 | 0.3±0.1 | 1.2±0.2 | 0.9±0.1 | 1.6±0.3 | | 1.0,0.4 | 0.9,1.1,0.3,0.7,0.2 | 3.10 |
| **PHg/TC** | ng g$^{-1}$ | 932±75 | 1059±229 | 156±65 | 37±13 | 189±12 | 120±21 | 7±1 | | | | |
| **Anhydrosugars /TC** | % | 4.59±0.47 | 0.69±0.27 | 12.00±2.03 | 8.93±2.21 | 10.12±1.76 | 3.62±1.17 | 2.77±0.31 | | | | |
| Levoglucosan/TC | % | 4.34±0.43 | 0.67±0.26 | 7.79±2.57 | 8.05±2.16 | 9.68±1.57 | 2.51±0.96 | 2.03±0.34 | | 8.9,7.4,6.3<br>7.8 | 12.2,4.1<br>3.2,15.7 | |
| Mannosan/TC | % | 0.25±0.09 | 0.02±0.01 | 4.21±0.59 | 0.89±0.17 | 0.43±0.19 | 1.12±0.37 | 0.74±0.21 | | 0.45 | 0.57 | |
| **Sugar Alcohols/TC** | % | 0.03±0.02 | <0.001 | 0.05±0.02 | 0.02±0.01 | 0.01±0.00 | 0.01±0.00 | 0.25±0.11 | | | | |
| Inositols (allo, myo, scyllo) /TC | % | 0.02±0.02 | <0.001 | 0.01±0.00 | <0.01 | <0.01 | <0.01 | 0.19±0.10 | 0.023 | 0.012 | | |
| Arabitol/TC | % | <0.01 | <0.0001 | 0.04±0.02 | 0.02±0.01 | 0.01±0.01 | 0.01±0.00 | 0.07±0.02 | 1.18 | 0.05, 0.13 | 0.21 | |
| **Resin acids/TC** | % | 10.42±4.67 | 0.55±0.15 | 30.40±11.63 | 26.87±11.31 | 9.21±1.41 | 5.25±4.00 | 1.82±1.11 | | | | |
| Dehydroabietic acid/TC | % | 10.38±4.66 | 0.54±0.15 | 28.15±10.62 | 25.44±10.81 | 9.11±1.33 | 4.90±3.71 | 1.70±1.05 | | 3.1,0.3 | 0.53,3.37 | |
| Pimaric acids/TC | % | ND[a] | <0.01 | 1.12±0.65 | 0.56±0.28 | 0.01±0.01 | 0.04±0.04 | 0.02±0.01 | | 0.23,0.003 | 0.13,0.29 | |
| Abietic acids/TC | % | 0.04±0.03 | 0.01±0.01 | 1.13±0.45 | 0.88±0.24 | 0.09±0.08 | 0.31±0.26 | 0.09±0.05 | | 0.002 | 1.52,0.42 | |
| **Lignin derivatives/TC** | % | 0.02±0.01 | <0.01 | 0.22±0.05 | 0.08±0.02 | 0.01±0.00 | 0.18±0.16 | 0.58±0.23 | | | | |
| 4-hydroxybenzoic acid/TC | % | 0.01±0.01 | <0.01 | 0.03±0.01 | 0.04±0.01 | 0.01±0.00 | 0.03±0.02 | 0.13±0.05 | | 0.057 | | |
| pyrogallol/TC | % | <0.01 | <0.001 | 0.18±0.05 | 0.04±0.02 | <0.001 | 0.15±0.14 | 0.42±0.17 | | | | |
| shikimic acid/TC | % | ND | <0.0001 | <0.01 | <0.001 | <0.0001 | <0.001 | 0.04±0.02 | | | | |
| **Sum of polar organics /TC** | % | 15.06±4.34 | 1.28±0.37 | 42.66±9.97 | 35.90±13.32 | 19.35±3.17 | 9.07±4.36 | 5.42±0.97 | | | | |
| **Ratios** | | | | | | | | | | | | |
| Levoglucosan/K$^+$ | µg µg$^{-1}$ | 6.0±1.2 | 0.8±0.2 | 6.0±1.5 | 51.5±19.0 | 8.6±2.8 | 3.1±1.5 | 1.5±0.3 | 2.00 | 8.8[b],20.6[c] | 17.8,2.9,75.7 | |
| Levoglucosan /mannosan | µg µg$^{-1}$ | 44.7±19.2 | 53.7±19.0 | 2.2±0.9 | 10.8±3.5 | 25.5±7.3 | 9.6±7.0 | 3.5±0.8 | 53.5 | 14.2 | 16.7,5.6,7.8 | |

[a]: ND: below detection limit

# ELEMENTAL COMPONENTS OF ATMOSPHERIC AEROSOLS AT COASTAL AND RURAL AREAS IN TANZANIA.

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## ABSTRACT

While many investigations on atmospheric aerosols have been conducted in Europe, North America, South America and various parts of Asia, only a handful of such studies have been reported for Sub Saharan Africa. Atmospheric aerosols which are associated with atmospheric pollutants, may cause a wide spectrum of effects. Active bulk collection of particulate matter with an aerodynamic diameter > 0.4 µm, from three sampling sites representing coastal, semi-urban and rural areas in Tanzania were investigated during dry and wet seasons of 2005 –2007. The analytical technique for qualitative and quantitative analysis was Epsilon 5 Energy Dispersive X–ray spectrometer using 3D optics. Particulate matter over coastal areas and rural areas showed an enrichment in non-crustal elements. A total of seventeen elements (Si, K, Ca, Ti, Fe, Se, Sr, Cr, Ni, Mn, Cu, Zn, As, Pb, Al, S and Cl) were identified and of these, eight elements (Si, K, Ca, Fe, Zn, Al, S and Cl) had an average concentration higher than 0.5 ugm$^{-3}$. Most of the concentrations were observed to decrease with increasing distance from the coastline. However, the average elemental concentrations were substantially higher in the dry season than in the wet season, by approximately an order of one and a half. Backward air mass trajectories revealed that the transport air corridors to the study area were clearly bounded and defined. The wind usually blew within a range of ENE-E-SSE (ocean to continental) and rarely to S-SSW which is the continental side. Long time mean wind data (30 years < ) indicated an average speed during wet and dry seasons in the range of 3-4 ms$^{-1}$ and 3.5 – 4.25 ms$^{-1}$ respectively. These results contribute to a data set of atmospheric aerosols and/or composition in Sub-Saharan Africa, where information is either scarce or non-existence.

**Keywords:** EDXRF, Sub Saharan Africa

**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# PHOTOCATALYTIC PRODUCTS FOR THE CONSTRUCTION INDUSTRY

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## ABSTRACT

Photocatalytic products have been used for many years in numerous applications. $TiO_2$-based photocatalysts are being used today in air purification devices and as surface treatment additives in ceramics, cement, paints and coatings, construction materials and glass. These products are being utilized for their de-pollution, self-cleaning, anti-fungal attributes. Photocatalytic coatings can be effectively used to combat air quality issues. Many trials have been carried out using photocatalytic products. For the first time, trials have shown quantitatively the de-pollution effect using continuous monitors over extended periods. This allows unambiguous statistical analysis which proves this technology is an effective practical solution to air pollution problems. In this presentation we evaluate the efficiency of two types of photocatalytic products for the removal of hazardous NOx pollution: photocatalytic paints and transparent clear coatings for concrete surfaces.

**Keywords:** Photocatalysis, Titania, Titanium Dioxide, de-pollution, construction materials

## 1. INTRODUCTION

This paper focuses on two different coating trials.
The first trial was performed in the Camden Council area of London, where we tested a transparent photocatalytic $TiO_2$ surface treatment utilizing continuous NOx monitoring.
In the second trial discussed in this paper, we evaluated the reduction of $NO_2$ by photocatalysis using a photocatalytic styrene acrylic coating which has been applied to a train station in central Manila, Philippines.

## 2. CAMDEN BOROUGH TRIAL, LONDON

There are 33 Councils in the city of London. The borough of Camden in the centre of London experiences some of the city's highest air pollution levels within the area declared as an AQMA (Air Quality Management Area).

30 London boroughs are supplying measurements from air monitoring stations to the London Air Quality Network, formed in 1993 to coordinate and improve air pollution monitoring in London.

The Air Quality Standard stipulates two objectives for $NO_2$: an annual mean of $40\mu g/m^3$ and an incident based objective of $200\mu g/m^3$ as an hourly mean not to be exceeded more than 18 times per year.

During 2005 and 2006 the annual mean target was exceeded in all but 2-3 of the boroughs, with the total number of sites measuring an increase in the annual mean concentration being nearly twice the number measuring decreases.

Despite initiatives to control traffic, the Camden area continued to exceed its air quality standards. Photocatalysis was proposed as an innovate means to help achieve the targets for $NO_2$ reduction.

The project had the objective to evaluate the effectiveness of a photocatalytic $TiO_2$ treatment applied to a wall in a sheltered courtyard at St Martin's Art College in Holborn. 135m$^2$ of the target wall inside the courtyard were coated with a transparent $TiO_2$ photocatalytic treatment (CristalACTiV™ PC-S7)

A continuous $NO_x$ analyser was set up in front of the wall. Two NOx sample probes are used, sampling the air at two different distances from the wall (Figure 1)

The reference values for pollution are obtained from other analysers located in proximity of the test area, as well by monitoring the test area prior to the application of the photocatalytic surface treatment.

A weather station is located alongside of the NOx analyzer to understand the influence of temperature, humidity, sunlight and rainfall on the effectiveness of the coating.

Figure 1.

As said, the NOx monitoring station was set up in July 2007, prior to the application of the photocatalytic coating, in order to establish a baseline for NOx at the site.

A transparent surface treatment based on photocatalytic $TiO_2$ was spray-applied on the test wall on March 16, 2009. Data monitoring has been active since that time for more than two years.

The reduction of overall NO on the test site is shown here below (Figure 2). The graph is clearly showing a very significant reduction in NO depending upon the time of day, thanks to the photocatalytic coating.

When the active surface is covered with wooden boards to de-activate the effect of photocatalytic treatment, the pollutant levels return at the initial values recorded before the application of the photocatalytic treatment on the wall.

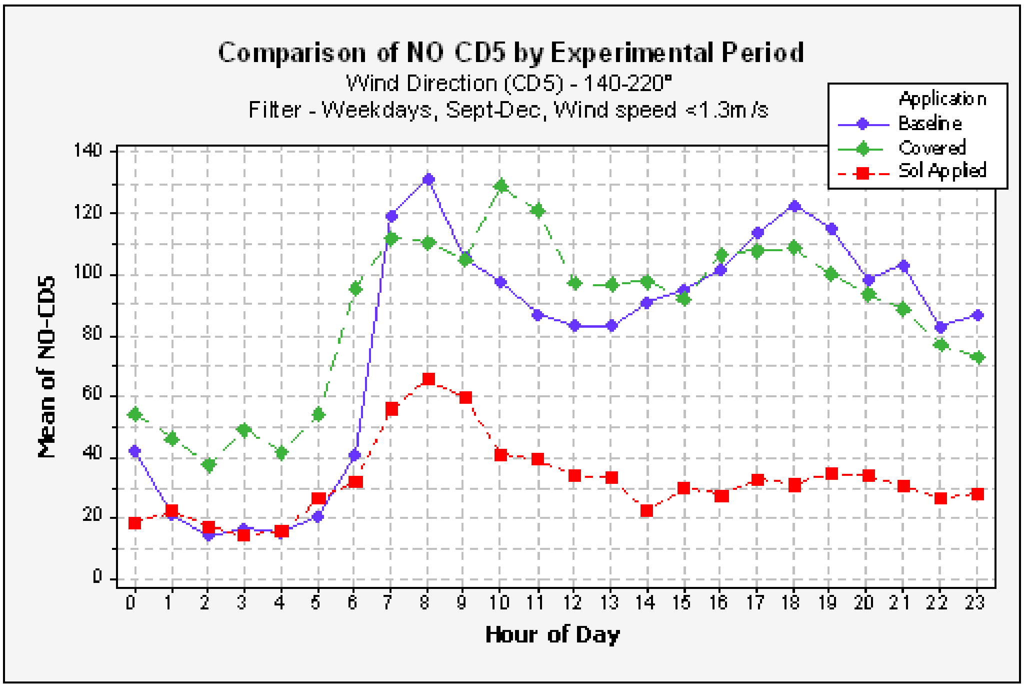

Figure 2.

The trial results, after an extensive analysis of the data collected, showed that the surface treatment used can achieve the following main performance:

- NOx depollution up to 0.5g/m$^2$/day
- 300m$^2$ of a façade coated with CristalACTiV™ material treat the NOx emission of 50 average cars travelling 20Km/day each.

## 3. MRT STATION, MANILA, PHILIPPINES

With the support of local city authorities and of a local paint manufacturer, a large scale trial was set up at the Guadalupe Train Station in Manila.

A parallel monitoring campaign was conducted in which we simultaneously monitored background $NO_2$ while measuring changes in $NO_2$ levels at the target sites.

In addition, nitrate build up was controlled using boxes developed for this trial, in which paint strips are used to determine quantitatively the amount of nitrates build-up, thus the actual $NO_2$ conversion that is taking place

In this evaluation the photocatalytic coating was applied over a surface of 6200sqm, including indoor and outdoor surfaces. The coating used in this evaluation is a styrene acrylic water-based coating containing CristalACTiV™ photocatalytic $TiO_2$.

18 stations consisting of $NO_2$ monitors and nitrate strips were set up. $NO_2$ monitors were placed at each location, boxes containing nitrate strips were put at 4 significant locations. In total, 5 monitors were evaluating baseline $NO_2$, both indoor and outdoor and 13 $NO_2$ monitoring stations were set up at the trial locations, both indoor and outdoor.

Background measurements started in January 2009 and were taken at locations 1, 10, 16, 17 and 18 at positions 250 metres away south and north of Guadalupe station (see picture below, Figure 3)

Figure 3.

It is important to note that $NO_2$ accumulation can be quite different by location, so monitors were set up in a variety of positions, including street level where traffic flow and emissions could be observed.

Other monitors were set up in more sheltered areas where $NO_2$ accumulation was observed and where reduced air movement creates higher levels of $NO_2$.

Inside monitors were set in areas where passenger exposure levels could be evaluated.

Painting took place in March 2009. Monitoring of the sampling stations was done every 5 days between mid-March and mid-June, then it was increased to every 2 days from mid June onwards.

In addition a weather station was placed on the MRT station to measure wind speed, temperature, humidity, barometric pressure, radiation and precipitation.

Traffic monitoring was established to develop information about the impact of traffic on $NO_2$ in the area.

Evaluations are being made on the influence of: surface area treated (type and size); confined and non-confined areas; direct and diffused sunlight.

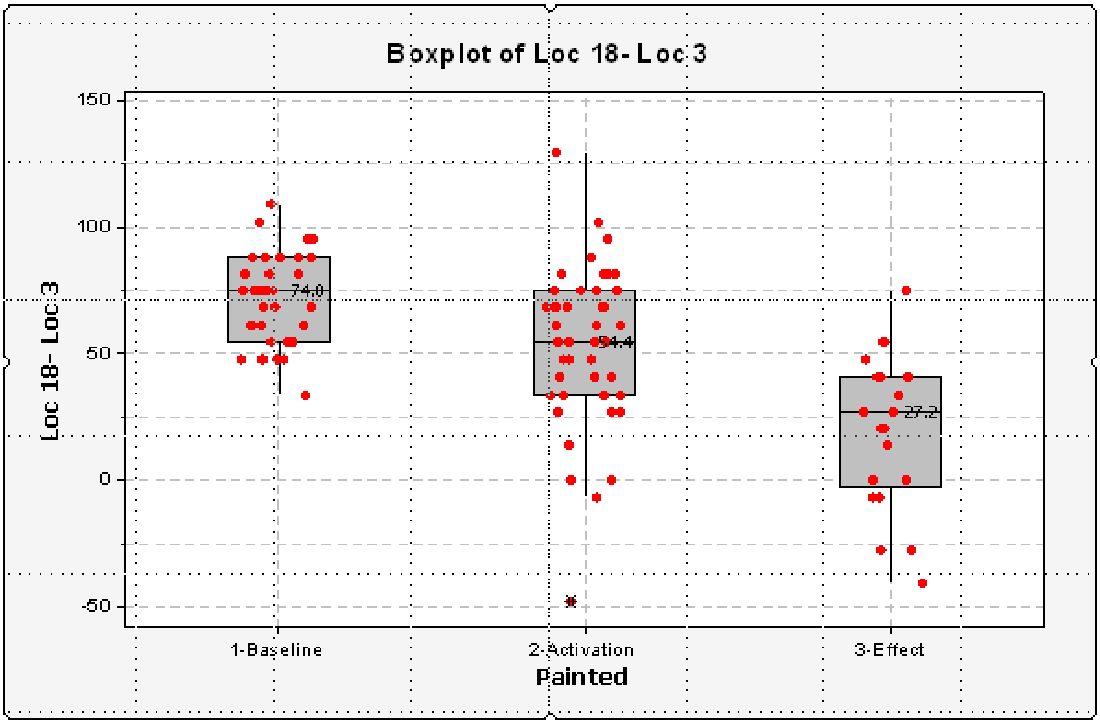

Figure 4.

The chart reported as Figure 4 compares the data generated at baseline monitor #18 (measuring background $NO_2$) versus monitor #3 (situated in an area of high $NO_2$ concentration).

The data plotted in the chart is the difference between the $NO_2$ measurements taken at the baseline monitor and the data observed at a location treated with the photocatalytic paint.

Three distinct measurement levels can be seen: baseline, activation and full effect of the photocatalytic coating

The efficiency of the NOx photodegradation is measured testing the accumulation of nitrates on dedicated test strips.

Results are reported in the chart below (Figure 5).

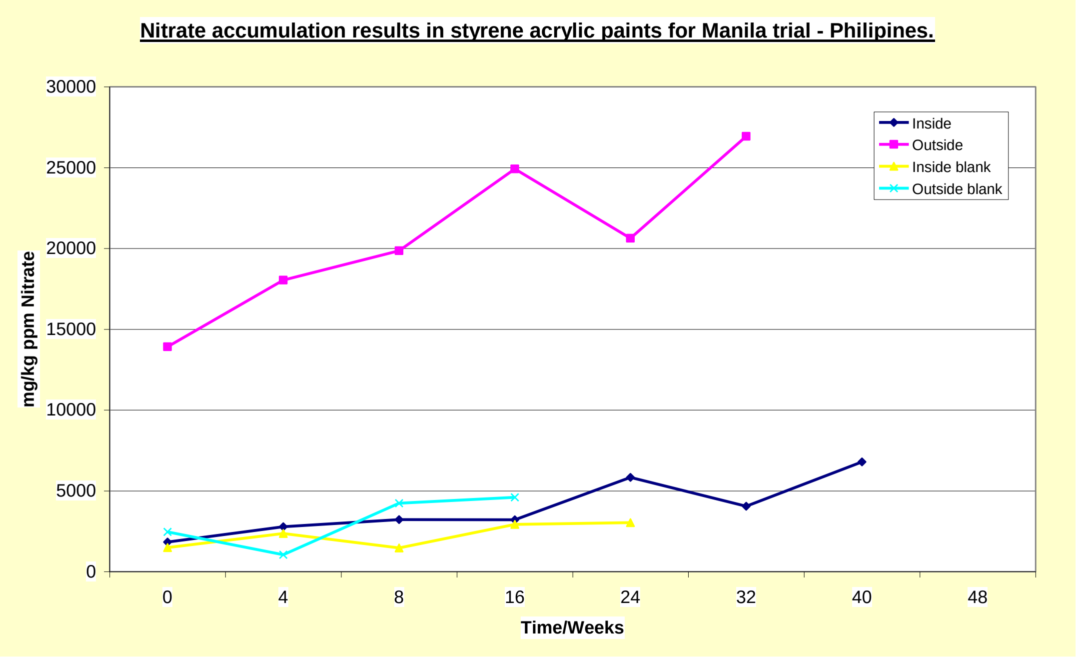

Figure 5.

The nitrate accumulation results demonstrate that $NO_2$ conversion is occurring and this is found to be a reliable measure of $NO_2$ conversion as the nitrate cannot come from any other source.

After only a few months of data, we saw 5 test locations that showed statistically significant NOx reductions.

The more confined areas (i.e. tunnels), combined with high levels of NOx are showing the highest NOx reduction rates as the pollutants in those areas have more than one chance to be converted and hit the monitor for detection.

The measures made confirm that the photocatalytic paint used shows the following performances:

- Outside the train station, 100m$^2$ treated with the photocatalytic paint can clean up to 26g of NOx per day
- The total surface of the trial removes >300kg of NOx per year
- Each square metre treated can clean the NOx emissions of ~1.7cars/day (*) passing in front of the test site
- The whole trial can clean the NOx emissions of ~7,000 cars (*)
  (*) calculation based on average emission of regulated cars

## CONCLUSIONS

Representative field trials as the ones presented in this article, showed the photoactivity of properly formulated coating materials. These surface treatments are most effectively deployed where large surface areas can be treated using either paint or transparent coatings.
Coatings and Paints based on photocatalytic $TiO_2$ are commercially viable solutions for addressing air quality issues in the world’s cities and be applied to just about any construction infrastructure.

Computational Fluid Dynamic calculations, via the European Framework 5 project PICADA, have already shown that products with this level of activity in laboratory testing can make a real impact on air quality in cities.

Since 2003, Cristal Global’s product and application developments have led to significant improvements in the efficiency of photocatalytic coatings and in the variety of coatings that are available.

Coatings formulations as well as the specific CristalACTiV™ $TiO_2$ photocatalysts developed for these purposes are available from transparent coatings for ornate buildings, to a wide range of colored paints for application to building facades. These materials are available for use on buildings, transportation infrastructures, paving and roofing materials, on new realizations as well as during refurbishment of existing structures.

Photocatalytic materials can be implemented as additional pollution control measures, complementary to the existing solution for the control of pollution at source.

# LOCAL and REMOTE SOURCES of BLACK CARBON (BC) AEROSOLS in the EASTERN MEDITERRANEAN ATMOSPHERE

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## ABSTRACT

Daily $PM_{10}$ aerosol samples were collected at a rural Eastern Mediterranean (EM) site (Antalya, 30.34°E, 36.47°N) between 1993 and 2001. In addition to large suite of variables, Black Carbon (BC) content of the collected samples was analyzed by means of Optical Transmissometer (OT-21, Magee Scientific). The average concentration of BC was found as 818±286 ng $m^{-3}$ (n=721). NOAA HYSPLIT4 model was run to compute the backward trajectories arriving to the sampling site. Nine clusters were retained in the K-means cluster analysis to interpret the origin of air masses. It has been found out that highest BC concentration was associated with the trajectories originating from western part of Turkey, Greece and countries around the Black Sea. Meteorological parameters were used to find the local sources of BC content of $PM_{10}$ samples collected at Antalya station.

**Keywords:** Backward Trajectory, Cluster Analysis, BC, Meteorology

## 1. INTRODUCTION

Black Carbon (BC) was suggested to be the second effective contributor to global warming after carbon dioxide by absorbing the direct and reflected solar radiation (Ramanathan and Carmichael, 2008). BC is released to the atmosphere through a range of incomplete combustion processes such as biomass burning and fossil fuel combustion (Bond et al., 2004). Since it is refractory and hydrophobic in nature (Weingartner et al., 1997) and associated with the fine mode of particles (Kondo et al., 2006), it is less effectively scavenged from the atmosphere, which further implies that BC particles are transported over the long distances.

The objectives of this study: (1) To find whether a trend exists in BC concentration over 9-year period, (2) To explore the seasonal variation of BC, (3) To determine the remote and local sources influencing BC content of $PM_{10}$.

## 2. EXPERIMENTAL

### Sampling

Sampling was performed at a rural area on Turkish Mediterranean coast, Antalya (30.34°E, 36.47°N). Daily $PM_{10}$ samples were collected on Whatman No.41 cellulose filters using Hi-Vol sampler (Sierra-Andersen Model SAUV-10 H PM10). Sampler was housed in a field laboratory mounted on a 4 m x 4 m concrete platform located on a rock structure 20 m above sea level. The field laboratory consists of a container (3 m x 2 m x 2 m), a storage area, a refrigerator to preserve the samples prior to shipment to a central laboratory in Ankara, and an area to change the samples. Details of the sampling location and sampling are given in Güllü et al. (1998). Sampling was initiated in 1993 and completed in 2001.

### Analysis

Collected samples were initially divided into four and different set of analytical techniques were employed to determine the chemical composition in terms of major ions and metals (Güllü et al., 1998; Öztürk et al., 2010; Öztürk et al., 2011). The remaining quarter of the samples (n=721) was analyzed by means of Optical Transmissometer (OT-21, Magee Scientific) in terms of black carbon (BC). This instrument was selected since it is portable, non-destructive and suitable for different type of filters. There are no filter standards that can be used to specifically validate BC measurements, however, OT-21 method was validated by Ahmed et al. (2009). The precision of the measurements was found to be 6 %. BC data presented in this manuscript were acquired with 880 nm channel. A detailed description of the applied technique can be found elsewhere (Khan et al., 2010).

### Cluster Analysis Methodology

Cluster analysis of trajectories has been generally employed to classify the large amounts of trajectories into similar sub-groups, which are called as ‘clusters’. The 5-day long backward trajectories arriving to Antalya station at 1500 m height were computed using the web version of the NOAA Hybrid Single Particle Langrangian Integrated Trajectory (HYSPLIT-4) model (http://ready.arl.noaa.gov/HYSPLIT.php) for the 9-year study period. Trajectories of 5 day-long was selected for this analysis since the typical lifetime of BC is around one week (Cape et al., 2012). K-means clustering, which was previously proposed by Dorling et al. (1992), was used to classify the trajectories. This algorithm is a routine available in SPSS (SPSS Inc., 2004). The 121 longitudinal and 121 latitudinal coordinates in hourly time resolution was used as input to cluster analysis run. Rectangular data matrix including the variables of latitude and longitude in columns and rows correspond to each days was formed (He et al., 2003; Kim et al., 2005). The methodology used in finding cluster numbers was previously proposed and employed in many studies (e.g., Cape et al., 2000; Brankov et al., 1998; Taubman et al., 2006; Owega et al., 2006).

## 3. RESULTS and DISCUSSION

BC concentration, [BC], where [X] refers to the concentration of X, of $PM_{10}$ samples (n=721) was analyzed by OT-21 and corresponding data was presented in this manuscript. The comparison of [BC] in the Mediterranean region was presented in Table 1. Rural stations, which are not under the direct influence of emission sources, were selected for comparison. Sciare et al. (2008) reported the [EC] for Crete as 310 ng $m^{-3}$ for the samples collected between 2001 and 2004, which is lower than the one found in this study ([BC]=818 ng $m^{-3}$). Lower [EC], 134 ng $m^{-3}$ was reported for the same site by Koulouri et al. (2008) for the period of 2004-2006. It is clear from table that Antalya station had the highest [BC] as compared to other stations cited.

**Table 1.** Comparison of BC concentrations in the Eastern Mediterranean Region

| Location | Period | Reference | [BC] (ng m$^{-3}$) |
|---|---|---|---|
| Antalya* | 1993-2001 | This Study | 818±286 |
| Crete Island (Greece) | 2001-2004 | Sciare et al. (2008) | 310±70 |
| Crete Island (Greece) | 2004-2006 | Koulouri et al. (2008) | 134±128 |
| Toulon (France)* | 2005-2006 | Saha and Despiau (2009) | 642±20 |
| Athens (Greece) | 2008 | Pateraki et al. (2012) | 440 |
| Malarco Isle (Spain) | 2009 | Pey et al. (2009) | 500 |
| Trisaia (Italy) | 2010 | Malaguti et al. (2012) | 340±230 |

*[BC] was used in the comparison for these two studies. [EC] was data presented in other cited references

## Temporal Variations

The long-term variation of [BC] was illustrated in Figure 1. Daily [BC] was presented with the blue circles and purple line represents five points box smoothing of [BC]. Highest mean [BC], about 1200 ng m$^{-3}$, was measured in 1996 during the study period, which can also be seen from Figure 1. However, it is not obvious from figure that whether a trend exists between 1993 and 2001. For this reason, seasonal Kendall (SK) test was applied to the [BC] data. Data do not have to conform any particular distribution in SK test. In addition, SK test can handle with the seasonality in the data, which is common for atmospheric compounds and it can be safely applied to data with missing values (Gilbert, 1987). Results of the SK test show that there is a declining trend in [BC] though it is not significant at p=0.05 significance level. The decreasing trend is obvious for the Crete Island, which is also on the Eastern Mediterranean region, as presented in Table 1.

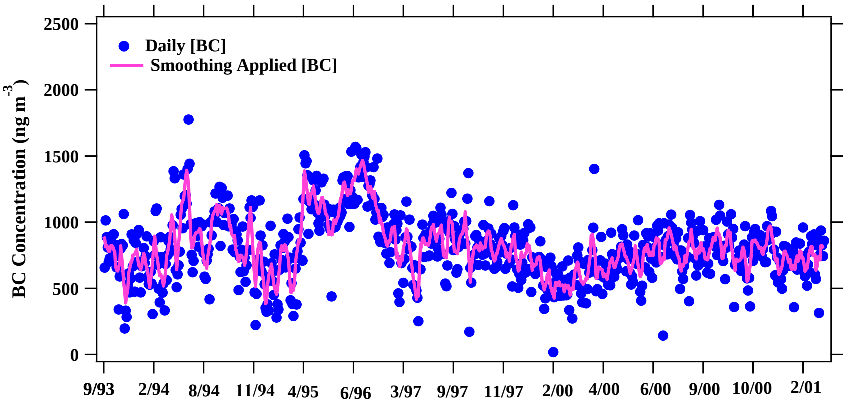

**Figure 1.** Long term variation of [BC]

The seasonal variation of [BC] was presented in Figure 2. The whiskers represent 10th and 90th percent, stars inside the boxes represent the median, and lower and upper values of the boxes represent 25th and 75th percent of the [BC]. Moreover, the smoothing was applied to the monthly data as described by Sciare et al. (2008) and it is shown by the orange continuous line in Fig.2. [BC] data showed well defined seasonal cycle and peaked in July. This observed pattern is in a good agreement with the [EC] seasonality reported by Sciare et al. (2008) for the Crete Island. Authors identified two peak periods, the early spring (March/April) and the summer months (July/September), which was then attributed to the intense emissions from biomass burning in the countries surrounding the Black Sea (Bulgaria, Romania, Moldavia, Ukraine, and Russia). In addition to this, forest fires increased in summer in a typical Mediterranean climate. Unfortunately, there is no forest fire inventory available for this period, which may provide clues about the impact of forest fire emissions on the observed [BC] in collected $PM_{10}$ samples.

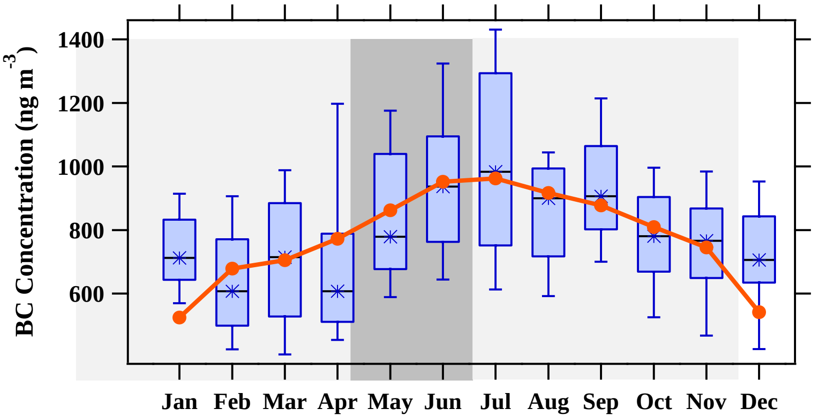

**Figure 2.** Seasonal variation of [BC]

## Local BC Sources

Daily meteorological data (wind speed and direction) were obtained from State Meteorological Works for the study period. The vector mean of wind speed and direction were calculated (www.webmet.com). The variation of [BC] with respect to wind direction was depicted in Figure 3. It is clear from Fig.3 that the most strong wind (>0.8 m $s^{-1}$) blew from 135°-180° direction. Fig.3 also indicates that there two local major contributors of [BC] ([BC]>1500 ng $m^{-3}$). First one is located in 90°-135° direction. This is associated with the sea breezes polluted by the ship emissions. The second contributor is an inland source and located in 225°-270°. The second source might be related with the fossil fuel combustion, biomass burning and traffic emissions.

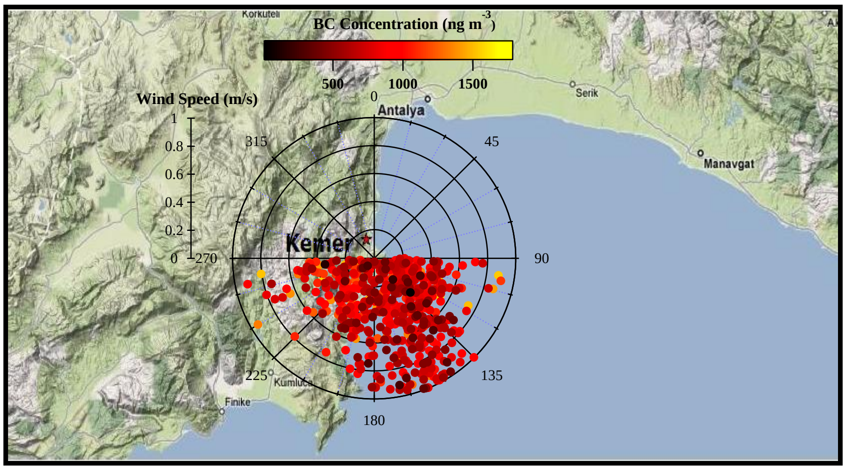

**Figure 3:** Variation of BC with respect to wind direction in Antalya region

## Remote BC Sources

Nine clusters that influence the Antalya station were identified from the cluster analysis and air masses assigned to each cluster were depicted in Figure 4. The percent of trajectories allocated to a particular cluster was also shown in parenthesis in Fig.4. It is clear from Fig.4 that air masses assigned to cluster 2, 3, 4, 8 and 9 have the long-fetch, fast moving, trajectories as compared to the rest of the clusters.

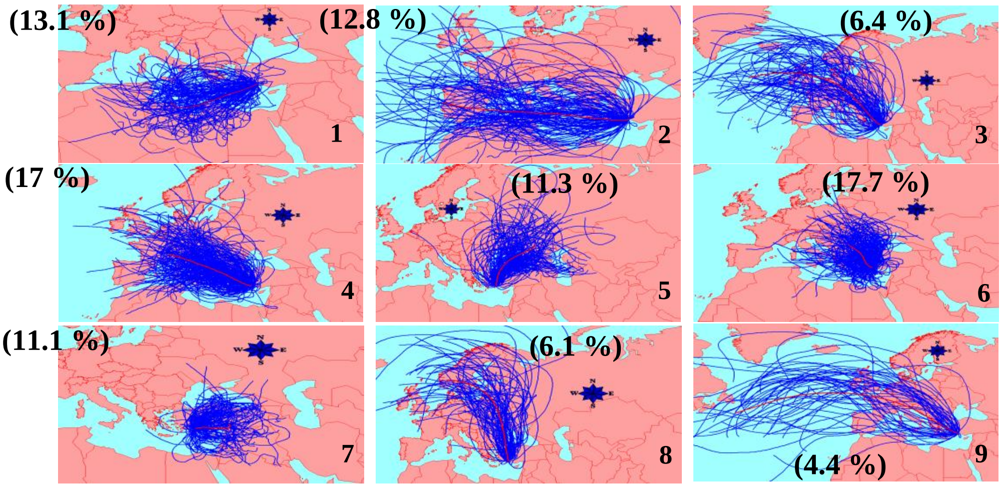

**Figure 4.** Cluster analysis results

The percent of trajectories allocated to Cluster 6 is about 18 %, which is the dominant direction and includes short-fetch, slow moving trajectories, originating from western part of Turkey and some eastern Europe countries. The second most frequent air masses originating from Western Europe and contain 17 % of the trajectories. The associated air masses in this cluster include long-fetch and slow moving trajectories. The variation of [BC] with respect to clusters is depicted in Figure 5. The non-parametric Kruskal-Wallis test (Abdalmogith and Harrison, 2005) was used to test inter- cluster variation of [BC].

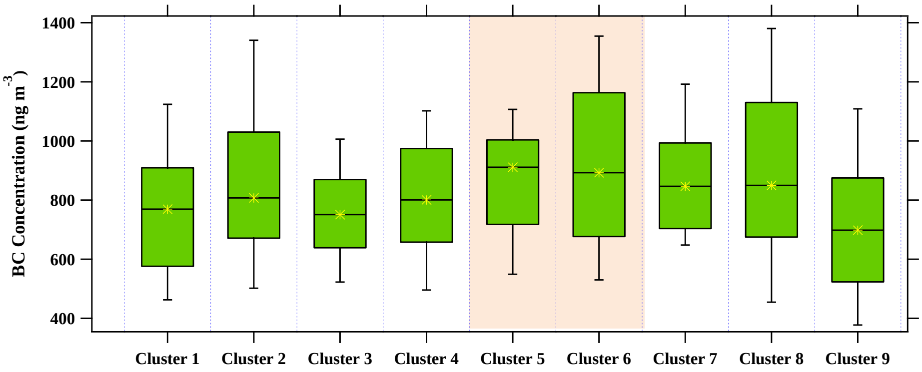

**Figure 5:** Variation of BC with respect to clusters

This test indicated significant difference ($p<0.5$) in the [BC] among the clusters. The highest [BC] is associated with Cluster 5, for which the median [BC] was found as 911 ng m$^{-3}$. The Cluster 5 encompasses whole Black Sea and countries surrounding the Black Sea. As discussed previously, Sciare et al. (2008) identified that the countries around the Black Sea emit considerable amount of BC as a result of biomass combustion, which explains why highest [BC] is associated with the air masses coming from the north direction. The second highest [BC], 893 ng m$^{-3}$, was corresponding to the Cluster 6, covering an area of northwestern part of Turkey and some eastern European countries. The long-fetch trajectories arriving to Antalya station from Atlantic Ocean makes the lowest contribution, 698 ng m$^{-3}$, to observed [BC].

## 4. CONCLUSION

[BC] in PM$_{10}$ samples collected at Antalya station was evaluated in this study in term s of temporal variations, local and remote sources. The SK test indicated no statistically significant trend for [BC] between 1993 and 2001. It has been found out that there is a well - defined seasonal pattern in [BC] peaked in summer, particularly, June and July, and relatively lower values were recorded in colder months. There are two dominant local sources with [BC] >1500 ng m$^{-3}$ influencing the sampling site: (1) the sector encompasses the area of 90°-135°. (2) The sector covering the area of 225°-270°. It was stand out that air masses arriving to sampling station from western part of Turkey, Eastern European countries, and countries located around the Black Sea contain significant amounts of BC.

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# CHARACTERISTIC OF AIRBORNE PARTICULATE MATTER SAMPLES COLLECTED FROM TWO SEMI INDUSTRIAL SITES IN BANDUNG, INDONESIA

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## ABSTRACT

Air particulate matter concentrations, black carbon as well as elemental concentrations in two semi industrial sites were investigated as a preliminary study for evaluation of air quality in these areas. Sampling of airborne particulate matter was conducted in July 2009 using a Gent stacked filter unit sampler and a total of 18 pairs of samples were collected. Black carbon was determined by reflectance measurement and elemental analysis was performed using particle induced X-ray emission. Elements Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Cu, Zn and As were detected. Twenty four hour $PM_{2.5}$ concentration at semi industrial sites Kiaracondong and Holis ranged from 4.0 to 22.2 µg $m^{-3}$, while the $PM_{10}$ concentration ranged from 24.5 to 77.1 µg $m^{-3}$. High concentration of crustal elements, sulphur and zinc were identified in fine and coarse fractions for both sites. The fine fraction data from both sites were analyzed using a multivariate principal component analysis and for Kiaracondong site, identified factors are attributed to sea-salt with soil dust, vehicular emissions and biomass burning, non ferrous smelter, and iron/steel work industry, while for Holis site identified factors are attributed to soil dust, industrial emissions, vehicular emissions with biomass burning, and sea-salt. Although particulate samples were collected from semi industrial sites, vehicular emissions constituted with S, Zn and BC were identified in both sites.

**Key Words**: airborne particulate matter, semi industrial sites, principal component analysis, PIXE

## 1. INTRODUCTION

Air pollution has become an important problem that requires serious attention due to its impact on human health and environmental quality. A large number of epidemiological studies have shown that air pollution causes adverse human health effects (Dockery et al., 1993; Katsouyani, 2005). Studies of air pollution in Indonesia are, however, very limited and regulatory decisions must be made based on pollution models from other countries (Tri Tugaswati, 1993; Browne et al., 1999). There is a need to establish baseline air pollution data across the country, to identify the major sources of air pollution, and to investigate the spatial and temporal patterns of transport and deposition of particular air pollutants to the Indonesian environment. Some publications related to air pollution level in urban Bandung and suburban Lembang has been published. Santoso et al. (2008) reported on the composition and source apportionment of fine and coarse particle samples collected in Bandung and Lembang, Indonesia between 2002 and 2004. The mean values of $PM_{2.5}$ concentrations at Bandung and Lembang were 14.03±6.86 and 11.88±6.60 µg $m^{-3}$, respectively. The mean values of $PM_{10-2.5}$ concentrations at Bandung and Lembang were 17.64±9.42 and 7.10±7.04 µg $m^{-3}$, respectively (Santoso et al., 2008). Only limited publications of air pollution in Indonesia are available, and the data of air quality in industrial area are still limited. Industrial emissions are believed to be one of major contributor to particulate matter, therefore in this study will assess the $PM_{2.5}$ and $PM_{10}$ level in industrial areas particularly in Bandung. Besides that, the objective of this research is also as a pre-study to identify the sources that could contribute to the particulate mass especially from industrial emissions in the areas.

## 2. MATERIALS AND METHODS

### 2.1 Sampling

Samplings were carried out in semi industrial areas, Kiaracondong and Holis street in Bandung. Bandung is the capital city of West Java Province and the third largest city in Indonesia, located at 768 metres above sea level, approximately 140 km southeast of Jakarta. The city surrounded by volcanoes. This topography characteristic made Bandung has lower temperatures year-around than most other Indonesian cities and can be classified as humid with the average temperature is 23.6 °C throughout the year. In general, Bandung has two seasons, dry season (April to September) and wet season (October to March). Bandung has estimated population of 2.39 million based on population census 2010 (Statistic Indonesia, 2010). Many small scale factories are located in and around the city. Commercial activities are mostly concentrated in the center, while industrial activities are concentrated in the west and east side of the city. There are several pockets of slum areas, where housing conditions are poor, waste disposal systems are lacking, green space is negligible, and in addition industry and residential development occur together. The rapid growth of industry, population and motor vehicle usage has strongly affected the city's environmental quality. The disparity in number of motor vehicles and available road has created a traffic jam problem almost in every section of the city, and has caused the air quality deterioration. Pollution sources that have significant effects on the city are secondary sulfate, soil dust, road dust, motor vehicles, biomass burning and industry (Santoso et al., 2008; Lestari et al., 2009).

The sampling sites Kiaracondong and Holis areas are not only surrounded by many small scale industries but also mixed with residential, school and commercial activities. Kiaracondong is located in the east of the city, and there is one big scale industry in that area. Holis is located in the western part of the city, and there are many small and big scale industries dominated by textile and paper industries. The location of sampling sites is shown in Figure 1. The distance between these locations is 6 km away.

Samples were collected from 6 July to 31 July 2009 using a Gent stacked filter unit sampler provided by International Atomic Energy Agency that capable for collecting particulate matter in the $PM_{2.5-10}$ (coarse) fraction and $PM_{2.5}$ size (fine) fraction (Hopke et al., 1997). The coarse fraction $PM_{2.5-10}$ samples were collected on an 8.0 μm nuclepore filters, whereas the fine fraction $PM_{2.5}$ samples were collected on 0.4 μm nuclepore filters. Sampling was performed at a flow rate of 15-18 $L.min^{-1}$ for 24 hours with a frequency of twice to three times per week over 3 to 4 week periods. Sampler was placed on the rooftop of a building 5 m above ground level and the intake nozzle of the sampler is located 1.8 m above the roof. The total of 18 pairs of $PM_{2.5}$ and $PM_{2.5-10}$ samples were collected from both areas.

Figure 1. Sampling sites of semi industrial area Kiaracondong and Holis, Bandung

### 2.2 Mass concentrations, BC and elemental analysis

The particulate matter mass of each fine and coarse fractions were determined by gravimetric using a six digits microbalance. The filters were stored for 24 hours prior to weighing in controlled environmental condition room. Mass concentrations of $PM_{2.5}$ and $PM_{2.5-10}$ ($\mu g.m^{-3}$) were obtained by dividing the gravimetric mass by the volume of air that passed through the filter. The concentration of black carbon (BC) in the samples was determined by reflectance measurement using an EEL Smoke Stain Reflectometer model 43D. Secondary standard of known reflectance were used to calibrate the reflectometer. Elemental analysis was performed using particle induced x-ray emission at the Institute of Geological and Nuclear Sciences (GNS), New Zealand. The X-ray spectra were analyzed using the computer code GUPIX (Maxwell et al., 1995) and calibration of the PIXE system was performed by irradiating suitable Micromatter thin target standards (Cohen et al., 2004).

### 2.3 Factor Analysis

Most factor analysis has been based on an eigenvector analysis. The simplest form of factor analysis is principal component analysis (PCA). This method attempts to simplify the description of a system by determining a minimum set of basis vectors that span the data space to be interpreted. Since PCA can only be performed n a set of samples in which the various sources contribute different amount of particles to each samples, the mass balance needs to be expanded to a matrix equation: Z = A x F, where, Z is a matrix of sample vectors, A is the matrix of loading vectors related to the source compositions and F is the matrix of scores that are related to the contribution of that source type to the variance of that particular measured variable. PCA has been widely used in studies of airborne particulate matter composition data (Hopke, 1999)

## 3. RESULTS AND DISCUSSION

### 3.1 Particulate matter and black carbon concentrations

$PM_{2.5}$, $PM_{10}$ and BC concentrations for each site are summarized in Table 1. Twenty four hour $PM_{2.5}$ concentration at semi industrial sites Kiaracondong and Holis ranged from 4.0 to 22.2 $\mu g\ m^{-3}$, while the $PM_{10}$ concentration ranged from 24.5 to 77.1 $\mu g\ m^{-3}$. $PM_{2.5}$ and $PM_{10}$ concentrations for both sites are shown in Figure 2. The mean $PM_{2.5}$ concentrations for Kiaracondong and Holis sites were 15.9 and 13.9 $\mu g\ m^{-3}$, respectively, while the mean $PM_{10}$ concentrations were 43.4 and 48.3 $\mu g\ m^{-3}$, respectively. Assuming that these 4 weeks of sampling can represent the annual mean of $PM_{2.5}$ level, most of the $PM_{2.5}$ concentrations in sampling site Kiaracondong would exceed the Indonesian national ambient air quality standard of an annual mean $PM_{2.5}$ value of 15 µg $m^{-3}$ (Government Regulation, 1999). However, none of $PM_{2.5}$ and $PM_{10}$ concentrations in each sampling sites exceeded the twenty four hour Indonesian NAAQS for $PM_{2.5}$ and $PM_{10}$ (65 and 150 µg $m^{-3}$, respectively).

Table 1. The sampling data, mean mass and BC concentrations (µg $m^{-3}$)

| **Sampling site** | **Number of samples** | **$PM_{2.5}$** | | **$PM_{10}$** | | **BC** | |
|---|---|---|---|---|---|---|---|
| | | **Range** | **Mean** | **Range** | **Mean** | **Range** | **Mean** |
| Kiaracondong | 10 | 4.0-22.2 | 15.9 | 34.1-56.8 | 43.4 | 0.8-3.7 | 2.6 |
| Holis | 8 | 4.1-20.5 | 13.9 | 24.5-77.1 | 48.3 | 0.8-3.6 | 2.7 |

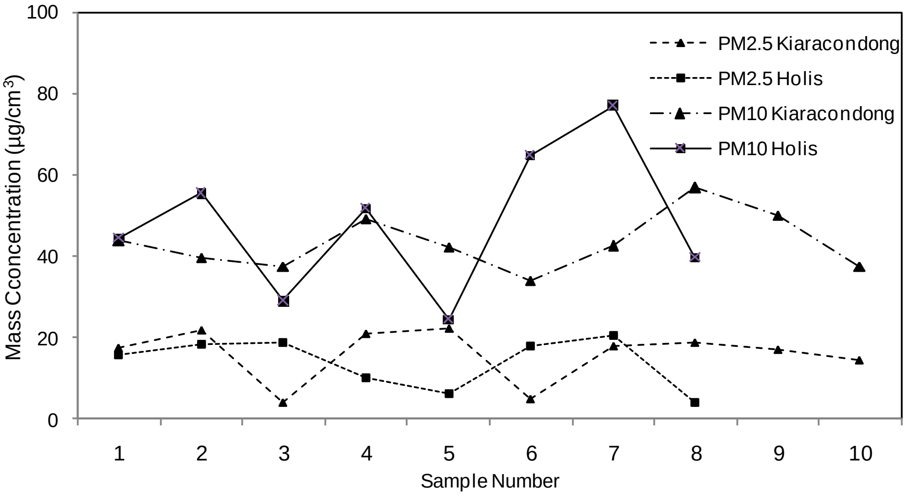


Figure 2. PM mass concentrations at the two semi industrial sampling sites in July 2009

The mean of BC concentrations in Kiaracondong and Holis were 2.6 and 2.7 µg $m^{-3}$, respectively. The average ratio of BC to $PM_{2.5}$ concentrations at these sampling sites ranged from 13-31%. These values do not differ significantly with the values reported in industrial area in Serpong area in 2008 (13-26%) which used the same sampling method and analytical procedure (Santoso et al., 2011). Transport related emissions are the major source of BC and long-range transport from fossil fuel related sources and biomass burning could be other substantial sources of BC (Begum et al., 2009).

Table 2. Elemental concentrations (ng.m$^{-3}$) in fine and coarse fractions collected in July 2009 in Kiaracondong Sampling Site

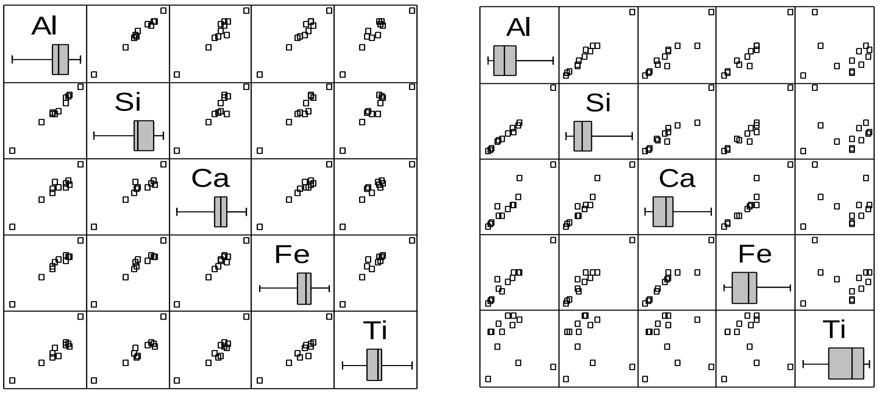
| **Element** | **Fine-Kiaracondong** | | | | **Coarse-Kiaracondong** | | | |
|---|---|---|---|---|---|---|---|---|
| | **Mean** | **Stdev** | **Min** | **Max** | **Mean** | **Stdev** | **Min** | **Max** |
| Na | 131.88 | 88.89 | 45.14 | 286.01 | 677.38 | 153.13 | 396.09 | 913.30 |
| Mg | 51.65 | 15.73 | 26.02 | 76.18 | 251.73 | 54.70 | 148.98 | 324.62 |
| Al | 72.56 | 27.77 | 28.13 | 114.90 | 843.14 | 166.31 | 555.65 | 1135.42 |
| Si | 129.25 | 46.81 | 54.72 | 191.06 | 1607.43 | 342.36 | 1074.77 | 2166.32 |
| P | 19.58 | 8.74 | 4.79 | 30.04 | 109.52 | 19.24 | 77.48 | 148.20 |
| S | 669.32 | 298.92 | 135.50 | 1124.21 | 505.95 | 100.24 | 347.89 | 689.37 |
| Cl | 38.58 | 18.03 | 19.52 | 88.71 | 549.67 | 287.26 | 158.20 | 1024.69 |
| K | 149.80 | 59.10 | 38.20 | 209.50 | 176.54 | 38.02 | 125.82 | 243.53 |
| Ca | 44.30 | 18.83 | 14.69 | 79.23 | 743.03 | 153.35 | 512.18 | 1095.26 |
| Ti | 3.73 | 2.49 | 0.78 | 7.37 | 50.34 | 16.65 | 30.06 | 90.88 |
| Cr | 1.21 | 1.07 | 0.24 | 3.74 | 3.72 | 2.00 | 1.00 | 6.17 |
| Mn | 1.75 | 1.90 | 0.14 | 6.42 | 14.33 | 5.09 | 10.03 | 26.93 |
| Fe | 54.32 | 24.36 | 17.04 | 91.05 | 657.66 | 133.60 | 426.69 | 932.98 |
| Cu | 1.65 | 0.72 | 0.44 | 2.93 | 5.28 | 4.53 | 1.00 | 13.30 |
| Zn | 20.31 | 11.57 | 8.40 | 40.35 | 28.07 | 10.77 | 11.12 | 39.74 |
| As | 3.56 | 2.56 | 1.12 | 7.47 | 7.87 | 5.52 | 2.15 | 18.17 |

Table 3. Elemental concentrations (ng.m$^{-3}$) in fine and coarse fractions collected in July 2009 in Holis Sampling Site

| **Element** | **Fine-Holis** | | | | **Coarse-Holis** | | | |
|---|---|---|---|---|---|---|---|---|
| | **Mean** | **Stdev** | **Min** | **Max** | **Mean** | **Stdev** | **Min** | **Max** |
| Na | 98.13 | 54.50 | 25.65 | 182.76 | 605.13 | 161.43 | 368.75 | 842.46 |
| Mg | 55.60 | 21.24 | 29.36 | 93.68 | 263.07 | 100.81 | 35.89 | 430.52 |
| Al | 110.15 | 81.89 | 18.57 | 317.29 | 1164.21 | 489.60 | 23.47 | 1878.29 |
| Si | 216.76 | 173.02 | 35.41 | 674.81 | 2410.60 | 975.83 | 51.96 | 3920.32 |
| P | 28.91 | 15.94 | 2.11 | 57.08 | 132.51 | 56.26 | 8.70 | 206.05 |
| S | 473.47 | 331.55 | 84.37 | 1076.80 | 607.40 | 375.12 | 14.02 | 1174.16 |
| Cl | 60.44 | 52.29 | 19.75 | 197.01 | 585.23 | 370.76 | 8.00 | 1071.52 |
| K | 182.63 | 113.40 | 20.91 | 380.06 | 285.40 | 134.48 | 8.73 | 465.91 |
| Ca | 114.37 | 97.00 | 3.98 | 329.46 | 1310.72 | 567.90 | 21.97 | 2215.66 |
| Ti | 4.65 | 5.37 | 0.42 | 19.25 | 71.78 | 31.69 | 1.46 | 125.90 |
| Cr | 1.78 | 0.65 | 0.96 | 2.91 | 8.98 | 4.28 | 0.21 | 14.43 |
| Mn | 3.52 | 1.56 | 1.87 | 5.93 | 20.57 | 8.25 | 0.44 | 29.77 |
| Fe | 75.45 | 55.90 | 5.58 | 209.66 | 931.22 | 413.61 | 11.90 | 1548.19 |
| Cu | 1.79 | 1.19 | 0.61 | 4.01 | 11.78 | 6.67 | 1.09 | 23.68 |
| Zn | 12.48 | 9.07 | 2.21 | 28.58 | 31.46 | 12.26 | 4.69 | 53.55 |
| As | 2.23 | 1.45 | 1.36 | 4.39 | 7.22 | 3.05 | 4.99 | 14.47 |

### 3.2 Elemental concentrations

Several elements were detected by PIXE in fine and coarse fractions. Elements such as Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe and Zn were detected in the most of the filters (over 90%), Cu and As were present in more than 30% of the samples, while V, Br, Hg and Pb were detected in less than 10% of the samples. The average elemental concentrations in coarse and fine particulate matter in Kiaracondong and Holis sampling sites are shown in Table 2 and Table 3, respectively. High concentration of Al, Si, Ca, Fe and Mn which are crustal elements, S and Zn were identified in $PM_{2.5}$ and $PM_{10}$ for both sites. Figure 3 shows the correlation plot for the five major soil component of Al, Si, Ca, Fe and Ti for each site. For Kiaracondong site, it shows good correlations for all elements while for Holis site there were good correlations between Al, Si, Ca and Fe, but with Ti. Element associated with Ti is suggested from other source at least this site has more than one source of Ti besides soil component.



(a) Kiaracondong sites (b) Holis sites

Figure 3. Correlation plot for the five major soil components for fine fractions from all sites

Sulfur in airborne particulate matter is generally present because of the atmospheric conversion of $SO_2$ to sulfate through homogenous processes (Hopke et al., 2008). Thus in general, only a portion of the particulate sulfate is the result of local sources because there is insufficient time to allow substantial conversion. Zinc is emitted from municipal solid waste, galvanizing operations, and non-ferrous metal smelting. All of these sources contribute to the fine fraction. However, the two stroke engine emissions can provide substantial zinc contribution to the urban street dust and thus also be found in coarse fraction (Hopke et al., 2008).

### 3.3 Principal component analysis

The trends in data monitored were analyzed using an approach based on factor analysis to identify quantitatively the source contributing to the pollution. To address the air quality issues, it is always necessary to have information on possible source contribution. A multivariate principal component analysis using Statgraphics Software was applied to the fine fraction data set to identify the major elements associated with the sources. Factors with two or more elements having factor loadings above 0.5 have been highlighted. The varimax factor loadings after rotation are presented in Table 4 and Table 5. The loadings are considered a correlation coefficient between the original variables and new factor variables that represent a linear combination. Loading values over 0.50 are generally considered significant although smaller ones may still provide insights into the nature of the sources (Hopke, 1999).

### a. Kiaracondong sampling site

Factor analysis for data from Kiaracondong site was identified four factors. The identified sources are attributed to soil, biomass burning and vehicle emissions, non ferrous smelter and iron/steel work industry. The first factor is crustal elements Al, Si, Ca, Fe and Ti which are recognized as typical soil indicators. It also can be seen from the correlation among these elements that it has strong correlation for each element. There is additional loading from Na which indicates that soil factor is also mixed with sea-salt. The second factor has the characteristic of high BC, S, K and Zn. This combination of elements suggests the contribution from biomass burning which is indicated by potassium that is strongly related to the biomass combustion, and vehicular emissions indicated from high S and Zn (Santoso et al., 2011). Bandung still has a large area of rice fields which is the main source of biomass burning and open solid waste burning from residential activity is also a potential source of biomass burning (Lestari et al., 2008). High concentration of S is attributed to the low fuel quality. Sulfur comes from diesel vehicles emissions since Indonesia still has high sulfur content in diesel fuel (Santoso et al., 2008). There is a fly-over road about 500 m to the west side of the sampling site, with many heavy vehicles pass through this area. The third factor is related to Cu from non ferrous smelter. In this sampling site, there is one big scale metal workshop industry which estimates to contribute to this factor. This industry also contributes to the fourth factor that has high factor loading for Cr. This element would be expected to be related to the iron/steel works (Hopke, 1999). It would have been more logical if Fe also has high positive loading on this factor, but due to the limited numbers of data the clearly correlation was not obtained.

### b. Holis sampling site

Factor analysis for data from Holis site was identified four factors. The first factor is crustal elements represent soil component. The second factor has high loading for Ti, Cr and Mn which indicated as the fingerprint of industrial activities. Ti could be expected from paint pigment plant that produces $TiO_2$ and is a major source of fine particle titanium. In this sampling site, there are several painting textile industries which may contribute to this source. This Ti source was clearly showed up when plotting the correlation of crustal elements for soil component (Figure 3 (b)). It shows that apparently there is another Ti source, since Ti appears having a negative correlation with the other crustal elements. The third factor is related to BC, S, K and Zn. This factor would be expected from vehicular emission especially from diesel vehicles mixed with biomass burning which also emits large quantity of black smoke. The fourth factor is clearly sea-salt by the presence of Na and Cl correlation. But it appears to be quite number of loading for BC and K which indicates that biomass burning could be mixed with this factor.

Table 4. Factor analysis with varimax rotation for fine fraction data from Kiaracondong site

| Parameter | Factor 1 | Factor 2 | Factor 3 | Factor 4 |
|---|---|---|---|---|
| BC | -0.6601 | **0.5637** | 0.2031 | 0.0586 |
| Na | **0.8374** | -0.5036 | -0.0372 | -0.0448 |
| Al | **0.9746** | 0.0779 | -0.0444 | 0.2423 |
| Si | **0.9637** | 0.1259 | -0.0902 | 0.2326 |
| S | -0.1944 | **0.9281** | 0.0508 | -0.0013 |
| K | 0.3200 | **0.8363** | 0.3990 | -0.0124 |
| Ca | **0.9863** | -0.0369 | -0.0497 | 0.0984 |
| Ti | **0.9554** | 0.1904 | 0.0401 | -0.0051 |
| Cr | -0.0244 | -0.0254 | 0.0260 | **0.9749** |
| Mn | **0.8881** | -0.1147 | 0.3587 | -0.2157 |
| Fe | **0.9926** | -0.0214 | 0.1550 | 0.2046 |
| Zn | 0.0640 | **0.9641** | -0.1642 | 0.0043 |
| Cu | 0.3777 | 0.0352 | **0.9238** | -0.0161 |

Table 5. Factor analysis with varimax rotation for fine fraction data from Holis site

| **Parameter** | **Factor 1** | **Factor 2** | **Factor 3** | **Factor 4** |
|---|---|---|---|---|
| BC | 0.6627 | 0.0228 | **0.5162** | 0.4355 |
| Na | 0.0597 | 0.1090 | 0.0953 | **0.9503** |
| Al | **0.9263** | -0.1046 | 0.2594 | 0.2012 |
| Si | **0.9434** | -0.1158 | 0.1900 | 0.2038 |
| S | 0.2162 | 0.0768 | **0.9331** | -0.1520 |
| Cl | 0.4258 | 0.1880 | -0.1084 | **0.8251** |
| K | 0.2812 | -0.0657 | **0.6293** | 0.6386 |
| Ca | **0.9559** | -0.0365 | 0.1540 | 0.1437 |
| Ti | -0.1073 | **0.8965** | 0.0788 | 0.0286 |
| Cr | -0.1809 | **0.9289** | 0.0642 | -0.1083 |
| Mn | 0.1113 | **0.8200** | -0.2565 | 0.3947 |
| Fe | **0.8940** | -0.0714 | 0.3738 | 0.2061 |
| Zn | 0.3737 | -0.0644 | **0.8772** | 0.1058 |

## 4. CONCLUSIONS

The airborne particulate samples collected from two semi industrial sites Kiaracondong and Holis in Bandung, Indonesia were characterized using particles induced x-ray emission to investigate the sources of pollution, as a preliminary study in step to the evaluation of air quality in these areas. Concentrations of crustal elements, S and Zn were found in high levels for both sites. A multivariate approach of principal component analysis has revealed four factors in each site. For Kiaracondong site, identified factors are attributed to sea-salt with soil dust, vehicular emissions and biomass burning, non ferrous smelter, and iron/steel work industry, while for Holis site identified factors are attributed to soil dust, industrial emissions, vehicular emissions with biomass burning, and sea-salt. Although particulate samples were collected from semi industrial areas, vehicular emissions especially diesel vehicles constituted with S, Zn and BC were identified in both sites. Additionally, a few different sources such as non ferrous smelter and iron/steel work industry sources have also been obtained due to sampling site characteristic difference.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
**4th International Symposium and IUAPPA Regional Conference**
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# PARTICLE NUMBER ESTIMATION IN AMBIENT AEROSOLS USING A CASCADE IMPACTOR

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## ABSTRACT

The purpose of this study is to determine the number of particles that are being exposed in an urban area. An 8 stage non-viable cascade impactor was utilized to resolve size distributions of ambient aerosols at an urban site in Istanbul. As air quality legislations are based on mass concentration of particulate matter, it is also crucial to know the particle number concentration for a complete assessment. The sampling campaign was from March 2009 to February 2010 but to make a comparison with previous studies only Spring 2009 values are taken into consideration. According to aerodynamic cut-off diameter and deposited aerosol mass value, particle number is predicted. Estimated particle number values are compared to those present in the literature for the same sampling zone and period. Mean values of both studies are in accordance. It is suggested that cascade impactor can also be used to make particle number concentration estimation.

**Keywords:** Particle number, cascade impactor, particle counter

## 1. INTRODUCTION

Particulate matter is from the major components of airborne pollutants. Thus, PM has always been an important subject for researchers. PM sampling techniques have developed over a 40 year period. According to health experts $PM_{100}$ is considered as inhalable while $PM_{10}$ is considered as thoracic fraction due to its effect on human thoracic health, and $PM_{4.0}$ is known to have detrimental effect on respiratory tract (Perez et al., 2008). Gomez-Moreno also expressed the relation of particulate diameter and health effects, as the diameter determines the place where the particle will be deposited. For that reason it is not practical to collect the whole particulate size spectrum suspended in the air. Since PM size bigger than 10 µm diameter doesn't have a significant effect on health, most legislations now have limit values of $PM_{10}$ and $PM_{2.5}$.

Above referred limits are according to mass concentration. However, Wichmann et al. (2000) suggested that the number rather than the mass per unit volume of fine particles can be more related with adverse health effects. Moreover, in some toxicological studies it is implied that toxicity per unit mass increases with the decreasing particle diameter (Lingard, et al., 2005; Oberdorster, 2000). PM concentration, composition, toxicity and as well as size distribution are important factors affecting human health (Hieu and Lee, 2010). As trace elements are present in all size ranges, generally fine PM contains much higher heavy toxic metals than coarse PM fraction (Fang et al.,2000).

Another fact is that, aerosols play an important role in global climate through the Earth's radiation budget (IPCC, 2007). A comprehensive knowledge has to be known to predict direct and indirect forcing (Gomez-Moreno, et al., 2011). This knowledge infrastructure can be formed by measuring both particle size and number distribution.

The goal of this study is to determine whether it is practical to convert the results achieved from cascade impactor to particle number distribution. Estimated results were checked with the ones sampled through a particle counter present in the literature (Borucu, et al., 2010). For a better understanding of the effects of aerosols both on climate and health it is indispensable to determine particle size and number distribution.

## 2. MATERIALS AND METHODOLOGY

### 2.1. Sampling Site and Device

An eight stage low volume cascade impactor (Andersen 20-800) was installed near Barbaros Avenue within the Yildiz Technical University Campus area. The device is 5 meters apart from the connection road between Barbaros Avenue and E-5 highway. Dense traffic is present at rush hours. At this time of the day fleet velocity decreases to approximately 5 km.hr$^{-1}$.

The impactor consists of nine stages. At the preceding eight stages particles are segregated according to impaction mechanism. At the last stage particles are collected by filtration mechanism which is called back-up filter. After a pre-seperator of 10 µm, cut-off diameters of the impactor are 9.0, 5.8, 4.7, 3.3, 2.1, 1.1, 0.65, 0.43 and <0.43 µm, in the collection order. Flow rate was operated constantly at 28.3 L.min$^{-1}$.

Quartz filters were used as the collection medium. Filters were dried in the oven at 103$^0$C over night and stabilized under constant temperature and humidity conditions as, 20±2 $^0$C and 50±2%, respectively. Filters were weighted with AND GR202 analytical microbalance. Field blanks were taken with each set. More information of sampling device and weighting method is present somewhere else (Kuzu and Saral, 2010).

Particle counter was set 400 m away from our sampling point. It consists of six channels of 0.3-0.5, 1.0-2.5, 2.5-5.0, 5.0-10.0 and >10.0 µm size ranges. The device was operated during Spring.

### 2.2. Estimation Methodology

Particles are collected on each stage according to their aerodynamic diameter. This diameter term is the diameter of a sphere with a unit density (1 g/cm$^3$) that has aerodynamic behavior identical to that of the particle in concern.

Starting from this point each collected mass was divided to the density stated above and thus volume of the particles were calculated. To estimate the particle number, an assumption had to be made. It was assumed that only particles of having cut-off diameter are collected. After estimating particle number, they were divided by the samples air to compute the number concentrations.

Impactor and counter devices don’t have particulate intervals in the same order. To refine the cut-off diameters of impactor according to counter, an estimation was used which was also followed by Hieu and Lee (2010). In this method, theoretical impaction curves was used which was supplied by the manufacturer and shown in Figure 1.

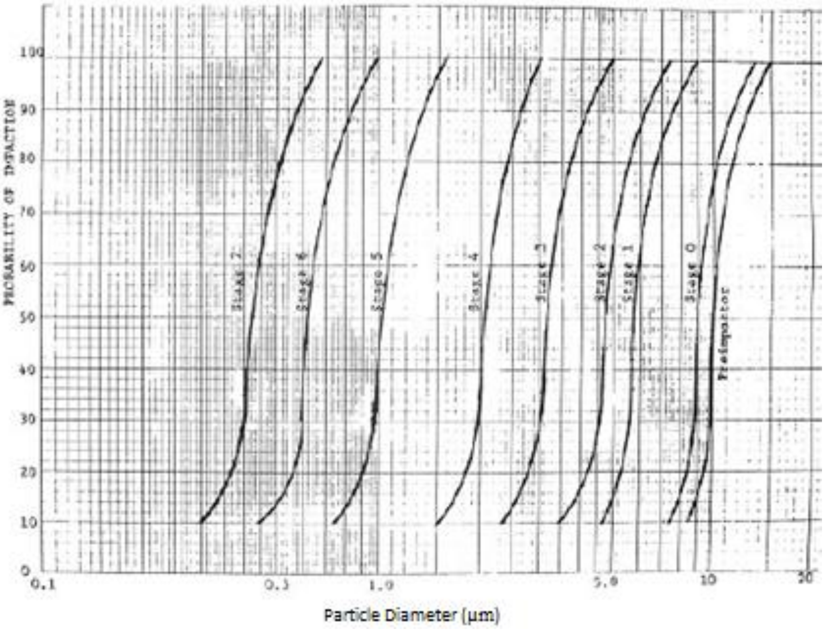

Figure 1. Theoritical impaction curves for Andersen low volume cascade impactor (Thermo Scientific, 2007)

Mass fractions corresponding to particle counter was estimated by adding the masses from previous stages together with the correction factor, acquired from intercepting the theoretical impaction curve with the diameter in concern. Calculation procedure is shown in Table 1.

Table 1. PM mass correction

| Particle diameter ranges (µm) | Calculation formula |
|---|---|
| 10.0 - 5.0 | Stage 0 X0.78 + Stage 1 X 0.86 + Stage 2 X 0.30 |
| 5 - 2.5 | Stage 2 X 0.70 + Stage 3 + Stage 4 X 0.14 |
| 2.5 - 1.0 | Stage 4 X 0.86 + Stage 5 X 0.60 |
| 1.0 - 0.5 | Stage 5 X 0.40 + Stage 6 X 0.86 + Stage 7 X 0.24 |
| 0.5 - 0.3 | Stage 6 X 0.14 + Stage 7 X 0.76 |

## 3. RESULTS AND DISCUSSION

Predicted and measured particle number concentration results for corrected size ranges are given below in Table 2.

Table 2. Comparison of measured and estimated particle numbers

| Particle diameter ranges (µm) | Measured Mean PM Number concentration (number/m$^3$) | Estimated Mean PM Number concentration (number/m$^3$) |
|---|---|---|
| 10.0 - 5.0 | 1.3E+05 | 1,34E+04 |
| 5 - 2.5 | 7.1E+05 | 8,74E+04 |
| 2.5 - 1.0 | 1.9E+06 | 3,74E+05 |
| 1.0 - 0.5 | 1.7E+07 | 8,33E+06 |
| 0.5 - 0.3 | 1.2E+08 | 1,64E+07 |

From the table it can be seen that results of the prediction underestimates. These results were plotted on graph to determine the correlation. The graph is shown in Figure 2. Correlation between two devices was found to be 0.86. This finding is better than the estimation stated Tittarelli et al. (2008). They used a particle counter in estimating particle mass concentration. Correlation of their estimated concentration values with PM10 was found to be 0.73. Their assumption method was based on assuming the particles are sphere, and all the particles had the same density. In fact, density of the particle changes according to its origin. This may be the one reason of a lower correlation. Another factor that could be the lower correlation is the selection of mean particle diameter. It was calculated as the arithmetic mean of the stated size interval for first forth channels and a value closer to the lower extreme was used for the fifth channel due to wider size range (2.5-10 µm).

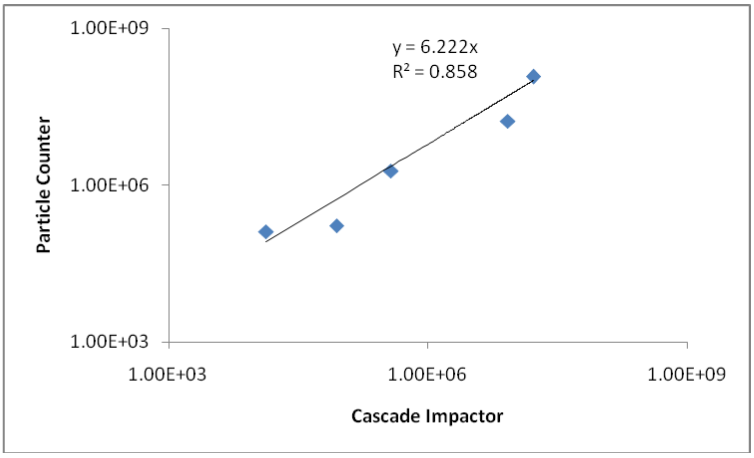

Figure 2. Correlation between cascade impactor and particle counter

After correlating the two devices, it is seen that reasonable results are achieved with a higher correlation than predicting mass concentration from a particle counter.

In Table 3 number size distribution was plotted. The curve is similar to normalized traffic influenced aerosol size distribution drawn by Morawska et al. (1999).

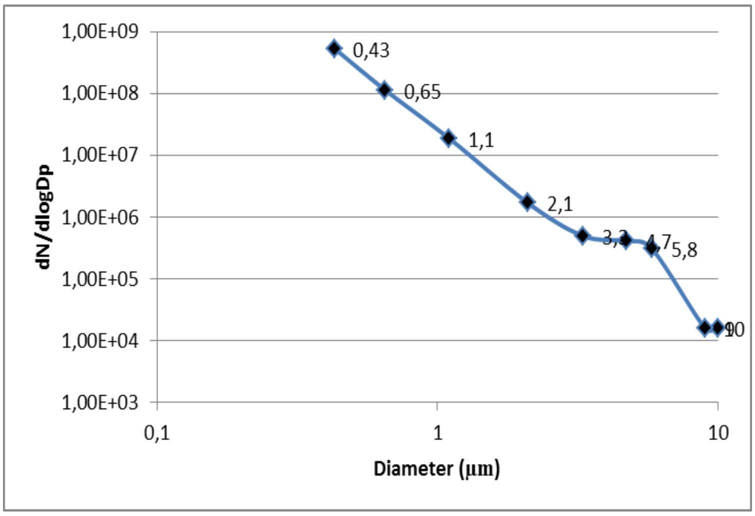

Figure 3. Estimated particle number distribution

This outcome is in accordance with our sampling location. The estimation is also reasonable by means of number size distribution.

## 4. CONCLUSIONS

Airborne particulate matter sampled utilizing a low volume cascade impactor. The results of spring season were matched with a particle counter running at the same time, 400 m apart from our sampling point to determine the correlation between two devices.

Results achieved from cascade impactor stages were corrected according to theoretical impaction curves to fit the particle counter cutoff diameters. New values were used to reveal the correlation of the devices. When line is plotted by intercepting the origin, a 0.86 correlation was found. This is better than the study made before in the literature. It should also be noted that cascade impactor underestimates the particle number per volume. Number size distribution plotted by the values achieved from estimation.

This study can further be supported by using different devices (high volume cascade impactor, different type of particle counter) and sampling at different seasonal conditions to identify the better relevance of different sampling methods.

## ACKNOWLEDGEMENTS

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# INVESTIGATION OF AEROSOL-PRECIPITATION INTERACTIONS IN NORTH-EASTERN NORTH AMERICA

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## ABSTRACT

We will report an investigation of the effects of changes in aerosols on clouds and precipitation patterns using the online meteorology/chemistry model (WRF-Chem) version 3.2. The domain covers much of north-eastern North America, with a focus on southern Canada, at a 12-km grid resolution. The purpose of the study is to asses the effects on clouds and precipitation of changes in aerosols that may occur due to future changes in population and emissions regulations.  This presentation will cover the initial stages of the work. The base case anthropogenic and biogenic hourly emissions for the WRF-Chem simulations were created from the 2008 annual, state- or county-wide total emission inventories for area, point and mobile sources from the U.S. EPA and the corresponding Canadian 2006 emission inventories, provided by Environment Canada.  Surrogate files for the allocation of emissions from area and mobile sources were created from GIS shape files using the Surrogate Generator Tool. The speciated, gridded and hourly emission data needed for the WRF-Chem simulation were then created using the Sparse Matrix Operator Kernel Emissions (SMOKE) system version 2.7. Satisfactory performance of the model was confirmed by comparing several one-month simulations with measured data.  Following this, preliminary studies of the effects of anthropogenic and biogenic aerosols on precipitation patterns were undertaken to establish parameters for more detailed studies to be carried out later.  These initial scenarios included runs with zero emissions (*i.e.* no chemistry), biogenic-only emissions and biogenic plus anthropogenic emissions.  The results of these will be discussed in this report, along with their implications for the design of the more detailed scenarios to follow.  In the latter, we will address the effect on precipitation in North America of changes in aerosols due to expected population and regulatory changes in the next few decades.

**Keywords:** Aerosol, cloud, precipitation, WRF-Chem, emissions

# ANALYZING AMOUNT OF HEAVY METALS OF ARSENIC AND VANADIUM IN THE SOIL OF ESFAHAN PROVİNCE

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## ABSTRACT

Nowadays, there are a numerous researches about the effect of Heavy metals pollution such as Arsenic and Vanadium in soil. Varying and destroying the physical and chemical features of soil, food chains, biodiversity and agriculture are the consequence of even the infinitesimal rising in these metals concentration. In order to do this research a region of 6800 kilometers square was selected in Esfahan province (which is located in the central land of Iran).Afterwards, sampling was done by the method of Stratified Random Sampling of the soil (with four kinds of land use types namely, urban, Industry, Agriculture, Rangeland).Results of 255 soil samples indicated that the average concentration of Arsenic in the discussed area was about 10.49 mg/l. maximal amount of Arsenic had found in industrial land(11.07 mg/l).Also Vanadium average was determined 83.41 mg/l .The highest amount of Vanadium had existed in agricultural region (89.87 mg/l ).As a result , it seems that to pollute soil, industry and agriculture sections have been played a monumental roles in this area. Existence of huge industrial factories, mines, farming lands have caused increasing concentration of these Heavy metals compared with universal standards.

**Keywords:** soil pollution, Heavy metal, Arsenic, Vanadium, Land use.

**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
**4th International Symposium and IUAPPA Regional Conference**
**10-13 September 2012 Istanbul –Turkey**

# "AIRBORNE CHEMICALS OVER RIMAC BASIN (LIMA - PERÚ), ITS SIGNIFICANCE AND DISPERSION"

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## ABSTRACT

Lima, a Metropolis (near to ten millions inhabitants) is situated at 12º L.S. and 77º M.W. That means in theory, is located in a semitropical zone, but presence and action of another odd phenomenes, like Peruvian Stream and Los Andes mountain influence, makes this city in middle of desert. Orographically, Lima occupies delta of river Rimac, a river which comes down, in only 132 Km from near 4500 m.o.s.l. until Pacific Ocean. Over this corridor it was made a novel survey of air quality, considering not only classic pollutants like particulated matter (STP, PM10), gases (CO, $SO_2$, $NO_x$), but also, heavy metals (Pb, Zn, Cr), potential oncogens (As, Cr). In a first step used process, were known methods in sampling (Hi-Vols, gases samplers), and laboratory analysis, however, in second time we assay pioneer labor, between us, by scanning microscopy. This paper intends to present the activities and results of upper mentioned survey made from sea shore to near 4500 m high.

## BACKGROUND

A vision from abroad substantiate opinions that in developing countries environmental problems, mainly pollution, actually may be "starting", and it will became important in future. It is not always true.

Here, in Peru, since long time, like 1923 (before Meuse Valley episode, 1930, considered initial pollution history), we had claims, evaluations, amendments, due to put in operation a big metal smelter and refinery, located in a small mountain community to 3700 m above sea level, and 170 km east of Lima. Simultaneous treatment of Pb, Cu and Zn, ores, smelter produces various types of metallic goods, but at sometime a mixture of airborne rich in As, Sb, Pb, particles, and other chemicals. Free generated pollutants, that time caused damage on natural pasture and by tropic chain, to domestic poor fauna, adopted at those highland cold areas. As results turn up a devastator epidemical decease, which annulet locomotion of cows and sleep. The consequences were the installation of cotrell systems, and construction of a 181 m high stack, as principal structural pollution controls. At present smelter and refinery are still going on, but are ranked, with exaggeration, among top-ten polluters in the world, by an international institute named Blacksmith.

End of fifties (xx age). **Fishing industries**. The boom of anchovy (Euralis rigens) transformation in fluor, glutted atmosphere of Lima, with loathsome adors. It was time when mass media, hence gross public, began to know and speak about "our" pollution.

In our air pollution gross events, an other landmark concern to a new smelter, specialized in Cu ores treatment, settling in 1960, this time in a littoral area, one thousand km south from Lima. Pollution generated, plenum in sulfuric gases, usually dispersed to north direction, time to time, change to south, where there is a narrow valley rich in olive crops. Sulfuric gases, in particular meteorological conditions damaged the olive, year after year during three decades. This fitotoxic action compeled to economic compensations, by appraisement of environmental authority. At present, a structural controls were established by a sulfuric acid manufacturing plant.

At finals of seventies (last contury), is announced the construction of a Zn refinery, 25 km near to Lima center. The announce provoked public alarm due to mass media comments, affirming this case will be similar, in danger, with episodes reffered above. Any way, it was very usefull to take provisions in different sences. Became urgent to make the first Environmental Impact Assessment (EIA). It was done extended during 1979-80 period. As consequence were taken important decisions previous to plant construction.

Main worries were concern to minimized generation of sulfuric gases, and after, to manage fail emissions adequeately. In this purpose was decided the use of “double contact” method in manufacturing the sulfuric acid (notwith standing 30% more costly than normal). Residual gases must be evacuate in a concentration less than 500 ppm over 690 m above sea level, dimension imposed to gain inversion layer semi-permanent in this area. In same sence was necessary to build a chimmeny. Of 260 m, which was made with special shape, carred, and because its high, supported in a knoll.

In realization of practices upper described was put in action by the Instituto de Salud Ocupacional (Occupational Health Institute), founded in 1947, which principal duties concerned in the beginning to security and welfare in the beginning to security and wefare of mining workers. After, in face to environmental raid problems, thanks its structure very well equipped in expert and materials, besides its important autonomy.

In 1992 (xx century), was promulgated the “Código del Medio Ambiente y Recursos Naturales” (Code of Environment and Natural Resources). As a consequence, it was organized a National Council, frequented with environmental authorities in each ministries. At present these governmental agencies have, in general vision a “scattered responsabilities and ineffective management, under legalistic “command and control” principle. Scientific aspects has been lagged.

## ESCENARIOS

If describe up background outcomes show singularness characteristics, the survey scenarios, biotic and abiotic, are all too peculiar.

**Orographically**, Lima occupies delta of Rimac. The scenario in question is a mountain-valley which rises from Pacific Ocean to near five km up. It is shapped by river Rimac which craggy waters descend 132 km E-W from snow capped highlands (over 4800 m), where starts to its end in the sea.

Landscape of this basin comprehended in study is so abrupt, shielding by mountains, with a slope changing between three to four m, so, in short 140 km, reached to near 5000 m up. In general **meteorological** component in Lima urban area considered adverse for better or for worse because prevalent conditions. Permanent presence of inversion layer over its atmosphere at 690 m high in average (CORPAC, 2010), which impose its grey or dark sky “waterproof” to vertical dispersion of emissions. Other parameters concern to stable temperatures, profiles of low winds speedy, absence of rainfall, no precipitations, local influences and seasonal changes.

The actual worsening of air quality, in Lima, until to be considered “mayor public health evil” finds in **antrophologic** topics, well defined and wide spread sources. One in base is incontrolled increase of population. There is an influx of rural people from rural to urban areas together with the transfer of agriculture labours to secondary and tertiary activities. Hence, poverty expands the city, and escals vehicle fleets, joint to considerable air quality challenges. An other concomitant factor. Comes from existence of government multifarious environmental agencies with diverse responsabilites and effective management. Also it is very important at this respect the individual and social behaviour.

**Lima near to sea**

**Middle of Rimac basin**

## THE SURVEY

Necesity of scoping the local levels of pollution enliven to bind over in a survey driven in Rimac Valley. Unlike background studies made encircled in downtown, this one covered such multifarious long area, divided at this purpose in “low” “medium” and “high”, well differentiated parts, as that altitude.

The aim and scope was a preliminary attempt to gain a broader understanding about pollutants and how them are cleaning or not. This, related study is designed to revise pollution levels by reviewing part the open history, and in same time to get a reasonable and scientifically defensible new adequate information. The survey, unbiased and “independent” addresses to ensure that acceptable and comparable collected data.

## FIELD TASKS

Air novel quality monitoring project began operations, in general, under “classic” criteria for sampling, testing, and analysis methods, but in a second step was assayed pioneer labor, for us, by scanning microscopy.

Collected samples were related not only to common pollutants like particulate matter (STP, $PM_{10}$), gases (CO, $SO_2$, $NO_x$), but also to a set of relative exotic heavy metals (Pb, Zn, Cd), and potential oncogens (As, Cr, VOC). All these, released by a wide spectrum of sources. Author classified these sources (aside natural ones), as generated in mining and metallurgic industries, in fisheries, in other dispersed, formal or informal factories, in public transport (tantamount to chaos in Lima) and, in very significant way, the bad habits of citizenry, including some public services.

For evaluation propouses it has been used a methodology capable to provide baseline measurements and understanding issues.

## MEASUREMENTS

Main details of the monitoring framework which has been put in place are connected first with schedule, with localization of sampling stations, and of course with measurement devices, plus accredited laboratories.

The monitoring project began operations in center city, having a twin sampler, simultaneously operating in an advanced sub-urban place. Thus, by itinerant moving two and two, synchronously, pollutant collect processes mounted to 3500 m. from sea shore in only 140 km far a way. The evaluations were carried out during one year and half, in discontinuous periods. This methodology not was decided by operators. It was imposed because the economic grant support of study was stipulated by an official agency, which policy was to deliver shares, only after approbation of partial reports and lost time proceedings.

Already a wide variety of concerns have been raised during exercise, all of which, will need to be considered to a greater or lesser degree in a wholly vision for understanding significance and behavior of pollutants over Rimac basin, up waters.

For instance, a limited number of 22 air samples has been taken using classic well classified divices, ones for particles (high-volume sampler) others for gases and vapors (manual or automatic testers). These divices were placed in sampling stations, above levels, directly influenced by random facilities. They made possible to witness air quality on urban areas (residential, industrial, commercial), and rural zones (residences, villages, flora), and other potentially sensitive receptors.

After field tasks air samples dedicates toward specialized laboratories (very short between us), where analytical procedures have abilities to give numerical data. Hence, primary objective demonstrated compliance with the applicable environmental standards. A secondary objective questioned if can be revealed existence of other unknown pollutants, plus than analized "common" ones?. Answer comes from a pioneer essay (for us) using **scanning microscopy** method.

## FINDINGS AND DISCUSSION

As consequence of comparison among data from those various sources with the particular magnitudes used in Ecology issues (ppm, pphm, µg/m$^3$), the principal substantiations may be sum up in followings:

**Particulates.** The observed mean concentrations levels were in general higher. Valors varied from 67 to 418 µg/m$^3$. For comparison purposes concentration of particulate matter distribution plots include the daily U.S. Environmental Protection Agency (EPA), shown as dashed lines. (Figure 1). Mean concentration levels determined for all sites were substantially higher than national and international standards. So, particles are most important pollutants during survey period. But it is to consider that particulates are a conglomerate of complex substances, which dangerousness depends to know the included chemicals in Hi-Vol samples, as heavy metals and oncogenes. (Figure 1)

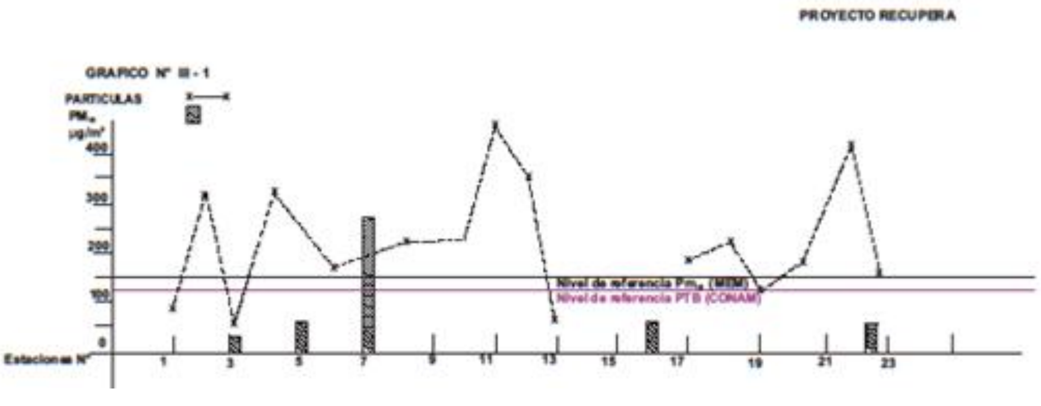


**Figure 1: STP x-------x P▨$_{10}$**

**Heavy Metals.** Peru is a miner country, so pollutants in here, are everywhere. Collected dusts were analyzed for Pb, Zn and Cd. Pb concentrations are below known standards, but its presence is spread. At this respect addition of organic compound of this metal to essence has been forsaken recently, four years ago. In relation to Cd, it has been detected in haigh concentration (58,1, 6,61, 3,0 µg/m$^3$), near to particular places where seems to exist informal, and may be clandestine activities. **(Figure 2)**

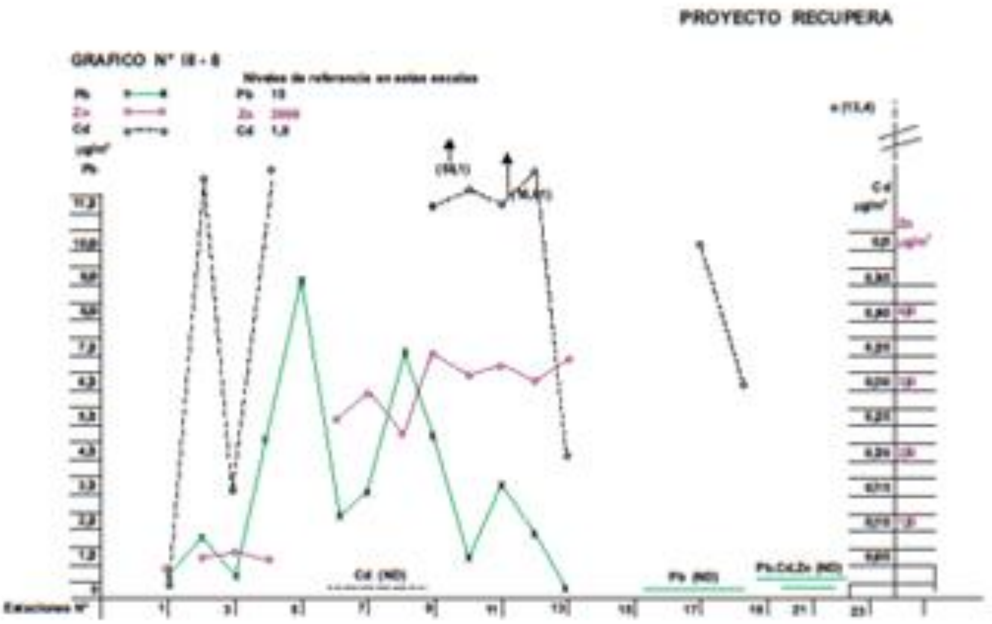


**Figure 2: PB x-------x Zn o------o Cd x…….x**

**Potential Oncogens.** Considered As, Cr, and VOC (Figure 3). They have presence in considerable concentrations. In case of As, it is common and abundant in Peruvian soils, so its presence in air maybe of natural source. The other ones exist, in some place high, e.i. 27 µg/m$^3$ for Cr total, in coincidence with station where also Cd was enough. (Figure 3)

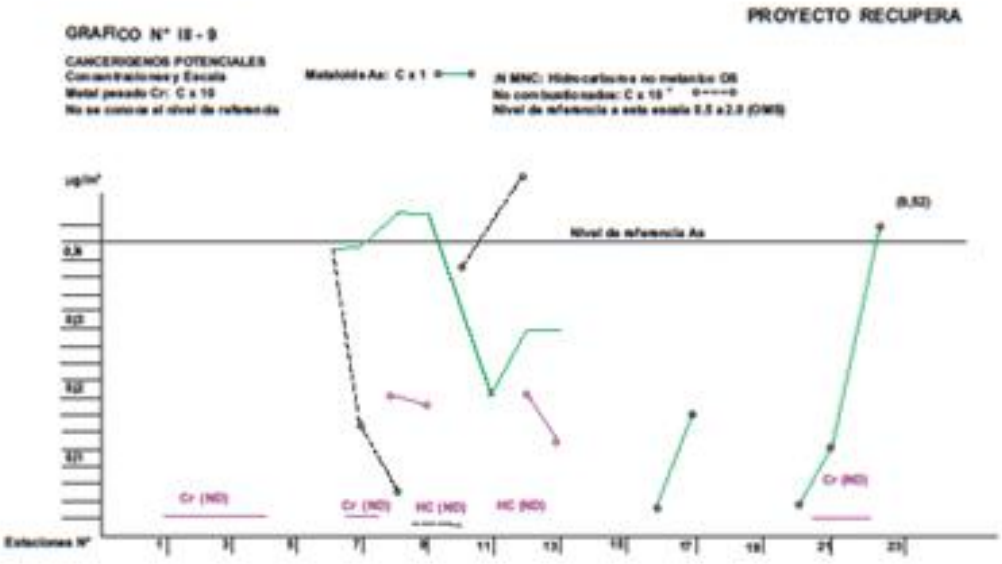


**Figure 3:** Cr ------- As o------o VOC o…….o

**Gases.** "Classic gases", $SO_2$, $NO_x$, CO, were detected, and results in general showed low magnitudes, but each one has its particularities. $SO_2$ increased its concentrations in a sub-urban town, at 800 m high and 40 km, from Lima Centre. This data is very interesting and will be refered in avance. Considered main source of this pollutant is combustible Diesel which contains more or less, 500 ppm of sulphur-s. The other pollutant ($NO_X$, CO, VOC), have multifarious sources, but mainly are concern to our public transport chaos. (Figure 4)

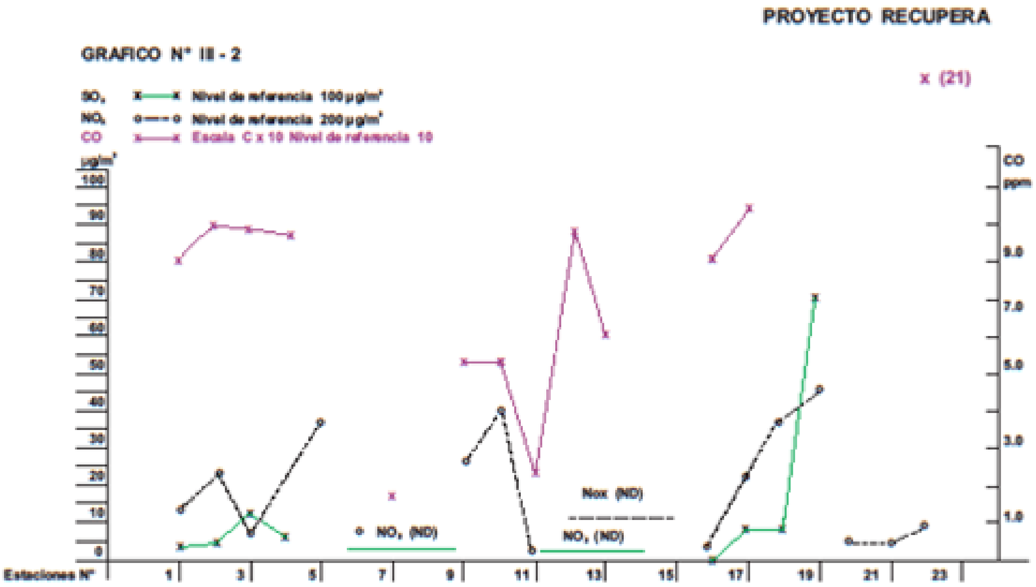


**Figure 4:** $SO_2$ x-------x $NO_X$ o…….o CO x------x

**Ozone-$O_3$.** Presence and generation of this secondary troposphere pollutant is a central point in actual survey. It means almost direct evidence, of its initial hypothesis, which defend that urban pollutants are moved from central city to up waters by winds and valley structure.

Analysis with samples get near ocean indicated concentrations less than 20 ppb (valeurs in normal air is around 60 ppb). But, measurements in samples taken in a town to 40 km (up waters), from Lima centre and 800m, above sea level revealed a phenomene of great importance. Its shows shape increasing $O_3$, hour after hour. (Figures 5 and 6).

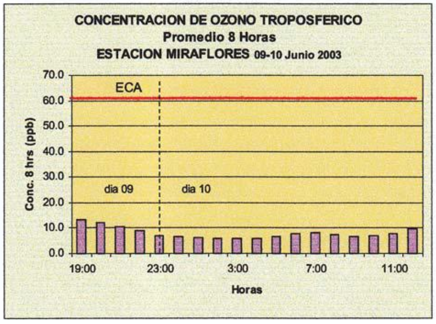


**Figure 5 Sea shore**

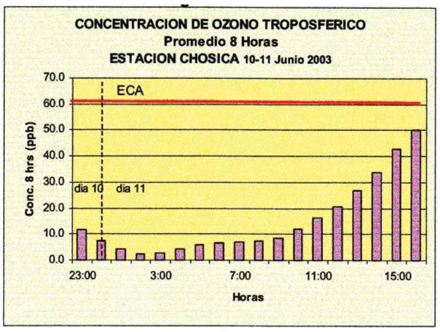


**Figure 6 at 800 m up**

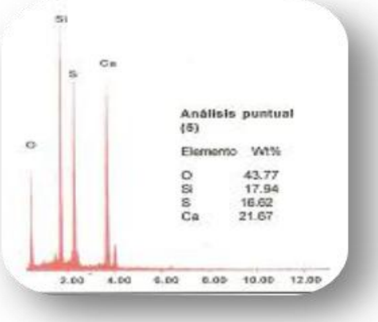
Why?. Because at that altitude sun shines plenarily, in opposite to dark (or grey) Sky over Capital. So, it reasonable to think that reaction (photolisis) is similar to those observed in smog chamber studies of auto exhaust. In other words polluted air mass generated in metropolis, raise and meet the energy necessary to ozone formation.

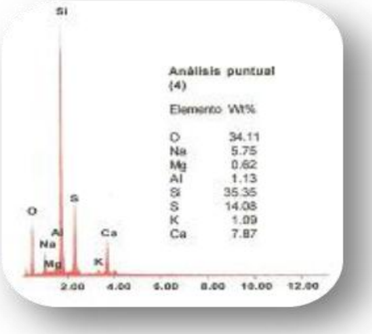
## CONCLUSIONS, APPRAISEMENT OF FINDINGS, AND PROPOSALS

The most significant conclusion of this study suggests that nature forces clean polluted air of Lima Metropolis “channeling” bad airs over corridor Rimac, up waters, transformed in an “horizontal chimney”.

Other preliminary conclusions sound:

- Presents the scope of this initial environmental evaluation out of Lima Centre.
- A general description has been presented, in which determining air borne were out lined.
- Evidence a panoramic over view of various factors not well understood or adreessed by authorities yet.
- Management and proceeding are backing, although some progess in that direction has been recently noted.
- It is obvious that the authorities attention would be draw to improve information, because is still bing generated at a hectic pace.
- Although the present results are promising, they may be confirmed by more extensive data obtained at location varying in nature from industrial and residential to rural areas, and this during different seasons of the year.





**Two addenda plus:**

- Use of **scanning microscopy**, gave us interesting data, reaffirming presence of heavy metals, and mark presence of As, Si, Al, in relative abundance, put in question if some pollutants come in of natural sources.
- In middle arca of raised valley, where was observed $O_3$ generation it is proposed to organize "green houses" for vegetables (or others) farming, thanks to **"climatic changes"** observed there.
- Finally, survey provides data against which any future changes in environmental quality can be judget.

**"Environmental care starts in knowlodge"**

**Mobil Environmental Laboratory for $O_3$**

**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
**4th International Symposium and IUAPPA Regional Conference**
**10-13 September 2012 Istanbul -Turkey**

# ICP MS DETERMINATION OF METALS IN TOTAL DEPOSITED MATTER IN ZAGREB, CROATIA

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## ABSTRACT

Monthly samples of deposited matter were collected over a one-year period at five different sites in Zagreb, Croatia: city centre, northern, southern, western and eastern parts of the city. Bergerhoff-type samplers were used to collect bulk deposition. After determining total deposited matter gravimetrically, the samples were analyzed for metals (Mn, Ni, Cu, Zn, As, Cd, Tl, Pb) by inductively coupled plasma mass spectrometry (ICP MS). Concentrations of metals were below the limit values set by the Croatian air protection legislation. Statistical methods were used to analyze the measurement data. T-test of individual samples showed a statistically significant difference between sampling sites for lead, zinc and copper. The regression analysis showed significant correlations between metals (Pb-Mn, Pb-As, Mn-Cu, As-Mn, As-Tl, Mn-Tl) at different sampling sites.

**Keywords:** atmospheric deposition, toxic metals, urban area

## 1. INTRODUCTION

Deposited matter contains substances in solid, liquid and gaseous phases, which are not integral parts of the air. They accumulate on the ground by gravity (dry deposition) or precipitation (wet deposition) from the atmosphere and contaminate soil, vegetation, materials and indirectly affect people. Total deposited matter (TDM) or bulk deposition is defined as the total dry and wet fallout collected in a container placed in an open field (Tripathi et al., 1993).

Heavy metals may spread both from natural (soil dust, sea spray, volcanic and Earth's crust activity) and anthropogenic sources (industrial and power plant emissions, civil heating systems, vehicular traffic, waste incinerators). They are generally associated with airborne particulate matter and may be transported over long distances (Morselli et al., 2003). Heavy metals emitted by combustion processes usually have relatively high solubility and reactivity, especially under low pH conditions. (Hou et al., 2005). Some heavy metals play an important role in the nutrition of plants, animals and humans (Mn, Ni, Cu, Zn), but if they occur in excess, they may produce certain toxic effects, while others (Cd, Pb) are toxic even at very low concentrations (Merešova et al. 2008). Since heavy metals generate high toxicity and high lability in atmospheric fallout, their monitoring is important both in urban and rural areas (Azimi et al., 2003).

During the past few decades, many studies on bulk deposition of metals in urban areas have been widely used to estimate the influence of atmospheric inputs of metals on the surface environment (Mijić et al., 2010).

The aim of this paper is to present the measuring results on the total atmospheric deposition of Mn, Ni, Cu, Zn, As, Cd, Tl and Pb for 2011 in order to evaluate the impact of airborne heavy metal pollution load in the urban area of Zagreb.

## 2. MATERIALS AND METHODS

Monthly samples of total deposited matter were collected over a one-year period (2011) at five different sites in Zagreb (Fig.1): city centre (C), northern (N), southern (S), western (W) and eastern (E) parts of the city.

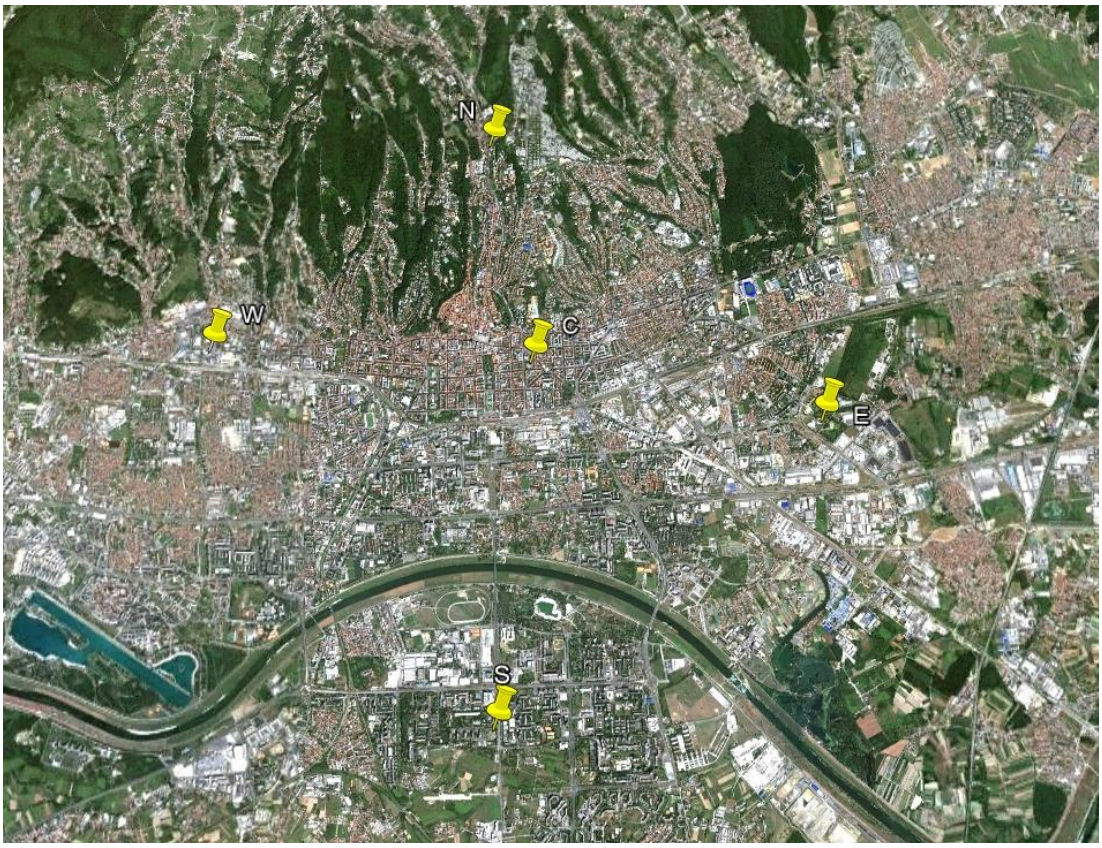

Fig. 1. Map of the sampling sites in Zagreb, Croatia.

The sampling device used to collect total deposited matter was a Bergerhoff-type deposit gauge (EN 15841:2009). Main assembly is consisted of a plastic-coated stand with a removable bird guard and bottle holder, with the overall height of 2 m and weighing approximately 6 kg. The volume of the PET collecting bottle is 1.5 L and the aperture is 120 mm in diameter. This device is used for the quantitative determination of soluble and insoluble contents of total deposited matter (Čačković et al. 2008). Atmospheric fallout was collected monthly; samples were analyzed for metals both in soluble (in this study this refers to the fraction of metals passing through an 8 μm membrane filter) and insoluble fractions (particulate fractions retained by filters). The sum of these two fractions of metal content gave the total monthly flux of that metal. The preparation of samples is shown in Fig. 2.

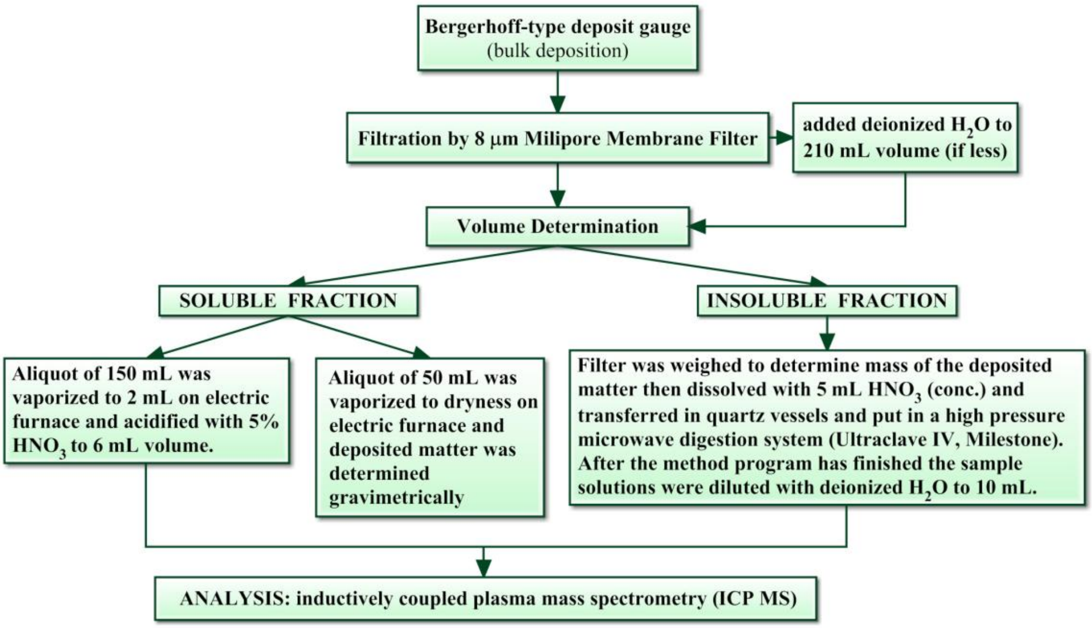

Fig. 2. Flow chart of the experimental steps

The ICP MS spectrometer was tuned to obtain an oxide ratio and doubly charged ratio less than 2 %. The carrier and make-up gas flow rate were optimized to maximize the sensitivity and minimize interferences. ICP MS analysis parameters are shown in table 1.

Table 1. ICP MS parameters

| **ICP MS operating parameters** (Agilent technologies model 7500cx) | |
|---|---|
| RF power (kW) | 1550 |
| RF matching (V) | 1.72 |
| Carrier + make up gals flow rate (L/min) | 1.07 |
| Helium gas flow rate (mL/min) | 4.0 |
| Peristaltic pump flow (rps) | 0.05 |
| Selected isotopes | $^{55}$Mn, $^{60}$Ni, $^{65}$Cu, $^{66}$Zn, $^{75}$As, $^{111}$Cd, $^{205}$Tl, $^{206}$Pb |
| Number of measurements per pek | 3 |
| Integration time per point | 0.5 for As and Cd and 0.1 for all others isotopes |
| Internal standards | Sc, Ge, Rh, Lu |
| Number of repetitions | 3 |

Data analysis included the calculation of Mn, Ni, Cu, Zn, As, Cd, Tl and Pb monthly deposition fluxes of total deposited matter expressed as microgrames per cubic meter. Descriptive statistics, t-tests and linear regression were used to analyze the measurement data. Statistical data analysis was performed using STATISTICA (version 10).

## 3. RESULTS AND DISCUSSION

Annual values of TDM and analyzed metal measured in 2011 at five sites in Zagreb are shown in Table 2. Values of TDM and metals (Ni, As, Cd, Tl, Pb) were all below the limit values set by the Croatian air protection legislation (Regulation on limit values of pollutants in the air). Limit values for Mn, Cu and Zn in TDM are not given in the Croatian air protection legislation.

The highest average value of TDM was found in the southern and the lowest in the eastern part of the city. The highest average value for Mn, Ni, Zn and Cd was found in the western part of the city, for As and Pb in the eastern and for Cu in the northern part of the city. The lowest average value for Ni, Cu and Zn was found in the eastern part of the city, for Mn, As and Cd in the southern and for Pb in the northern part of the city.

Table 2. Descriptive statistics of metals analyzed in total deposited matter at five sampling sites in Zagreb, collected over 2011

| **Sampl. site** | **Statist. param.** | **Mn** | **Ni** | **Cu** | **Zn** | **As** | **Cd** | **Tl** | **Pb** | **TDM** |
|---|---|---|---|---|---|---|---|---|---|---|
| | | **($\mu$g/m$^2$d)** | | | | | | | | (mg/m$^2$d) |
| **C** | **Range** | 12-30 | 2-6 | 9-27 | 22-44 | 0.2-0.9 | 0.1-0.4 | 0-0.04 | 2-7 | 25-173 |
| | **Average** | 19.96 | 3.05 | 19.59 | 32.61 | 0.52 | 0.20 | 0.02 | 4.57 | 68 |
| | **SD** | 4.89 | 1.07 | 5.49 | 7.42 | 0.21 | 0.14 | 0.01 | 1.16 | 38 |
| **N** | **Range** | 8-33 | 1.6-4 | 6-52 | 10-65 | 0.2-1.1 | 0.1-0.3 | 0-0.03 | 1-4 | 29-126 |
| | **Average** | 18.37 | 2.87 | 25.20 | 25.33 | 0.61 | 0.14 | 0.01 | 2.69 | 61 |
| | **SD** | 7.32 | 0.82 | 15.89 | 16.31 | 0.28 | 0.32 | 0.01 | 0.72 | 28 |
| **S** | **Range** | 9-30 | 0.4-7 | 5-17 | 12-65 | 0.1-0.8 | 0.1-0.3 | 0-0.02 | 1.6-4.5 | 35-125 |
| | **Average** | 16.41 | 2.95 | 11.30 | 26.37 | 0.43 | 0.13 | 0.01 | 2.85 | 69 |
| | **SD** | 6.36 | 1.71 | 3.67 | 14.65 | 0.21 | 0.05 | 0.01 | 0.94 | 24 |
| **E** | **Range** | 1-50 | 1.5-6 | 0.8-12 | 10-27 | 0.3-0.9 | 0.1-0.4 | 0-0.06 | 0.9-31 | 17-80 |
| | **Average** | 16.92 | 2.56 | 6.83 | 19.31 | 2.81 | 0.17 | 0.02 | 5.76 | 49 |
| | **SD** | 12.26 | 1.62 | 3.31 | 5.16 | 8.28 | 0.09 | 0.02 | 8.14 | 20 |
| **W** | **Range** | 13-31 | 1-47 | 6-29 | 21-69 | 0.2-0.8 | 0.1-1.1 | 0-0.04 | 2.9-14 | 32-121 |
| | **Average** | 20.51 | 7.67 | 16.82 | 36.06 | 0.51 | 0.26 | 0.02 | 5.28 | 64 |
| | **SD** | 5.81 | 12.59 | 5.21 | 13.66 | 0.21 | 0.29 | 0.01 | 2.90 | 26 |

T-test of individual samples showed a statistically significant difference between sampling sites for some metals. Lead content in TDM in the centre and western part of the city was significantly higher than the lead content in northern, southern and western parts of the city. Zinc content in the city centre and western part of the city was higher than in the eastern part. Copper content was found to be significantly different between all sampling sites except between the western part of the city and city centre.

Correlation coefficients (r) for all five sampling sites are shown in Table 3.

Table 3. Correlation coefficients between analyzed metals in total deposited matter at five sampling sites in Zagreb collected over 2011

| Sampling site | | Pb | Mn | Cd | Tl | Ni | As | Cu |
|---|---|---|---|---|---|---|---|---|
| **C** | **Mn** | 0.72* | | | | | | |
| | **Cd** | -0.01 | -0.02 | | | | | |
| | **Tl** | 0.58* | 0.67* | -0.11 | | | | |
| | **Ni** | -0.45 | -0.31 | -0.26 | -0.47 | | | |
| | **As** | 0.63* | 0.67* | 0.02 | 0.97* | -0.47 | | |
| | **Cu** | 0.53 | 0.38 | 0.23 | 0.11 | -0.17 | 0.16 | |
| | **Zn** | 0.11 | 0.40 | 0.17 | 0.00 | -0.30 | 0.03 | 0.00 |
| **N** | **Mn** | 0.72* | | | | | | |
| | **Cd** | -0.53 | -0.34 | | | | | |
| | **Tl** | 0.58 | 0.67* | -0.15 | | | | |
| | **Ni** | 0.06 | 0.25 | -0.56 | 0.06 | | | |
| | **As** | 0.63* | 0.67* | 0.10 | 0.72* | 0.04 | | |
| | **Cu** | 0.68* | 0.82* | -0.32 | 0.70* | 0.26 | 0.69 | |
| | **Zn** | -0.13 | 0.01 | 0.81* | -0.19 | -0.63 | 0.01 | -0.46 |
| **S** | **Mn** | 0.41 | | | | | | |
| | **Cd** | -0.08 | 0.05 | | | | | |
| | **Tl** | 0.03 | 0.49 | -0.26 | | | | |
| | **Ni** | -0.11 | -0.38 | 0.73* | -0.35 | | | |
| | **As** | 0.17 | 0.70* | -0.28 | 0.48 | -0.51 | | |
| | **Cu** | 0.20 | 0.84* | 0.11 | 0.34 | -0.25 | 0.69* | |
| | **Zn** | 0.08 | 0.76* | 0.26 | 0.35 | -0.22 | 0.48 | 0.79* |
| **E** | **Mn** | 0.48 | | | | | | |
| | **Cd** | -0.17 | 0.21 | | | | | |
| | **Tl** | 0.41 | 0.78* | 0.20 | | | | |
| | **Ni** | 0.40 | 0.26 | 0.47 | 0.75* | | | |
| | **As** | 0.42 | 0.74* | -0.06 | 0.89* | 0.43 | | |
| | **Cu** | 0.69 | 0.75* | 0.37 | 0.30 | 0.29 | 0.29 | |
| | **Zn** | 0.47 | 0.75* | 0.02 | 0.28 | -0.13 | 0.29 | 0.72* |
| **W** | **Mn** | 0.71* | | | | | | |
| | **Cd** | 0.46 | 0.76* | | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **Tl** | 0.77* | 0.87* | 0.72* | | | | |
| **Ni** | -0.41 | -0.32 | -0.33 | -0.41 | | | |
| **As** | 0.66* | 0.47 | -0.04 | 0.44 | -0.14 | | |
| **Cu** | 0.48 | -0.15 | -0.13 | 0.10 | -0.38 | -0.28 | |
| **Zn** | -0.70* | -0.36 | -0.16 | -0.45 | 0.04 | -0.27 | -0.44 |

* statistically significant, $p<0.05$

A significant correlation was found between manganese and copper in northern (0.82), southern (0.84) and eastern (0.75) parts of the city. Also, there was a significant correlation between lead and manganese (0.71 – 0.72), and lead and arsenic (0.63 – 0.66) found in the centre, northern and western parts of the city and between manganese and cadmium (0.76) in the western part of the city. Byeong-Kyu and Gee-Hyeong (2010) obtained similar results of the correlation of the above mentioned metals and traffic emissions.

A significant correlation was found between arsenic and manganese (0.67 – 0.74) and arsenic and thallium (0.72 – 0.97) at the centre, northern and eastern sampling sites. Table 3 data for manganese and thallium shows their significant correlation in the centre (0.67), northern (0.67) and eastern (0.78) parts of the city.

## 3. CONCLUSION

Annual values of the TDM and metals (Ni, As, Cd, Tl, Pb) measured at five sampling sites in Zagreb are all below the limit values set by the Croatian air protection legislation.

Statistical information shows that lead content in the centre and western part of the city is significantly higher than at other sampling sites, and that copper differs significantly between sampling sites (except for the centre and western part). Manganese content differs at eastern and western sampling sites, thallium between southern and western sites and zinc content at the city centre and western part from the eastern part of the city.

Linear regression analysis shows significant correlations between some metals. At the city centre correlations between lead, manganese and arsenic were found. Correlations between arsenic, manganese and thallium were found and the centre, northern and eastern sampling site. At the western part of the city correlation between lead and arsenic, and manganese and cadmium were found. This correlations may indicate that these metals probably come from the same sources (traffic emission, industrial facilities or road dust).

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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**10-13 September 2012 Istanbul -Turkey**

# PMF ANALYSIS OF RAINWATER DATA GENERATED FOR BLACK SEA ATMOSPHERE

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## ABSTRACT

The main objective of this study to find the sources and source regions influencing the chemical composition of rainwater samples collected at Amasra (32.38°E, 41.75°N) station located at the Black Sea coast of Turkey. Modified automated Andersen rainwater sampler was used to collect 452 wet only samples between 2005 and 2011. Collected samples were analyzed in terms of major ions ($SO_4^{2-}$, $NO_3^-$, $Cl^-$, $NH_4^+$, $Na^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$) by employing Ion Chromatograph (Dionex, DX120). Selectra 2001 model pH meter was used to measure the acidity of the samples. The volume weighted mean pH value for the rainwater samples was found as 4.88 and about 40 % of the time samples had pH lower than that of natural rainwater implying that acidity is an issue for the site. Well defined seasonal pattern for the fractional acidity ($[H+]/[\ SO_4^{2-}]+[NO_3^-]$) can be attributed to the dominance of alkaline species in atmosphere in summer season. Rainwater composition data was subjected to EPA Positive Matrix Factorization (PMF) to find the probable source profiles. PMF identified three factors as crustal, free acidity, ammonium rich and sea salt.

**Keywords:** Rainwater Chemistry, PMF, Major Ions, Black Sea

## 1. INTRODUCTION

The rainwater composition is significantly determined by the atmospheric pollution. Rainwater scavenges considerable amount of atmospheric pollutants while falling from the atmosphere and hence, forming complex mixtures (Chate and Devara, 2009; Tiwari et al., 2012). Because of its composition, rainwater has important role on the ecosystem quality. Excess wet scavenging of atmospheric pollutants particularly N and S may adversely affect the forests and grassland and results in the acidification and eutrophication of water ecosystems (Stevens et al., 2004; Bouwman et al., 2002; Tian et al., 2011). Studies of precipitation chemistry are mainly focusing on the soluble major ion concentrations (Al-Momani et al., 1995; Das et al., 2005; Alagha and Tuncel, 2003; Tuncer et al., 2001).

The chemical composition of precipitation samples collected at Amasra station was evaluated in this study by investigating the temporal variation of the measured variables. In addition, Positive Matrix Factorization (PMF) was employed to apportion the sources influencing the chemical composition of precipitation.

## 2. METHODS

Daily precipitation samples were collected by automated Andersen rain sampler between 2005 and 2011 at a station (32.38°E, 41.75°N) in Amasra, which is on the Turkish Black Sea coast. The collected precipitation samples were analyzed by a combination of analytical techniques in terms of major ions, pH and conductivity. The major ions ($SO_4^{2-}$, $NO_3^-$, $Cl^-$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, and $Na^+$) were determined by the Dionex DX120 Ion Chromatography (IC). Selectra 2001 model pH meter was used to measure the acidity of the samples.

## 3. RESULTS and DISCUSSION

### a. Comparison with Literature

The measured ionic composition of rainwater at Amasra station was tabulated in Table 1. In addition, literature values of similar stations were compiled and provided in Table 1 in order to make a comparison of values obtained from this study.

Relatively higher concentration of $Ca^{2+}$ is recorded for the Mediterranean sites (i.e., Jordan, Galilee, Antalya, Zonguldak, Istanbul and this study), which can be attributed to the influence of dust transport from North Africa. In addition, it has been previously pointed out that local soil in Turkey is also rich in terms of $Ca^{2+}$ (Başak and Alagha, 2004). As it is expected, the lowest marine tracer ($Na^+$ and $Cl^-$) concentrations were recorded for the Anatolia site due to being an inland site. Although the Istanbul station is also classified as an inland site, which is about 5 km away from the Marmara Sea shore, that is why comparably higher concentrations of marine markers were recorded for this site than the Anatolia site. The lowest pH was recorded for Amasra station as compared to other Turkish sites. However, the recorded value is higher than the ones reported for coastal China (Aas et al., 2007) and USA (Song and Gao, 2010) sites. It is interesting to note that USA site has comparably lower concentrations of acidic components ($SO_4^{2-}$ and $NO_3^-$) than the ones recorded in this study though it has the lowest rainwater acidity, which can be explained by the effective neutralization of acidic species with the higher concentration of crustal alkaline species measured in precipitation samples collected at Amasra station.

**Table 1**Comparison of measured variables with the literature (μeq/l)

| Site | Country | Time | Type | pH | $Cl^-$ | $NO_3^-$ | $SO_4^{2-}$ | $Na^+$ | $NH_4^+$ | $K^+$ | $Mg^{2+}$ | $Ca^{2+}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| This Study | Turkey | 2005-2011 | Coastal | 4.88 | 98.15 | 22.22 | 53.35 | 82.24 | 45.00 | 8.70 | 33.61 | 87.13 |
| RRL[1] | India | 1995-1997 | Coastal | 6.7 | 18 | 10 | 19.0 | 15.0 | 18.7 | 1.80 | 5.20 | 20.20 |
| Eshidiya[2] | Jordan | 2003-2004 | Coastal | 6.62 | 121.50 | 63.70 | 121.50 | 85.10 | 43.00 | 51.00 | 133.60 | 192.10 |
| LXH, GuangDong[3] | China | 2003 | Coastal | 4.57 | 18.0 | 9.0 | 86.0 | 33.00 | 13.00 | 12.00 | 9.00 | 41.00 |
| Anatolia[4] | Turkey | 1993-1998 | Inland | 6.13 | 18.00 | 28.00 | 56.00 | 16.00 | 64.00 | 8.40 | 11.00 | 74.00 |
| Galilee[5] | Israel | 1981-1990 | Coastal | 6.02 | 202 | 15.3 | 97 | 166 |  | 8.1 | 64.4 | 108 |
| Newark[6] | USA | 2006-2007 | Coastal | 4.57 | 1.08 | 1.38 | 2.64 | 0.60 | 0.64 | 0.06 | 0.05 | 0.21 |
| Antalya[7] | Turkey | 1992-1994 | Coastal | 5.17 | 390 | 70 | 113 | 450 | 1.56 | 12.1 | 94 | 140 |
| Zonguldak[8] | Turkey | 1995-1999 | Coastal | 5.15 | 42 | 27.4 | 56.45 | 139 | 85.56 | 95.14 | 161 | 137 |
| İstanbul[9] | Turkey | 2001-2002 | Inland | 5.36 | 215.11 | 78.41 | 231.89 | 113.13 | 16.41 | 73.60 | 259.84 | 473.60 |

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[1] Das et al. (2005)
[2] Al-Khashman (2005)
[3] Aas et al. (2007)
[4] Tuncer et al. (2001)
[5] Herut et al. (2000)
[6] Song and Gao (2010)
[7] Al-Momani et al. (1995)
[8] Alagha and Tuncel (2003)
[9] Başak and Alagha (2004)

### a) pH and Fractional Acidity

The frequency distribution of pH in precipitation samples was depicted in Figure 1. The pH of the rainwater in the pristine environment is around 5.6 due to dissolution of $CO_2$ in rainwater droplets (Boubel et al., 1994). It can be revealed from Figure 1 that about 40 % of the time precipitation pH is lower than 5.6, which further implies that these samples are not fully neutralized due to either presence of excess acidity or absence of bases in the precipitation.

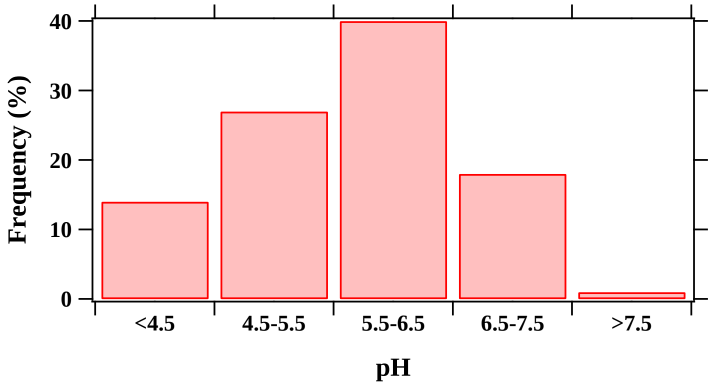

**Figure 1:** Frequency distribution of pH in precipitation samples

Annual change of mean pH value was illustrated in Figure 2. The yellow shaded area represents the ± 10% measurement uncertainty of the pH measurements. The green squares and black line correspond to annual pH values and best fitted regression line, respectively. Figure 2 showed that annual pH value in Amasra was significantly decreasing ($R^2$=0.69, $p<0.05$) with the average rate of -12 % $yr^{-1}$. Recently, Öztürk et al. (2012) found a decreasing trend for the crustal components of the particulate matter samples collected at Antalya station operated between 1993 and 2001. Although there is no concurrent data available for this study, the increase in the acidity of the precipitation observed in this study can be attributed to the decrease of the airborne crustal material that is effective in the neutralization of acidity.

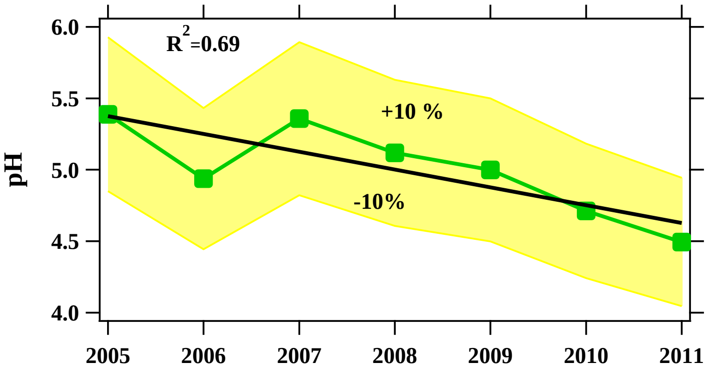

**Figure 2:** Annual volume weighted mean (VWM) pH of rainwater

Figure 3 shows the seasonal variation of fractional acidity of rainwater samples collected at Amasra station. The equivalent ratio of $H^+$ to the sum of $SO_4^{2-}$ and $NO_3^-$ provides information on the degree of neutralization capacity of precipitation. Monthly values of the corresponding ratio range from 0.03 to 0.73 in this study. Well defined seasonal pattern was observed in this ratio. The lower values of the ratio in summer imply that elevated neutralization owing to the increase airborne crustal material in this season.

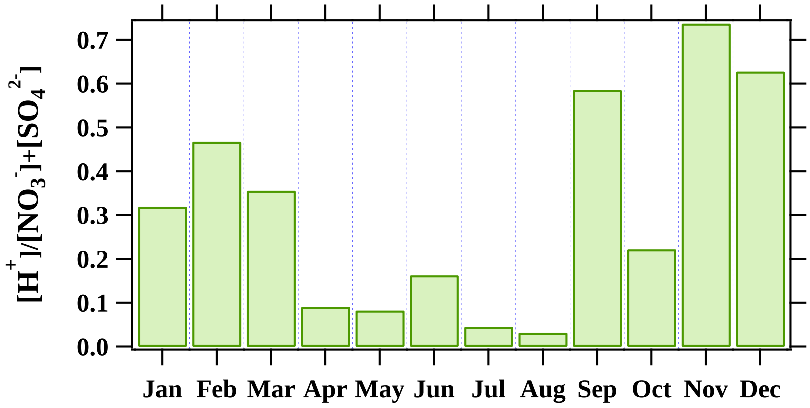

**Figure 3:** Seasonal variation of fractional acidity of rainwater

The monthly average pH and major ion concentrations measured in the precipitation samples were depicted in Figure 4. Measured variables and pH showed the similar pattern and peaked in May and August. Significantly higher mean pH value recorded in August indicating that the neutralization capacity of precipitation due to cationic variables ($NH_4^+$,$Ca^{2+}$, $Mg^{2+}$ and $K^+$) is high enough to drop the acidity resulting from the presence of major anions ($SO_4^{2-}$ and $NO_3^-$). The soil derived variables ($Ca^{2+}$, $Mg^{2+}$ and $K^+$) become easily airborne in summer since the resuspension of soil particles is enhanced by the dry soils. In contrast to this, damp soil conditions in winter prevent soil to uplift by the action of wind, which explains why winter concentrations of crustal variables are lower as compared to summer. The similar monthly pattern observed for the acidic and basic variables is due to the neutralization of secondary inorganic pollutants ($SO_4^{2-}$ and $NO_3^-$) by the cationic species on the particulate matter, which is further scavenged out from the atmosphere with rain.

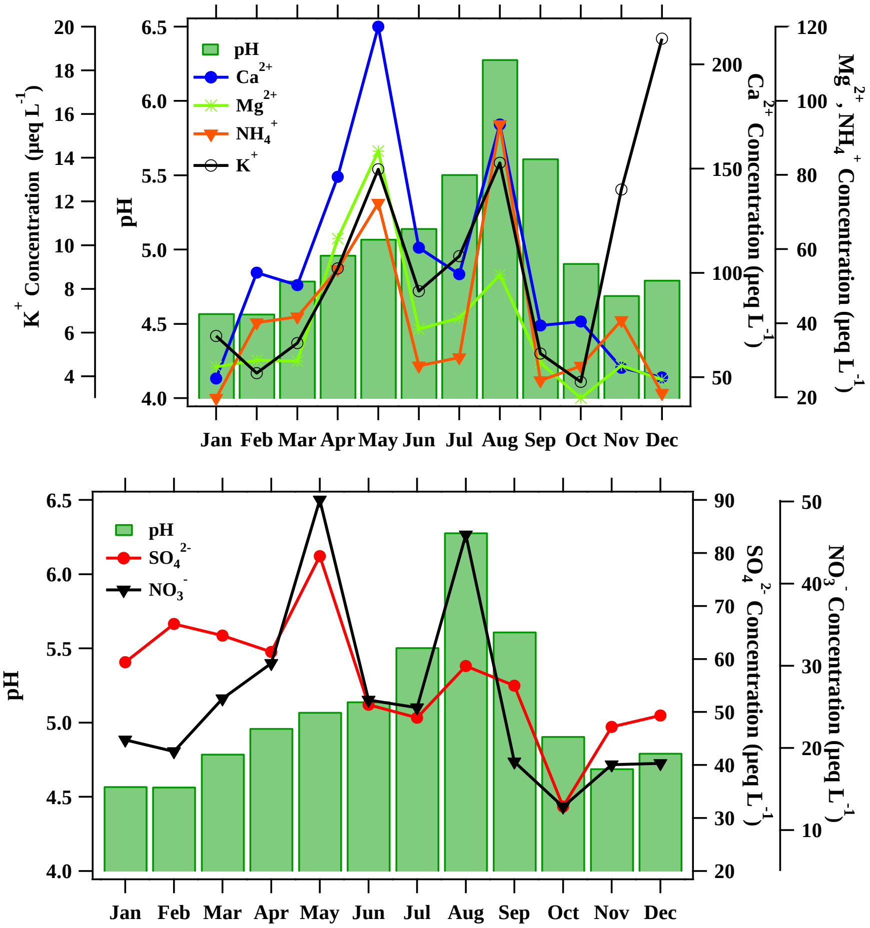

**Figure 4:** Monthly average variability of pH and major ion concentrations

## b) Positive Matrix Factorization (PMF)

In order to find the sources affecting the chemical composition of precipitation samples collected in Amasra station, EPA PMF 3.0, henceforth it will be referred to as “PMF”, (USEPA, 2008) was applied to the generated data set. This software utilizes ME-2 as the underlying engine to solve the PMF algorithm (Paatero, 1999; Mooibroek et al., 2011). The data set generated for precipitation is formed into a matrix X (nxm), where ‘n’ refers to the number of samples and ‘m’ is equal to the number of parameters in the data set. In PMF, the matrix X is divided into two sub-matrixes, G (nxp) and F (pxm), where ‘p’ is the number of sources resolved by the PMF and a residual matrix E, which accounts for the unexplained portion of the precipitation. The target “Q value” suggested by the PMF manual is the matrix size (nxm) of the concentration file (USEPA 2005). The other fit diagnostics guidelines specified in the user manual were also followed to determine the optimal number of factors in adddition to “Q value”(Chan et al., 2011; USEPA, 2008). As described by Baumann et al. (2008), an uncertainty value corresponding to each variable was calculated. The methodology reported by Kim and Hopke (2008) was used for the handling of missing and below detection limit (BDL) data. Based on the PMF analysis, four factors (sources) were retained as the final solution. Figure 5 shows the resolved source profiles.

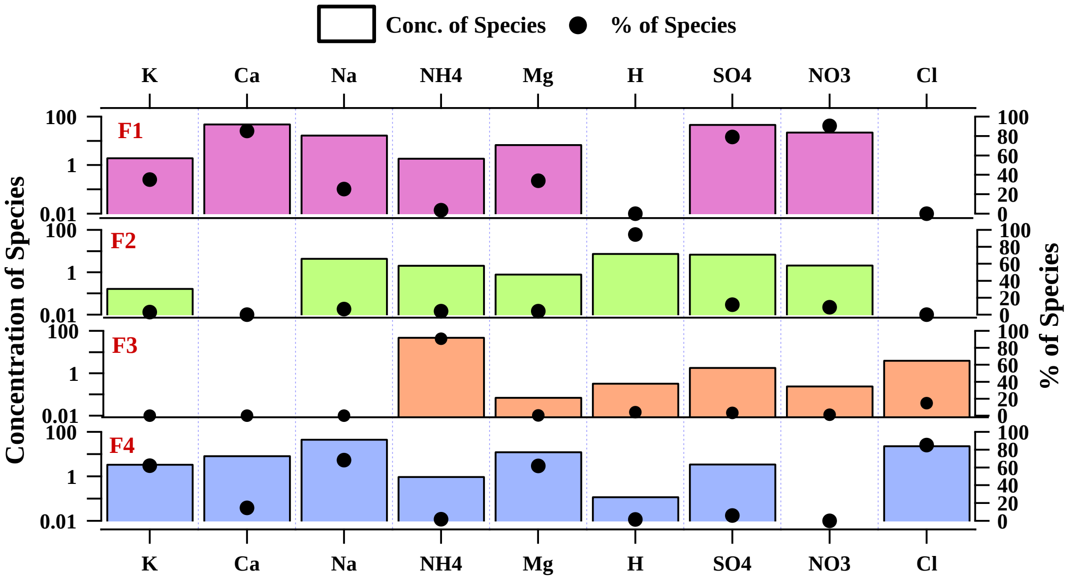

**Figure 5:** Factor profiles resolved by PMF analysis at Amasra site

Factor 1 (F1) has high loading of $Ca^{2+}$, $SO_4^{2-}$ and $NO_3^-$. The composition of this factor represents soil particles mostly in the form of $CaCO_3$ which neutralizes $H_2SO_4$ and $HNO_3$. The factor contribution plot (not shown herein) is also consistent with the temporal variability of the crustal materials (Figure 4) and peaked in the summer months. Almost 95 % of the $H^+$ is apportioned to Factor 2 (F2), which stands for the free acidity. This factor contribution plot (not shown herein) corresponding to this factor shows very similar pattern with the Figure 2. Factor 3 (F3) is an ammonium rich factor and this factor is accounted for almost 90 % of the measured $NH_4^+$. The temporal variation of this factor is completely different than the rest of the factors indicating that sources contributing to this factor are different and/or scavenging of gaseous ammonia is the main contributor to this factor. The last factor (F4) has high loadings of $Na^+$, $Mg^{2+}$ and $Cl^-$, which implies that this factor represents sea salt components of precipitation. The salts of NaCl and $MgCl_2$ associated with the particles are scavenged out with the precipitation. Since station is located on the coast, it is not surprising to observe this factor in this source apportionment study.

## 4. CONCLUSION

The following conclusions can be drawn based on the precipitation composition at Amasra stations between 2005 and 2011.

1. The volume weighted pH in the range of 4.5 to 5.4 with a mean of 4.89 and 40 % of the samples has pH lower than natural rainwater indicating forty percent of the time precipitation is acidic
2. There is a statistically significant decreasing trend in pH of the precipitation between 2005 and 2011 implying that either acidic components increased or basic species decreased during this period
3. Fractional acidity showed well defined seasonal pattern. Summer minimum is attributed to the increase of neutralization due to airborne crustal material
4. PMF identified four factors (crustal, free acidity, ammonium rich and sea salt) determining the chemical composition of the precipitation at Amasra

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# SOURCE APPORTIONMENT OF PARTICULATE MATTER POLLUTION IN THE MAJOR URBAN AREAS OF TEXAS

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## ABSTRACT

Texas, the second largest state in the United States, has several large and fast-growing urban areas and it is also home to major industrial and energy complexes located along the ports of Houston and Corpus Christi. There is an increasing concern about fine particulate matter ($PM_{2.5}$) pollution in Texas attributed to local anthropogenic sources and long-range transport of secondary aerosols. The primary objective of this study was to identify and quantify the local as well as regional sources contributing to particulate pollution in the urban areas of Brownsville, Corpus Christi, Dallas-Fort Worth and Houston. An advanced factor analysis technique, positive matrix factorization (PMF3), was employed on the measured ambient PM levels in order to identify and quantify the sources. Conditional probability function (CPF) and potential source contribution function analysis (PSCF) were employed to identify the probable local and regional source regions affecting the measured. PMF3 identified optimal solution of eight sources affecting Corpus Christi and Brownsville, nine sources in the Dallas-Fort Worth metroplex, while ten to eleven sources were apportioned for monitoring sites located in the Houston area. Secondary sulfates were identified to be the major contributor in all urban areas accounting for nearly 40% in Houston and Dallas Forth Worth, 30% in Corpus Christi, and 27% in Brownsville. The other common sources identified included traffic emissions (10-17%), biomass burns (8 -13%), crustal dust (10-13%), sea salt (4-19%) and secondary nitrates (6-10%). The PSCF analysis highlighted long range transport of secondary sulfates from anthropogenic diesel emissions in Mexico, and the continental haze from highly industrialized upwind regions in Texas, Louisiana, and along the Ohio River valley and Mississippi River region. The study results provide stake-holders and policy-makers with a detailed knowledge of the impact of local versus regional sources contributing to $PM_{2.5}$ levels in the urban areas of Texas.

**Keywords:** PMF3, potential source contribution function analysis (PSCF), coastal regions.

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# IDENTIFICATION AND APPORTIONMENT OF OZONE FORMING POTENTIAL IN AN URBAN ATMOSPHERE BY PCA-MLR

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## ABSTRACT

The aim of this study was to estimate ozone-forming potential (OFP) in ambient air through measurement of ambient volatile organic compounds (VOCs), as well as identify and apportion the sources of ambient OFP by a receptor modeling tool. For this purpose, a sampling campaign was initiated within Davutpasa Campus of Yildiz Technical University, Istanbul between March 24 and June 9, 2011. A total of 133 samples was collected representing the daytime-hour profiles of VOC concentrations. The measurement results were employed in a principal component analysis (PCA) coupled with a multiple linear regression (MLR) analysis to identify and apportion the effective sources of ambient VOCs followed by the integration of maximum incremental reactivities (MIRs) of ozone precursors to estimate ozone forming potentials of each sources. The results suggested that six major sources were effective on the formation of ambient OFP, namely solvent use (45.3%), industrial paint use (17.6%), gasoline exhaust (16.1), evaporative emissions (7.1%), diesel exhaust (10.1%), and biogenic emissions (3.6%). The results showed that although estimated lower in VOC contributions, diesel and biogenic emissions pose the highest OFP per unit emission followed by gasoline and evaporative emissions. Lowest potentials were estimated for solvent and paint use. The data obtained from such a study could provide valuable information for local authorities and decision makers for a proper control and management strategy.

**Keywords:** Istanbul, Volatile Organic Compounds, Ozone-Forming Potential, PCA-MLR

## 1. INTRODUCTION

One of the most important air pollutants in the atmosphere, tropospheric ozone, acts as an important greenhouse gas (Mickley et al., 2001) and contributes to global warming and climate change (Kulkarni et al., 2011). Several papers have been dedicated to the study of tropospheric ozone in last decades (Aneja et al., 1999; Guicherit and Roemer, 2000; Brodin et al., 2010). For instance, Jonson et al. (2001) estimated tropospheric ozone concentrations in a number of European cities including Mace Head (Ireland), Voss (Norway), Noia (Spain), and Yarner Wood (England). They reported that the concentration of tropospheric ozone ranges from 2 to 95 ppb over these cities in July. Zheng et al. (2010) measured maximum hourly tropospheric ozone concentrations as ranging from 36 to 88 ppb in Pearl River Delta (China). In an earlier paper, Zheng et al. (1998) reported similar values with a wider range in Chongqing (China).

Atmospheric photochemical reactions of especially a group of volatile organic compounds (VOCs), called ozone-precursors, is the main source of elevated ozone concentrations in the troposphere (Wark et al., 1998; Seinfeld and Pandis, 1998). This is the main reason of why most researchers focused on ambient concentrations of VOCs (Gee and Sollars, 1998; Muezzinoglu et al., 2001; Na et al., 2001; Ohura et al., 2006; Khoder, 2007; Wang and Zhao, 2008; Demir et al., 2011) and identification and apportionment of sources of ambient VOCs (Lawrimore and Aneja, 1997; Vega et al., 2000; Villarrenaga et al., 2004; Jorquera and Rappenglück, 2004; Guo et al, 2004; Song et al., 2007; Elbir et al., 2007; Demir 2011; Demir et al., 2012). VOCs are released to the atmosphere from both natural and anthropogenic sources, including, but not limited to, driving a car, painting, starting a fire, cooking, grass cutting, smoking, etc. Plants also release VOCs to the atmosphere during their metabolism. Reimann and Lewis (2007) stated that emissions related to fossil fuel production and utilization are the most important sources of anthropogenic VOCs in the atmosphere. Biomass burning, industrial emissions, biofuel utilization and waste handling activities are the other global major sources.

Most studies related to sources of ambient VOCs focus on the estimation of local sources by the use of a receptor modeling tool. For instance, Vega et al. (2000) measured 45 simultaneous samples at three different sampling stations in Mexico City (Mexico) and found that motor vehicle emissions were the most dominant sources at all stations. In another study, Santarsiero and Fuselli (2008) applied a receptor modeling tool to ambient measurement results finding out that six factors were effective on the ambient profile of VOCs. Abdul-wahab et al. (2005) also reported a source identification study, in which seven pollutant species along with four meteorological parameters were evaluated by a receptor modeling tool. In Turkey, two VOC source identification/apportionment studies were reported by Elbir et al. (2007) and Demir et al. (2012).

Current paper presents the results of a volatile organic compound source identification and source apportionment study. The identification of sources of 40 ozone-precursor species measured in ambient air was done by a receptor modeling tool, Principal Component Analysis (PCA). The contributions from the sources identified by PCA were estimated by a Multiple Linear Regression (MLR) on total ambient concentrations of volatile organic compounds. Finally, the ozone-forming potentials of the sources were calculated using Maximum Incremental Reactivities (MIR) of individual VOC species.

## 2. METHODOLOGY

### 2.1. Sampling Site

The samples were collected within the Davutpasa Campus of Yildiz Technical University, chosen for its proximity to major roads, major industrial sources, heavy residential areas, and the central bus station of Istanbul. A map of the campus and the surrounding areas is shown in Fig. 1. The campus is surrounded by a great number of light and heavy industries on the west, south, and the east sides. There are heavy residential zones extending from north-west to south of the campus. The central bus station of Istanbul is located about 1.5 km north of the campus. As expected, the campus is surrounded by highways and connection roads in all sides.

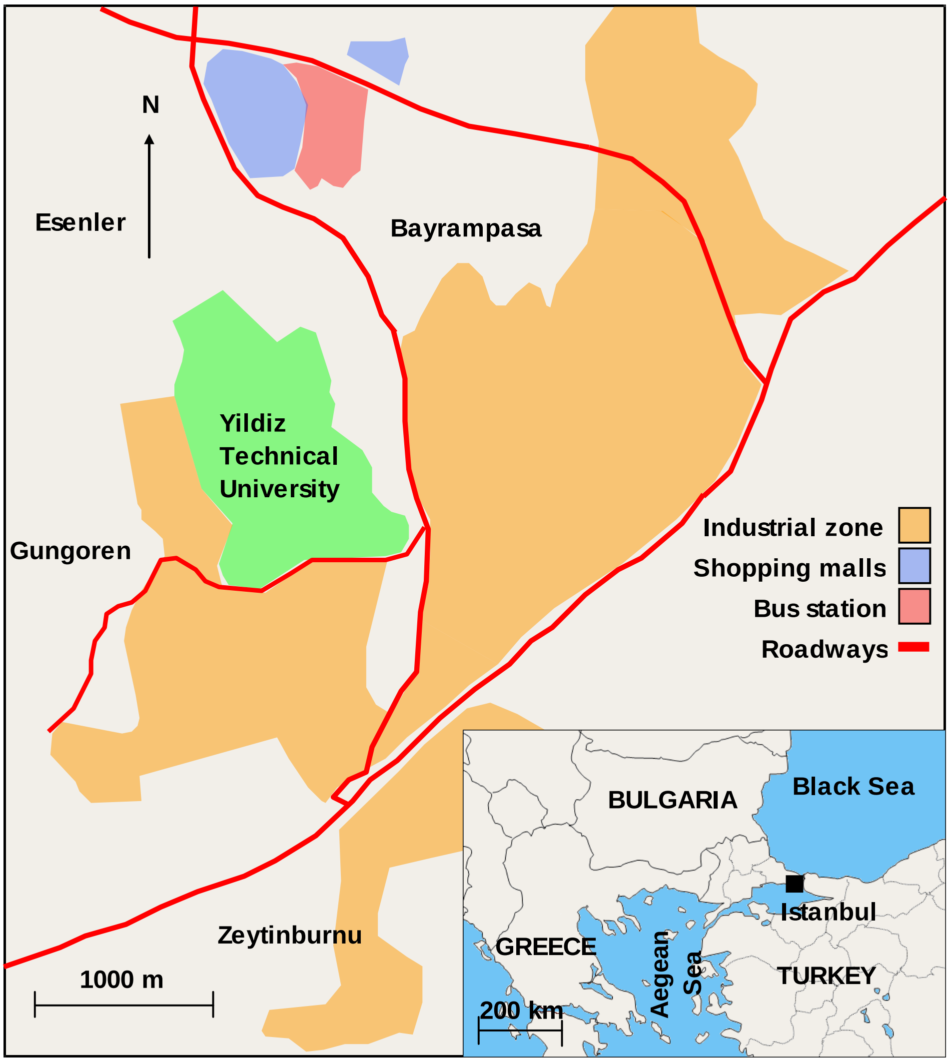

**Figure 1.** Map of Davutpasa Campus of Yildiz Technical University (Istanbul) and surrounding area (previously appeared in Demir et al., 2011).

## 2.2. Sampling and Analysis

A total of 133 ambient air samples representing daytime conditions were collected within Davutpasa Campus of Yildiz Technical University between March 24 and June 9, 2011. EPA Method TO-17 was strictly followed during the sample collection. The samples were collected by passing ambient air through Perkin-Elmer type, preconditioned adsorption tubes packed with 60 mm of Carbopack B$^{TM}$ at flowrates ranging from 40 to 100 mL.min$^{-1}$. Total sample volumes were between 25 and 60 L. The tube contents were analyzed by a Perkin-Elmer TD-GC-MS combination. The details of calibration, limits of detection, and performance measures along with QA/QC procedures were previously given in Demir et al. (2012).

## 2.3. Source Identification and Apportionment

Identification of sources of ambient volatile organic compounds were performed by application of a principal component analysis on the daytime measurement results (Demir et al., 2012). Principal component analysis is a factor analytical method to search for dominant factors behind a physical phenomenon by reducing multivariable data sets to interpretable factors. It can be used for identification of sources of volatile organic compounds measured at a receptor site (Guo et al., 2006). In order to employ PCA to reveal possible sources in a receptor site, a great number of ambient measurements of several VOC species is necessary. PCA suggests that this dataset includes fingerprints of the major sources around. The details of PCA theory can be found in Seinfeld and Pandis (1998).

PCA can only be used for source identification. The results of a PCA analysis reveals eigen values and corresponding eigen vectors of a correlation matrix, which is formed using the concentration matrix. In order to estimate the source contributions, a multiple linear regression analysis can be employed. For MLR, the rotated eigen vectors are used as independent variables and the total VOC concentrations are the dependent ones. The regression constants are then interpreted for source contributions.

Finally, the source profiles (rotated eigen vectors of the correlation matrix) from the PCA were used to estimate ozone-forming potentials (OFPs) for each individual source category. OFP for each source was estimated by multiplying Maximum Incremental Reactivity (MIR, Table 1) of each individual VOC species with factor loading of that VOC in the associated source profile. The results were combined with the MLR results and interpreted for contributions of sources to total OFP.

**Table 1.** Maximum incremental reactivities of individual VOC species (Partly adapted from Demir and Saral, 2012)

| **Species** | **Abbreviation** | **MIR*** **(g $O_3$ / g VOC)** | **Species** | **Abbreviation** | **MIR** **(g $O_3$ / g VOC)** |
|---|---|---|---|---|---|
| 2-methylbutane | 2MBTN | 1.38 | b-pinene | BPINEN | 4.4 |
| 2,3-dimethylbutane | 23DMBT | 1.07 | Cyclopentane | CPNTAN | 2.4 |
| 2-methylpentane | 2MPNTN | 1.5 | Methylcyclopentane | MCPNTN | 2.8 |
| 3-methylpentane | 3MPNTN | 1.5 | Cyclohexane | CHXAN | 1.28 |
| Hexane | HEXANE | 0.98 | Methylcyclohexane | MCHXN | 1.8 |
| 2,4-dimethylpentane | 24DMPT | 1.5 | Benzene | BENZEN | 0.42 |
| 2-methylhexane | 2MHXN | 1.08 | Toluene | TOLUEN | 2.7 |
| 2,3-dimethylpentane | 23DMPT | 1.31 | Ethylbenzene | ETBNZN | 2.7 |
| 3-methylhexane | 3MHXN | 1.4 | m&p-xylene | MPXLN | 7.4 |
| Heptane | HEPTAN | 0.81 | Styrene | STIREN | 2.2 |
| 2-methylheptane | 2MHPTN | 0.96 | o-xylene | OXLEN | 6.5 |
| 3-methylheptane | 3MHPTN | 0.99 | Isopropylbenzene | IPBNZN | 2.2 |
| Octane | OCTAN | 0.6 | Propylbenzene | PRBNZN | 2.1 |
| Nonane | NONAN | 0.54 | p-ethyltoluene | PETOLN | 2.16 |
| Decane | DECAN | 0.46 | m-ethyltoluene | METOLN | 2.16 |
| Undecane | UNDCN | 0.42 | o-ethyltoluene | OETOLN | 2.16 |
| 1-pentene | 1PNTEN | 6.2 | 1,2,4-trimethylbenzene | 124TMB | 8.8 |
| t-2-pentene | T2PNTN | 8.8 | 1,2,3-trimethylbenzene | 123TMB | 8.9 |
| c-2-pentene | C2PNTN | 8.8 | 1,3,5-trimethylbenzene | 135TMB | 10.1 |
| a-pinene | APINEN | 3.3 | 1,4-diethylbenzene | 14DEBN | 1.98 |

* Maximum incremental reactivities are from Carter (1994)

## 3. RESULTS

Average daytime concentrations of 40 species of VOC along with their standard deviations and several other descriptive statistics are given in Demir (2011). The four factors extracted by the application principal component analysis are shown in Table 2.

**Table 2.** Factors extracted by principal component analysis (Adapted from Demir, 2011)

| VOC Species | Factor 1 | Factor 2 | Factor 3 | Factor 4 |
|---|---|---|---|---|
| **EigenValues** | 29.91 | 3.74 | 1.58 | 1.34 |
| 2MBTN | 0.289 | 0.361 | 0.311 | 0.657 |
| 23DMBT | 0.897 | 0.206 | 0.363 | 0.101 |
| 2MPNTN | 0.930 | 0.166 | 0.310 | 0.065 |
| 3MPNTN | 0.938 | 0.158 | 0.287 | 0.065 |
| HEXANE | 0.950 | 0.157 | 0.238 | 0.085 |
| 24DMPT | 0.907 | 0.261 | 0.309 | 0.084 |
| 2MHXN | 0.699 | 0.251 | 0.578 | 0.252 |
| 23DMPT | 0.653 | 0.472 | 0.496 | 0.265 |
| 3MHXN | 0.589 | 0.499 | 0.579 | 0.212 |
| HEPTAN | 0.464 | 0.544 | 0.637 | 0.192 |
| 2MHPTN | 0.444 | 0.589 | 0.574 | 0.256 |
| 3MHPTN | 0.354 | 0.445 | 0.499 | 0.390 |
| OCTAN | 0.277 | 0.778 | 0.466 | 0.065 |
| NONAN | 0.324 | 0.731 | 0.504 | 0.110 |
| DECAN | 0.497 | 0.459 | 0.666 | 0.198 |
| UNDCN | 0.447 | 0.623 | 0.591 | 0.140 |
| 1PNTEN | 0.133 | 0.130 | 0.133 | 0.784 |
| T2PNTN | 0.209 | 0.889 | 0.262 | 0.163 |
| C2PNTN | 0.082 | 0.940 | 0.086 | 0.06 |
| APINEN | 0.110 | 0.734 | 0.258 | 0.358 |
| BPINEN | 0.142 | 0.855 | 0.153 | 0.283 |
| CPNTAN | 0.674 | 0.521 | 0.154 | 0.260 |
| MCPNTN | 0.948 | 0.184 | 0.228 | 0.090 |
| CHXAN | 0.907 | 0.262 | 0.289 | 0.115 |
| MCHXN | 0.535 | 0.469 | 0.616 | 0.253 |
| BENZEN | 0.089 | 0.405 | 0.243 | 0.716 |
| TOLUEN | 0.696 | 0.334 | 0.572 | 0.145 |
| ETBNZN | 0.341 | 0.250 | 0.753 | 0.335 |
| MPXLN | 0.394 | 0.208 | 0.827 | 0.263 |
| STIREN | 0.239 | 0.256 | 0.854 | 0.097 |
| OXLEN | 0.378 | 0.251 | 0.733 | 0.373 |

| | | | | |
|---|---|---|---|---|
| IPBNZN | 0.340 | 0.694 | 0.516 | 0.246 |
| PRBNZN | 0.465 | 0.570 | 0.624 | 0.233 |
| PETOLN | 0.470 | 0.565 | 0.641 | 0.172 |
| METOLN | 0.422 | 0.625 | 0.609 | 0.166 |
| OETOLN | 0.451 | 0.610 | 0.606 | 0.173 |
| 124TMB | 0.459 | 0.611 | 0.605 | 0.191 |
| 123TMB | 0.494 | 0.556 | 0.636 | 0.157 |
| 135TMB | 0.452 | 0.618 | 0.594 | 0.192 |
| 14DEBN | 0.351 | 0.601 | 0.541 | 0.182 |

The factors shown in Table 2 were interpreted by Demir (2011) and summarized here. The first factor was rich especially in hexane, 2-methylpentane, 3-methylpentane, methylcyclopentane, and cyclohexane. This factor was interpreted as emissions related to "*industrial solvent use*". The highest eigen value was obtained for this factor, representing the strength of solvent use emissions. The second factor was characterized by high loadings of octane, nonane, undecane, t-2-pentene, and some alkylbenzenes, which represent diesel vehicle emissions. The factor was also rich in pinenes, the characteristic emissions from biogenic sources. Thus, the second factor was named as "*diesel vehicle + biogenic emissions*". The higher loadings of especially xylenes, styrene, decane, and some other alkyl benzenes suggested that this factor stands for "*general industrial paint use*." Finally, the fourth factor, being rich especially in benzene and 1-pentene along with 2-methylbutane, was attributed to "*gasoline vehicle + evaporative emissions*".

Contributions of these sources to ambient VOC concentrations within Davutpasa campus of Yildiz Technical University were estimated by regressing these source factors on the total VOC concentrations (Demir, 2011). A simple assumption from Demir (2011) that biogenic indicators are only pinenes (α-pinene and β-pinene) could further categorize the interpretation of contributions from both diesel vehicle emissions and biogenic emissions. A similar approach can be employed to further separate gasoline vehicle emissions and evaporative emissions by simply assuming that the only indicator of evaporative emissions is 2-methylbutane. These simplifying assumptions made it possible to separate these two groups of sources that PCA was not able to. Finally, the factor loadings in each source profile obtained by the application of PCA were multiplied by MIR values of associated VOC species to calculate ozone-forming potential profiles from these source categories. The contributions of individual sources and estimated OFPs are shown in Table 3.

**Table 3.** Estimated contributions of interpreted sources to ambient VOC and OFP (partly adapted from Demir, 2011)

| **Source** | **Mass Contribution (μg.m$^{-3}$)** | | **Percent Contribution (%)** | | **Average potential (g O$_3$ per g VOC emitted)** |
|---|---|---|---|---|---|
| | **To ambient VOC** | **To ozone-forming potential** | **To ambient VOC** | **To ozone-forming potential** | |
| Solvent use | 37.62 | 94.1 | 50.4 | 45.3 | 2.50 |
| Paint use | 12.34 | 36.5 | 16.5 | 17.6 | 2.96 |
| Gasoline exhaust | 11.03 | 33.52 | 14.8 | 16.1 | 3.04 |

| | | | | | |
|---|---|---|---|---|---|
| Evaporative emissions | 4.83 | 14.68 | 6.5 | 7.1 | |
| Diesel exhaust | 6.47 | 21.28 | 8.7 | 10.3 | 3.29 |
| Biogenic emissions | 2.28 | 7.5 | 3.1 | 3.6 | |
| **Total** | **74.6** | **207.6** | **100.0** | **100.0** | |

The highest contribution to ozone-forming potential was from the emissions related to the solvent use (45.3%) followed by paint use (17.6%) and gasoline exhaust (16.1%). The lowest potential was estimated for biogenic emisisons (3.6%). The results were similar for contributions of each individual source to ambient VOC concentrations.

## 4. CONCLUSIONS

Source identification and apportionment of ozone-forming potentials were performed in this study. The source identification was done by the use of principal component analysis on the measurement results of 40 ambient VOC species (ozone-precursors) in 133 samples representing daytime conditions from March 24 to June 9, 2011. The source contributions were determined by multiple linear regression of source factors extracted by PCA on the total concentration of ambient VOCs. Although PCA extracted six source categories in four factors, a simplifying assumption was employed to further separate the source categories into six individual groups, namely solvent use, paint use, gasoline exhaust, evaporative emissions, diesel exhaust, and biogenic emissions. Average contributions of these sources to ambient VOC concentrations were 37.62, 12.34, 11.03, 4.83, 6.47, and 2.28 µg.m$^{-3}$, respectively summing up to 74.6 µg.m$^{-3}$ (the total concentration of these VOC species were 74.8 µg.m$^{-3}$ on average). It was found that most ambient VOCs originate from anthropogenic sources (96.9%) and a minor fraction from natural sources (3.1%).

Although emissions related to solvent use were estimated to contribute 50.4% of the total ambient VOC concentrations, their contribution to OFP was slightly lower (45.3%). In contrast, percent contributions of all other source categories to OFP were slightly higher than ambient VOC concentrations. The main reason for this difference was distinct loadings of each individual VOC species in different source profiles extracted by PCA, as a result of which estimated OFPs varied between sources. The lowest OFP was calculated for solvent use (2.50), leading to lower contribution to OFP, while the OFP for biogenic emissions and diesel vehicle exhaust was the highest (3.29). However, it should be noted that although lower in average OFP, anthropogenic sources contribute a considerably major fraction of tropospheric ozone formation potential due to their high abundance in ambient air.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# AIR QUALITY OF MUMBAI WITH SPECIAL REFERENCE TO VARIATION IN GROUND LEVEL OZONE CONCENTRATIONS

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## ABSTRACT

In the present work secondary data was obtained from Maharashtra Pollution Control Board's (MPCB) continuous air quality monitoring site at Bandra (Mumbai) from 2008-2009 and analyzed with special reference to ground level ozone. The hourly permissible limit of Central Pollution Control Board was exceeded 119 times, whereas the 8-hourly permissible limit exceeded 21times. The maximum concentration of ozone (379.6µg/$m^3$) was observed in post monsoon season. The correlation of ozone concentrations with meteorological parameters and precursor pollutants was also studied. The study supports the findings that formation of ozone is not just dependent on the availability of precursors but is also dependent upon various other meteorological parameters as well.

**Keywords:** Ground Level Ozone, Mumbai, Air pollution, Secondary pollutant, Correlation of Ozone.

## 1. INTRODUCTION

Ozone ($O_3$) is a colourless, reactive oxidant gas that is a major constituent of atmospheric smog. Unlike other air pollutants it is not emitted by any specific source; but is formed in the atmosphere as a secondary pollutant by the photochemical reactions of sunlight (U.V. rays) and nitrogen oxides (NOx), facilitated by a variety of volatile organic compounds (VOCs), which are photo chemically reactive in nature ***(Liu et al., 1987, World Bank Group, 1998)***. Ground Level Ozone (GLO) thus is increasingly becoming a major topic of concern not only because of its increasing concentrations but also because of its adverse impacts on plants and animals including humans caused, even at low concentrations.

The effect on humans and animals occur above 50 ppb, which include reduced lung function, lung irritation and in extreme cases and mortality ***(WHO, 2006)***. Clinical studies have documented an association between short-term exposure to ground-level ozone at concentrations of 200–500 µg/$m^3$ and mild temporary eye and respiratory irritation as indicated by symptoms such as cough, throat dryness, eye and chest discomfort, thoracic pain, and headache ***(WHO, 1987)***.

In the present study secondary data of precursor pollutants and meteorological parameters is obtained from MPCB and analysed to study the trend of ground level ozone.

## 2. METHODOLOGY

The site is surrounded on the western side by Arabian Sea, while the southern side is marked by urban areas of the city of Mumbai. A small portion on the south-west of the city is covered by a bay (Mahim Bay); whereas the suburban areas cover the adjoining boundaries on the north and east side of the city. It is also important to note that both airports of the city are situated on the North and North-East side and the major one being on the North-east side is a domestic and international airport. Western express highway runs very close to the monitoring site which experiences a heavy traffic during peak hours. Data is obtained from MPCB's continuous air quality station located at Govt. Polytechnic College, Bandra **(Figure 1)**. The continuous monitoring system has been installed at the present site in the year 2007, which is manufactured by Chemtrols and provides data on instantaneous and hourly basis for all the pollutants monitored. But for the present study the data is obtained for hourly average basis from 1st Jan 2008 to 31st Dec 2009. The details regarding the sampling procedure and the detection methods for the parameters monitored are provided in **Table 1**.

Mumbai being located in the tropical climatic zone experiences distinct seasons. Summer is marked by hot and dry climate which lasts from March to May which is then followed with a seasonal precipitation commonly known as monsoon during June to September. During this season most part of the country experiences precipitation and thus the air quality is relatively cleaner in this season. The Post monsoon is experienced in October and November, where the temperature again rises and hot and humid climatic conditions prevail. Moderately cold season of winter is experienced from December to February.

## 3. RESULTS AND DISCUSSION

The hourly data obtained from MPCB was divided into four seasons and filtered for any outliers by administering the 4sigma test in statistics. For the purpose of correlation, values lying outside the range were replaced by median value for each parameter. The annual average concentration of $PM_{10}$ was observed to be 157.45 $\mu g/m^3$ and 150.84 $\mu g/m^3$ in 2008 and 09 respectively, which is twice more than the prescribed standards of 60$\mu g/m^3$ by the Central Pollution Control Board (CPCB). In case of NOx and CO the observed concentration reported as 65.54, 2.06 and 74.26, 2.26 $\mu g/m^3$ in 2008 and 2009 respectively exceeded the annual average standard marginally. (NOx: 40$\mu g/m^3$; CO: 2$\mu g/m^3$). The annual average of Benzene was found to be below standard of 5$\mu g/m^3$. The hourly average for ozone during the monitoring period was observed to be 27.87 and 34.93 in 2008 and 2009. The reason for the standard deviation to be higher than mean can be explained with high skewness (2.28) of the data which was observed to be skewed on the left.

The one hourly permissible limit of CPCB (180 $\mu g/m^3$) was exceeded 42 times in 2008 and 149 times in 2009; whereas the 8 hourly permissible limit (100 $\mu g/m^3$) was exceeded 21 and 67 times in 2008 and 2009 respectively. The descriptive statistics of precursor pollutants and meteorological parameters are described in **Table 2.**

**Seasonal variations:** It is known that ozone is a secondary pollutant formed by the photochemical reactions, among primary pollutants and major one of them is NOx. The reactions which lead to the formation of ozone has been explained elaborately elsewhere ***(Guttikunda, 2009 and Royal Society, 2008)***. In the present study ozone peak was observed during post monsoon season and the highest value was observed to be 252.10 $\mu g/m^3$ and lowest was 1 $\mu g/m^3$. The seasonal variation of GLO for entire monitoring period is depicted in **Figure 2**. The same season experienced the highest number of hourly excedances i.e 89 times and eight hourly standard 40 times of the prescribed standards. Similar concentration was observed in Pune, western part of India, where ozone concentrations are reported the highest (80–100 μg/m$^3$) in summer and lowest (8–14 μg/m$^3$) in monsoon (***Debaje and Kakade, 2009).*** Other studies conducted in the city of Ahmadabad were peak concentrations of 93.8±27.6 μg/m$^3$ were observed in winter season ***(Lal et al., 2000)***. Many studies conducted for assessing the seasonal variation in GLO agree that the concentration of ozone is lowest during the monsoon season ***(Naja and Lal, 1996, Naja et al., 2003, Debaje et al. 2003; Debaje and Kakade, 2009).*** There is a slight variation in ozone concentration in other cities, Delhi (68-252 µg/m$^3$) in winter high altitudinal zone of Mt. Abu (206 µg/m$^3$) where maximum concentration was reported in winter season ***(Singh et al., 1997; Naja et al., 2003)***.

The variability in the ozone maxima at different locations can be due to the change in wind pattern of the study area ***(Naja et al., 2003)***. The higher concentrations in summer can be attributed to the increase in surface temperature and increase in precursor gas concentrations ***(Debaje and Kakade, 2003)***. While, due to the change in wind pattern in the country after the monsoon season, the polluted wind from urban areas gets transported to the downwind sites, thereby increasing the precursor gas concentration in the respective region. Also the other reason for increase in concentration can be due to the lack of vertical mixing experienced during winter, which traps the gases and also allows a higher lifetime for ozone.

**Diurnal Variation:** Since ozone formation is dependent upon photochemical reactions GLO is supposed to reach peak near afternoon and decrease during the evening. Most of the studies so far reported that the ozone concentration follows the typical diurnal trend showing an increase in the afternoon and low concentration during the night time (***Debaje and Kakade, 2006; Londhe et al., 2008***). The average diurnal variation, shows that maximum average $O_3$ concentration was 74.16 µg/m$^3$ in the afternoon (16:00h), while the highest hourly concentration was observed to be 250.8 µg/m$^3$ (at 18:00h) and minimum average was 17.08 µg/m$^3$ in the morning (07:00h), whereas, the lowest concentration of 1 µg/m$^3$ was observed several times at night.

**Correlation of Ozone with Meteorological Parameters and Pollutants:** The correlation of ozone was carried out using the Pearson's correlation method in the statistical software SPSS version 17. Initially correlation was carried out for 19 parameters; the correlation of ozone with rainfall, air pressure, Sulphur dioxide ($SO_2$) and Vertical wind speed was negligible in all the seasons and hence is not reported. The correlation for rest of the parameters is presented is **Table 3**.

**Correlation with Pollutants:** Pearson's correlation test was applied to the seasonal data sets at the significance level of 0.01. The correlation of ozone with the precursor pollutants at the monitoring site is mixed in nature and hence it is difficult to decide their role in ozone formation. The correlation of ozone with all the precursor pollutants is negative in post monsoon and winter season, but mixed in summer and monsoon. $NO_x$ exhibits strong negative correlation of -0.460 with ozone in winter season. Study conducted by ***Naja et al.,2003***; at Mt Abu a high altitude site shows that a weak negative correlation of ozone with NO but a weak positive correlation with CO was reported explaining a possibility of incomplete photochemical processes. But in the present study it is observed that CO expresses a weak negative correlation with ozone in all the seasons except monsoon. This can be explained as, since the study area is located in coastal zone, there is a possibility of completion of photochemical processes due to higher ambient temperatures and solar radiation.

In some cases the relationship of ozone with $PM_{10}$ is reported to be negative suggesting destruction of GLO (***David et al., 2010)***. The correlation with $PM_{10}$ as well as $PM_{2.5}$ was observed to be positive in summer and monsoon while it was negative in the post monsoon and winter during which high ozone concentrations were recorded.

**Correlation with Meteorological Parameters:** Amongst the meteorological parameters considered in the **Table 2** the correlation of ozone is positive with temperature (0.505) in winter season, similar observation was reported by ***Debaje and Kakade, 2006 and Salve et al., 2007***. The correlation of ozone with relative humidity was found to be strongly negative in summer and weak in post monsoon and winter. One of the reasons for higher concentration of ozone in post monsoon season can be due to the wind direction which has a weak positive correlation with ozone.

It is important to note that during post monsoon and winter season the predominant wind direction to the monitoring site is from north, north-east and north-west. It has been already mentioned earlier that there are two airports located on the north forming an arc from north-east to north-west direction. So there is a possibility that the air pollutants from aeroplane exhausts are brought to the monitoring site thereby increasing the concentrations.

There are other studies which also report similar findings that in spite of favourable conditions in summer season the concentration of ozone is higher in winter ***(Debaje and Kakade, 2006).***

## 4. CONCLUSIONS

The diurnal, seasonal and annual variation of ozone was studied to find out the factors influencing ozone formation at the present site. It was observed that the permissible limits for $NO_x$ ad CO marginally exceeded the annual standards prescribed by the CPCB, whereas the ozone concentrations exceeded consistently exceeded the standards in post monsoon and winter season. To understand the behaviour of ozone in detail, Pearson’s correlation was applied to seasonally divided data sets. From the findings of the study it can be said that ozone varies greatly from season to season. In present study GLO concentration is higher in post monsoon season which is unlike other studies reported in India. The relationship of precursor pollutants changes with GLO change in season. Major influence of meteorology not only on ozone formation but on the precursors as well needs to be studied in further detail.

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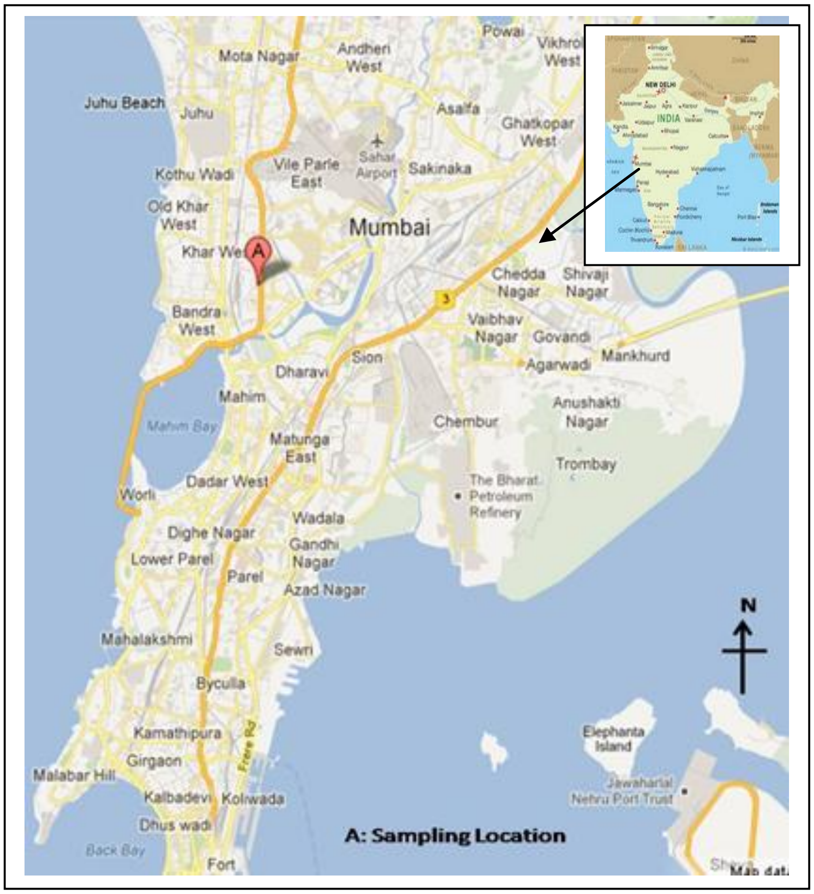

**Figure 1 : MPCB Monitoring Location at Bandra, Mumbai**

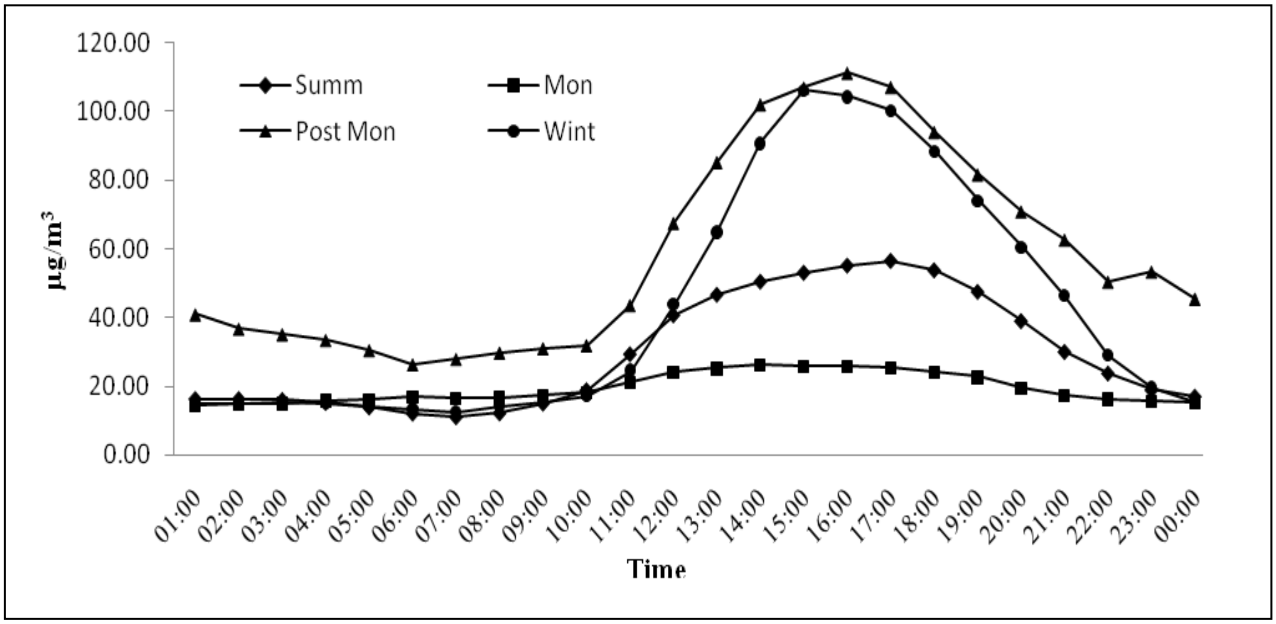

**Figure 2 : Seasonal Variation of Ozone During the Monitoring Period**

**Table 1 : Sampling Methodology and the Detection Methods**

| Sr. No. | Pollutant | Technique | Range | Detection Limit |
|---|---|---|---|---|
| **1** | Sulphur Dioxide | UV Fluorescence | 0-50 ppb, 0-20 ppm | 0.4 ppb |
| **2** | $H_2S$, TRS, TS | UV Fluorescence | 0-50 ppb, 0-20 ppm | 0.4 ppb |
| **3** | Oxides of Nitrogen $NO-NO_2-NOx$ | Chemiluminescence | 0-50 ppb, 0-20 ppm | 0.4 ppb |
| **4** | Ammonia | Chemiluminescence | 0-50 ppb, 0-2000 ppb | 1 ppb |
| **5** | NOy | Chemiluminescence | 0-50 ppb, 0-2000 ppb | < 50 ppt |
| **6** | Carbon Monoxide | Gas Filter correlation | 0-1000 ppm | 0.04 ppm |
| **7** | Carbon Dioxide | Gas Filter correlation | 0-2000 ppm | <0.2 ppm |
| **8** | Nitrous Oxide $N_2O$ | Gas Filter correlation | 0-1000 ppm | <0.04 ppm |
| **9** | Ozone | UV Photometric | 0-100ppb, 0-10ppm | <0.6 ppb |
| **10** | Total Hydrocarbon | FID | 0-1000 ppm | 0.03 ppm |
| **11** | Benzene , Toluene, Ethyl Benzene, | Gas | 0-1000ppb | <0.01 ppb |

| | | | | |
|---|---|---|---|---|
| | Xylene, BTEX | Chromatography | | |
| **12** | Particulates (TSP, $PM_{10}$, $PM_{2.5}$) | Beta attenuation | 0-5000 µg/$m^3$ | < 1 µg/$m^3$ |
| **13** | **Meteorological Sensors**<br>WS,WD, Ambient Temp., RH, Barometric Pr., Solar Radiation, Rain Gauge | | | |

## Table 2 : The Descriptive Statistics of Precursor Pollutants (2008 -2009)

| | | **$PM_{10}$** | **$PM_{2.5}$** | **$SO_2$** | **NOx** | **CO** | **$O_3$** | **Benzene** | **Toluene** | **Ethyl benzene** | **M+P Xylene** | **O Xylene** | **Wind Speed ( m/s)** | **Temperature (°C)** | **Relative Humidity (%)** | **Wind Direction (Deg)** | **Solar Radiation (W/M²)** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sum** | **Min** | 18 | 4 | 1.3 | 3.2 | 0.5 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 21.70 | 20.70 | 0.00 | 0 |
| | **Max** | 388 | 164 | 37.4 | 226 | 6.2 | 141 | 33 | 91.6 | 12.9 | 27.2 | 14.4 | 1.2 | 40.60 | 96.50 | 360.00 | 1063.70 |
| | **Avg.** | 124 | 40.8 | 13.8 | 44.1 | 2.6 | 27.6 | 2.7 | 11.4 | 1.7 | 2.5 | 0.9 | 0.25 | 29.69 | 67.73 | 215.49 | 177.08 |
| | **SD** | 61 | 25.9 | 5.6 | 38.1 | 0.9 | 23.1 | 4.3 | 14.1 | 1.9 | 3.9 | 1.9 | 0.26 | 2.91 | 12.17 | 115.32 | 264.99 |
| **Mon.** | **Min** | 0 | 1 | 1.6 | 0.5 | 0.1 | 1 | 0 | 0 | 0 | 0 | 0 | 0.00 | 24.00 | 53.90 | 0.00 | 0.00 |
| | **Max** | 386 | 103 | 34.5 | 188 | 4.7 | 73.4 | 15 | 71.1 | 9.4 | 30.8 | 12.8 | 1.70 | 35.30 | 99.90 | 360.00 | 971.50 |
| | **Avg.** | 69.3 | 25.5 | 12.1 | 40.3 | 1.3 | 19.1 | 1.4 | 8 | 0.7 | 1.4 | 0.6 | 0.28 | 28.43 | 83.72 | 189.39 | 112.01 |
| | **SD** | 36.8 | 14.9 | 4.65 | 30.2 | 0.5 | 12.9 | 1.9 | 11.7 | 0.9 | 2.9 | 1 | 0.32 | 2.08 | 9.47 | 123.39 | 194.05 |
| **Post Mon.** | **Min** | 12.9 | 1 | 4.30 | 2.9 | 0.1 | 1 | 0.04 | 0 | 0 | 0 | 0.02 | 0.00 | 20.80 | 15.40 | 0.00 | 0.00 |
| | **Max** | 657 | 334 | 85.4 | 546 | 7.6 | 252 | 51.4 | 164 | 9.6 | 30.7 | 14.8 | 1.40 | 38.90 | 99.90 | 360.00 | 956.30 |
| | **Avg.** | 186 | 82.8 | 24.3 | 114 | 2.3 | 48.1 | 3.3 | 10.6 | 0.99 | 3.1 | 0.8 | 0.15 | 28.94 | 65.53 | 154.60 | 117.56 |
| | **SD** | 95.4 | 44.7 | 13.7 | 99 | 1.3 | 44.9 | 4.4 | 14.3 | 1.5 | 3.97 | 1.4 | 0.32 | 3.44 | 18.42 | 135.32 | 209.49 |
| **Win** | **Min** | 39.7 | 8.6 | 1.3 | 1.9 | 0.1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 7.3 | 15.3 | 0 | 0 |
| | **Max** | 653 | 333 | 91.6 | 422 | 7.1 | 228 | 46.6 | 142 | 30.8 | 54.1 | 39.9 | 13.5 | 37.6 | 96.2 | 360 | 823.3 |
| | **Avg.** | 234 | 109 | 22.3 | 96.2 | 2.2 | 41.6 | 6.1 | 23. | 2.3 | 5.7 | 1.8 | 0.22 | 25.69 | 58.68 | 171.81 | 118.62 |
| | **SD** | 102 | 56 | 13.5 | 80.9 | 1.2 | 44.6 | 6.9 | 27.9 | 3.8 | 7.8 | 3.8 | 0.38 | 4.13 | 14.71 | 142.46 | 194.82 |

* Sum- Summer, Mon –Monsoon, Post Mon- Post monsoon and Win – Winter

All values are in µg/$m^3$ except meteorological parameters

**Table 3 : Person Correlation of Ozone with Precursor Pollutant and Meteorological Parameters**

| | **Summer**<br>(n=4416) | **Monsoon**<br>(n=5776) | **Post Monsoon**<br>(n=2925) | **Winter**<br>(n=4201) |
|---|---|---|---|---|
| **Precursor Pollutants** | | | | |
| **$PM_{10}$** | 0.118 | 0.144 | -0.016 | -0.239 |
| **$PM_{2.5}$** | 0.133 | 0.064 | -0.025 | -0.222 |
| **$NO_X$** | -0.225 | -0.188 | -0.099 | **-0.460** |
| **CO** | -0.051 | 0.018 | -0.204 | **-0.363** |
| **Benzene** | 0.040 | 0.008 | -0.192 | -0.156 |
| **Toluene** | -0.035 | -0.221 | -0.257 | -0.204 |
| **Ethyl benzene** | 0.100 | 0.057 | -0.227 | -0.120 |
| **M+P Xylene** | 0.077 | -0.100 | -0.321 | -0.217 |
| **O Xylene** | 0.097 | 0.043 | -0.217 | -0.112 |
| **Meteorological Parameters** | | | | |
| **Wind Speed** | **0.430** | **0.483** | 0.178 | 0.313 |
| **Temperature** | **0.470** | 0.367 | 0.365 | **0.505** |
| **Relative Humidity** | **-0.477** | -0.292 | -0.230 | -0.253 |
| **Wind Direction** | 0.265 | -0.180 | 0.313 | **0.395** |
| **Solar Radiation** | 0.313 | 0.328 | 0.275 | 0.294 |

* Significance Level 0.01

AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES
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# ANALYSIS OF SURFACE OZONE AND NITROGEN OXIDES AT URBAN, SEMI-URBAN AND RURAL SITES IN ISTANBUL, TURKEY

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## ABSTRACT

Continuous observations of ozone ($O_3$) and nitrogen oxides ($NO_x$) were conducted at three different sites in Istanbul (urban/traffic, semi-rural and rural/island) from 2007 to 2009 in order to determine the diurnal, monthly and seasonal variations of $O_3$ and to study the regional influences on its levels. The diurnal variations are characterized with afternoon maxima and the night minimum. The monthly concentrations start to increase in March reaching their maxima in summer. The $O_3$ concentrations for weekends were higher than those on weekdays at each site. High ozone-day periods were examined by applying the HYSPLIT back-trajectory model and the results pointed potential influence of highly polluted upwind regions to the air quality downwind.

**Keywords:** Istanbul, ozone, HYSPLIT, cluster analysis

## 1. INTRODUCTION

Ozone ($O_3$) is a major component of photochemical smog that is formed through a series of photochemical reactions in the presence of volatile organic compounds (VOCs) and nitrogen oxides ($NO_x$) under the intense solar radiation (Seinfeld and Pandis, 1998). As a result of complex meteorological influences and photochemical mechanisms, precursor emissions ($NO_x$ and VOCs) can lead to elevated levels of surface $O_3$ locally and downwind (Solomon et al., 2000).

In Istanbul, limited number of studies has focused on the $O_3$ levels due to the limited network of ambient $O_3$ measurements. In contrast to the large geographical extend and the population of Istanbul, only a few measurement stations can monitor $O_3$ levels since 1999, which are operated by the Istanbul Metropolitan Municipality (IBB) (Incecik et al., 2010). This dataset has been statistically investigated for different periods in a number of studies. (Topcu and Incecik, 2002 and 2003; Im et al., 2006 and 2008). In common, these studies found that $O_3$ mixing ratios generally increase with increasing temperature in the ozone season and were characterized by southwest and west – southwest winds and calm conditions. They have reported that the diurnal variations of $O_3$, $NO_x$ and VOCs supported the buildup of $O_3$ during rush hours.

Due to the limited number of studies conducted for the $O_3$ levels in Istanbul and considering the urban focus of all these studies, $O_3$ levels in Istanbul (Asian side) were measured at three new different sites (urban/traffic, semi-rural and rural/island) in frame of the Cost -728 Action in order to better represent the geographical features of $O_3$ within the extended area. This study aims to determine the diurnal, monthly and seasonal variations of $O_3$ at each site and to study the possible regional influences using back-trajectory analysis.

## 2. MATERIALS AND METHODS

In the present study, new continuous $O_3$ and $NO_x$ measurements have been carried out at three different sites of Istanbul in frame of the Cost -728 Action. These sites provide large $O_3$ variations with different emission characteristics, particularly $NO_x$, and regional characteristics. These stations are:

1. Göztepe (40.99N, 29.07E, 40 m asl): It is a urban/traffic site that has been located just a few meters away from a major highway (E-5), where about 200,000 motor vehicles pass daily. Therefore, the site is strongly influenced by high traffic emissions, particularly $NO_x$, throughout the day. The site is also close to residential areas and therefore, traffic and household emissions are the dominant source influencing the station that is typical of an urban/traffic site.

2. Kandilli (41.06N, 29.06E, 124 m asl): This air quality station has been located at the yard of Kandilli Observatory of Bogazici University over the Bosphorus and represents a typical semi-rural site. There is low traffic density compared to the Göztepe site and is mostly surrounded with residential areas. Additionally, the close proximity of the site to the Bosphorus strait leads to exposure to shipping emissions that can have significant influences on the air quality levels over the city (Im et al., 2011a).

3. Büyükada (40.51N, 29.07E, 210 m asl): This background measurement site has been established at the crest of the Prince’s Island (Büyükada) which is 2.5 km away from the main land. The island has a population of about 7400 in winter season while in summer, its population increase to at least 20,000. There is no motor traffic (except for a few municipal cars and the fire department) and no industrial activity on the island. Therefore, the only local source of anthropogenic emissions is wintertime residential heating. However, due to its close proximity to Istanbul urban area, the dominant northerly winds can transport plumes that are rich in $O_3$ precursors to the island.

$O_3$ mixing ratios were continuously measured using a UV photometric analyzer (Thermo 49i) at each station. Additionally, NO and $NO_2$ mixing ratios at the two sites (Büyükada and DMO) were measured by a Thermo 42*i*-LS low source NO-$NO_2$-$NO_x$ analyzer. Back-trajectories arriving to Kandilli at 1200 LST were calculated using the Hybrid Single – Particle Lagrangian Integrated Trajectory (HYSPLIT)) model (Draxler and Hess, 1998) for 72-h periods at an elevation of 1000 m above ground level. This 3-day time scale is well suited to capture the long-range transport (LRT) of air pollutants since most pollutants will be deposited within couple of days.

## 3. RESULTS AND DISCUSSION

### 3.1. Monthly mean ozone mixing ratios

The monthly mean $O_3$ mixing ratios at the three sites, averaged over each month in the 2007-2009 period are shown in Fig 1a. The highest $O_3$ levels were observed at the Büyükada site (35.4 ppb), followed by Kandilli (31.3 ppb). The lowest $O_3$ levels were observed at Göztepe air quality station (23 ppb) due to very high $NO_x$ emissions from the traffic titrating $O_3$ locally, as well as the insufficient time to form $O_3$ close to the sources. The figure shows an increase in the monthly mean $O_3$ mixing ratios from March (spring) to August (summer) followed by a decrease from August to December. $O_3$ levels peak during late spring and summer months are due to favorable temperature and abundance of solar radiation, thus promoting photochemical reaction.

### 3.2. Diurnal and seasonal variability of ozone mixing ratios

As seen in Figure 1b-d, the diurnal pattern of $O_3$ on seasonal basis is characterized by maximum concentrations in the afternoon and minimum concentration during early morning hours. Its variation at the three sites generally coincides with the increase of solar radiation where $O_3$ reaches to a peak value in the afternoon hours, and then continuously decreases until midnight. Observations at the sub-urban and rural sites (Kandilli and Büyükada; Figure 1c-d) present much different levels of $O_3$ from those at the urban/major traffic Göztepe station (Figure 1b) at each season. As seen in the figure, the highest $O_3$ values were monitored in Büyükada at each season (19.2 ppb in winter, 37.5 ppb in spring, 44.8 ppb in summer and 21.9 ppb in fall).

The low values of $O_3$ in this heavy traffic site at daytime were attributed to the destruction of $O_3$ by rapid reactions between $O_3$ and nitric oxide (NO-titration). Diurnal variation of the hourly-averaged $NO_x$ mixing ratios at Göztepe site presents a maximum during the morning rush hours (~108 ppb), a minimum (~55 ppb) at around 1200-1500 LST when $O_3$ reaches its maximum. The two peaks (nocturnal and daytime peaks) are clearly seen in winter season. However, the nocturnal peak in Göztepe during the winter season is slightly higher than its daytime peak due to the high $NO_x$ emitted all day long and accumulate at the surface do to the frequent inversions and calm winds during night (Im et al., 2006).

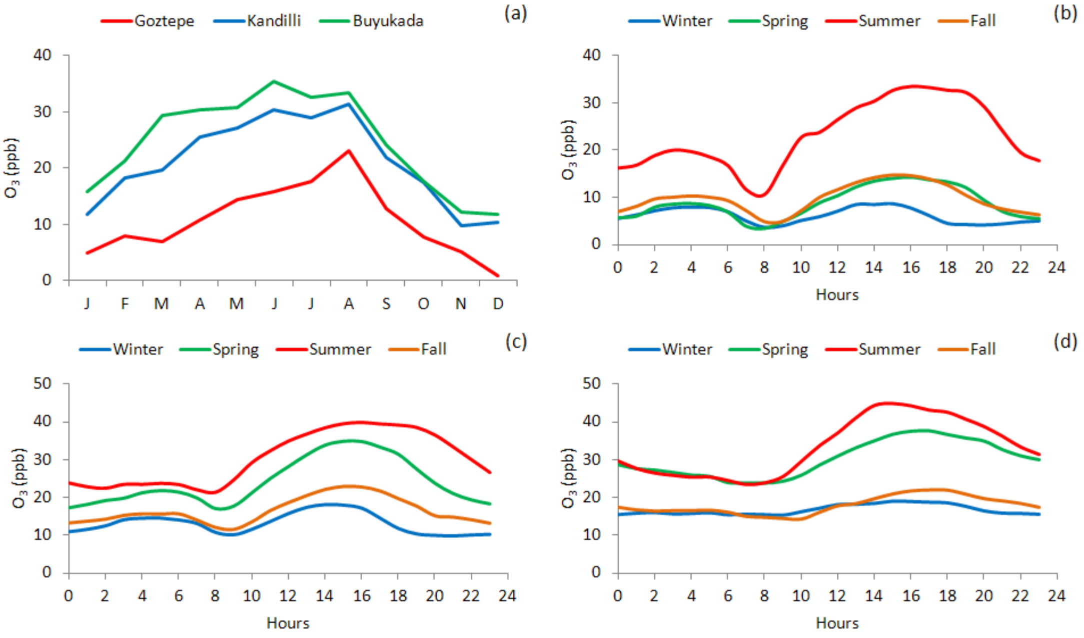

Figure 1. Monthly $O_3$ levels at three sites (a) and diurnal variations of $O_3$ in each season at Göztepe (b), Kandilli (c) and Büyükada (d).

Figure 1c shows that Kandilli site presents typical semi-rural site characteristics with the nocturnal and daytime peaks that are clearly seen at each season and are characterized by similar but higher $O_3$ levels compared to the Göztepe site. On the other hand, the diurnal cycle is almost identical to that of Göztepe, representing the same peak and low hours. Due to the decrease in the traffic and residential emissions in summer, a less pronounced minimum is observed in summer (Figure 1c) compared to the other seasons. At the Büyükada station, the minimum $O_3$ mixing ratios were observed during morning hours between 0700 and 0900 LST (Figure 1d). $O_3$ levels start increasing with the increasing solar radiation and reaches the highest levels at around 1400-1500 LST.

### 3.5. Ozone variations with nitrogen oxides

Significant correlations (*r*) were found between $NO_x$ and $O_3$ at Göztepe (r=-0.64) and Büyükada (r=-0.54). Higher correlations at the Göztepe station indicates more interactions between $O_3$ and $NO_x$ at this site, which is due to the fresh traffic emissions just a few meters away from the air quality station. As seen in Figure 3a, $NO_x$ levels at the traffic site can reach up to more than 1 ppm that is much larger than at the Büyükada site (Figure 3b). A correlation of ~0.76 is calculated between NO and $NO_2$ at the Göztepe site pointing identical sources of NO and $NO_2$, which, in this case, is traffic. r between NO and $NO_2$ at Büyükada air quality station is calculated to be 0.62, suggesting that transport of precursor emissions from upwind is more important than the local emissions in terms of $O_3$ formation compared to the Göztepe site.

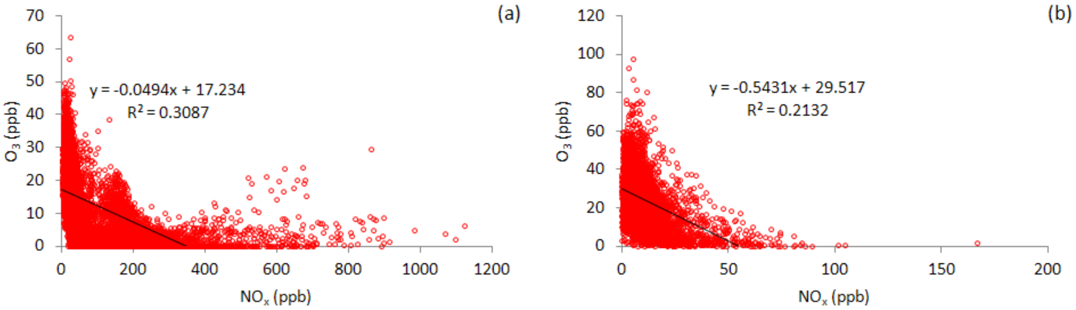

Figure 3. Scatter diagrams of $O_3$ and $NO_x$ at Göztepe (a) and Büyükada (b).

### 3.3. Weekday/weekend surface $O_3$ mixing ratios based on ozone season

Figure 2 shows the weekday and weekend diurnal variations of $O_3$ at the three sites. As seen in Figure 2a, $O_3$ mixing ratios at Göztepe air quality station were calculated to be higher on weekend days than on weekdays, a finding that is associated with the decreased volume of vehicular traffic and, consequently, lower fresh NO that destroys $O_3$. Weekend $O_3$ mixing ratios were 14% higher for the afternoon peak $O_3$. On the other hand, $NO_x$ mixing ratios were 25% lower during the afternoon $O_3$ peak time on weekends. On the other hand, because Göztepe air quality station is established nearby a high-density traffic, it is impacted mostly by high traffic emissions even in weekends (Figure 2a). Furthermore, secondary nocturnal $O_3$ peak at this site was observed in the early morning hours at around 0300 LST and 0500 LST during both weekend and weekdays.

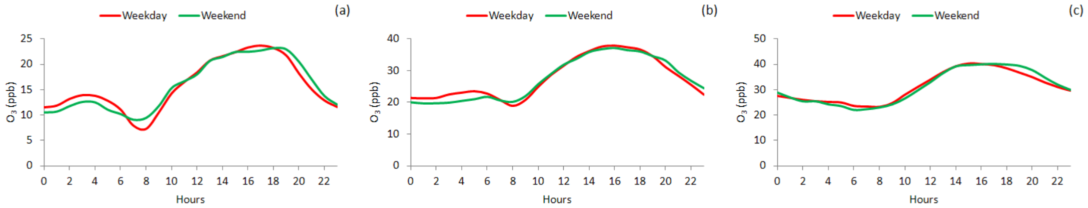

Figure 2. Weekend effect at Göztepe (a), Kandilli (b) and Büyükada (c).

At the Kandilli site, peak $O_3$ levels were calculated to be higher in weekdays compared to the weekends by about 2% (Figure 2b). On the other hand, the morning minima during weekend were up to 7% higher in weekends than in weekdays, similar to the Göztepe site. At weekdays and weekends, the maximum diurnal $O_3$ mixing ratio was calculated to be 37.8 ppb (1600 LST) and 37.0 ppb (1600 LST), respectively. Similar to the Kandilli site, $O_3$ mixing ratios at the Büyükada site were slightly higher (up to 7%) on weekdays than on weekends, a finding that may be associated with the increased shipping from the main land to the island during weekends, providing more $NO_x$ to destroy $O_3$ at this site (Figure 2c). The maximum diurnal $O_3$ mixing ratios at Büyükada is calculated to be 40.2 ppb (1500 LST) for weekdays and 40 ppb (1700 LST) for weekends, respectively.

## 3.6. Backward Trajectory Analysis

In order to better understand and characterize the relationship between transport and $O_3$ levels in the city, we have also examined the air masses for two high ozone days (4-6 August 2008; 15-17 May, 2009) by HYSPLIT model and cluster analysis. HYSPLIT backward trajectory results for August 2008 and May 2009 high ozone days periods are presented in Figure 4. Trajectories show that the main transports follow the pathways of west/northwest, and south for 2008 and 2009 episodes, respectively. Pollutants originating from Europe, Balkans and the Black Sea can be transported to Istanbul. The results of the HYPSLIT model clearly show the strong influence of the Balkan regions on Kandilli.

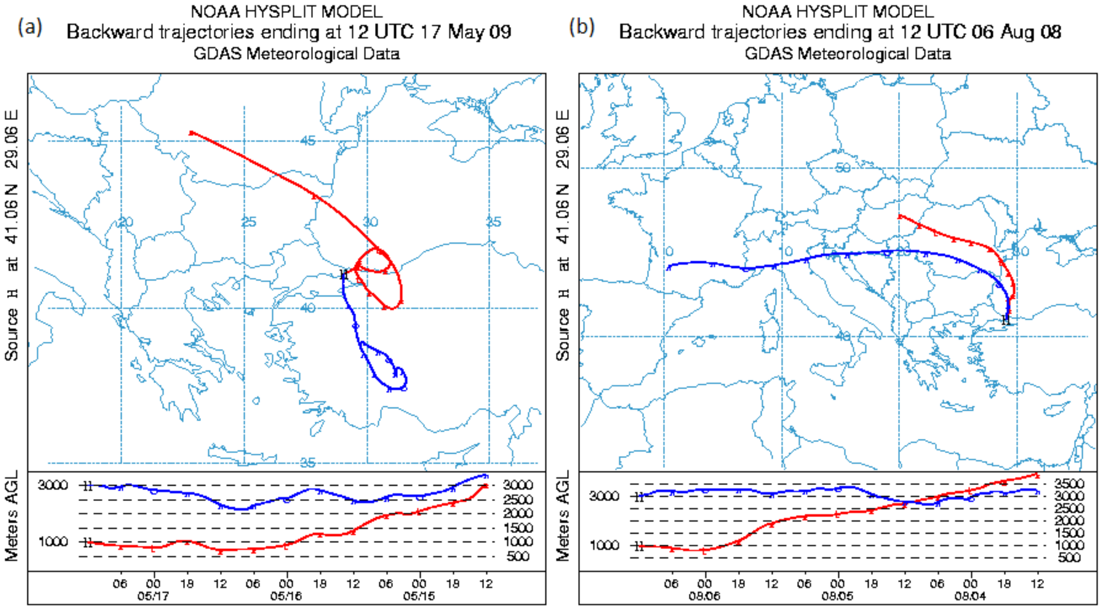

Figure 4. HYSPLIT back-trajectory results for the two high ozone days: a)4-6 August 2008 and b) 15-17 May, 2009.

## 4. CONCLUSIONS

Diurnal, monthly and seasonal profiles of $O_3$ mixing ratios at three different sites in Istanbul (traffic/urban, semi-rural and rural/island) were identified and discussed based on the two years of hourly measurements from July 2007 to December 2009 in Istanbul. Results showed that at the three stations, there is a clear seasonal variation exhibiting a maximum in summer and a minimum in winter. Both monthly and daily evolutions indicate that the highest $O_3$ mixing ratios were observed during spring and summer Surface $O_3$ levels at the rural site were generally higher compared to the semi-rural and the traffic sites. The lowest $O_3$ mixing ratios were measured at the traffic site where the titration effect of local high $NO_x$ emissions is important, which is a clear indication of traffic areas in the city.

$O_3$ mixing ratios for the weekend days were slightly higher than that on weekdays at the Göztepe site, while the differences between weekend and weekday did not exceed 9 ppb at any station. On the other hand, differences in the time of observed peak $O_3$ and the variability during the rush hours were notable, particularly at the traffic site. The sharp decrease in the morning rush hour $O_3$ levels during weekdays were not observed in weekends. The back-trajectory analysis clearly showed that particularly during the high ozone days, transport is mainly from Europe, Balkans and the Black Sea to Istanbul. Elevated levels of $O_3$ might be attributed to a mix of transport and local production.

## 5. ACKNOWLEDGEMENTS

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# INVESTIGATION OF TROPOSPHERIC OZONE VARIATION WITH RESPECT TO METEOROLOGICAL PARAMETERS IN BOLU

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## ABSTRACT

Ozone and meteorological parameters were monitored in suburban region of Bolu, Turkey for three years period. During sampling, $O_3$ concentration showed well-defined seasonal pattern, significantly higher values were obtained in summer as compared to winter. The correlation between $O_3$ and meteorological parameters were explained by statistical methods like multiple linear regression (MLR) to understand the impacts of meteorological parameters on ozone concentration. Factor analysis was performed (FA) to figure out the relation among the monitored parameters.

**Keywords:** Ozone, Multiple Linear Regression, Factor Analysis, Meteorology

## 1. INTRODUCTION

An essential constituent of the stratosphere, ozone is an undesirable pollutant in the troposphere that causes a photochemical smog. Tropospheric ozone is a major secondary air pollutant produced from photochemical reactions and some anthropogenic processes. However, the presence of ozone in the troposphere is understood to arise from two basic processes. The first one is; tropospheric/stratospheric exchange that causes the transport of stratospheric air, rich in ozone, into the troposphere and the second is the production of ozone from photochemical reactions occurring within the troposphere (Duenas et al., 2002; Barrero et al., 2006).

## 2. MEASUREMENTS and METHODS

### 2.1. Sampling location:

The monitoring site, Abant Izzet Baysal University Campus, is located at 40° 42.864′ N and 31° 31.035′ E. Instruments were placed on the roof of the presidency building in the campus at 15 m from ground level and 874 m from sea level. The distance between university and D-100 or TEM highways and the city center is 1.5 km and 10 km, respectively. Due to the closeness of the sampling site to the city center and the dense agricultural zones around it, the sampling area is defined as suburban region. In the selection of sampling point safety of the instruments, the facility of electricity and non-existence of any buildings around the sampling area that restrict the wind flow were considered.

### 2.2. Ozone and meteorology monitoring instruments:

Real time $O_3$ concentrations were measured with Thermo Scientific 49i UV ozone analyzer during three years (March 2009-March 2012). The lower detectable limit of the instrument is 1.00 ppb. Ozone concentration measurements based on ultraviolet absorption photometry and the data was recorded as 5 minutes means.

Meteorological parameters were measured with WeatherLink Meteorology station which can measure 30 parameters at the same time. Mostly used parameters-temperature, relative humidity, rain, solar radiation, wind speed and wind direction- were measured with an hour interval.

## 3. RESULTS and DISCUSSION

### 3.1. Overall evaluation of ozone concentration and meteorological parameters:

Ozone concentrations and meteorological parameters measured during three years sampling were summarized as daytime and night time (nocturnal) in Table 1. In order to understand the reaction mechanism of photochemical $O_3$ production, the data were evaluated by dividing in two parts as daytime and night time. As indicated in Table 1, average temperature and solar radiation which are the basic parameters that affect the photochemical reactions were higher at daytime than at night time. However, the relative humidity got higher at night which plays a role in the destruction of $O_3$.

Table 1. Statistical summary of ozone concentration and meteorological parameters

| | N | Mean | Stdev. | Max. | Min. | Median |
|---|---|---|---|---|---|---|
| ***Daytime*** | | | | | | |
| Ozone (ppb) | 15562 | 30.1 | 14.9 | 125.5 | 1.0 | 29.8 |
| T ($^o$C) | 14249 | 11.5 | 8.4 | 35.3 | -13.1 | 11.6 |
| Wind speed (m $s^{-1}$) | 12012 | 2.4 | 1.7 | 8.5 | 0.4 | 1.8 |
| Wind direction (deg) | 13185 | 199.4 | 78.6 | 337.5 | 0.0 | 247.5 |
| Solar Rad. (W $m^{-2}$) | 12387 | 324 | 282 | 1078 | 1.0 | 244 |
| Rel. Humi. (%) | 14249 | 71 | 22 | 100 | 0.2 | 74 |
| ***Night time*** | | | | | | |
| Ozone (ppb) | 10832 | 17.8 | 11.3 | 95.8 | 1.0 | 16.4 |
| T ($^o$C) | 10076 | 8.2 | 7.0 | 26.2 | -15.4 | 8.6 |
| Wind speed (m $s^{-1}$) | 7836 | 1.7 | 1.1 | 8.5 | 0.4 | 1.3 |
| Wind direction (deg) | 8872 | 227.6 | 62.2 | 337.5 | 0.0 | 247.5 |
| Solar Rad. (W $m^{-2}$) | 589 | 21 | 25 | 135 | 1.0 | 10 |
| Rel. Humi. (%) | 10076 | 82 | 18 | 100 | 0.4 | 89 |

### 3.2. Temporal variation of ozone

#### 3.2.1. Diurnal variation:

Evaluation of $O_3$ variation over the diurnal scale can provide meaningful information about emissions and chemical and physical processes during the whole day (Duenas et al., 2002). The average diurnal variation of $O_3$ concentrations with standard deviations showed minimum (~14.6±10.7) in the early morning (04:00) and maximum (38.3±14.3 ppb) at 14:00 as illustrated in Figure 1. The maximum average $O_3$ concentration was obtained around afternoon hours (13:00-15:00). As a result, $O_3$ production is mostly observed in daylight hours (06:00-19:00) when the solar radiation is active. Low concentrations in early morning and at night are mostly due to ozone depletion reactions, dilutions and dispersion processes (Shan et al., 2009).

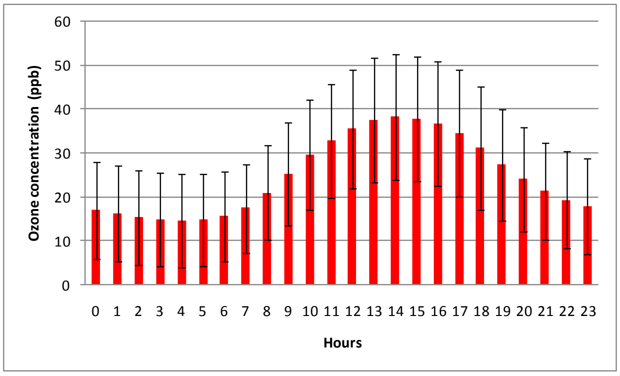

Figure 1. Diurnal variation of $O_3$ concentrations

Beside photochemical reactions and anthropogenic emissions, meteorological conditions also play an important role in the diurnal variation of $O_3$ concentration (Tu et al., 2007). Comparison of the average values of hourly $O_3$ concentrations with temperature and wind speed showed close relationship as indicated in Figure 2. Variations of $O_3$ concentrations and temperature were parallel to each other, that means they reached their maximum and minimum values at the same time. However, this same trend was not obtained between $O_3$ and wind speed. Ozone reached its maximum value at 14:00 whereas wind speed reached its maximum at 16:00.

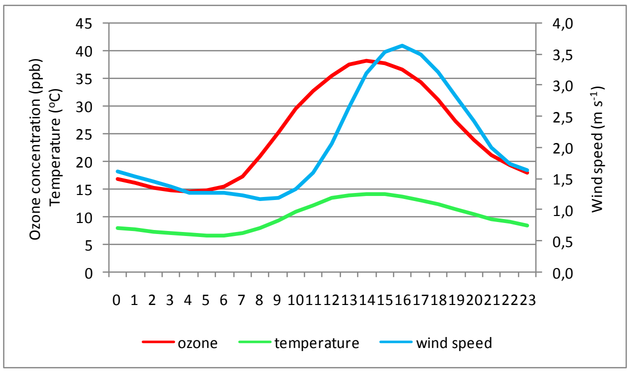

Figure 2. Diurnal variations of $O_3$ concentration, temperature and wind speed

### 3.2.2. Annual, monthly and seasonal variations

Through whole sampling period (3 years (or 37 months)), ozone concentrations showed same tendency in each year (Figure 3) as maximum in warm seasons and minimum in cold seasons. The seasonal difference in concentrations of secondary air pollutants was also discussed in literature (Permadi et al., 2008; Tu et al., 2007; Barrero et al., 2006; Duenas et al., 2002). The highest maximum $O_3$ concentration (125 ppb) was obtained in 2009 which was the highest value of the last three years. The maximum average $O_3$ concentrations were around 30-35 ppb from June to September in each year. Between these months average ambient temperature was higher than 15$^{o}$C and the maximum temperature was higher than 30$^{o}$C, average solar radiation was higher than 400 W m$^{-2}$ and relative humidity was around 75-85 %. During the whole sampling period average wind speed was not changed and it was around 2.0 m s$^{-1}$.

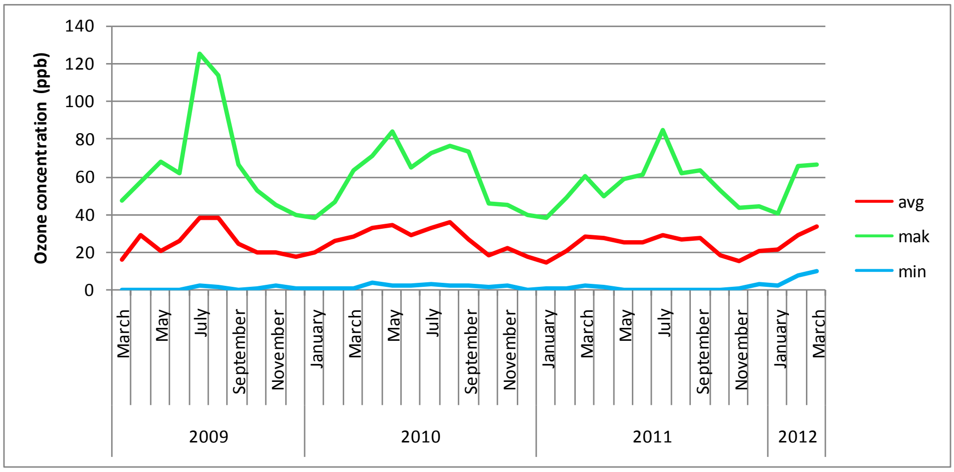

Figure 3. Trends of ozone concentrations during sampling period

Although there are some uncertainties to explain the temporal variations of $O_3$, classifying months as homogeneous groups is much more effective to evaluate the variation in concentration (Tu et al., 2007; Duenas et al., 2002; Nair et al., 2002). In Bolu, distinct grouping is impossible because cooler periods are a little bit longer than warmer ones. However, this negligible difference did not considered and months were grouped as winter (December, January, February), spring (March, April, May), summer (June, July, August) and autumn (September, October, December). Maximum average values of $O_3$ concentration and meteorological parameters were observed in summer. Average ozone concentration, temperature, wind speed, solar radiation and relative humidity were 30.7 ppb, 18.1°C, 2.4 m $s^{-1}$, 420.5 W $m^{-2}$ and 79.5 %, respectively. Average $O_3$ concentration in each season and in each wind direction was shown in Figure 4. Maximum $O_3$ concentrations (~38 ppb) were obtained in E and SSE directions in summer.

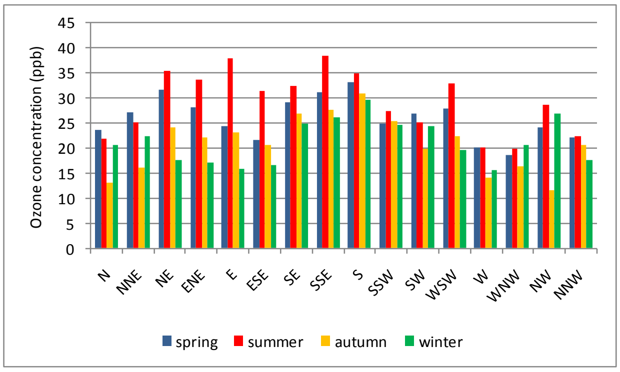

Figure 4. Average $O_3$ concentration in each direction for each season

### 3.2.3. Ozone concentrations in growing season

The harmful effects of $O_3$ on vegetation, forests and human health are generally seen during growing season. The main reason is the effective photochemical reactions in this season (Dawson et al., 2007; Lengyel et al., 2004; Duenas et al., 2002). Gvozdic and his colleagues conducted their study in order to determine the influences of meteorological conditions on $O_3$ concentration between June and October (Gvozdic et al., 2011). In this study the growing season covers the period between April to September when plant growth takes place in Bolu. The average $O_3$ concentration was around 25 ppb in this period. The average values of three significant parameters in the growing seasons that affect the production of $O_3$ directly;

temperature, solar radiation and relative humidity were 14°C, 400 W m$^{-2}$ and 76 % in 2009; 16°C, 385 W m$^{-2}$ and 79 % in 2010; 14°C, 370W m$^{-2}$ and 83 % in 2011, respectively.

Beside these parameters wind speed and wind direction should be analyzed. The direction of transport of $O_3$ containing air mass can play an important role in the description of formation and movement of $O_3$ (Camalier et al., 2007). In growing season average $O_3$ concentration in each wind direction was indicated in Figure 5. Maximum average $O_3$ concentration was around 35.5 ppb and seen in SSE and S directions, however in dominant wind direction (WSW) average concentration value was 31 ppb.

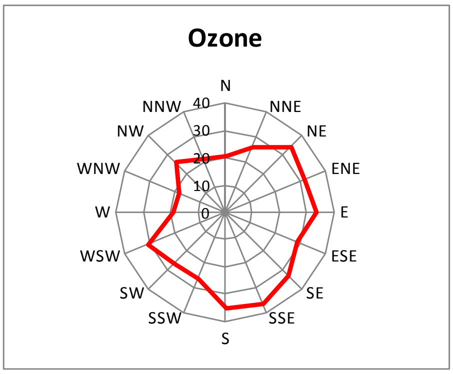

Figure 5. Average $O_3$ concentration in growing season with respect to each wind direction

High wind speed often implies high speed transport of air parcel, which is resulted in rapid dilution of primary pollutants, but this fact is much more complex for $O_3$ (Shan et al., 2008). Duenas and his collegues (Duenas et al., 2002) categorized the wind strengths as calm (<0.2 m s$^{-1}$), soft (0.2-2 m s$^{-1}$), moderate (2-4 m s$^{-1}$) and strong (>4 m s$^{-1}$). In growing season the percents of soft, moderate and strong winds were 40%, 32% and 28%, respectively. The dominant wind direction in this season was WSW direction. Figure 6 shows the variation of maximum $O_3$ concentration in each direction with the wind strength. The highest maximum $O_3$ concentration (125 ppb) was seen in WSW direction when the strong winds was blown and the lowest maximum $O_3$ concentration (~40ppb) in SW and WNW directions where strong and moderate winds were dominant. In the rest of other directions soft winds were observed and average maximum $O_3$ concentration was found around 66 ppb.

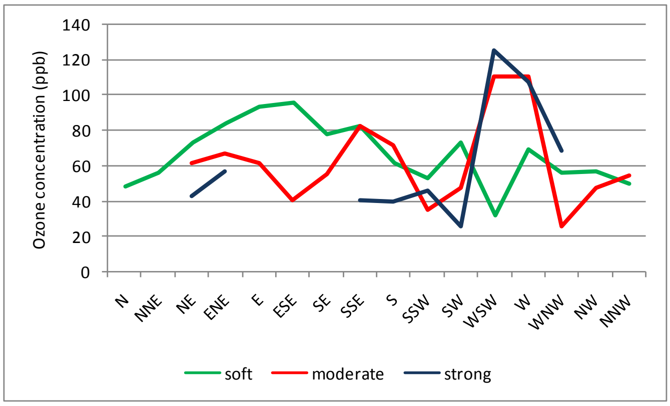

Figure 6. Maximum $O_3$ concentrations in each wind direction within each wind strength in growing season

### 3.2.4. Multiple regression analysis

Multiple linear regression (MLR) is one of the widely used methods that allows to predict the processes involved in $O_3$ formation in dependence of meteorological parameters (Gvozdic et al., 2011; Özbay et al., 2011; Kovac-Andric et al., 2009; Barrero et al., 2006; Lengyel et al., 2004). MLR was achieved by using hourly $O_3$ concentrations (dependent value) and meteorological parameters (independent values) in the growing seasons. In order to construct a meaningful relationship between $O_3$ and meteorological parameters 24-h in a day was classified as early morning (05:00-08:00), morning (08:00-11:00), midday (11:00-14:00), afternoon (14:00-19:00), evening (19:00-22:00) and night (22:00-05:00). In each part of the day MLR was applied and the coefficients were given in Table 2. The highest $R^2$ value was obtained at the evening hours (0.301). The highest coefficients of temperature (0.834) was in the midday, at night and in the early morning wind speed has coefficients 4.151 and 4.439, respectively. The relationship between $O_3$ and wind direction was obtained only at night however, the value of the coefficient indicates that it can be negligible beside other parameters. Between relative humidity and $O_3$ there is a negative relation that means $O_3$ concentration decreases when the relative humidity increases as in early morning, morning and at night.

Table 2. Multiple linear regression coefficients of $O_3$ concentration and meteorological parameters

| | **Temperature** | **Wind Speed** | **Wind Direction** | **Relative Humidity** | **$R^2$** |
|---|---|---|---|---|---|
| Early morning | 0.247 | 4.439 | - | -0.235 | 0.144 |
| Morning | 0.701 | 2.748 | - | -0.273 | 0.265 |
| Midday | 0.834 | 1.517 | - | -0.154 | 0.278 |
| Afternoon | 0.645 | 1.056 | - | -0.138 | 0.301 |
| Evening | 0.365 | 2.643 | - | -0.155 | 0.190 |
| Night | 0.182 | 4.151 | -0.024 | -0.228 | 0.176 |

### 3.2.5. Factor analysis

Factor analysis can be used for classification of data to find connections between variables, finding similarities and detecting outliers in a data set (Gvozdic et al., 2011; Lengyel et al., 2004). In this analysis average daytime (06:00-19:00) $O_3$ concentrations in the growing seasons was used as an input. Three factors that have eigen values greater than 1 by varimax rotation were obtained (Figure 7) and these three factors explained approximately 69.2 % of the total variance. First factor explained 30.8 % of the total variance and $O_3$, temperature, solar radiation and relative humidity were the components in this factor. The second factor included only wind speed and it explained 20.2 % of the total variance. Rain is the unique component of the third factor which explained only 18.2 % of the total variance.

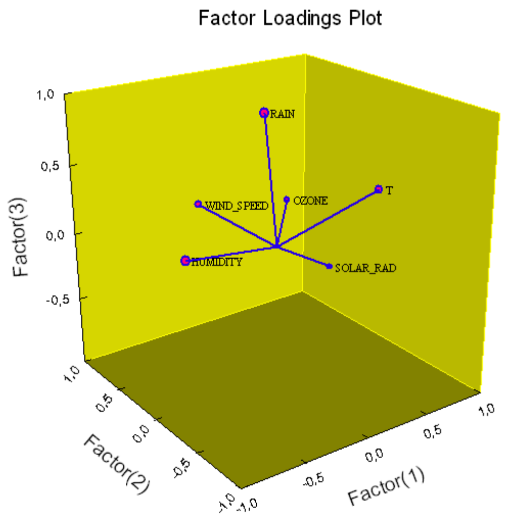

Figure 7. Graphical representation of factor analysis results

## 4. CONCLUSION

Basic statistical evaluation of $O_3$ concentration and meteorological variables, evaluation of temporal variations in each parameter and finally application of MLR and FA for each parameters in the growing seasons was discussed for three-years data. The results of analysis showed that solar radiation which is known as the main parameter for $O_3$ production was not effective as indicated in literature, however notable effect of wind speed and temperature on $O_3$ variation was obtained. In order to construct a meaningful relationship between these parameters wind sector and back-trajectory analysis should be applied as aimed to be done in the future works.

## ACKNOWKEDGEMENTS

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
**4th International Symposium and IUAPPA Regional Conference**
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# METHODS OF PREPARATION OF ELECTRODE PLATE WITH THIN ACTIVATED CARBON FILM FOR SIMULTANEOUS GAS AND DUST REMOVAL IN AIR POLLUTION

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## ABSTRACT

Concerns about the environmental pollution across the world have gradually moved from water to air. Major substances consisting of air pollutants include dust, volatile organic compounds, and odor among others. A novel activated carbon electrode has been developed to supplement the weakness of an electrostatic precipitator widely used for controlling them. As a result of the research, the proper binder was PVA (polyvinylacetate) and black carbon was additionally injected to reduce electric resistance in the activated carbon. The proper ratio of the activated carbon : black carbon was 1:0.3:0.2 and the activated carbon electrode showed good efficiency for dust collecting and odor reduction.

**Key words:** Electrostatic Precipitator, Activated Carbon Electrode, Air Pollution

## 1. INTRODUCTION

According to the intensified urbanization and industrialization due to the industrial development, air pollutants from smokes from cars and factories have gradually emerged as the social problem not only for our surrounding indoor living spaces but also public living spaces including tunnels, subway stations and theaters among others, along with more accelerated consensus on the national awareness of air pollution control over the recently frequent occurrence of yellow dust. Major substances consisting of air pollutants as such include dust, volatile organic compounds, and odor among others.

Among methods to control these air pollutants, the most widely used method is the electrostatic precipitation method. An electrostatic precipitator consists of an electrification room where dust is led to electric charge by corona discharge and a dust removal room where the charged dust is attached to an electrode plate and removed thereafter(Bologa et al., 2009). However, there are problems such that much of electricity is consumed as direct current in high voltage is required for corona discharge, and that dust is not evenly attached to an electrode surface because current density is concentrated only on the edge of the electrode plate, as well as a normal iron plate has the low specific surface area where dust is attached although a stainless steel or iron plat is normally used for the electrode plate. In addition, an ozone removal device should be installed to the back end of a dust removal room because ozone is generated due to the reaction with oxygen in the air during the corona discharge in an electric dust collecting device. Moreover, only dust can be removed, but VOCs such as benzene and toluene or odor substances such as ammonia, hydrogen sulphur cannot be removed(Long and Yao, 2010).

To overcome technological problems in removing air pollutants using an electrode plate in the past, it is necessary to widen the area to which dust is attached by increasing the specific surface area of an electrode plate, distribute current density evenly to an electrode for the uniform attachment without any bias of the dust attachment to a place, and enable the simultaneous removal of VOCs and odor(Liu et al., 2008).

To use the activated carbon as an electrode, the activated carbon from textiles is normally used because there is a problem with the growing resistance in an electrode if there is any metallic salt such as iron, manganese and magnesium among others. However, it is necessary to have plans to remove metallic ions from the activated carbon from the nature or coal which is very cheap and use it because the activated carbon from textiles is very expensive at around 100,000 won per kg. In addition, it is necessary to have a binder for the attachment between the particles of the activated carbon and to the conductor surface for the coating in a thin film over the conductor surface in an effort to use the activated carbon as an electrode(Kim et al., 2004). Also, it is necessary to have plans to open micropores even after the mixing with a binder because the ability to remove pollutants will be lost if micropores over the activated carbon are clogged during the mixing with a binder to the activated carbon(Lei et al., 2011). Moreover, it is necessary to reduce electrical resistance in the activated carbon to prevent the flow of electric current from any hindrance. This was solved by combining carbon black with high electric conductivity(Nadakatti et al., 2011).

As a result, this study aimed at inventing an electrode where the activated carbon is coated in a thin film with its live and unique functions using micropores in the activated carbon even with the use of a binder, as well as lowering electric resistance by modifying the activated carbon from plants or textiles in an effort to overcome problems in the existing technology. Experiments were carried out for the ability to remove air pollutants using the activated carbon electrode which was manufactured in this method.

## 2. MATERIALS AND METHODS

### 2.1 Pretreatment on activated carbon

Although the activated carbon from textiles has been used when an activated carbon electrode is manufactured, this study substituted the activated carbon from general coconuts for the activated carbon from textiles in this study because the activated carbon from textiles is very expensive. The activated carbon was used after pretreatment due to concerns about the occurrence of resistance when electric current is applied after an electrode plate is made because any normal activated carbon contains metallic ions massively. To remove tar and heavy metals which are stained to the activated carbon above all, it was used after it was washed many times with hot water at 100°C, and cleaned and dried after the washing with the distilled water after it was boiled in hydrochloric acid at about 1N. The concentration of heavy metals in the washing water after the cleaning was measured with ICP.

### 2.2 Preparation of binders

To find out a proper mixing ratio and a proper binder between the powdered activated carbon and the binder before a thin film electrode in the activated carbon, PTFE (polytetraflouoroethylene), NMP (n-methyl-2-pyrrolidinone), PVdF (polyvinyllidene fluoride) and PVA (polyvinylacetate) were compared to decide a binder. These binders are much used in the study on the double layer capacitor and their electric resistance is not high as they were selected for the use to store much electricity.

## 2.3 Fabrication of activated carbon electrode

To identify resistance per mixing ratio of each material in the production method for the thin film of the activated carbon, it was made from the mixing of materials such as PVA, PVA and activated carbon, PVA and activated carbon with black carbon as conductor on an aluminum plate in about 0.5mm of thickness and 5cm of diameter (⍰) 5cm. PVA was selected for a binder because the activated carbon was stained from an electrode due to the lacking adhesiveness for other binders such as PTFE or PVdF even though the quantity larger than that of PVA is used. The mixing ratio between PVA and the activated carbon was fixed at 0.3 because the adhesiveness is weak in a range of less than 0.3 and electric resistance increases in a range of not less than 0.3.

## 2.4 Dust collection

The experimental device, identifying the mass of dust attachment per electrical load at each activated carbon electrode, consists of three components including an electrode holder, an electrode and a current supply. The electrode holder has grooves to install electrode plates at a positive electrode and a negative electrode on the styrene foam which is an insulator. It was installed horizontally at an interval of about 2cm between the positive electrode and negative electrode. An aluminum plate was used for a control electrode and a thin film from PVA and activated carbon + PVA + black carbon was made on an aluminum plate for experiments, where experiments for the mass of dust attachment per current were carried out in a range of 1.5KV - 8KV respectively.

After batch experiments, the continuous flow dust collection experiments were carried out. The aluminum plate electrode was used for a control electrode, while an electrode which was made from mixing the activated carbon, PVA and black carbon at 1: 03 : 0.2 on an aluminum plate for the experimental electrode. The content of black carbon was 0.2 according to the experimental results for electrical characteristics. The electrical load was fixed at 5kV in reference to the experimental results from the preceding stage, while the mass of kaolin attachment was being identified for each electrode.

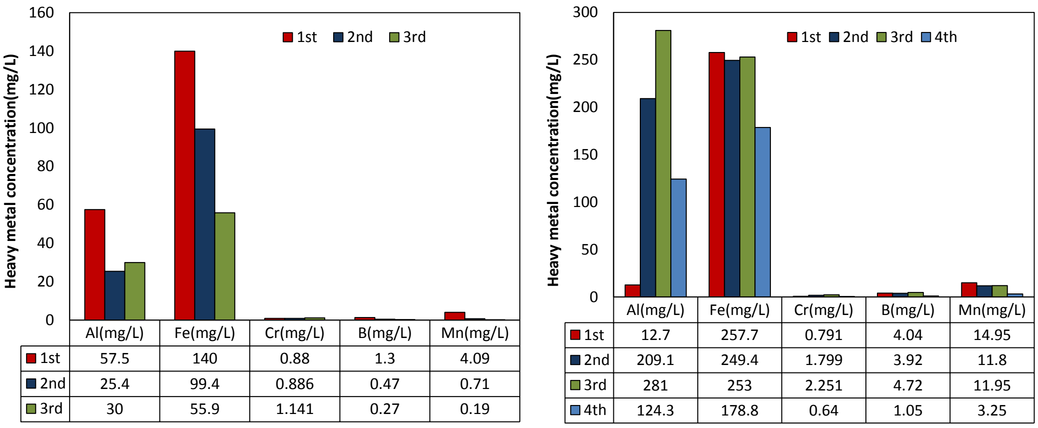
## 2.5 Odor reduction

To identify the ability of the activated carbon to which an aluminum plate is attached in removing air pollutants, experiments to remove ammonia gas and the emulsified gas were carried by peeling it off and crushing it. The concentration and input amount were different respectively because ammonia gas could be easily removed and the removal speed of the emulsified gas might be lower. The measurement of the gas concentration was done by suction with the gas-detecting tube (Gastech).

# 3. RESULTS AND DISCUSSION

## 3.1 Heavy metal removal from activated carbon

The powered activated carbon was put into hot water and washed many times to remove tar in this study. It was again washed about 4 times in the hydrochloric acid solution at about 1N to remove metallic ions. Fig. 1 shows results measured from supernatants which were flown out per washing in the hydrochloric acid solution. It shows that the activated carbon has the most iron and aluminum with a very small amount of manganese and other metals were nearly undetected. In addition, the method by the acidic cleaning is appropriate because the concentration of each metal becomes lower as the round of once, twice and three times is repeated when the hydrochloric acid cleaning is carried out.



| | Al(mg/L) | Fe(mg/L) | Cr(mg/L) | B(mg/L) | Mn(mg/L) |
|---|---|---|---|---|---|
| 🟥 1st | 57.5 | 140 | 0.88 | 1.3 | 4.09 |
| 🟦 2nd | 25.4 | 99.4 | 0.886 | 0.47 | 0.71 |
| 🟩 3rd | 30 | 55.9 | 1.141 | 0.27 | 0.19 |

| | Al(mg/L) | Fe(mg/L) | Cr(mg/L) | B(mg/L) | Mn(mg/L) |
|---|---|---|---|---|---|
| 🟥 1st | 12.7 | 257.7 | 0.791 | 4.04 | 14.95 |
| 🟦 2nd | 209.1 | 249.4 | 1.799 | 3.92 | 11.8 |
| 🟩 3rd | 281 | 253 | 2.251 | 4.72 | 11.95 |
| 🟦 4th | 124.3 | 178.8 | 0.64 | 1.05 | 3.25 |

Fig. 1 Residual heavy metal concentration in supernatant along with series washing.

### 3.2 Binder selection

To make an activated carbon electrode plate, a binder is necessary for injecting the binder into the powdered activated carbon and fixing it to an aluminum plate. Carbon powder should not be stained or separated from the aluminum plate after the activated carbon is fixed by the binder. Also, there should be no crack on the surface.

Table 1 shows results after the binding characteristics are identified with the different mixing ratio with each binder based on 1g of the powdered activated carbon. The attaching conditions were observed after the drying with the use of ethanol, methanol and acetone as a solvent as well as the use of a fluorine binder PTFE and PVdF, and a vinyl binder PVA.

When PVA is used, the adhesiveness to an aluminum electrode plate was very excellent without crushing, staining or scratch after drying even though the mixing ration with the activated carbon is made only to 1 : 0.2. Accordingly, PVA is used for the binder of all the activated carbon electrode plates thereafter.

Table 1. Observation of adhesion characteristics of binders

| Binder | Solvent | Mixing ratio (Wt) (activated carbon : binder) | Adhesion | Remarks |
|---|---|---|---|---|
| PTFE | Ethanol | 1 : 0.03 | x | Adhesiveness disappears after drying. |
| | | 1 : 0.05 | x | |
| | | 1 : 0.1 | x | |
| | | 1 : 1 | x | |
| PTFE + NMP | Ethanol | 1 : 0.03 | x | Injection of NMP increases adhesiveness, but it is lost after drying. |
| | | 1 : 0.05 | x | |
| | | 1 : 0.1 | △ | |
| | | 1 : 1 | △ | |

| | | | | |
|---|---|---|---|---|
| PVdF | Acetone | 1 : 0.03 | △ | Adhesiveness disappears after drying. |
| | | 1 : 0.05 | △ | |
| | | 1 : 0.1 | △ | |
| | | 1 : 1 | △ | |
| PVA | Methanol | 1 : 0.1 | △ | The mixing ratio of 1 : 0.2 or more shows very high adhesiveness with no staining. |
| | | 1 : 0.15 | △ | |
| | | 1 : 0.2 | ○ | |
| | | 1 : 0.5 | ○ | |

x: No binding, △: Binding is done but staining happens when it is scrubbed with hands, ○: Good binding with no staining when it is scrubbed with hands.

### 3.3 Electrical resistance of electrode

Electric resistance of an aluminum plate was very low at 0.1Ω. However, resistance was infinite to the extent of an insulator when a thin film on an aluminum plate was made only from PVA. Nevertheless, resistance became lowered to a range of 400-500Ω in case of a thin film by mixing PVA and the activated carbon, resulting in confirmation that the powdered activated carbon, which is used by washing the activated carbon with hydrochloric acid in this study, can be used for a carbon electrode. Again, resistance became lowered to 15-25Ω if black carbon is added as a conductor to the powdered activated carbon, resulting in the fact that the injection of black carbon is essential for the manufacturing of an electrode in the thin film of the activated carbon and the weight ratio of 1 : 0.3 : 0.2 respectively for the mixing ratio is appropriate.

### 3.4 Batch type experiments

Table 2 shows the measurement results for the mass of kaolin attachment per electric load to an electrode plate. The mass of dust attachment was expected to be more in case of a thin film of the activated carbon where black carbon is injected to lower resistance in the thin film of the activated carbon. Nevertheless, it was identified that there was no great difference from the case where only the activated carbon was injected. The mass of kaolin attachment per unit area ($cm^2$) of an activated carbon electrode is done up to $150mg/cm^2$. An activated carbon electrode showed the mass of attachment about twice as much as that of a general aluminum plate.

Table 2. Dust collection amount of different electrode and voltage, 1.5 kV, 3 kV, 5 kV & 8 kV

| Binder mixing weight ratio (A.C.:PVA:B.C.) | Initial weight of thin film (g) | 1.5 kV | | 3 kV | | 5 kV | | 8 kV | |
|---|---|---|---|---|---|---|---|---|---|
| | | After attachment (g) | Mass of attachment (g) | After attachment (g) | Mass of attachment (g) | After attachment (g) | Mass of attachment (g) | After attachment (g) | Mass of attachment (g) |
| Aluminum plate | 1.02 | 1.04 | 0.02 | 1.32 | 0.3 | 2.09 | 1.07 | 2.53 | 1.51 |
| 1 : 0.2 : 0 | 1.43 | 1.48 | 0.05 | 2.16 | 0.73 | 3.42 | 1.99 | 4.41 | 2.97 |
| 1 : 0.3 : 0.2 | 1.55 | 1.59 | 0.04 | 2.36 | 0.81 | 2.85 | 1.3 | 4.53 | 2.98 |

Attached to one side of a ▯ 5cm electrode plate (area = 19.6cm$^2$)

### 3.5 Continuous dust collection

As shown in Table 3, the mass of attachment is more to the positive electrode than the negative electrode if current is applied. The mass of attachment tends to increase gradually over time. This happens because the electric charge of dust is electrified with anions. On the other hand, the mass of attachment is very small on an activated carbon electrode and an aluminum electrode plate where current is not applied. As a result, it is necessary to supply current to an electrode in an effort to increase the mass of dust attachment and it is identified that the maximum mass of attachment per area of an electrode was about 14 mg/cm$^2$ after two hours.

Table 3. Amount of dust collected continuously at 1 hour and 2 hours

| Time | Number | Binder mixing weight ratio (A.C. : PVA : B.C.) condition | Electrode | Weight of the manufactured thin film (g) | Weight after 1 hour (g) | Mass of the attached kaolin (mg) | Mass of attachment (mg/cm$^2$) |
|---|---|---|---|---|---|---|---|
| 1 hour | 1 | 1 : 0.3 : 0.2 (5kV) | - pole | 1.5025 | 1.6765 | 174 | 8.8 |
| | 2 | | + pole | 1.5029 | 1.6963 | 193 | 9.8 |
| | 3 | | - pole | 1.4670 | 1.5968 | 130 | 6.6 |
| | 4 | | + pole | 1.4475 | 1.5843 | 137 | 7.0 |
| | 5 | | - pole | 1.4885 | 1.5683 | 80 | 4.1 |
| | 6 | 1 : 0.3 : 0.2 | No pole | 1.5450 | 1.6108 | 66 | 3.4 |
| | 7 | Aluminum plate | No pole | 1.0241 | 1.0329 | 9 | 0.46 |
| 2 | 1 | 1 : 0.3 : 0.2 | - pole | 1.5025 | 1.737 | 235 | 12 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| hours | 2 | (5kV) | + pole | 1.5029 | 1.788 | 285 | 14.5 |
| | 3 | | - pole | 1.4670 | 1.690 | 223 | 11.4 |
| | 4 | | + pole | 1.4475 | 1.714 | 266 | 13.6 |
| | 5 | | - pole | 1.4885 | 1.641 | 153 | 7.8 |
| | 6 | 1 : 0.3 : 0.2 | No pole | 1.5450 | 1.620 | 75.2 | 3.8 |
| | 7 | Aluminum plate | No pole | 1.0241 | 1.040 | 16.2 | 0.8 |

### 3.6 Odor reduction

Fig. 2 shows graphs after the concentration of the residual ammonia and hydrogen sulphur gas was measured. The experiment was carried out by lowering the injected amount to 0.05g because breakpoints could be hardly seen as the reaction was too quick although 0.5g was injected during the experiment for ammonia gas. Despite the high concentration of ammonia gas in the beginning, 80% of the removal ratio was shown as the most of reaction was carried out in about 10 minutes when 0.05g of the activated carbon was injected. Most of the reaction for hydrogen sulphur gas was ended in about 10 minutes by injecting 0.5g of the activated carbon and 95% or more of removal ratio was seen.

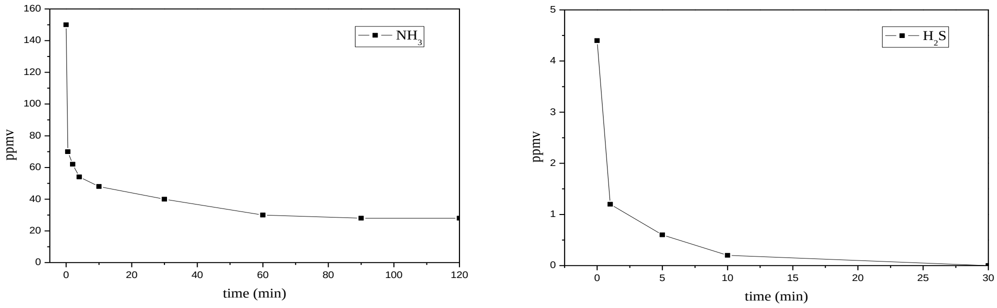


Fig. 2 Ammonia and hydrogen sulphur gas concentration in test bag by time.

## 4. CONCLUSION

The following is the summary for the experimental results to remove dust and air pollutants with the characteristics of an activated carbon electrode which was made from attaching the activated carbon in a thin film to an aluminum plate. Adhesiveness or strength was excellent without peeling off when the mixing ratio of the activated carbon : binder becomes 1: 0.2 or more if PVA is used. Dust collection amount up to about 14mg/cm$^2$ was possible at 3kV. As a result of carrying out the experiment to remove odor by peeling off an activated carbon electrode, about 80% of removal ratio was shown in 10 minutes for ammonia gas when 0.05g was injected, while about 95% or more of removal ratio was shown in 10 minutes for hydrogen sulphur gas when 0.5g was injected. Given these findings, it is considered that an activated carbon electrode can replace the existing electrode in an electric dust collection device, so that the increase of dust collection efficiency and removal of gas substances may be done at the same time.

## ACKNOWLEDGEMENT

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# EQUIVALENCE OF AUTOMATIC SAMPLERS TO GRAVIMETRIC SAMPLERS FOR PM10 FRACTION

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## ABSTRACT

We performed equivalence testing by comparing mass concentrations of PM10 particle fraction measured by β-attenuation and by gravimetric method. Samples were collected during the period 1 January 2010 - 31 December 2011. The comparison was performed between gravimetric method described in EN12341 on a non-referent sampler (HVC Digitel HD-80) and an automatic analyzer (ESM ANDERSEN FH 61 IR). Results were analyzed using a computer spreadsheet, "Orthogonal regression and the test equivalence Utility v.2.8" developed at the RIVM (Dutch Institute for Public Health and the Environment, Dep. Centre for Environment Monitoring). Annual correction of results shows a satisfactory degree of equivalence for year 2010, but not for 2011. Seasonal correction meets the requirement of equivalence of the results for both years of measurement.

**Key Words:** PM10, correction factors, Utility v.2.8

## 1. INTRODUCTION

Determination of equivalence and consequent correction of the measured results at each measurement point are necessary primarily due to objective factors such as composition of airborne particles, characteristics of the measuring site and the impact of increased operating temperature in the automatic device which causes the loss of volatile components from already collected particles, as well as with regard to subjective factors, primarily the manner and frequency of maintenance of the measuring device. The purpose of this study was to determine the correction factors for automatic analyzer of airborne particles in Zagreb at the measuring station Zagreb1 of National network for air quality monitoring located at the intersection of Miramarska and Vukovarska streets in Zagreb, declared as a traffic sampling site. For the determination of the PM10 mass concentration two methods are used: β-ray attenuation method and the gravimetric method according to EN 12341:2006.

## 2. MATERIAL AND METHODS

Samples of PM10 particle fraction were simultaneously collected using automatic analyser ESM ANDERSEN FH-61 IR and HVS Digitel DH-80 sampler.

The total of 721 daily samples of PM10 particle fraction on quartz fibre filters (Whatman QMA) were collected during the period 1 January 2010 - 31 December 2011 using HVS Digitel DH-80. Filters were conditioned and weighed before and after sampling. Weighing was preformed after 48 hours conditioning at (20±1) °C and relative humidity of (50±5) %. Mass concentrations were determined gravimetrically using a Mettler Toledo AX205 balance.

Results were analysed using a computer spreadsheet, "Orthogonal regression and the test equivalence Utility v.2.8" developed at the RIVM (Dutch Institute for Public Health and the Environment, Dep. Centre for Environment Monitoring).

## 3. RESULTS

Table 1: Annual average concentrations and number of the daily limit value exceedances of 50 µg m$^{-3}$

| | **Gravimetric method** | **Automatic method** | | |
|---|---|---|---|---|
| | | **Original data** | **Annual correction** | **Seasonal correction** |
| **2010.** | | | | |
| **N** | 362 | 362 | 362 | 362 |
| **Avg (µg/m$^3$)** | 33,5 | 28,1 | 32,1 | 33,4 |
| **>50 (µg/m$^3$)** | 65 | 36 | 60 | 63 |
| **2011.** | | | | |
| **N** | 359 | 359 | 359 | 359 |
| **Avg (µg/m$^3$)** | 36,1 | 32,0 | 35,1 | 36,0 |
| **>50 (µg/m$^3$)** | 86 | 57 | 79 | 85 |

Table 1 shows that number of the daily limit exceedances of 50 µg m-3 (according to EU CAFÉ Directive 2008/50/EC) during the calendar year obtained from the results of automated methods is lower for both years compared to the number obtained by gravimetric method. Correction of results with an annual correction function gives comparable numbers of annual excess of daily limit values obtained by gravimetric method, and the correction with seasonal correction function is even more effective. Correction of the results with an annual correction function achieves comparable values of annual mean concentrations obtained by the gravimetric method, and correction with seasonal correction function is again more effective.

Table 2: Comparison of the annual set of original, corrected annually and seasonally corrected data from an automatic analyzer with the data obtained by gravimetric analyzer.

| **Result of orthogonal regression** | | | **Correction function** | **N** |
|---|---|---|---|---|
| **Original data** | **Annual correction** | **Seasonal correction** | | |
| **2010.** | | | | |
| $y=0,749x+3,030$<br>$R^2=0,948$<br>U=**41,7%** | $y=1,008x-1,607$<br>$R^2=0,948$<br>U=23,5% | $y=1,002x+0,082$<br>$R^2=0,972$<br>U=16,5% | $y_1=1,335y-4,044$ | 362 |
| **2011.** | | | | |
| $y=0,800x+3,182$<br>$R^2=0,942$<br>U=**34,7%** | $y=1,007x-1,237$<br>$R^2=0,942$<br>U=**27,4%** | $y=1,003x-0,129$<br>$R^2=0,959$<br>U=22,5% | $y_1=1,250y-3,977$ | 359 |

Correction of results with an annual correction function (Table 2) gives the slope coefficient close to one with a statistically insignificant intercept. Correction of results with seasonal correction functions gives even better results. Corrected results meet the requirements for the relative expanded combined measurement uncertainty <25%.

Table 3 : Comparison of original and seasonal corrected data from an automatic analyzer with the data obtained by gravimetric method.

| | **Original data** | **Correction data** | **Correction function** | **N** | **$R^2$** |
|---|---|---|---|---|---|
| **2010** | **Winter** | | | | |
| | y=0,761x-0,135<br>U=**50,2**% | y=1,003x-0,091<br>U=18,8% | $y_1$=1,313y+0,177 | 89 | 0,981 |
| | **Spring** | | | | |
| | y=0,787x+1,070<br>U=**41,4**% | y=1,024x-0,961<br>U=21,6% | $y_1$=1,217y-1,360 | 92 | 0,828 |
| | **Summer** | | | | |
| | y=1,230x-3,534<br>U=**33,2**% | y=0,991x-0,362<br>U=11,5% | $y_1$=0,813y+2,873 | 91 | 0,915 |
| | **Autumn** | | | | |
| | y=0,881x-0,298<br>U=**29,5**% | y=1,004x-0,092<br>U=18,8% | $y_1$=1,135y+0,339 | 90 | 0,935 |
| **2011** | **Winter** | | | | |
| | y=0,803x-0,387<br>U=**44,1**% | y=1,003x-0,071<br>U=20,9% | $y_1$=1,246y+0,482 | 85 | 0,969 |
| | **Spring** | | | | |
| | y=0,853x+1,943<br>U=**27,1**% | y=1,008x-0,624<br>U=20,4% | $y_1$=1,172y-2,278 | 92 | 0,909 |
| | **Summer** | | | | |
| | y=1,348x-5,590<br>U=**51,1**% | y=0,943x-0,066<br>U=24,4% | $y_1$=0,742y+4,148 | 91 | 0,691 |
| | **Autumn** | | | | |
| | y=0,819x-4,403<br>U=**32,4**% | y=1,006x-1,423<br>U=**33,4**% | $y_1$=1,220y-5,373 | 91 | 0,945 |

Table 3 shows that the correction functions differ with seasons for both years of measurement. The slopes of correction function in the warm periods of the year were considerably lower compared to the slopes obtained for the cold periods of the year.

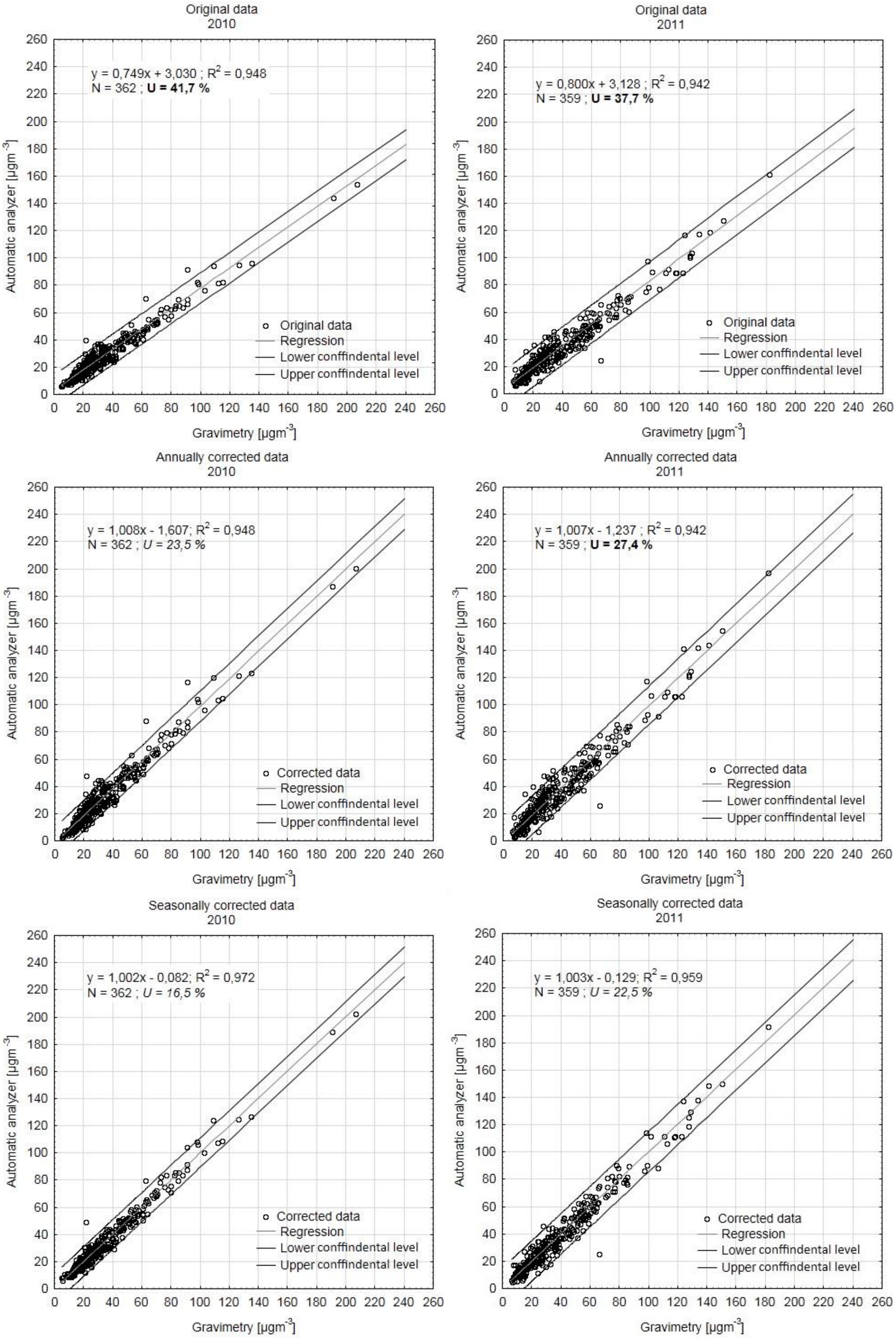

Figure 1 : The results of orthogonal regression of original, annually and seasonally corrected data of automatic method with gravimetric method for 2010 and 2011.

## 4. CONCLUSION

The requirement of equivalence is that the relative expanded measurement uncertainty is <25%. Annual correction of the results shows a satisfactory equivalence for the year 2010, but not for 2011. Seasonal correction meets the requirement of equivalence of the results for both years of measurement. In the year 2010, the difference in the number of exceedances of the daily concentration limit value between gravimetric data and corrected β-attenuation data was 7,7%, while this difference for the year 2011 was 8,1%. After seasonal correction was performed those values fell to 3% and 1,2%, for the years 2010 and 2011 respectively. These preliminary results show the need for use of correction factors, especially seasonal, in order to achieve the equivalence of the results obtained by non-referent method.

Recommendation is to correct results using seasonal correction functions, which as result gives the regression line close to $y = x$, almost identical annual average concentrations and nearly identical number of days exceeding the daily limit concentration of PM10 particle fraction. A necessary condition for use of automated devices ESM ANDERSEN FH-61 IR in order to assess the air quality is the proper maintenance and calibration of the equipment, including regular (annual, semi-annually) correction due to the activity of β-source. Regular corrections would provide consistent correction functions, and corrections could be implemented through a certain number of years without re-testing of equivalence.

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# TEMPERATURE AND HUMIDITY DEPENDENCE OF DIFFUSIVE UPTAKE RATES OF BTEX COMPOUNDS FOR PASSIVE SAMPLERS

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## ABSTRACT

Passive sampling is a commonly preferred method for sampling volatile organic compounds from ambient air due to the fact that diffusive sampling methods do not require active pumping of ambient air and eliminate high operational and maintenance costs of air pumps. With passive sampling techniques, the passive samples are analyzed and the collected masses of target analytes are correlated with ambient concentrations through diffusive uptake rates for the given adsorbent material. It is the common application that uptake rates from literature data are used in the calculation. However, uptake rates are known to be dependent mostly on ambient concentration of the target analyte (i.e. the concentration gradient) and environmental conditions, especially temperature and humidity. The purpose of this study is to simultaneously collect active and passive samples to estimate diffusive uptake rates of BTEX compounds for Perkin Elmer type, Carbopack B-filled adsorption tubes under differing ambient conditions. Measurement results will provide opportunity to seek out mathematical correlations between ambient conditions and the uptake rates. In an attempt to formulate the dependency of passive sampling to ambient conditions, samples will be collected during 4, 8, and 12 hour exposure periods. The results of the study will help contribute to passive sampling literature.

**Keywords:** BTEX, Passive Sampling, Uptake Rate, Ambient Conditions

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# BIOACCESSIBILITY OF THE INHALABLE FRACTIONS OF URBAN ROAD DUST

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## ABSTRACT

In-vitro and animal toxicological studies confirmed that the chemical composition of inhaled particles play a major role in its toxic, genotoxic and carcinogenic mechanisms, but the component-specific toxic effects are still not understood. Particle-bound airborne transition metals can also lead to the production of Reactive Oxygen Species in lung tissue; a special concern amongst particularly susceptible cohorts. The bioaccessibility of the fine fraction is evidently of importance for public health. Size-fractioned road dust collected from one of the highest trafficked roads in the United Kingdom, were characterised for its bulk elemental composition with EDXRF and ICP-OES, and its molecular composition with micro Raman spectroscopy (mRS). It was found that the fine fraction (< 38 µm) had the highest Pb (238 ppm) and Cr (171 ppm) concentrations. Concentrations of both Pb and Cr decreased substantially in the larger fractions. The mRS data showed that the Cr was mostly present as lead chromate and therefore in the Cr(VI) oxidation state. Apart from rather alarmingly high concentrations of oxidative stressors (Cu, Fe, Mn) obtained from the elemental analysis, the carcinogenic potential of the respirable fraction is evident from the mRS data. These same fractions underwent in-vitro testing to assess the mobility of toxic and carcinogenic components by leaching with artificial body fluids. Leachates were analysed for Cr, Cu, Zn, V, Pb, Mn, Cd, Fe, Ni, Al and As concentrations at time intervals from 1 hour to 8 weeks. In general, most of the elements leached in the ppb range and concentrations decreased with increase in particle size. Although the mobility in the artificial body fluids of the various elements varied, up to half the Cr, all of the Pb and most of the Ni were released.

**Keywords:** Road dust, respirable, bioaccessibility, artificial body fluid, toxicology.

## 1. INTRODUCTION

Metropolitan areas worldwide have ever-growing road networks to support the vast amount of traffic flowing through cities. A large array of literature underlines the growing concern for the environmental impact of particulate matter from anthropological sources in urban settings (Yuen et al., 2012; Meister et al., 2012; Sorenson et al., 2012). Particles of specific interest are those which gather as curb-side sediment poised to be pulverised and perturbed hence suspended by the action of vehicles making use of the road (Abu-Allaban et al., 2003; Atiemo et al 2012). These particles may be referred to as road dust (RD). Evidence from across the globe suggests that RD is responsible for a large portion of total suspended particulate matter. For example, research from Ho Cho Minh City, Vietnam, indicates that resuspended road dust accounts for 74% of the total suspended particulate matter (Hien et al., 1999). The most appealing aspect of RD from an analytical standpoint is the already well-documented abundance of transition metals, many of which toxic and in some incidences carcinogenic (Unceta et al., 2010). The acute consequences of exposure to such metals have previously been outlined using in-vitro and in-vivo and animal toxicology studies (Camner et al., 1978; Devlin et al., 2005; Klien et al., 2011) .

The contamination of roads with transition metals is suspected to be a result of a large range of sources including industrial processes, weathering of roads and buildings, combustion engines, abrasive actions on different parts of vehicles. All of these can result in the production of fine matter containing harmful metals (Hares et al., 1999; Zhong et al., 2012; Lueng et al., 2008; Yuen et al., 2012; Davis et al., 2000; Lin et al., 2002; Zhao et al 2012; Luo et al., 2012 ) . (See table 1)

**Table 1.** Anthropological sources of metals in RD and effects on human health

| ***Metal*** | ***Source*** | ***Health concerns*** |
|---|---|---|
| ***Al*** | Car bodies | Linked to Alzheimer's |
| ***Cd*** | Tires | Carcinogenic |
| ***Cr*** | Road markings, industry | Carcinogenic in +6 state |
| ***Fe*** | Road surface | Causes eye problems |
| ***Mn*** | Brakes | Dermatological conditions |
| ***Ni*** | Fuels | Carcinogenic |
| ***Pb*** | Road markings | Affects brain and nervous system |
| ***V*** | Fuels | Affects nervous system |
| ***Zn*** | Tires | Dermatological conditions |

Characterisation of these particle-bound transition metals in road dust is an avenue which has been thoroughly explored and usually produces fairly concurrent results (Cesari et al., 2012; Tanner et al., 2008; Han et al., 2011; Chen et al., 2012). Collection and analysis methods are usually carried out in a similar manner also. However, the component specific toxic effects are still relatively unknown. Naturally the ability of such metals to become available to the body is of keen public interest. Currently there is relatively little literature available on the interactions of RD with bodily fluids. Therefore, the aim of this study is to provide results regarding these issues, using two different types of artificial lung fluid, one synonymous with the more acidic fluid of the upper respiratory tract, and one with the deep lung fluid. The former is known as artificial lysosomal fluid (ALF) and has a fixed pH of 4.55. The latter is Gamble's solution, with a pH of 7.4 (Colombo et al., 2008).

Bioaccessibility of metals within road dust can be regarded as the percentage of trace substances made available to the body via the gastrointestinal or respiratory tracts (Charlesworth et al., 2011). This can be calculate by simply finding the concentration of a particular metal leached into a bodily fluid over the bulk concentration of the original dust.

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RD was collected from Oxford Road, Manchester, one of the main routes into the city centre, passing along two of the largest universities in the UK supporting over 70,000 students. Oxford Road is widely believed to be one of the busiest bus routes in Europe (Pidd., 2007), as well as being heavily laden with cars and taxis, giving it the potential to be a highly anthropogenically polluted area. This is further exasperated by the Mancunian Way raised motorway lying adjacent to Oxford Road. The intention of the study is to expose said road dust to artificial lung fluids previously mentioned, incubate at human body temperature for varying periods of time, then analyse them for content of transition metals. Comparing the results from this leaching analysis to concentrations of the bulk road dust will give bioaccessibility information on each metal.

## 2. EXPERIMENTAL

### 2.1 Sampling

Sampling was carried out on a traffic island using a plastic dustpan and brush, a similar process to that carried out by Charlesworth and Lees (1999). One sampling site was deemed to be representative of the 550 meter stretch of road by rigorous analysis and statistical testing carried out by on Oxford Road previously (Barrett., 2010). A mass of 10 kg of RD collected from the sampling site was air dried at a temperature of 21 °C for 14 days. The resulting sediment was separated into different grain size fractions using standard sieve methods. The finest three grain size fractions achieved using this technique were selected to be analysed for this study (125-63 µm, 63-38 µm and <38 µm). It has been previously assumed that only matter sized <10 µm is able to enter the respiratory tract. However, there is evidence to suggest that in particles as large as 100 µm maybe respirable, hence the use of these fraction sizes for this experimentation (Kenned et al., 2002; Erdal et al., 1995).

### 2.2 Bulk Analysis

Bulk composition analysis of the RD fractions were carried out by preparing each of the fractions of RD as pellets with a binding agent of cellulose and then analysing them with an Epsilon 5, ED-XRF instrument, using a Gd anode x-ray tube at an accelerating voltage of 25-100 kV and a 0.5-34 mA current.

### 2.3 Leaching

0.15 g ± 0.0015 g of each of the three fractions of road dust previously mentioned were measured out into universal vials containing 15 ml of lung fluid measured accurately. Samples were shaken in an incubator at 37 °C for time periods of (1 h, 1 d, 1, 2, and 8 weeks). A total of forty five samples were prepared: three fraction sizes in three different mediums (ALF, Gamble solution and deionised water) for 5 different time periods.

On removal from the incubator shaker, samples were given five minutes cooling time before being filtered using 0.2µm Whatman PVDF syringe filters into clean universal vials. The samples were then acidified using spectral grade $HNO_3$ (310µl) and stored in at 4 ºC until analysis could be performed.

Analysis of the leachates was carried out primarily using an argon plasma Varian, Vista AX, CCD simultaneous ICP-OES, with a spray chamber and glass nebuliser to determine the concentrations of metals quantitatively. These were: Al, Cd, Cr, Fe, Mn, Ni, Pb, V, Zn. Further analysis was carried out for Cr, Ni and Pb using a Varian AA2407 GFAAS with autosampler using a temperature control programme 85-2600 ºC and a flow rate of 0.3 L/min. The chromium absorbance was measure at wavelength of 429nm and the nickel at 351.5nm.

## 3. RESULTS AND DISCUSSION

The results from the XRFS bulk analysis are represented in table 2. Most are expressed in the parts per million range. However, due to the high concentration of Al and Fe, they are expressed in % of total RD. The largest component of the fragments in each case was Si, which made up at least 20 % of each fraction. The results seem to agree reasonably well with data collected in characterisation studies previously mentioned. The usual trend is Al & Fe > Zn > Pb & Cr >V & Ni. The elements shown grouped between inequality signs are usually of very similar concentrations (Cesari et al., 2012; Chen et al., 2012; Okorie et al., 2012).

Data of this nature has previously been subjected to the Risk Assessment Information System (RAIS) (Potgieter-Vermaak et al., 2011), where the daily intake for recreational exposure to metals in road sediment was used to calculate the chronic illness risk due to inhalation or ingestion of harmful metals (refer to http://rais.ornl.gov/tools/rais_chemical_risk_guide.html). However the aim of this study is to investigate the effects of metals once gained entry to the body, therefore the progressive step is to consider the risk of leached metals using the RIAS.

**Table 2**. Elemental concentrations of elements of health interest determined by XRFS.

| ***Metal*** | ***Al (%)*** | ***Fe (%)*** | ***Cr (ppm)*** | ***Mn (ppm)*** | ***Ni (ppm)*** | ***Pb (ppm)*** | ***V (ppm)*** | ***Zn (ppm)*** |
|---|---|---|---|---|---|---|---|---|
| ***<38*** | 4.93 | 3.82 | 171 | 612 | 54 | 238 | 71 | 1055 |
| ***63-38*** | 3.98 | 3.26 | 179 | 517 | 42 | 169 | 71 | 750 |
| ***125-63*** | 4.27 | 2.52 | 142 | 372 | 41 | 109 | 69 | 477 |

The leaching data provides interesting reading. In general the ALF data provided consistent results indicating that leaching increases with time and usually is higher for those particles of a finer grain size. The Gamble solution and deionised water media proved less consistent data and the expected trends were not always seen. Figure 1 illustrates the leaching data for Pb from the data gathered using the ICP-OES technique. It can be seen that there is a rough progression in the percentage of Pb leached over time for the more acidic ALF, and somewhat for the Gamble solution, although the main function of this figure is to illustrate the large difference in percentage leaching between ALF and gamble.

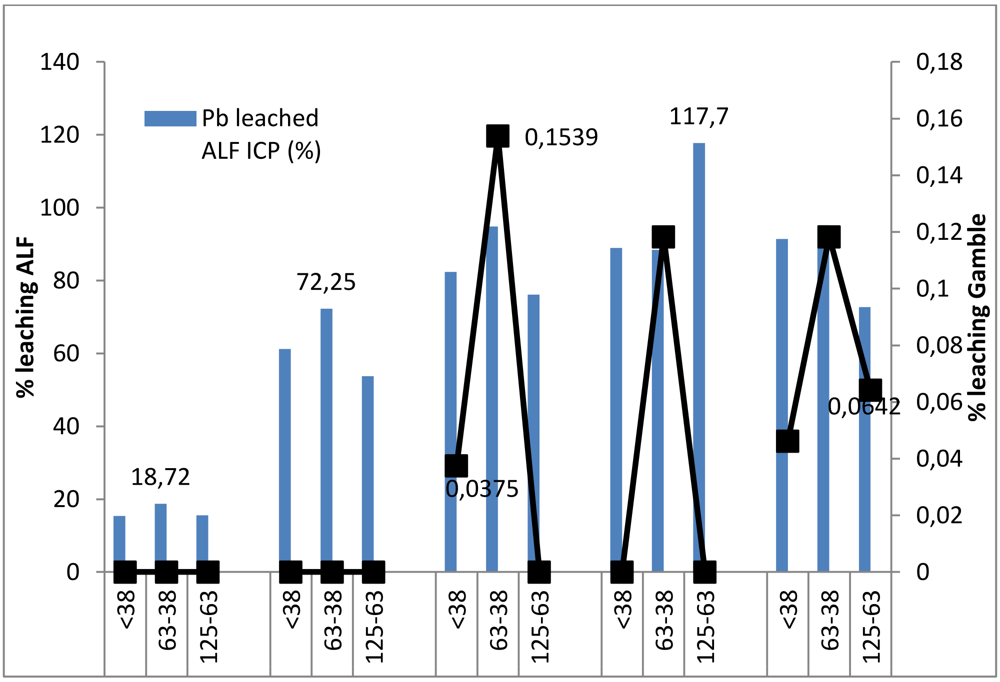

**Figure 1.** Percentage leaching of Pb onto ALF and Gamble solution over time.

As can be seen from the scale on the Y-axis the concentration leached onto the ALF is considerably more than that of the Gamble solution, this is owed to the significantly lower pH of the ALF compared to the other two mediums, and is concurrent with previous literature (Zereini et al., 1997).

Tables 3 exhibits the percent leached of each metal analysed by comparing the concentration of leachates to the bulk concentration of each metal. Bioaccessibility information given in table 3 is used to construct figure 2, which gives the reader a visual representation of how percentage leaching increases over time. The increase in leaching over time can be mapped mathematically by comparing the rate of increase between each metal to get correlation values using the Pearson formula, and is illustrated in Table 4. The lowest value is 0.714, (excluding the outliers of Ni by GFAAS), suggesting a strong correlation.

**Table 3.** Percent leached of each metal in ALF relative to the bulk elemental

| ALF | Cr | Cr GFAAS | Pb | Pb GFAAS | Ni | Ni GFAAS | Fe | Mn | Al | Zn |
|---|---|---|---|---|---|---|---|---|---|---|
| **<38 1h** | 0.99 | 1.70 | 15.4 | 13.3 | 2.11 | 5.65 | 1.05 | 11.1 | 0.86 | 17.2 |
| **63-38 1h** | 0.74 | 0.78 | 18.7 | 18.5 | 2.19 | 4.90 | 0.94 | 10.9 | 0.75 | 22.5 |
| **125-63 1h** | 0.48 | 0.44 | 15.5 | 18.9 | 1.10 | 8.78 | 0.61 | 7.74 | 0.31 | 18.5 |
| **<38 24h** | 9.63 | 25.8 | 61.2 | 48.0 | 16.2 | 21.4 | 16.3 | 53.5 | 3.62 | 60.4 |
| **63-38 24h** | 7.16 | 20.4 | 72.3 | 57.1 | 17.7 | 14.2 | 15.3 | 59.1 | 3.14 | 60.9 |
| **125-63 24h** | 5.11 | 13.7 | 53.7 | 51.3 | 9.02 | 0.00 | 11.7 | 40.6 | 1.55 | 48.8 |
| **<38 1w** | 15.3 | 25.4 | 82.4 | 67.8 | 30.6 | 222 | 22.4 | 68.3 | 6.70 | 71.0 |
| **63-38 1w** | 11.7 | 30.1 | 94.9 | 84.0 | 28.6 | 30.7 | 22.8 | 76.0 | 5.43 | 65.9 |
| **125-63 1w** | 9.64 | 22.4 | 76.1 | 48.7 | 18.9 | 64.2 | 23.4 | 62.2 | 2.94 | 59.6 |
| **<38 4w** | 18.7 | 54.6 | 88.9 | 86.0 | 38.4 | 100 | 27.2 | 73.2 | 8.65 | 73.9 |
| **63-38 4w** | 16.3 | 43.2 | 88.5 | 84.0 | 45.9 | 98.2 | 31.1 | 81.7 | 7.31 | 70.2 |
| **125-63 4w** | 12.3 | 31.9 | 117 | 95.1 | 29.2 | 34.6 | 31.4 | 63.1 | 4.21 | 62.2 |
| **<38 8w** | 20.3 | 44.4 | 91.4 | 87.8 | 40.5 | 88.9 | 28.0 | 74.3 | 9.93 | 76.6 |
| **63-38 8w** | 18.0 | 37.3 | 95.2 | 97.3 | 49.9 | 93.8 | 33.3 | 85.2 | 8.74 | 76.4 |
| **125-63 8w** | 15.2 | 32.5 | 72.7 | 74.1 | 29.1 | 70.7 | 33.7 | 73.3 | 5.58 | 75.3 |

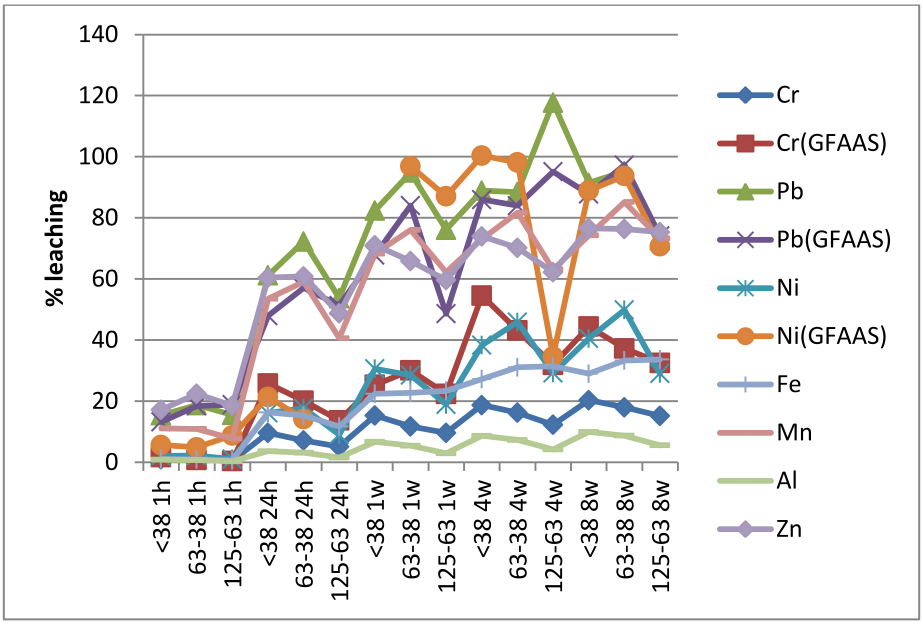

**Figure 2.** Time dependent leaching profile all metals in ALF analysed by ICP-OES and GFAAS **as %.**

**Table 4.** Pearson correlation table, showing correlation between metals in ALF

| | *Cr* | *Cr(GFAAS)* | *Pb* | *Pb(GFAAS)* | *Ni* | *Ni(GFAAS)* | *Fe* | *Mn* | *Al* | *Zn* |
|---|---|---|---|---|---|---|---|---|---|---|
| **Cr** | 1 | | | | | | | | | |
| **Cr(GFAAS)** | 0.9542 | 1 | | | | | | | | |
| **Pb** | 0.8476 | 0.8488 | 1 | | | | | | | |
| **Pb(GFAAS)** | 0.9081 | 0.9025 | 0.9560 | 1 | | | | | | |
| **Ni** | 0.9557 | 0.9201 | 0.8494 | 0.9268 | 1 | | | | | |
| **Ni(GFAAS)** | 0.7073 | 0.5596 | 0.5590 | 0.5498 | 0.6628 | 1 | | | | |
| **Fe** | 0.9246 | 0.8937 | 0.9173 | 0.9370 | 0.9164 | 0.5838 | 1 | | | |
| **Mn** | 0.9239 | 0.9013 | 0.9215 | 0.9294 | 0.9220 | 0.6532 | 0.9475 | 1 | | |
| **Al** | 0.9733 | 0.9229 | 0.7654 | 0.8624 | 0.9520 | 0.6978 | 0.8352 | 0.8617 | 1 | |
| **Zn** | 0.9364 | 0.9033 | 0.8997 | 0.9091 | 0.8855 | 0.6451 | 0.9341 | 0.9788 | 0.8642 | 1 |

Figure 3 shows cumulative leaching over the course of the 8 weeks for each metal analysed quantitatively using ICP-OES in the ALF, as discussed earlier. It is striking how high the percentage leaching of some metals is, but also the rate at which this occurs. It can be observed that around half of the overall amount leached happens within the first 24 hours of the lung fluids exposure to RD.

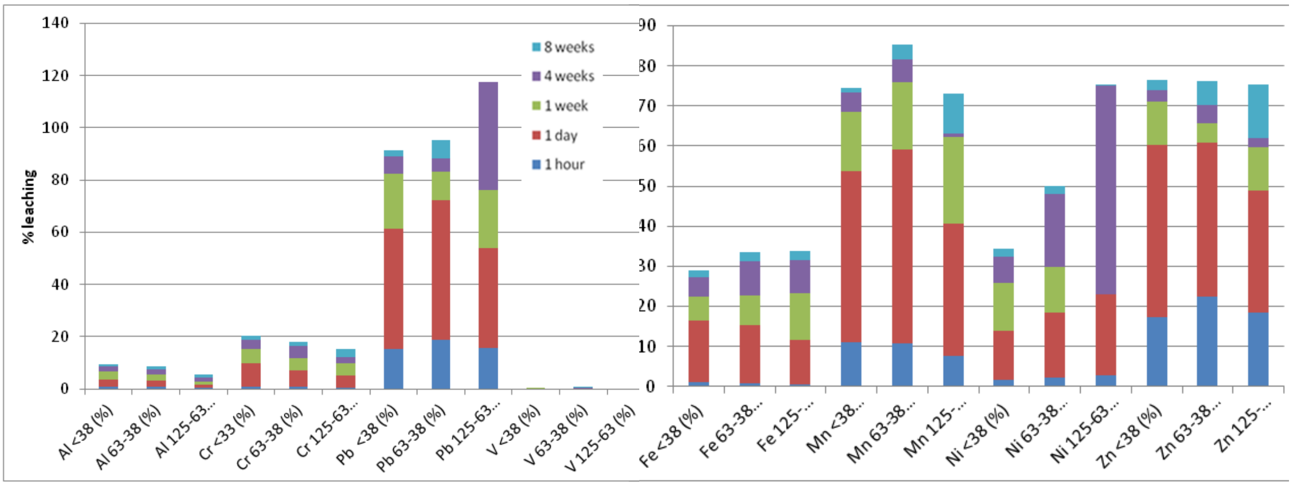

**Figure 3.** Cumulative leaching for each metal over the 8 week period the samples were in incubation.

The RAIS previously mentioned was used to apply a risk rating to each fraction of RD for the leaching part of the experiment to provide a more comprehensive view on the possible effects that the metals studied may have on the body once entry has been gained. The RAIS places a large amount of inputs into a comprehensive calculation to gain a unitless value representing the excess likelihood of an individual suffering consequences related to the selected chemicals. The body weight inputs for the calculation were adjusted to represent the average body weights for adults and children in the UK (84 kg for adults, 21 kg for children).

Tables 5 and 6 show the RAIS calculator results for the non-cancer related hazard index for adults and children respectively. Literature suggests that any value larger than 0.1 shows significant risk to health (Luftig et al., 1997), calculations show that the HI for children is larger than 0.1 and is fairly close to this figure for adults too. Table 7 gives data regarding the carcinogenic risk related to inhaling and ingesting metals in the quantities shown it can be observed that the total risk is in the 1 in 100,000 range, this is recognised as a significant risk.

**Table 5.** RIAS data showing the hazard index (HI) among adults for bioaccessible fraction

| | **Metal** | **<38 µm fraction** | **63-38 µm fraction** | **125-63 µm fraction** |
|---|---|---|---|---|
| **Inhalation risk** | Al | $1.12 \times 10^{-3}$ | $8.15 \times 10^{-4}$ | $5.86 \times 10^{-4}$ |
| | Cr | $2.83 \times 10^{-3}$ | $2.63 \times 10^{-3}$ | $1.76 \times 10^{-3}$ |
| | Mn | $4.63 \times 10^{-3}$ | $4.54 \times 10^{-3}$ | $2.81 \times 10^{-3}$ |
| | Ni | $2.67 \times 10^{-4}$ | $2.56 \times 10^{-4}$ | $1.47 \times 10^{-4}$ |
| | Zn | $6.59 \times 10^{-4}$ | $4.67 \times 10^{-4}$ | $2.93 \times 10^{-4}$ |
| | Total per fraction | $9.52 \times 10^{-3}$ | $8.71 \times 10^{-3}$ | $5.6 \times 10^{-3}$ |
| | Grand total | 0.0238 | | |

**Table 6.** data showing the hazard index (HI) among children for bioaccessible fraction

| | **Metal** | **<38 µm fraction** | **63-38 µm fraction** | **125-63 µm fraction** |
|---|---|---|---|---|
| **Inhalation risk** | Al | 8.89 x $10^{-3}$ | 6.49 x $10^{-3}$ | 4.66 x $10^{-3}$ |
| | Cr | 2.26 x $10^{-2}$ | 2.1 x $10^{-2}$ | 1.41 x $10^{-2}$ |
| | Mn | 3.71 x $10^{-2}$ | 3.6 x $10^{-2}$ | 2.23 x $10^{-2}$ |
| | Ni | 2.14 x $10^{-3}$ | 2.06 x $10^{-3}$ | 1.17 x $10^{-3}$ |
| | Zn | 5.27 x $10^{-3}$ | 3.74 x $10^{-3}$ | 2.3 x $10^{-3}$ |
| | Total per fraction | 7.6 x $10^{-2}$ | 6.13 x $10^{-2}$ | 4.45 x $10^{-2}$ |
| | Grand total | 0.182 | | |

**Table 7.** RAIS data showing the carcinogenic chronic daily intake for the bioaccessible fraction

| | **Metal** | **<38 µm fraction** | **63-38 µm fraction** | **125-63 µm fraction** |
|---|---|---|---|---|
| **Inhalation risk** | Cr | 1.99 x $10^{-8}$ | 1.85 x $10^{-8}$ | 1.24 x $10^{-8}$ |
| | Pb | 7.05 x $10^{-12}$ | 5.21 x $10^{-12}$ | 2.75 x $10^{-12}$ |
| | Ni | 1.53 x $10^{-11}$ | 1.47 x $10^{-11}$ | 8.37 x $10^{-12}$ |
| | | | | |
| **Ingestion risk** | Cr | 1.82 x $10^{-5}$ | 1.69x $10^{-5}$ | 1.13 x $10^{-5}$ |
| | Pb | 4.65 x $10^{-7}$ | 3.44 x $10^{-7}$ | 1.69 x $10^{-7}$ |
| | Ni | N/A | N/A | N/A |
| | | | | |
| | Total per fraction | 1.87 x $10^{-5}$ | 1.73 x $10^{-5}$ | 1.14 x $10^{-5}$ |
| | Grand total | 4.74 x $10^{-5}$ | | |

## 4. CONCLUSION

The results of this study show that metals are far more soluble in the lower pH lung fluid, designed to mimic the upper respiratory tract, an area carefully protected by phagocyte white blood cells. However the rate at which this study has shown metals can dissolve in the lung fluid, coupled with other research which suggests that white blood cells work rate can be diminished by the presence of silica or organic dust leads to the suggestion that metals investigated in this study may well be accessible to the body (Fogelmark et al., 1983; Poole et al., 2008).

The objective of using the RAIS approach in the manner used in this study is to provide figures on the dangers of the selected transition metals when made bioaccessible. The outcomes have shown that despite the risk of the inhalation and ingestion of metals for the percentage of dust that will leach is less than if only the bulk is considered, it still provides a significant risk.

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# IDENTIFICATION OF POTENTIAL SOURCE REGIONS OF SULPHATE ION DETERMINED IN AEROSOL SAMPLES COLLECTED FROM CENTRAL ANATOLIA, TURKEY

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## ABSTRACT

In this study, potential source regions of aerosol $SO_4$ were identified in rural area at the Central Anatolia Station (33.10$^o$E, 40.10$^O$W) of Turkey, which is located at Çubuk. Concentrations of $SO_4$ measured in aerosol samples for the years 1995, 2000, 2004, 2005 and 2006 were used to determine source regions of $SO_4$ in the Central Anatolia. Major potential source regions were identified using potential source contribution function (PSCF) model which combines chemical and meteorological data. Five day backtrajectories for each day of years 1995, 2000 ,2004, 2005 and 2006 at 100, 500 and 1500 m above ground level were calculated using NOAA HYSPLIT model. %40 of the highest $SO_4$ concentrations were considered to be polluted trajectory group. PSCF results were calculated using combined trajectories for the years 1995 and 2000. These were compared with the results for the years 2004, 2005 and 2006.

The PSCF results showed that, Balkans is the most important source region strongly affecting $SO_4^{2-}$ concentrations at the central Anatolia, which is followed by Ukraine and Russian Federation. The Western Part of Europe have low PSCF values. Potential source locations of $SO_4^{2-}$ obtained using different time periods are in good agreements in the vicinity of the Balkan Countries. On the other hand, there are also differences between the distributions of PSCF values calculated for different periods. There is no significance differences in PSCF results with different trajectory starting altitude.

**Key Words:** Trajectory Statistics, Potential Source Contribution Functions, HYSPLIT

## 1. INTRODUCTION

As one of the air pollutants form, atmospheric aerosols having adverse impact on human health causes several environmental problems such as changing earth climate and cloud properties, acid rain, reduced outside visibility, influencing radiative balance of Earth (Begum et. al., 2005; Mihalopoulos et. al., 1997). Sulphate is one of the major components of aerosols and it is derived from gas- particle conversion processes of $SO_2$ oxidation. Sulphate-coated particles has effect on fog, haze and cloud droplets and so it causes acid rains (Ganor et al., 2000). Atmospheric sulphate levels in the eastern Mediterranean basin, including Turkey, are comparable to those over industrial areas of Europe and the United states (Luria et. al., 1996; Kouvarakıs et.al., 2002). Higher sulphate levels has been reported even in remote and rural areas of Eastern Mediterranean. Potential sources of these high atmospheric sulphate levels reported as local pollution, long-range transport from distant sources, transport of mineral dust from desert and biogenic sources in the area. But long-range transport has been recorded as major source for sulphate anomaly (Kallos et. al., 2007). Description of potential source regions affecting aerosol sulphate composition in the Mediterranean basin is important due to these high $SO_4^{2-}$ concentrations (Doğan et. al. 2010).

Apportionment of source regions in other words determination of sources contributions on observed levels of pollution in the regional scale is necessary information for air quality management and development of national policy for exchange of air pollutants with other countries (Hsu et al., 2003).

The Eastern Mediterranean Basin is surrounded by highly populated and industrialized area of South Europe on its northern side and northern Africa on its southern side. The area is subject to strong natural and anthropogenic pollutants emitted from several regional and local sources (Doğan et. al., 2010). Pollution in the area resulted from anthropogenic sources is mainly from Europe, Balkans and all of them are located to northern part of Turkey.

From the beginning of the 1980s, studies carried out in the eastern Mediterranean atmosphere are mostly focused on the composition of aerosols and contribution of natural and anthropogenic sources (Kubilay et. al., 1995; Mihalopoulos et. al., 1997; Güllü et al., 2000; Koçak et. al., 2007). On the other hand, fewer studies on source regions of pollutants restricted to some part of the area are available (Güllü et. al., 2005; Doğan et. al., 2010; Türküm et. al., 2008). Some studies have been conducted to determined aerosol sulphate composition and potential source areas in Black Sea and Mediterranean regions of Turkey (Doğan et. al., 2010; Güllü et. al., 2005; Doğan et al., 2008), but there is no data available for Central Anatolia.

In this study, potential source contribution function (PSCF) analysis (Ashbaugh et al., 1985) is used to define potential sources regions of $SO_4^{2-}$ measured in the aerosol samplescollected at the Central Anatolia Region, Çubuk. Similarities and differences of source regions in different year discussed. Effect of trajectory altitudes on PSCF values are also evaluated.

## 2. MATERIALS AND METHODS

### 2.1. Study area

The study area was selected as starting from west of the UK and extending to east of the Caspian Sea in east-west direction (20ºW and 60ºE longitude) and from the middle of the Siberia to almost to the equator in north-south direction (75ºN and 15ºN latitudes).

Central Anatolia Station (33.10$^o$E, 40.10$^o$N) in which aerosol samples collected is located at Çubuk, which is approximately 50 km away from the city of Ankara and having altitude of 1169 m AMSL. Çubuk is typical rural area remote from industrial and human activities.

Çubuk station is the only EMEP station situated in Turkey. The site selection, sampling and analytical procedures were based on the EMEP protocols, that were applied commonly in all EMEP stations in Europe. The station has been operated by the Ministry of Health, Refik Saydam Hygiene Institute since 1993. Daily aerosol and precipitation samples have been collected and the parameters of SO2, SO4, NO2, HNO3+NO3 and NH3+NH4 have been measured in air samples while SO4, NO3, NH4, Na, Mg, Ca, K, Cl, pH and conductivity parameters and precipitation amounts have been assessed using the precipitation samples at Çubuk station (NILU, 2010).

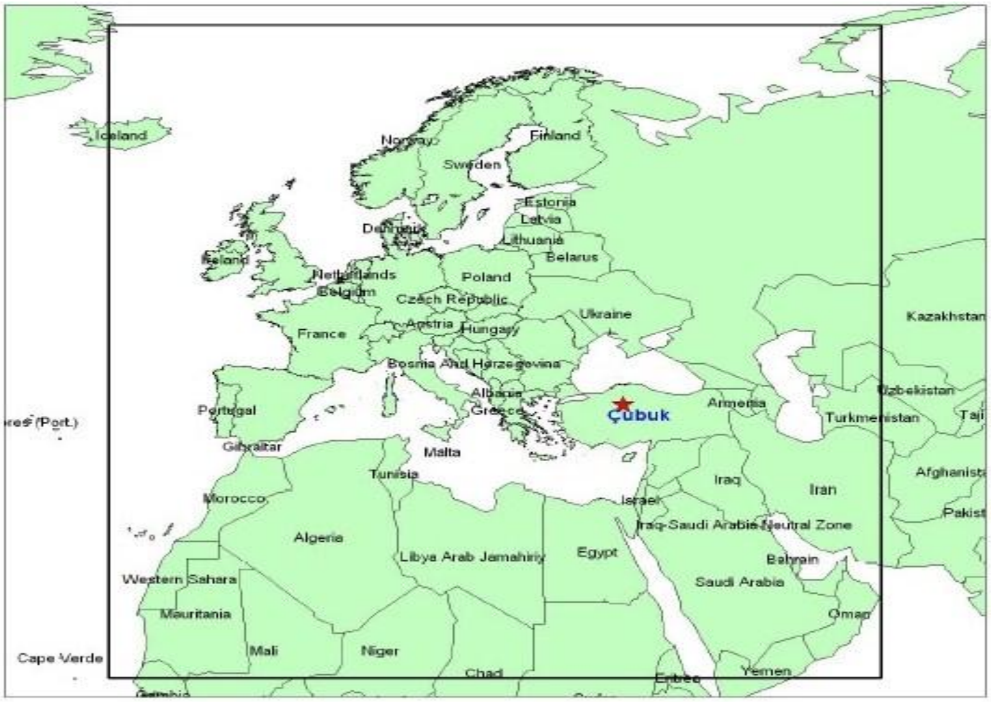


**Figure 1** Study area and locations of sampling stations.

## 2.2 SO$_4$ DATA

SO$_4^{2-}$ measurements of aerosol samples taken from Çubuk station were used. The station became operational in 1992 and air and precipitation samples are being collected since 1993. In this study, samples collected for the years 1995, 2000, 2004, 2005 and 2006 were used. In this period, 1477 daily aerosol samples had been collected and analyzed in the laboratories of Ministry of Health, Refik Saydam Hygiene Center.

## 2.3. AIR MASS BACKTRAJECTORIES

The Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model obtained by using ARL‟ s READY web application (ARL, 2009) was used to calculate air mass back trajectories. Using HYSPLIT model, back trajectories starting at 4 stations were calculated for each day of the years 1995, 2000, 2004, 2005 and 2006. Daily back trajectories were evaluated for 5 days for four different starting heights above the starting point at ground level (100m, 500m, 1500m)

## 2.4. POTENTIAL SOURCE CONTRIBUTION FUNCTION (PSCF)

Developed by Ashbaugh et al. (1985), PSCF was defined as the conditional probability that an air parcel with a level of pollutant concentration above a criterion value arrives at a receptor site after having passed through a specific geographical area. In the PSCF calculations, If pollutant specie emitted within the grid cell (*i*,*j*) and trajectory of an air parcel passes over this cell at the time of emission, it is assumed that air parcel collects the pollutant emitted in the cell and transported it along the trajectory to the receptor site.

The PSCF of an element *X* in *ijth* cell of a grid is calculated by using Eq. (1):

— (1)

where *nij* is the total number of trajectory segments in the *ijth* cell and *mij* is the total number of polluted trajectory segments in the same *ijth* cell that are related with exceeded a certain level during the study period. In this study, highest 40% of the concentration values was taken as pollution above the selected criterion and the backtrajectories started in the days when these high measurements occur were selected as polluted trajectories.

If the total number of segments in a grid cell, nij is small, it results in a high PSCF value with a high uncertainty. To minimize the effect of small values of nij, an arbitrary weighting function $W_{ij}$ as described in Zhao and Hopke (2006) was multiplied by PSCF value:

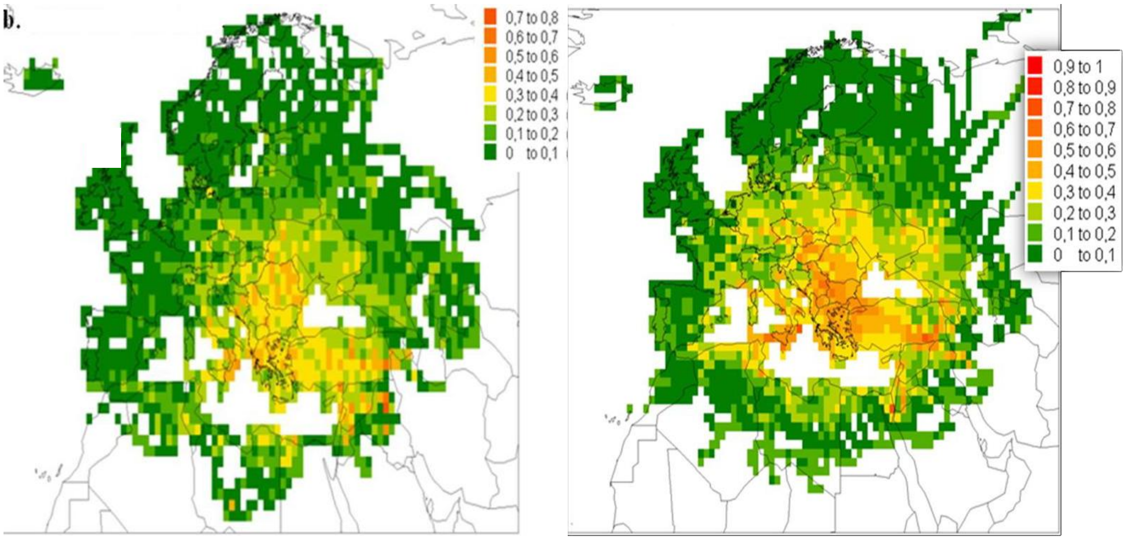
$$w(n_{ij}) = \begin{Bmatrix} 1.0 & n_{ij} > 2 \cdot n_{avg} \\ 0.75 & n_{avg} < n_{ij} \le 2 \cdot n_{avg} \\ 0.5 & n_{avg}/2 < n_{ij} \le n_{avg} \\ 0.15 & n_{ij} \le n_{avg}/2 \end{Bmatrix} \qquad (2)$$

## 3. RESULTS AND DISCUSSIONS

Potential source regions of $SO_4^{2-}$ affecting Central Anatolian Region were identified. For this purpose, $SO_4^{2-}$ levels measured in aerosol samples from Çubuk station and back trajectory calculations were used in the PSCF model.

In order to evaluate changes in the source regions in different years, PSCF calculations were performed using combined $SO_4^{2-}$ and trajectory data generated in Çubuk station in the years 1995, 2000 and 2004,2005,2006 separately. The result are given in Figure 2 and 3. These figures prepared with the combined trajectories from all starting altitudes. As can be seen in the figures, there is a general agreement between the source regions obtained by PSCF results calculated for different years. In both cases source regions affected sulphate concentrations at Çubuk are located in the Balkan region, particularly at the western part of Turkey, Greece, Romania, Bulgaria, Italy and Ukraine. Countries more distant from the receptor such as Scandinavian countries, Britain, Spain, France and Germany generally have small PSCF values. However, PSCF values of these countries for the years 2004-2006 are relatively higher. As distance from receptor increases, agreement between the source regions predicted for different years becomes worse. The numbers of trajectory segments calculated between 2004-2006 years are more than calculated segments for 1995 and 2000 years; this may be the reason for this situation. On the other hand, It is well documented that trajectory model-related uncertainties increase with distance from the receptor (Harris et al., 2005; Baumann and Stohl, 1997). So as can be seen in Figure 2 and 3, difference between PSCF values at distant areas from receptor can be arised from these model uncertainties.

There are two such well known $SO_2$ sources in our study domain. One of them is the Mt. Etna Volcano at Sicily, Italy and the second one is the Afşin Elbistan Power Plant at the Southeastern Turkey. Both of these sources are well identified in both PSCF results. Although the general agreement between the PSCF values in different years is good, there are also some disagreements between the results for different years. For example, Poland, which is a country with documented high $SO_2$ emissions (Kiuila, 2003) appears as a significant, as expected. However, PSCF values for 1995 and 2000 years in most of the grids in Poland are rather low. Although $SO_2$ levels in Poland atmosphere decreased from 1990s to 2000s (Olendrzyński et al., 2002), the reason for higher PSCF values calculated for the years 2004, 2005 ve 2006 can be that trajectory segment numbers falling in this region for the years 2004,2005 and 2006 are more than 1995 and 2000 years. Other potential source regions affected sulphate concentrations at Çubuk are located in southern Italy, and Northern Africa.



**a.PSCF values calculated for the years 1995,2000**

**b. PSCF values calculated for the years2004,2005 and 2006**

**Figure 2.** Distribution of PSCF values for %40 highest $SO_4^{2-}$ calculated for Çubuk stations for different the years (All trajectory height combined)

To assess influence of starting altitudes of trajectories on potential source regions, PSCF calculations were performed by using back trajectories for the years 1995, 2000 and with starting altitudes 100 m, 500 m and 1500 m. Results of PSCF calculations are depicted in Figure 4. The conclusions reached from combined trajectories in the previous paragraphs do not change significantly in these figures. There is no obvious difference in the agreements in PSCF values with different trajectory starting altitude, particularly in the areas with closer distance to the receptor. As demonstrated above, potential source regions strongly affected $SO_4$ compositions at Çubuk are of Balkan Countries, Western Part of Turkey and North of Turkey. More distant Countries such as Germany, France, Spain and Scandinavian Countries have lower contribution on $SO_4$ concentrations measured at Çubuk for all starting altitudes.

Since the starting altitude of trajectories did not show any expected differences between source regions the use of combined trajectories (trajectories at all starting altitudes) can be recommended in trajectory statistics. The reason is, combining trajectories results in larger number of segments in most of the grids and thus decreases the uncertainties arising from counting statistics. This would not be warranted if there were clear differences between the results of PSCF at different starting altitudes.

## CONCLUSIONS

The study aims mainly to find potential source regions affected sulphate concentration measured at Çubuk in Central Anatolian Region and to evaluate effect of trajectories with different starting altitudes on PSCF values. At the same time, differences between PSCF values for different years were also discussed.

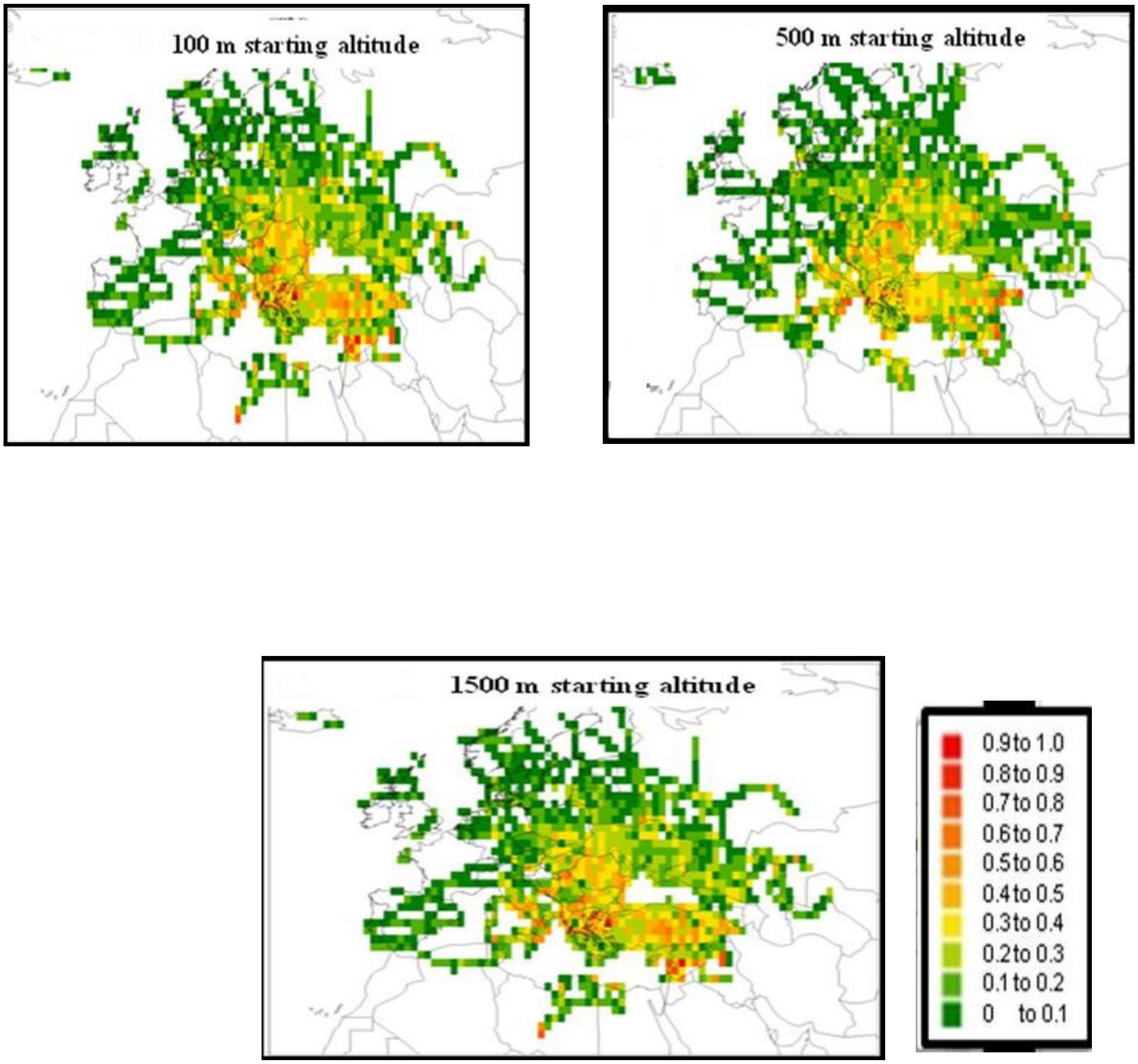


**Figure 4.** Distribution of PSCF values calculated for 1995 and 2000 at different trajectory starting altitudes

According to PSCF results, the main source areas affected $SO_4$ concentrations at Central Anatolian Area are located mainly at Balkan countries, Ukraine, Western and Southeastern parts of Turkey and South Italy. Areas relatively distant from receptor have lower PSCF values There is general agreement between the source regions determined by PSCF calculated for different years. However, PSCF results demonstrated that the agreement between source regions determined with different years becomes poorer with increasing distance from receptor. . In future studies, PSCF calculations could be performed with more years $SO_4$ and back trajectories data in order to observe better changes in potential source areas. PSCF values with different starting altitudes didn't show large difference. Therefore the use of combined trajectories can be recommended in trajectory statistics. The reason is this, combining trajectories results in larger number of segments in most of the grids and thus decreases the uncertainties arising from counting statistics.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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**10-13 September 2012 Istanbul -Turkey**

# AROMATIC HYDROCARBON LEVELS IN URBAN AIR OF ROME

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## ABSTRACT

Continuous measurements of 8 aromatic hydrocarbon, nitrogen dioxide ($NO_2$) and ozone ($O_3$) levels were carried out in the urban air of Rome during the years 2010 and 2011. The total aromatic hydrocarbon concentrations varied from 5.62 ppbV in the winter period to 2.39 ppbV in the summer. Toluene was the most abundant species, which contributed from 50% to 52% of the aromatic hydrocarbons. The profile of aromatic compounds follows traffic pattern, since maximum concentrations are achieved at traffic rush hours, morning, early and late afternoon. The aromatic hydrocarbon total concentration decreases of 50% in comparison with the levels measured in the same site in 2007. Based on the MIR scale developed by Carter, the highest contributors to ozone production in Rome were toluene (44%) and m-xylene (32%) and both are characteristic emissions from vehicular exhaust.

**Key Words**: aromatic hydrocarbons, urban air pollution, autovehicular traffic

## 1. INTRODUCTION

Aromatic hydrocarbons are one of the most important class of air pollutants in urban areas, their quantification in the atmosphere is important for assessment of the air quality and for understanding the mechanisms of smog photochemical formation. In fact aromatic hydrocarbons play an important role in the chemistry of the troposphere as precursors of ozone: in the presence of nitrogen oxides and sunlight, they react with the hydroxyl radical ($HO^{\cdot}$) to form ozone and other photochemical oxidants such as peroxyacetyl nitrate (PAN) and aldehydes (Carter, 1994, Atkinson, 2000). Several studies have shown that the dominant anthropogenic sources in the urban areas are vehicle exhaust, gasoline evaporation, emissions from the commercial and industrial use of solvents, and gas leakage from natural gas and liquefied petroleum gas (LPG) (Perry and Gee, 1995, Derwent et al., 2000, Barletta et al., 2008, Na et al., 2004, Na et al., 2005, Parra et al., 2009). Levels of aromatic hydrocarbons in ambient air are strongly dependent on the composition of the fuels used, types and ages of vehicles, traffic flow and speed as well as road and weather conditions in the city (Perry and Gee, 1995, Na and Kim, 2001).

Rome has the highest number of vehicles (~2.5 millions as on 31.12.2010) among Italian cities. Due to inadequacy of public transport system, traffic and scarce parking, motorcycles (~ 404.000) have become an important mode of transport in Rome. In this study, continuous concentration data of aromatic hydrocarbons, $NO_2$ and $O_3$ were obtained by means of an automatic gas chromatograph and a differential optical absorption spectrometer (DOAS), in the urban air of Rome during the years 2010 and 2011. We reported diurnal and seasonal variations of aromatic hydrocarbon levels and their influence on the formation of photochemical smog. Aromatic hydrocarbon mean concentrations are compared with data found in the same site in 2007. Moreover, the contributions of aromatic hydrocarbons to local ozone production was estimated using the Maximum Incremental Reactivity (MIR) developed of Carter (2010).

## 2. MAIN TEXT

This study was carried out at the ISPESL Pilot Station in downtown Rome (near S. Maria Maggiore Cathedral). A Syntech Spectras GC 955 gas-chromatograph equipped with a capillary column DB1 (30m x 0.32mm ID) and photoionization detector, was used for continuous measurements of 8 aromatic hydrocarbon concentrations with 30 minute time intervals.

$NO_2$ and $O_3$ concentrations have been measured by means of Differential Optical Absorption Spectroscopy (DOAS, OPSIS, Sweden). DOAS is based on Beer-Lambert's absorption law, which states the relationship between the quantity of light absorbed and the number of molecules in the light path. A typical DOAS instrument consists of a continuous light source, i.e. a Xe-arc lamp, and an optical setup to send and receive the light through the atmosphere (Platt, 1994).

Table 1. Seasonal variations of aromatic hydrocarbon concentrations (ppbV) in Rome

| | Winter | Spring | Summer | Fall |
|---|---|---|---|---|
| Benzene | 1.03 | 0.64 | 0.48 | 0.63 |
| Toluene | 2.81 | 2.08 | 1.25 | 2.19 |
| ethylbenzene | 0.10 | 0.06 | 0.04 | 0.07 |
| m & p-xylene | 1.39 | 0.79 | 0.48 | 0.91 |
| o-xylene | 0.13 | 0.08 | 0.06 | 0.09 |
| Styrene | 0.02 | 0.02 | 0.04 | 0.01 |
| 1,3,5 Trimethylbenzene | 0.09 | 0.05 | 0.03 | 0.05 |
| 1,2,4 Trimethylbenzene | 0.05 | 0.02 | 0.01 | 0.02 |
| *Tot* | *5.62* | *3.74* | *2.39* | *3.97* |

Table 1 lists the seasonal mean concentrations of aromatic hydrocarbons that varied from 5.62 ppbV in the winter period to 2.39 ppbV in the summer.

Aromatic hydrocarbon seasonal concentrations decreased from winter to spring until to reach minimum level in summer and increased from summer to fall with a winter maximum. The total concentration of aromatic hydrocarbons is reduced of 58% during summertime.

Toluene (2.81-1.25 ppbV) was the most abundant species, which contributed from 50% to 52% of the aromatic hydrocarbons, m & p-xylene (1.39-0.48 ppbV) was the second highest species (contribution to total aromatic hydrocarbons 25-20%), followed by benzene (1.03-0.48 ppbV) from 18% to 20% of the aromatics both in winter and in summer.

In figure 1 average daily concentrations of all sampling days during winter period are presented, showing the evolution of aromatics during weekdays and weekends. The aromatic hydrocarbon trend follows traffic pattern with maximum concentrations measured during traffic rush hours, early morning and late afternoon. Aromatic hydrocarbon concentrations are significantly lower on weekends.

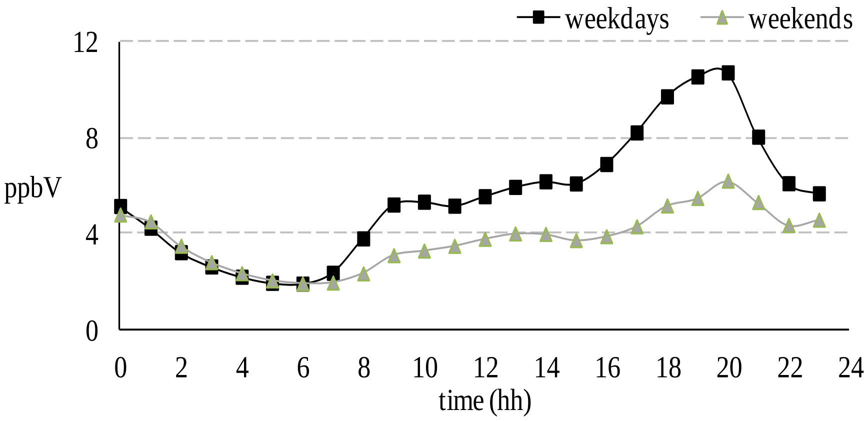

Fig. 1. Diurnal variations of aromatics during weekdays and weekend in winter period

The correlation coefficients between aromatic hydrocarbons are summarized in Table 2 for winter and summer, respectively. Strong correlation between aromatic volatile organic compounds during cold period evidences the common origin of the pollutants due to the autovehicular traffic. Besides, the daily trend of these compounds confirms that motor exhaust emissions are their dominant source.

Table 2. Summary of correlation coefficients (r) between aromatic hydrocarbons

| Compound | Benzene | Toluene | ethylbenzene | m & p-xylene | o-xylene | Styrene | 1,3,5 TMB | 1,2,4 TMB |
|---|---|---|---|---|---|---|---|---|
| *Winter* | | | | | | | | |
| Benzene | 1.00 | 0.91 | 0.82 | 0.92 | 0.92 | 0.76 | 0.84 | 0.83 |
| Toluene | | 1.00 | 0.91 | 0.99 | 0.99 | 0.80 | 0.92 | 0.85 |
| ethylbenzene | | | 1.00 | 0.91 | 0.91 | 0.84 | 0.84 | 0.66 |
| m & p-xylene | | | | 1.00 | 1.00 | 0.80 | 0.80 | 0.87 |
| o-xylene | | | | | 1.00 | 0.81 | 0.93 | 0.87 |
| styrene | | | | | | 1.00 | 0.88 | 0.56 |
| 1,3,5 TMB | | | | | | | 1.00 | 0.68 |
| 1,2,4 TMB | | | | | | | | 1.00 |
| *Summer* | | | | | | | | |
| Benzene | 1.00 | 0.42 | 0.59 | 0.58 | 0.71 | 0.77 | 0.56 | 0.41 |
| Toluene | | 1.00 | 0.75 | 0.73 | 0.73 | 0.38 | 0.68 | 0.51 |
| ethylbenzene | | | 1.00 | 0.97 | 0.94 | 0.44 | 0.90 | 0.71 |
| m & p- | | | | 1.00 | 0.94 | 0.38 | 0.93 | 0.72 |
| o-xylene | | | | | 1.00 | 0.57 | 0.89 | 0.70 |
| styrene | | | | | | 1.00 | 0.37 | 0.22 |
| 1,3,5 TMB | | | | | | | 1.00 | 0.73 |
| 1,2,4 TMB | | | | | | | | 1.00 |

Summer aromatic hydrocarbon concentrations show a poorer correlation between benzene and other aromatic hydrocarbons. For example, the correlation of benzene with toluene in the summer period (r = 0.42) is not clear as that in the wintertime (r = 0.91). This difference is probably due to the different photochemical reactivity of the two compounds. Also the correlation between toluene and other aromatic compounds decreases in summer compared with winter although this decrease is less marked.

In Table 3 are reported aromatic hydrocarbon annual means measured in the same site in 2007 (Fanizza et al., 2011) and the present data.

Table 3 Comparison of aromatic hydrocarbon levels (ppbV) measured in Rome in different periods

| | Averages 2007[(a)] | Averages 2011 |
|---|---|---|
| Benzene | 1.50 | 0.77 |
| Toluene | 2.60 | 2.23 |
| ethylbenzene | 1.00 | 0.07 |
| m & p-xylene | 2.10 | 1.01 |
| o-xylene | 0.80 | 0.10 |
| Styrene | 1.10 | 0.02 |
| 1,3,5 Trimethylbenzene | 0.50 | 0.06 |
| 1,2,4 Trimethylbenzene | 0.50 | 0.03 |
| *Tot* | *9.1* | *4.29* |

(a)Fanizza et al. 2011

The comparison between our data and the relative data of 2007 shows a reduction of 50% of aromatic hydrocarbon levels, in particular benzene concentration decreases from 1.50 ppbV to 0.77 ppbV and toluene level from 2.60 to 2.23 ppbV.

The aromatic hydrocarbon concentration reduction in 2010, compared to 2007, can be attributed to the progressive introduction of increasingly stringent emission standards. Directive 98/69/EC (Step 2), in force since January 2005, introduced the Euro 4 emission standard that required for gasoline passenger cars, additional reduction of 47% for HC and $NO_x$ emissions compared with Euro 3, while for diesel passenger cars the Euro 4 standard required vehicles to emit 50% less HC than the Euro 3 standard (EEA, 2009). Directive 2002/51/EC (Step 2) introduced the Euro 3 (2006) standards for motorcycles, with differentiated limits depending on the engine size: motorcycles below 150 $cm^3$ THC<0.8 g/km and motorcycles ≥150 $cm^3$ THC<0.3 g/km. In addition, as shown in figure 2 the number of circulating passenger cars in Rome complying with the Euro 0,1,2,3 emission limits decreases by 24% in 2010 compared to 2007, while cars with Euro 4 increase by 34% and the number of Euro 3 motorcycles increases by 52% (data from ACI).

Aromatic organic compounds play an important role in the formation of photochemical ozone. Ozone is formed in the complex reaction mechanism that involves volatile organic compounds (VOCs) and oxides of nitrogen in the presence of sunlight.

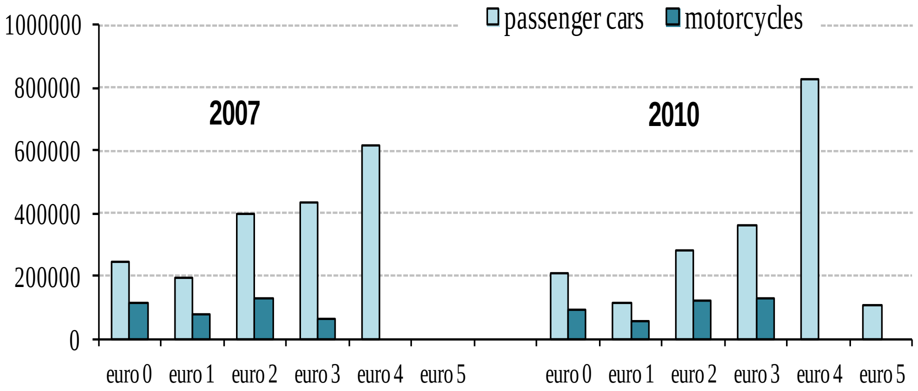

Fig. 2. Number of circulating passenger cars and motorcycles in Rome divided in terms of Euro categories for the years 2007 and 2010.

The dominant source of NO in urban locations is road traffic exhaust that in the troposphere is converted to $NO_2$ by reaction with $O_3$ and during daytime photodissociated back to NO according to the reaction:

$NO_2 + h\upsilon \rightarrow O_3 + NO$

This corresponds to a so called photostationary state and this would not lead to a significant net production of ozone. Therefore, for ozone formation an additional pathway is needed to convert NO to $NO_2$; one that will not destroy ozone. Ozone formation occurs when VOC are oxidized by hydroxyl radical ($HO^{\cdot}$), producing peroxy radicals that react with NO to form $NO_2$. This $NO_2$ can rapidly photolyze during the daytime to regenerate NO and form $O_3$. Figure 3 shows ozone and nitrogen dioxide daily trends from July 16th to 23rd, both photostationary state typical conditions ($O_3$ and $NO_2$ in opposite phase) and photochemical smog episodes (e.g. July 17th and 22nd) are detectable in the plot.

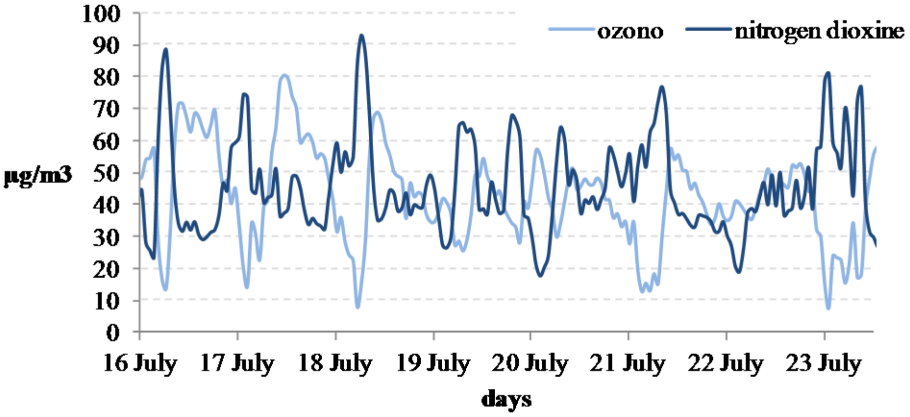

Fig. 3. Daily trends of ozone and nitrogen dioxide from July 17th to 23rd.

In this study the contributions of aromatic hydrocarbons to local ozone production was estimated using the Maximum Incremental Reactivity (MIR) developed by Carter (1994). MIR is the amount (in grams) of ozone formed per gram of VOC added to an initial VOC-$NO_x$ mixture, showing how much a compound may contribute to the ozone formation in the air mass. This dimensionless coefficient (gram of ozone formed per gram of VOC emitted), multiplied by the measured aromatic hydrocarbon concentrations indicates how much the compound may contribute to ozone formation in the air mass. The MIR coefficients used are those updated in 2010 by Carter.

To investigate ozone forming contribution to aromatic hydrocarbons, we used only the results measured in warmer months with the highest photochemical reactivity potential. Morning measurements (from 7 to 10) before photochemical reactions have a chance to take place have been used to evaluate the contribution of each aromatic hydrocarbon to ozone production. The gas chromatograph used in this study does not separate the p- from the m-xylene, but it reports the sum of these two compound concentrations. We preferred to calculate separately the contribution of these two compounds to ozone production because of high MIR of m-xylene and we used the m-xylene/p-xylene ratio (2.33) found by Monod et al. (2001) for urban air in several cities including Rome. As shown in Table 4, based on the MIR scale, the highest contributors to ozone production in Rome are toluene (44%) and m-xylene (32%) and both are characteristic emissions from vehicular exhaust.

Table 4 Photochemical ozone production by aromatic hydrocarbons estimated in urban air of Rome.

| Aromatic hydrocarbons | | MIR | $O_3$ formation | |
|---|---|---|---|---|
| | ($\mu$g m$^{-3}$) | (dimensionless) | ($\mu$g m$^{-3}$) | **(%)** |
| Benzene | 1.66 | 0.72 | 1.20 | 2.65 |
| Toluene | 4.93 | 4 | 19.73 | 43.68 |
| ethylbenzene | 0.17 | 3.04 | 0.53 | 1.17 |
| m-xylene | 1.48 | 9.75 | 14.39 | 31.84 |
| p-xylene | 0.74 | 5.84 | 4.31 | 9.54 |
| o-xylene | 0.26 | 7.64 | 1.99 | 4.4 |
| Styrene | 0.17 | 1.73 | 0.29 | 0.65 |
| 1,3,5 Trimethylbenzene | 0.20 | 1.76 | 2.31 | 5.11 |
| 1,2,4 Trimethylbenzene | 0.05 | 8.87 | 0.44 | 0.96 |
| *Tot* | | | *45.19* | |

## 3. CONCLUSION

The daily trend of aromatic hydrocarbons and the strong correlation between aromatic volatile organic compounds during cold period evidence the common origin of the pollutants due to the autovehicular traffic. The seasonal mean concentrations of aromatic hydrocarbons vary from 5.62 ppbV in the winter period to 2.39 ppbV in the summer. The daily trends of $NO_2$ and $O_3$ evidence smog photochemical episodes during hot period. The comparison between our data and data measured in the same site in 2007 shows a reduction of 50% of aromatic hydrocarbon levels, in particular benzene concentration decreases from 1.50 ppbV to 0.77 ppbV and toluene level from 2.60 to 2.23 ppbV. This reduction is attributable to the adoption of European Directives related to the introduction of more stringent emission standards and this evidences the effectiveness of European Directives above mentioned in reducing air pollution.

Based on the MIR scale, the highest contributors to ozone production in Rome are toluene (44%) and m-xylene (32%) and both are characteristic emissions from vehicular exhaust. The largest influence of a volatile aromatic compound over another on the formation of ozone can help to define future emission reduction strategies.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# NICKEL LEVELS IN FINE PARTICLES IN ZAGREB AIR

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## ABSTRACT

This paper presents the first results of nickel monitoring in fine particulate matter with aerodynamic diameter of less than 10 µm, 2.5 µm or 1 µm ($PM_{10}$, $PM_{2.5}$ or $PM_1$). Its levels were monitored at one measuring site in the northern part of Zagreb during 2011. Compared to nickel in $PM_{10}$ particles 78.1% was found in $PM_{2.5}$ and 64.5% in $PM_1$ particles, during winter period. In spring, compared to nickel in $PM_{10}$ particles 70.3% was found in $PM_{2.5}$ and 51.7% in $PM_1$ particles. Compared to nickel in $PM_{10}$ particles 72.4% was found in $PM_{2.5}$ and 42.6% in $PM_1$ particles, during summer period. In autumn, compared to nickel in $PM_{10}$ particles 81.3% was found in $PM_{2.5}$ and 54.0% in $PM_1$ particles.

**Keywords:** $PM_{10}$, $PM_{2.5}$, $PM_1$ particles, Seasonal Differences, Toxicity of Particles

## 1. INTRODUCTION

Nickel is released into the air from natural sources and man-made sources. In the air, nickel takes the form of particulate matter or is adsorbed on particulate matter. It is removed from air by dry and wet deposition. Its removal rate and distance travelled from the source depend on source characteristics, particle size, and wind velocity. Nickel compounds are human carcinogens by inhalation exposure. The International Agency for Research on Cancer (IARC) has classified nickel compounds as carcinogenic to humans (Group 1) and metallic nickel as possibly carcinogenic to humans (Group 2B).

Allergic skin reactions are the most common health effect of nickel, affecting about 2% of the male and 11% of the female population. Nickel content in consumer products and possibly in food and water are critical for the dermatological effect. The respiratory tract is also a target organ for allergic manifestations of occupational nickel exposure.

Nickel levels in the ambient air are in the range 1-10 ng $m^{-3}$ in urban areas, although much higher levels (110-180 ng $m^{-3}$) have been recorded in heavily industrialized areas and larger cities. There is, however, limited information on the species of nickel in ambient air (Air Quality Guidelines, 2000).

## 2. MATERIALS AND METHODS

Monitoring of nickel in $PM_{10}$, $PM_{2.5}$ and $PM_1$ particle fractions was provided at one measuring site in the northern part of Zagreb, the capitol of Croatia, in 2011 as an independent research project. During the monitoring period, 344 samples of each particle size were collected.

Particulate matter was collected from approximately 50 $m^3$ of ambient air on quartz filters every 24 hours. Samples were digested with nitric acid and microwaves while nickel content was determined with inductively coupled plasma mass spectrometry (ICP-MS). The limit of detection was 0.30 ng $m^{-3}$.

## 3. RESULTS AND DISCUSSION

The results of daily concentrations of nickel in $PM_{10}$, $PM_{2.5}$ and $PM_1$ particle fractions measured in 2011 are shown in Fig. 1.

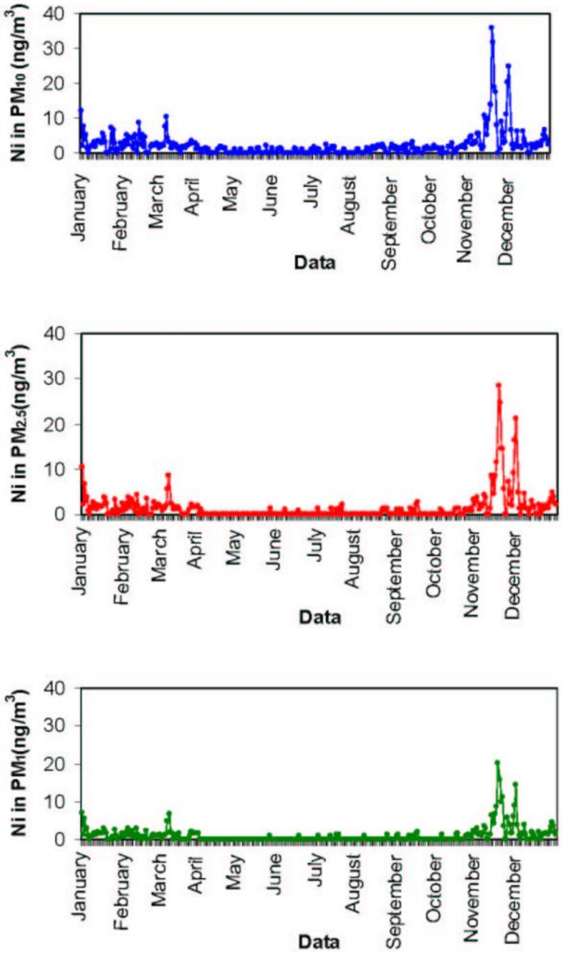

Fig. 1 Mass concentrations of nickel in $PM_{10}$, $PM_{2,5}$ and $PM_1$ particle fractions in 2011

The highest nickel concentrations were measured in the autumn and maximum daily values were 35.8 ng $m^{-3}$ for $PM_{10}$, 28.3 ng $m^{-3}$ for $PM_{2.5}$ and 20.2 ng $m^{-3}$ for $PM_1$ particles. In spring and summer nickel concentrations in $PM_{2.5}$ and $PM_1$ particle fractions were often under the limit of detection.

In Table 1 the mean annual values, mean seasonal values and the range of nickel concentrations in $PM_{10}$, $PM_{2.5}$ and $PM_1$ particle fractions measured in 2011 are shown.

Table 1 - Mean annual and seasonal values for nickel in $PM_{10}$, $PM_{2.5}$ and $PM_1$ particle fractions (ng $m^{-3}$) in 2011

| Measuring period | | N | C±STD | Range |
|---|---|---|---|---|
| Winter | Ni in $PM_{10}$ | 74 | 2.69±2.150 | n.d.-10.34 |
| | Ni in $PM_{2,5}$ | 74 | 1.73±1.541 | n.d.-8.47 |
| | Ni in $PM_1$ | 74 | 1.23±1.233 | n.d.-6.79 |
| Spring | Ni in $PM_{10}$ | 86 | 0.64±0.858 | n.d.-3.62 |
| | Ni in $PM_{2,5}$ | 86 | 0.18±0.499 | n.d.-2.11 |
| | Ni in $PM_1$ | 86 | 0.13±0.417 | n.d.-2.02 |
| Summer | Ni in $PM_{10}$ | 87 | 0.73±0.840 | n.d.-3.13 |
| | Ni in $PM_{2,5}$ | 87 | 0.24±0.553 | n.d.-2.81 |
| | Ni in $PM_1$ | 87 | 0.15±0.411 | n.d.-2.01 |
| Autumn | Ni in $PM_{10}$ | 86 | 4.20±6.583 | n.d.-35.77 |
| | Ni in $PM_{2,5}$ | 86 | 3.00±5.429 | n.d.-28.34 |
| | Ni in $PM_1$ | 86 | 2.18±3.736 | n.d.-20.21 |
| Whole year | Ni in $PM_{10}$ | 344 | 2.08±3.793 | n.d.-35.77 |
| | Ni in $PM_{2,5}$ | 344 | 1.31±3.065 | n.d.-28.34 |
| | Ni in $PM_1$ | 344 | 0.95±2.162 | n.d.-20.21 |

N – number of samples C –arithmetic means STD – standard deviations

In Croatia, the enforcement of the Air Protection Act (Air Protection Act, 2004) and the Ordinance on Limit Values of Pollutants in the Air (Ordinance, 2005) began in 2006. The latest amendments to the Air Protection Act (Air Protection Act, 2011) have been in force since 2011, as Croatian regulations now must be in agreement with European standards.

Following the European Council Directives, the Ordinance on Limit Values of Pollutants in the air provides the limit value (LV) for nickel in $PM_{10}$ particle fractions (20 ng $m^{-3}$) for annual mean value.

The 2011 Air Protection Act defines two categories of air quality:

1st category – clean air (the concentration levels of air pollution are below LV)

2nd category – polluted air (the concentration levels of air pollution are over LV).

In 2011 the annual mean value for nickel in $PM_{10}$ particle fractions was 2.08 ng $m^{-3}$ and was below LV (20 ng $m^{-3}$). The air was therefore classified as clean. Limit values for nickel in $PM_{2.5}$ and $PM_1$ particle fractions are not given in European Council Directives and Croatian Ordinance.

Compared to nickel in $PM_{10}$ particle fractions 78.1% was found in $PM_{2.5}$ and 53.2% in $PM_1$ particle fractions over the whole year.

Epidemiological studies have shown that particle size and chemical composition play a major role in the relative toxicity of particles. The obtained data have shown a high percentage of nickel in small particles, especially in the winter and autumn.

Fig. 2 shows the correlation between mass concentrations of nickel in $PM_{10}$ and $PM_{2.5}$ particle fractions over all four seasons in 2011.

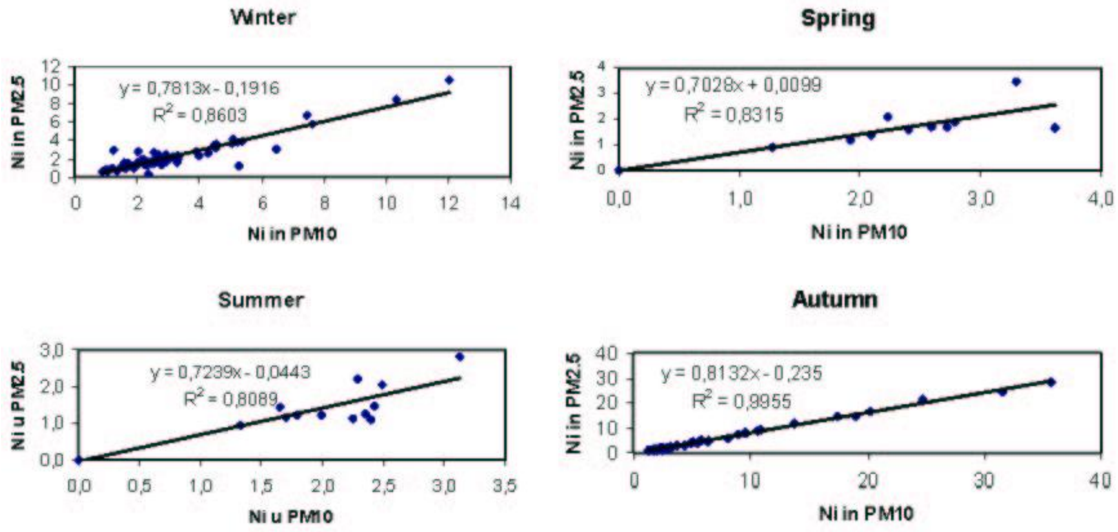

Fig. 2 - Correlation between mass concentrations of nickel in $PM_{10}$ and $PM_{2.5}$ particle fractions over all four seasons in 2011

Fig. 3 shows the correlation between mass concentrations of nickel in $PM_{10}$ and $PM_1$ particle fractions over all four seasons in 2011.

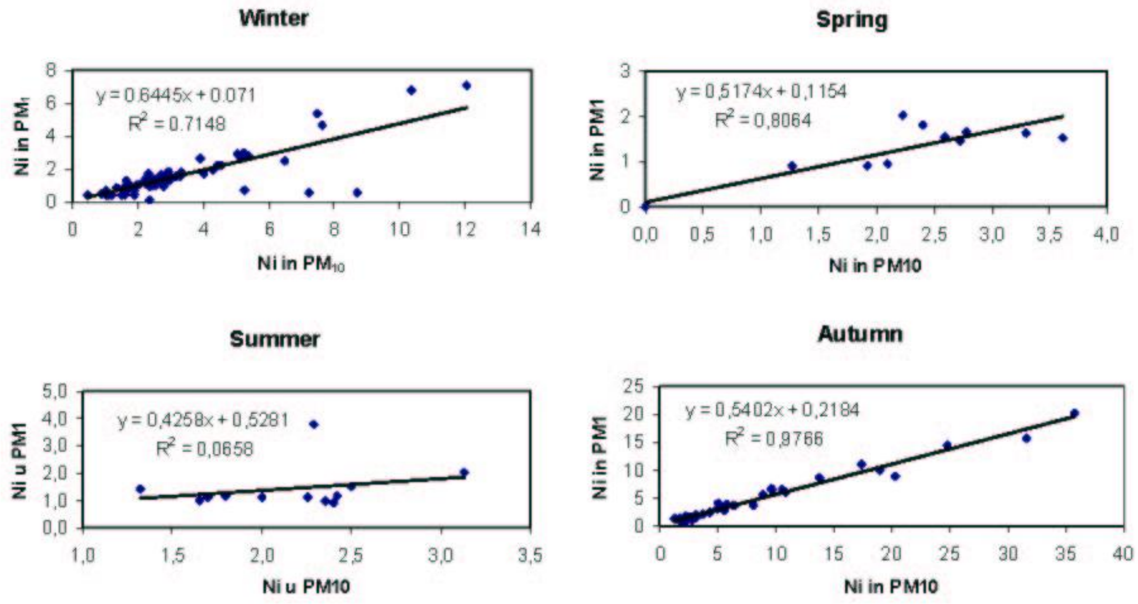

Fig. 3 Correlation between mass concentrations of nickel in $PM_{10}$ and $PM_1$ particle fractions over all four seasons in 2011

Fig. 4 shows the correlation between mass concentrations of nickel in $PM_{10}$ and $PM_{2.5}$ particle fractions and Fig. 5 in $PM_{10}$ and $PM_1$ particle fractions in 2011.

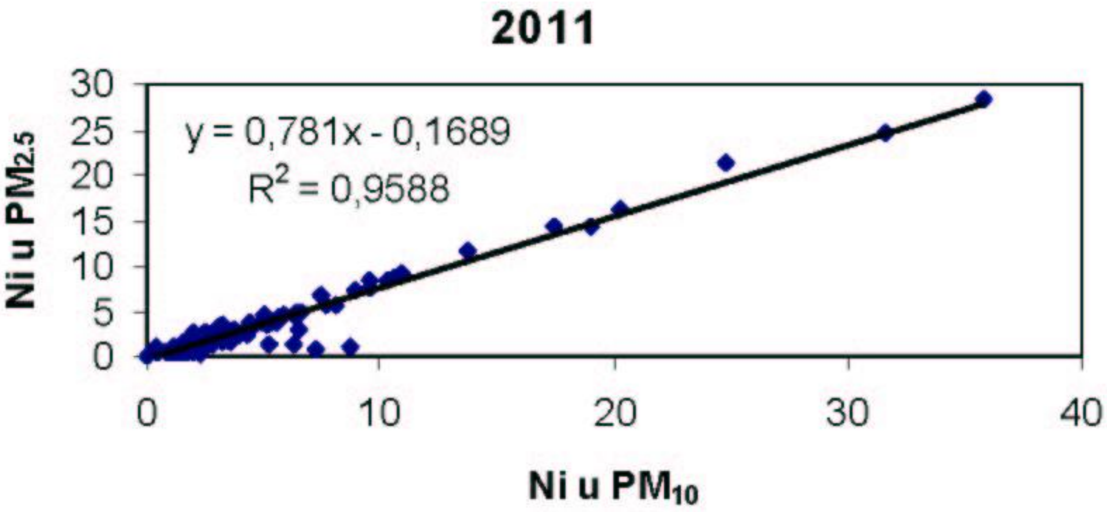

Fig. 4 - Correlation between mass concentrations of nickel in $PM_{10}$ and $PM_{2.5}$ particle fractions in 2011

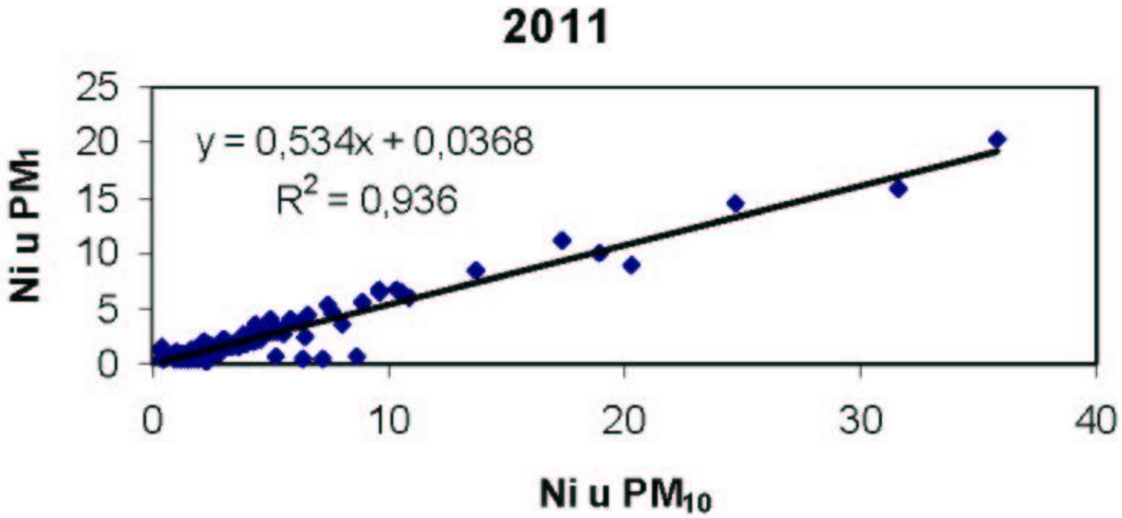

Fig. 5 - Correlation between mass concentrations of nickel in $PM_{10}$ and $PM_1$ particle fractions in 2011

In Table 2 the percentage of nickel in $PM_{2.5}$ and $PM_1$ particle fractions compared to their concentrations in $PM_{10}$ particle fractions in 2011 is shown.

Table 2 - The percentage of nickel in $PM_{2.5}$ and $PM_1$ particle fractions compared to their concentrations in $PM_{10}$ particle fractions in 2011

| Season | $PM_{2.5}$ | $PM_1$ |
|---|---|---|
| Winter | 78.1 | 64.5 |
| Spring | 70.3 | 51.7 |
| Summer | 72.4 | 42.6 |
| Autumn | 81.3 | 54.0 |
| Whole year | 78.1 | 53.2 |

Correlations between nickel in $PM_{10}$, $PM_{2.5}$ and $PM_1$ particle fractions showed seasonal differences in the percentage of nickel in $PM_{2.5}$ and $PM_1$ particle fractions compared to their concentrations in $PM_{10}$ particle fractions.

Compared to nickel in $PM_{10}$ particles 78.1% was found in $PM_{2.5}$ and 64.5% in $PM_1$ particles, during winter period. In spring, compared to nickel in $PM_{10}$ particles 70.3% was found in $PM_{2.5}$ and 51.7% in $PM_1$ particles. Compared to nickel in $PM_{10}$ particles 72.4% was found in $PM_{2.5}$ and 42.6% in $PM_1$ particles, during summer period. In autumn, compared to nickel in $PM_{10}$ particles 81.3% was found in $PM_{2.5}$ and 54.0% in $PM_1$ particles.

The results of mass concentrations determination of nickel in $PM_{10}$ and $PM_{2.5}$ particle fractions and the percentage of nickel in $PM_{2.5}$ compared to their concentrations in $PM_{10}$ particle fractions are in accordance with the results obtained in other countries like Italy (Lonati et al., 2005), Spain (Moreno et al., 2006; Querol et al., 2008), Sweden (Furusjö et al., 2007), Ireland (Byrd et al., 2010), Belgium (Bencs et al., 2010), France (Alleman et al., 2010) and on the south-eastern Mediterranean coast (Mamane et al., 2008).

In literature there are not publications with the results of nickel in $PM_1$ particle fraction. The measurement of metals in $PM_1$ particle fraction is at the very beginning of the research investigations.

## 4. CONCLUSION

Monitoring of nickel concentrations in $PM_{10}$ particle fractions in 2011 showed that its concentrations were not high. Annual mean value was below limit value.

Epidemiological studies have shown that particle size and chemical composition play a major role in the relative toxicity of particles.

The data obtained from nickel measurements in $PM_{10}$ respirable range particles in comparison with nickel in $PM_{2.5}$ and $PM_1$ thoracic range particles showed high percentage of nickel in small particles, especially in winter and autumn periods of measuring.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# DETERMINATION OF EMISSION PROFILES OF VOLATILE ORGANIC COMPOUNDS IN ANKARA ATMOSPHERE

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## ABSTRACT

Among the different types of VOC emission sources, emission profiles for motor vehicles including several fuel profiles are generated for Ankara during this study. Therefore Carbon numbers between 5 and 12, different VOCs were measured via GC-MS in Ankara atmosphere and 7 different source categories were prepared. The source categories for which the emission profiles are generated include running vehicle exhaust, cold-start, hot-soak (evaporative), whole gasoline, headspace gasoline, whole diesel and headspace diesel. Moreover, by using these source profiles a CMB study was also performed. However, in this study just whole gasoline profile was examined. Gasoline profiles generated in this work are presented, discussed and also compared with the profiles available in the literature.

**Key Words:** VOCs, Emission profiles, Urban air pollution, Vehicle exhaust, Gasoline

## 1. INTRODUCTION

VOCs are of concern in many urban areas not only due to their role in tropospheric $O_3$ formation but also due to their adverse impacts on human health. Many VOCs have been identified as toxic substances, and some of them are either known or suspected carcinogens.

The composition pattern of species emitted from a source category is referred to as a source profile or an emission profile. An emission profile can be expressed as the weight fraction, which is a ratio of each compound to the total mass of compounds in the source emission. Accurate speciated source profiles are needed for a successful development of emission control strategies.

VOC (Volatile Organic Compound) source profiles have been developed for several urban areas of the U.S.A., Canada, Japan and Australia. However, in Turkey, VOC emission inventories have not been generated yet. There are only a very few researches attempted at developing VOC emission profiles for Turkey during the last few years. It is postulated that potential major emission sources of VOCs in Ankara could be motor vehicles, residential heating and solvent use.

Running vehicle exhaust, cold-start, hot-soak (evaporative), whole gasoline, headspace gasoline, whole diesel and headspace diesel profiles were especially selected for the identification of the traffic originated organic compounds. Furthermore, a CMB (Chemical Mass Balance) study was also done to examine the contribution of the main VOC sources to the measured ambient VOC concentrations in Ankara atmosphere. However, in this work due to page limitation only whole gasoline source profile was examined.

## 2. ANALYSIS OF FUEL SAMPLES

Gasoline samples were analyzed to develop whole and headspace fuel fingerprints specific to Turkey for speciated VOCs. Two different brands of fuels namely British Petroleum (BP) and Petrol Ofisi (PO) were taken from the BP and PO gas stations located in Ankara.

Sample bottle filled with fuel sample waited at the room temperature for 5 min then it is submerged into water-bath that is at 60ºC. After 5 min, 1 mL of whole fuel sample was injected into a thermal desorption tube from its sampling end that was connected to the gas loading apparatus. Sample was purged for 5 min under 50 mL min$^{-1}$ of high purity $N_2$ flowing through multisorbent tube. Laboratory blanks were also analyzed and no contamination was found at a significant level. The tubes that were loaded with whole fuel sample were analyzed using short-path thermal desorber followed by gas chromatographyby a model 6890 GC system supplied by HP (Agilent Technologies Inc., Palo Alto, CA, U.S.A.) coupled to mass spectrometry by a model 5973 MS operated by a 90 L sec$^{-1}$ vapor-diffusion vacuum pump (SPDT/GC-MS) and equipped with an electron multiplier detector. Analytical column was a 60m×0.32mm J&W(Palo Alto, CA, USA) DB-1 with 1 _dimethlypolysiloxanecoating and He was used as a carrier gas.

The GC–MS parameters that were optimized for the determination of 98 target VOCs whose carbon numbers between 2 and 12. Retention times as well as target and qualifying ions used in the SIM mode of GC–MS operation. The optimum GC–MS parameters provided good chromatographic peak resolution for almost all target analytes. In order to attain the optimization of stability and response, optimum SPTD parameters have been obtained. The detailed information about optimization of the SPDT/GC-MS and method performanceparameters is given in a previous publication (Kuntasal et al., 2005).

A gas phase mixture of VOCs including 148 individual compounds (2–20gm$^{-3}$) ranging from C2 to C12 was supplied by Environment Technology Center, Environment Canada (Ottawa, Canada).A calibration gas containing 2–20gm$^{-3}$ of each compound was prepared in a pressurized 15 L SUMMA polished canister by mixing standards having purity of 98% or higher and seven different stock gas mixtures that were purchased from Scott Specialty Gases (Plumsteadville, PA, USA). The calibration gas was analyzed and quantified against standard reference material SRM 1800 (non-methane hydrocarbon compounds in nitrogen) and 1804a (volatile organics in nitrogen) provided by the National Institute of Standards and Technology (NIST) (Gaithersburg, MD, USA).

External standard calibration and internal standard addition method was used for the GC–MS quantification and bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d5, and 1-bromo-4-fluorobenzenewere used as internal standards. A 10mL of gas phase I.S. was added to all sample tubes prior to analysis. Quantification was performed according to relative response factor (RRF) calculations.

## 3. RESULTS AND DISCUSSION

Whole-gasoline profiles can be used to represent emissions of unburned gasoline during cold-start conditions, rapid accelerations, and running losses from saturated fuel-injection systems (Doskey et al., 1999). The compositions of two different fuel brands, which are sold in Ankara, are shown in Table 1. The given values are in weight percent and they are normalized for the compound set ranging from C5 to C12.

Composition of the whole gasoline profiles for Brand-1 and Brand-2 do not show a significant variation (± 10%). However, heavier aromatic compounds including n-propylbenzene, 3-ethyltoluene, 4-ethyltoluene, 1,3,5-trimethylbenzene, 2-ethyltoluene and 1,2,4-trimethylbenzene have higher contribution in Brand-1 Unleaded Gasoline than Brand-2 Unleaded Gasoline.

However, these compounds have lower contributions in Brand-1 Leaded Gasoline as compared to Brand-2 Leaded Gasoline.

Contribution of aromatic substances to Brand-1 Unleaded and Brand-2 Unleaded Gasoline profile compositions were found as 44% and 40%, respectively. In addition to this, total aromatic content of Brand-2 Leaded Gasoline is higher (i.e., 38%) than that of Brand-1 Leaded Gasoline (i.e., 35%). Benzene content of both brands was found almost same (i.e., 3%). However, Toluene content was slightly different for unleaded gasoline. Toluene content was higher in Brand-2 Unleaded Gasoline than the Brand-1 Unleaded gasoline.

Table 1. Whole gasoline profiles for two different brands.

| **Compound name** | **Brand-1 (Wt %)** | | **Brand-2 (Wt %)** | |
|---|---|---|---|---|
| | **Unleaded** | **Leaded** | **Unleaded** | **Leaded** |
| Pentane | 2.82 | 3.47 | 2.86 | 3.03 |
| 2,2-dimethylbutane | 1.80 | 2.87 | 1.67 | 2.76 |
| 2,3-dimethylbutane | 1.47 | 2.03 | 1.35 | 1.91 |
| t-4-methyl-2-pentene | 0.07 | 0.09 | 0.07 | 0.08 |
| 2-methylpentane | 4.52 | 5.87 | 4.17 | 5.34 |
| c-4-methyl-2-pentene | 0.08 | 0.10 | 0.08 | 0.10 |
| 3-methylpentane | 3.47 | 4.87 | 3.62 | 4.43 |
| 1-hexene/2-methyl-1-pentene | 6.65 | 9.24 | 6.84 | 8.44 |
| Hexane | 2.55 | 2.68 | 2.50 | 2.53 |
| c-3-methyl-2-pentene | 2.59 | 4.06 | 2.31 | 4.02 |
| 2,2-dimethylpentane | 0.35 | 0.27 | 0.31 | 0.25 |
| Methylcyclopentane | 1.29 | 2.04 | 1.19 | 2.02 |
| 2,4-dimethylpentane | 0.50 | 0.35 | 0.45 | 0.36 |
| Benzene | 3.16 | 2.60 | 3.19 | 2.64 |
| Cyclohexane | 0.45 | 0.85 | 0.41 | 0.80 |
| 2-methylhexane | 2.03 | 1.62 | 2.06 | 1.64 |
| 2,3-dimethylpentane | 0.95 | 0.72 | 0.90 | 0.69 |
| 3-methylhexane | 2.32 | 1.95 | 2.43 | 1.93 |
| 1-heptene | 0.12 | 0.13 | 0.11 | 0.12 |

| | | | | |
|---|---|---|---|---|
| Heptane | 1.88 | 1.44 | 1.85 | 1.47 |
| c-2-heptene | 2.85 | 2.09 | 2.72 | 2.14 |
| 2,2-dimethylhexane | 0.07 | 0.05 | 0.07 | 0.05 |
| Methylcyclohexane | 0.36 | 0.48 | 0.33 | 0.47 |
| 2,5-dimethylhexane | 0.14 | 0.10 | 0.13 | 0.10 |
| 2,4-dimethylhexane | 0.29 | 0.21 | 0.27 | 0.21 |
| Toluene | 6.63 | 7.37 | 8.97 | 7.13 |
| 3-methylheptane | 0.77 | 0.55 | 0.71 | 0.56 |
| c-1,3-dimethylcyclohexane | 0.07 | 0.09 | 0.06 | 0.10 |
| 2,2,5-trimethylhexane | 0.36 | 0.26 | 0.34 | 0.26 |
| Octane | 0.49 | 0.33 | 0.44 | 0.35 |
| Ethylbenzene | 2.47 | 1.89 | 2.41 | 2.04 |
| m,p-xylene | 8.18 | 7.56 | 9.20 | 7.95 |
| o-xylene | 4.14 | 3.33 | 3.96 | 3.59 |
| Nonane | 0.09 | 0.05 | 0.07 | 0.06 |
| iso-propylbenzene | 0.27 | 0.18 | 0.20 | 0.20 |
| n-propylbenzene | 1.04 | 0.70 | 0.74 | 0.85 |
| 3-ethyltoluene | 2.90 | 2.18 | 2.18 | 2.63 |
| 4-ethyltoluene | 1.76 | 1.22 | 1.24 | 1.45 |
| 1,3,5-trimethylbenzene | 2.15 | 1.50 | 1.40 | 1.85 |
| 2-ethyltoluene | 1.11 | 0.75 | 0.70 | 0.92 |
| 1,2,4-trimethylbenzene | 4.25 | 3.26 | 2.88 | 4.10 |
| iso-butylbenzene | 0.06 | 0.04 | 0.03 | 0.05 |
| sec-butylbenzene | 0.06 | 0.04 | 0.03 | 0.05 |
| 1,2,3-trimethylbenzene | 0.90 | 0.58 | 0.44 | 0.77 |
| 1,4-diethylbenzene | 0.90 | 0.60 | 0.32 | 0.92 |
| Naphthalene | 0.15 | 0.08 | 0.04 | 0.14 |
| **Paraffins** | **43.94** | **48.80** | **47.44** | **46.23** |
| **Olefins** | **11.97** | **16.36** | **12.83** | **15.50** |
| **Aromatics** | **44.09** | **34.84** | **39.73** | **38.27** |

Unleaded whole gasoline profile which was prepared for Ankara together with the whole gasoline profiles for Ottawa, Atlanta, Cairo and Seoul are shown in Figure 1. The data available in the literature were selected so as to enable comparison from different geographical regions. Only the unleaded gasoline profile developed for Ankara was compared with the literature since the data on leaded gasoline profile is scarce in the literature.

The whole gasoline profiles for Atlanta and Ottawa are very similar. The Seoul profile has a different composition from rest of the profiles for most of its compounds. Cairo profile has a similar pattern to that of Atlanta and Ottawa except its very high aromatic content including benzene, toluene, ethylbenzene, m&p-xylene and o-xylene.

Ankara profile has a distinct pattern showing similarities to Ottawa, Atlanta and Cairo profiles. Toluene content in the Ankara profile (i.e., 7.8%) is very similar to that of the Atlanta profile (i.e., 8.1%). Benzene content, on the other hand, is about two and three times higher than that of Atlanta and Ottawa profiles, respectively. Benzene content of the Ankara profile (i.e., 3.2%) is same as the Cairo profile. Benzene is a known human carcinogen thus its concentration in gasoline is limited to 1% in the EU and the U.S.A. (Gwilliam et al., 2004).

Ethylbenzene, m&p-xylene and o-xylene contents of the Ankara profile is approximately a factor of two higher than that of Atlanta and Ottawa profiles but it is lower than that of the Cairo profile. Comparing the contribution of aromatics for the profiles provided in Figure 2 shows that Ankara (i.e., 42%) and Cairo (i.e., 48%) profiles have significantly higher aromatic content than the rest. Gasoline specifications in the EU set a maximum content of aromatics to 35%. Thus, the aromatic content of the Ankara gasoline should be decreased. Ankara gasoline has the highest olefin content (i.e., 12.4%). Maximum olefin content of gasoline is set to 18% in the EU. Thus olefin content of the Ankara gasoline is lower than the EU limit value. Paraffin content of the Ankara gasoline (i.e., 46%) is lower than that of Ottawa (50%) and Seoul (55%) gasoline. This is due to high percent contribution of aromatics in Ankara gasoline.

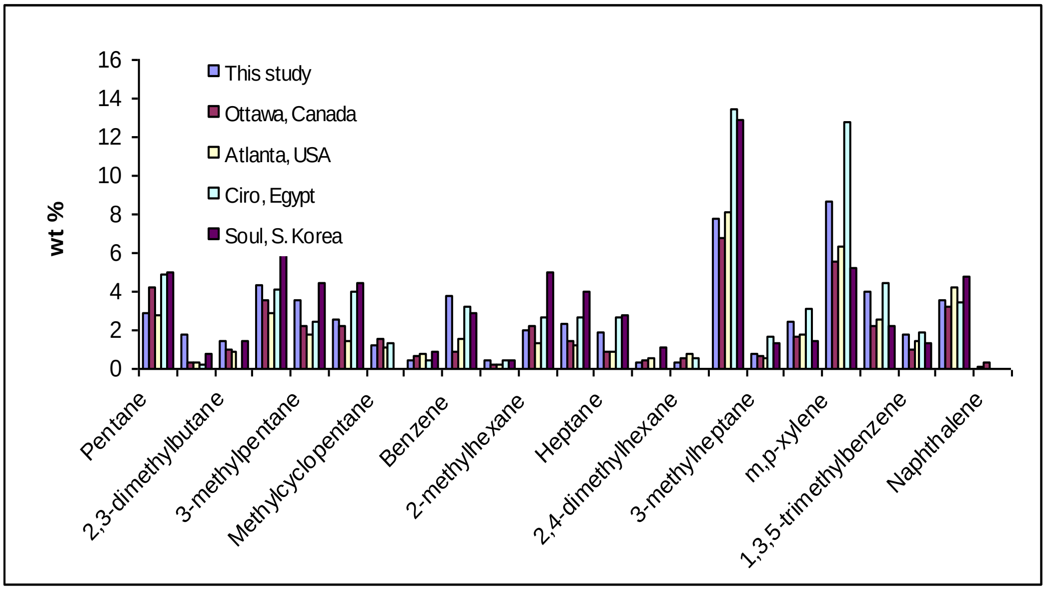

Figure 1. Comparison of the whole gasoline profiles (CPPI, 1994; Conner et al., 1995; Doskey et al., 1995; Na et al., 2002)

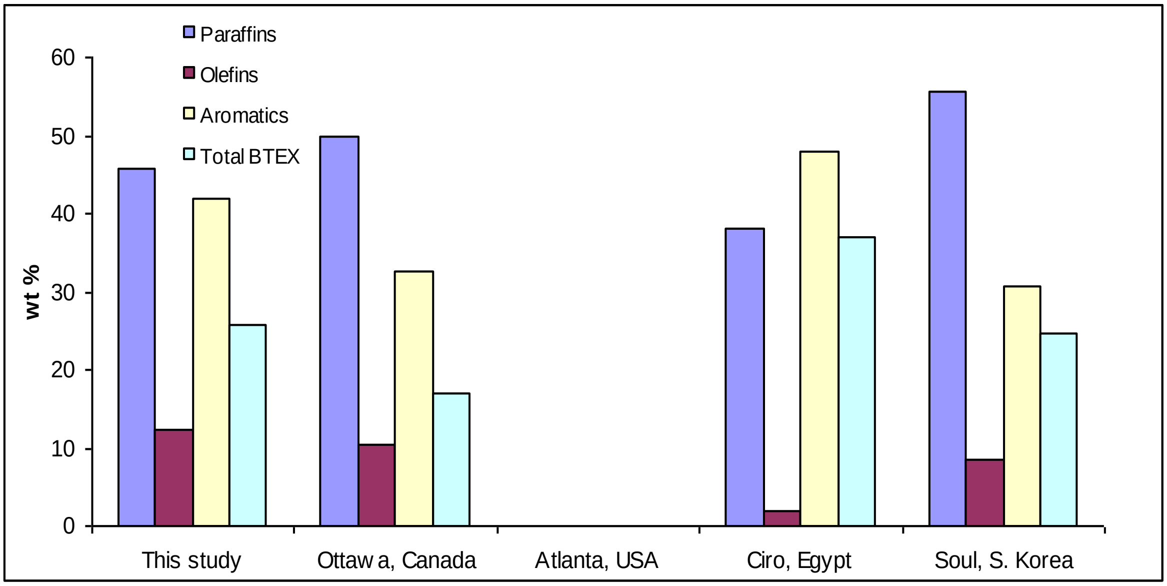

Figure 2. Comparison of groups for the whole gasoline profiles

## 4. CONCLUSION

Different brands investigated in this study have very similar whole gasoline compositions in Ankara. It is probably because these gas stations received gasoline from the same refinery.

Aromatic content of the Ankara gasoline is high. High contribution of aromatics is distinguished especially for unleaded gasoline indicating aromatics are used as octane enhancers. Fuel oxygenates as additive or reformulated gasoline can be considered to decrease high aromatic content of the unleaded gasoline.

Use of high aromatic content in the unleaded gasoline in Ankara without introducing catalytic converter to a significant share of the vehicles in use might result in significant increase in the toxic aromatic emissions.

Benzene content of Ankara gasoline is high (i.e., 3%).

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Na K., Kim Y.P, Moon I., Moon K.C., 2004. Chemical composition of major VOC emission sources in the Seoul atmosphere. Chemosphere 55, 585–594.

# RISK ASSESSMENT OF POLY CYCLIC AROMATIC HYDROCARBONS IN THE HOLY CITY OF MAKKAH, SAUDI ARABIA

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## ABSTRACT

Millions of pilgrims of different nations arrive in the Holy City of Makkah every year to perform Hajj and/or Umrah. Off course, increasing of pilgrims numbers is accompanied by the increase of their daily activities as well as the increase the demands of transportation means. Consequently, considerable quantities of either gaseous or solid pollutants are emitted to the atmosphere. In the current study, atmospheric concentrations of PAHs were evaluated in Makkah city to study particulate PAHs profiles during Hajj season of the year 1431H. Urban atmospheric particulate matter was collected using High Volume samplers. Samples of 24h were collected at three sampling sites (Al-Shebaikah, Al-Aziziah and Mina) whose characteristics were representative of the prevailing conditions. Eighteen PAHs were quantified by using GC technique, and total PAHs were ranged from 128.72 to 195.2 ng/m$^3$ with a mean value of 164.67 ng/m$^3$ for TSP, from 120.13 to 166.48 ng/m$^3$ with mean value of 137.81 ng/m$^3$ for PM$_{10}$ and from 103.5 to 184.95 ng/m$^3$ with a mean value 132.40ng/m$^3$ for PM$_{2.5}$, respectively. Makkah air quality is predominantly affected by road transport (automobiles) and is defined as heavy traffic and resuspended soils and road dust. Therefore, the percentage of the total carcinogenic compounds to the ΣPAH18 was calculated in the present study for different size of particulate matter in the three different locations. The higher percentages of the total carcinogenic compounds were recorded at Al-Shebaikah, with a maximum value of 63.5 % in PM$_{10}$ samples. The most carcinogenic PAHs, dibenzo[a]pyrene, was identified at very low concentrations. There is a lack of studying PAHs as environmental pollutants in Saudi Arabia. So that the current study focuses on studying of the risk assessment of polycyclic aromatic hydrocarbons (PAHs) In the Holy city of Makkah, Saudi Arabia. To the best of our knowledge, this study is considered as the first one in Saudi Arabia.

**Keywords:** Polycyclic Aromatic Hydrocarbons, Risk assessment, Makkah.

# TOXICITY EVALUATION AND SOURCE APPORTIONMENT OF PAHS AT THREE STATIONS IN ISTANBUL

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## ABSTRACT

This study focuses on the Polycyclic Aromatic Hydrocarbons (PAHs) in three monitoring stations in Istanbul, Turkey: Yildiz-URB1, DMO-URB2 (urban sites) and Kilyos-RUR (rural site). A total of 326 airborne samples were collected and analyzed for 16 PAHs and Total Suspended Particles (TSP) for the period of September 2006-December 2007. Benzo(a)Pyrene toxic equivalency factors (TEFs) to PAH concentration values were calculated indicating that the health risk of BaP and DiBenz(a,h)Anthracene (markers of traffic emissions) have the highest contribution compared to all of the other species measured at the sampling sites. In order to determine PAH sources, two different source apportionment techniques were applied to the measurements; diagnostic ratios and Positive Matrix Factorization.

**Keywords:** Polycylic Aromatic Hydrocarbons, Toxic Equvalency Factors, Positive Matrix Factorization, Diagnostic Ratios, Urban air

## 1. INTRODUCTION

Polycyclic Aromatic Hydrocarbons (PAHs) are semivolatile organic compounds consisting of two or more fused aromatic rings and produced mainly by incomplete combustion reactions of organic materials including fossil fuels at high temperatures (Li and Kamens, 1993). Though classified as persistent organic pollutants (POPs), PAH levels are affected by atmospheric removal and transformation processes (Galarneau, 2008).

The concentration of PAHs in urban air can range from trace to significant levels (Ravindra et al., 2001, 2006). Atmospheric concentrations are strongly depends on the size of airborne particulate matter with highest concentrations being in the respirable size range. (Baek et al., 1991; Venkataraman et al., 1994). PAHs are widely distributed in the atmosphere and are one of the first atmospheric pollutants that have been identified as suspected carcinogens. The recognized carcinogenic PAHs are mostly associated with particulate matter. As the molecular weight of a specific PAH increases, the carcinogenicity of PAHs also increases, and the acute toxicity decreases (Ravindra et. al. 2008).

The occurrence and sources of PAHs in the atmosphere have been widely studied especially in the last two decades. In most urban and rural areas, airborne PAHs mainly originate from automobile exhausts and/or combustion of fossil fuel (Khalili et al., 1995; Rogge et al., 1993; Ravindra et al., 2006; Sharma et. al., 2007; Singh et. al., 2008). In addition to diesel and gasoline engine vehicles, trains, aircrafts, ships also contribute significantly to the mobile sources of PAHs (Ravindra et. al., 2008). Residential heating is another important source group for PAHs. Besides coal combustion, natural gas burning is found to be a contributor to PAH concentrations in urban air (Yang and Chen 2004; Rogge et. al., 1993; Ravindra et. al., 2008).

Istanbul extends both on the European and the Asian sides of the Bosphorus, and is thereby is situated on two continents. Because of its unique location, transportation is one of the major problems in the city and is also one of the most important sources of air pollution. In this study, firstly PAH concentrations were determined in the city and these results were evaluated with respect to their toxicity aspect. Two different source apportionment techniques were applied to the results; diagnostic ratios and PMF and results o the source apportionment applications were evaluated in detail.

## 2. MATERIAL AND METHOD

**2.1 Study area:** Atmospheric concentration of PAHs and TSPs were measured in Istanbul from September 2006 to December 2007. Three monitoring stations, namely Yildiz, DMO and Kilyos were selected as measuring locations to characterize the PAH concentrations in ambient air in Istanbul (Figure 1).

Figure 1. Locations of sampling stations

Yildiz station (URB1), located in the campus of Yildiz Technical University, represents the urban atmosphere of the European part of the city. This sampling site has high traffic activity and is surrounded by residential and commercial areas. The sampler was sited 1.5 m above the ground level and about 4 m away from a busy road (50,000-75,000 vehicles per day). The second sampling site, DMO (URB2), was selected for being on the Asian part of the city and having urban atmospheric properties. This station is located just next to the Bosphorus Bridge Highway, which is one of the two intercontinental bridges in Istanbul. This sampling site was characterized by high traffic density and by being in a residential area, therefore was defined as an “urban” station. The sampler was sited about 1.5 m above the ground level and about 10 m away from the busy bridge highway (75,000-100,0000,000 vehicles per day). The third sampling station was selected for having rural area properties and being on the north of the city which is the upwind direction for dominant northerly winds. Kilyos (RUR), which is in the European side of the city, is located in Bogazici University Saritepe Campus. This site is on the Black Sea coast and is not populated, except for the campus building surrounding the station. This station was defined as a background “rural” site. In this station the sampling platform was about 15 m above the sea level.

**2.2 Ambient Measurements:** In the sampling sites, number of samples collected were 135, 129 and 62 for URB1, URB2 and RUR stations, respectively. Sampling days were chosen as the weekdays in the period of September 2006-December 2007. Airborne samples were collected using PS-1 samplers (GPS1 PUF Sampler, General Metal Work) to collect airborne particle-bound PAHs and TSP. All the sampled filters and glass cartridges were placed in appropriate soxhlet extractors and extracted with a n-hexane:diethylether mixture (9:1, v/v) for 20 h. Using procedures described by EPA Method TO13A and 3630C (USEPA 1999a,b). The analyses of all the extracts for PAHs were performed by the means of reversed-phase HPLC using UV-visible and fluorescence detectors in series. The HPLC system comprised a

Dionex 4500i chromatograph. Separation was performed by the means of a Vydac 201TP5415 column with a corresponding guard cartridge. Pre-analysis procedures, quality assurance and analysis were described in detail elsewhere (Hanedar et. al., 2010).

## 3. RESULTS

**3.1 PAH concentrations:** The seasonal data were statistically analysed and presented in Table 1, where the seasonal median, mean along with the minimum and maximum values of the concentration for each PAH compound and the total PAH concentration (sum of the single analysed compounds) were given. The total average PAH concentrations were 100.7±61.3, 84.6±46.7 and 25.1±13.3 ng $m^{-3}$ and the TSP concentrations were 101.2±53.2, 152.3±99.1, 49.8±18.6 µg m-3 for URB1, URB2 and RUR stations, respectively. As seen from Table 1, the maximum concentrations for all stations were observed for the Winter 2006 and the minimum values were observed for the Summer 2007 and Fall 2007 periods in terms of average values. In the literature, several other studies also indicated the peak concentrations of PAHs in urban areas were found in winter (Ravindra et. al., 2006; Muller et. al., 1998; Halsall et al., 1994; Smith and Harrison, 1996; Panther et al., 1999; Park et al., 2002; Guo et al., 2003, Sharma et. al. 2007). These elevated concentrations can be explained by higher emissions of PAHs in the winter from higher fuel consumption for heating purposes, more traffic volumes and the atmospheric stability processes that prevent the dispersion of the pollutants. For all stations, the concentrations measured for the year 2006 were higher than those measured in 2007 and the minimum seasonal effect was observed for the RUR station.

**3.2 Application of Toxic Equivalency Factors:** Risk assessment associated with inhalatory PAH uptake is often estimated on the basis of the BaP concentration in the air. Generally, in health risk studies, BaP is used as a marker substance because it was evaluated in most relevant studies, as being responsible for 50% of the carcinogenic potential of PAHs (according to recent knowledge) and scientific background concerning BaP seems to be sufficient for establishing a limit value (Petry et. al., 1996).

**Table 1.** Statistical information for the total PAHs concentrations (ng/m$^3$)
Sample number (n), minimum (Min), maximum (Max), average (Ave), standard deviation (SD)

| **URB1** | | | | | **URB2** | | | | | **RUR** | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **n** | **Min** | **Max** | **Ave** | **SD** | **n** | **Min** | **Max** | **Ave** | **SD** | **n** | **Min** | **Max** | **Ave** | **SD** |
| **2006 Fall (September-November 2006)** | | | | | | | | | | | | | | |
| 16 | 31,1 | 244,2 | 108,1 | 64,2 | 15 | 8,5 | 129,8 | 60,8 | 45,3 | 8 | 10,3 | 57,1 | 33,7 | 17,4 |
| **2006 Winter (December 2006-February 2007)** | | | | | | | | | | | | | | |
| 30 | 64,5 | 276,9 | 150,9 | 57,6 | 25 | 53,7 | 224,4 | 126,6 | 38,3 | 11 | 20,7 | 58,5 | 34,8 | 13,3 |
| **2007 Spring (March-June 2007)** | | | | | | | | | | | | | | |
| 32 | 7,5 | 283,3 | 101,1 | 66,1 | 41 | 48,2 | 194,9 | 106,8 | 42,7 | 6 | 13,2 | 49,8 | 30 | 15,9 |
| **2007 Summer (July-August 2007)** | | | | | | | | | | | | | | |
| 26 | 14,6 | 141,5 | 65,5 | 6,2 | 26 | 22,6 | 86,4 | 56,8 | 15,5 | 21 | 7,1 | 36 | 18,5 | 7,8 |
| **2007 Fall (September-November 2007)** | | | | | | | | | | | | | | |
| 31 | 21,5 | 216,8 | 77,3 | 45,8 | 22 | 14 | 76,1 | 44,8 | 19,5 | 7 | 7,2 | 34,9 | 17,6 | 9,9 |
| | | | | | | | | | | **2007 Winter (December 2007)** | | | | |
| | | | | | | | | | | 9 | 10,5 | 40,9 | 23,7 | 9 |

The establishment of TEFs for PAHs, helps to characterize the carcinogenic properties of PAH mixtures precisely. To date, only a few proposals concerning TEFs for PAHs are available. Nisbet and LaGoy (1992), completed a list of TEFs which seems to better reflect the actual state of knowledge on the relative potency of individual PAHs. Here, Nisbet and LaGoy (1992) approach will be used to evaluate the human health risk relating to inhalatory exposure to PAHs.

Table 2 indicates mean concentrations for individual PAH and TSP at the sampling sites with BaP equivalents. Total carcinogenic activity of PAHs at the sites were 2,16; 2,65 and 1,26 ng m$^{-3}$ for URB1, URB2 and RUR stations, respectively. BaP contribute to approximately the half of the activity for the sites. Carcinogenic acitivity of BaP reaches to elevated values in cold periods depending on the higher concentration values for all the sites. The second highest BaP equivalent compound was DBA, occupying 23,1; 25,8 and 31,8 % of total carcinogenic activity for URB1, URB2 and RUR sites, respectively.

Georgiadis et al. 1999, indicated that the range of airborne PAHs and examined exposure in various biomarker-based studies varies by several orders of magnitude. In their study, total PAH concentrations were around 20–200 ng m$^{-3}$ and BaP concentrations around 5–50 ng m$^{-3}$ for urban areas. Petry et al. 1996 indicated that the sum of BaP equivalency was about 0,96 ng m$^{-3}$ for city environment. Fang et al. 2004 investigated a total BaP equivalency of about 12,6 ng m$^{-3}$ for urban site, and BaP occupied about 50% of the activity. These researches indicate that the higher BaP concentration ratios occur in urban sampling sites due to traffic exhausts. In this study, BaP equivalency results indicated that the health risk BaP and DBA, which are markers of traffic emissions, have the biggest contribution among all the species in the urban sampling sites.

**Table 2.** Average concentrations for individual PAH and TSP with BaP equivalents

| **Individual PAHs** | **TEF Values Nisbet and Lagoy, 1992** | URB1 (n=135) | | URB2 (n=129) | | RUR (n=62) | |
|---|---|---|---|---|---|---|---|
| | | Conc. (ng/m$^3$) | Ave. BaP eq., (ng/m$^3$) | Conc. (ng/m$^3$) | Ave. BaP eq.. (ng/m$^3$) | Conc. (ng/m$^3$) | Ave. BaP eq. (ng/m$^3$) |
| Nap | **0.001** | 34.7 | 0.035 | 22.9 | 0.023 | 6.1 | 0.0061 |
| AcPy | **0.001** | 13.7 | 0.014 | 8.3 | 0.008 | 2.1 | 0.0021 |
| AcP | **0.001** | 2.1 | 0.002 | 1.7 | 0.002 | 0.7 | 0.0007 |
| Flu | **0.001** | 4.2 | 0.004 | 2.6 | 0.003 | 0.9 | 0.0009 |
| PA | **0.001** | 20.2 | 0.020 | 16.8 | 0.017 | 2.9 | 0.0029 |
| Ant | **0.01** | 5.2 | 0.052 | 7.9 | 0.080 | 2.5 | 0.025 |
| FL | **0.001** | 7.0 | 0.007 | 7.9 | 0.008 | 2.9 | 0.0029 |
| Pyr | **0.001** | 4.7 | 0.005 | 5.1 | 0.005 | 2.3 | 0.0023 |
| BaA | **0.1** | 1.4 | 0.135 | 1.7 | 0.173 | 0.7 | 0.07 |
| CHR | **0.01** | 1.7 | 0.017 | 2.5 | 0.025 | 1.1 | 0.011 |
| BbF | **0.1** | 1.2 | 0.121 | 1.4 | 0.144 | 0.7 | 0.07 |
| BkF | **0.1** | 0.4 | 0.041 | 0.5 | 0.045 | 0.3 | 0.03 |
| BaP | **1** | 1.1 | 1.112 | 1.3 | 1.288 | 0.6 | 0.6 |
| IND | **0.1** | 0.8 | 0.084 | 1.3 | 0.126 | 0.3 | 0.03 |
| DBA | **1** | 0.5 | 0.499 | 0.7 | 0.683 | 0.4 | 0.4 |
| BghiP | **0.01** | 1.7 | 0.017 | 1.9 | 0.020 | 0.5 | 0.005 |
| Total PAHs | **-** | **100.7** | 2.164 | **84.6** | 2.648 | **25.1** | 1.26 |
| TSP (µg m$^{-3}$) | | 101.2 | - | 152.3 | - | 49.8 | - |

## 3.3 Source Apportionment Applications

**3.3.1 Diagnostic Ratios:** One of the atmospheric PAHs source apportionment methods given in the literature is diagnostic ratios (DR). Ratio of specific PAHs to each other or total PAHs are used as an indicator of sources, especially for vehicle emissions. These relative amounts, which can be based on particle or total (gas+particle) concentrations, are typically presented as DRs of two isomeric species or as profiles representing several species at once (Galarneau, 2008). The most important advantage of this method is less calculation requirement. However, the method should be used with caution because it is often difficult to discriminate between some of the sources such as fuel differentation for vehicle sources or coal and other biomass fuels (Ravindra et al., 2006).

In Table 3, DRs from reviewed in Ravindra et. al. 2008 were given with application to PAH concentration determined in this study. There are eight different DR values tabulated. According to the results of this application, measured PAH concentrations in the urban stations originates mainly from traffic sources. In addition, diesel emissions were the dominant source types. In rural stations, it was likely that multiple PAH sources including motor vehicles may contribute to the PAH source profiles. However, diesel emissions were unexpectedly the dominant type here as well. A likely explanation for this unexpected result is the emissions from the ships which are waiting to pass to the strait which connects the Black Sea to the Marmara Sea.

Table 3. Diagnostic ratio application results

| **Diagnostic ratios** | **Value** | **Indicator Source** | **References** | **This Study** | | **Probable Sources** |
|---|---|---|---|---|---|---|
| | | | | **Station** | **Value** | |
| **IND/(IND+ BghiP)** | 0.18<br>0.35-0.70<br>0.56<br>0.62 | Cars<br>Diesel<br>Coal<br>Wood Burning | Ravindra et. al., (2006);<br>Kavouras et. al., (2001) | URB1 | 0.31 | Diesel |
| | | | | URB2 | 0.36 | Diesel |
| | | | | RUR | 0.28 | Cars |
| **Flu/(Flu+Pyr)** | >0.5 | Diesel | Rogge et. al. (19993a,b);<br>Fang et. al. (204);<br>Ravindra et. al. (2006) | URB1 | 0.48 | Diesel |
| | <0.5 | Gasoline | | URB2 | 0.6 | Diesel |
| | | | | RUR | 0.29 | Gasoline |
| **BaP/(BaP+ CHR)** | 0.5 | Diesel | Khalili et. al. (1995);<br>Guo et. al. (2003) | URB1 | 0.38 | Diesel |
| | 0.73 | Gasoline | | URB2 | 0.37 | Diesel |
| | | | | RUR | 0.4 | Diesel |
| **BbF/BkF** | >0.5 | Diesel | Pandey et. al. (1999);<br>Park et. al. (2002) | URB1 | 2.9 | Diesel |
| | | | | URB2 | 4.5 | Diesel |
| | | | | RUR | 5.8 | Diesel |
| **BaP/BghiP** | 0.5-0.6 | Traffic emission | Pandey et. al. (1999);<br>Park et. al. (2002) | URB1 | 1.04 | Traffic emission |
| | >1.25 | Brown coal | | URB2 | 1.15 | |
| | | | | RUR | 1.35 | Brown Coal |
| **IND/BghiP** | <0.4 | Gasoline | Caricchia et. al. (1999) | URB1 | 1.28 | Diesel |
| | ~1 | Diesel | | URB2 | 1.61 | Diesel |
| | | | | RUR | 0.85 | Diesel |
| **Pyr/BaP** | ~10 | Diesel | Oda et. al. (2001) | URB1 | 9.3 | Diesel |
| | ~1 | Gasoline | | URB2 | 9.02 | Diesel |
| | | | | RUR | 14.9 | Diesel |
| **FL/Pyr** | 0.6 | Vehicular | Neilson et. al. (1998) | URB1 | 3.6 | - |
| | | | | URB2 | 2.87 | - |
| | | | | RUR | 1.69 | - |

**3.3.2 Positive Matrix Factorization (PMF):** Receptor models are mathematical or statistical procedures for identifying and quantifying the sources of air pollutants at a receptor location. Beside various receptor modeling techniques including the chemical mass balance (CMB) method, principal component analysis, multiple linear regression and individual particle analysis, another factor analysis technique, PMF, has also been used for the source apportionment of urban aerosols. In PMF applications, all of the values in the solution profiles and contributions forced to be nonnegative, which is more realistic than solutions from other used methods. With careful selection of modeling parameters, PMF has been found to be more powerful in source identification than the other factor analysis techniques (Chan et. al., 2008; Huang et al., 1999).

There are number of studies about source apportionment of PAHs with receptor based models but a limited number of these studies consists of PMF application on PAH concentrations (e.g. Lee et. al., 2004; Larsen and Baker, 2003; Chan et. al., 2008).

EPA PMF1.1, which is used in out study, solves the general receptor modeling problem using constrained, weighted, least squares. The modeling procedures may be divided into three broad steps: (1) preparing data to be modeled (creation of data uncertainties, selection of the best number of factors); (2) processing the data with PMF to develop a feasible and robust solution (treatment of outliers) and (3) interpreting the solution.

**Modeling parameters:** In PMF application, two input files must be necessary, one file with the concentrations and one with the uncertainties associated with those concentrations (USEPA, 2005). PMF requires an uncertainty estimate for each variable. In the application, measurement precision for each compound was calculated by propagation of the error, taking into consideration the uncertainties in sampling, extraction, and analysis. In PMF application, Equation based uncertainties option was used as MDL and error percentages were prepared for each compound and uncertainties were calculated in the model. In processing 20 random starting points were applied in order to find the global minimum.

**Number of factors:** Careful selection of the number of factors is essential in getting sensible results from PMF analysis. This selection process is still largely determined by trial-and-error and the experiences of the other researchers reported in the literature (Paatero, 2004). In this study, DR results were used as a tool to decide on the number of factors. First of all, diesel and gasoline sources were performed separately in urban stations. This separation could be achieved by PMF technique, according to Larsen and Baker, 2003. Another suprising indication of the DR application is traffic source group being important for the rural station. Finally five factors were applied to the urban sites and four factors were applied to the rural site. Factors were named based on the information about the source profiles compiled using different literature studies.

## PMF results:

*PMF results for URB1:* 5 factors were applied to URB1. In PMF application AcPy ve AcP determined as “weak” species. Factor values were given in Table 4.

*Factor 1:* In this factor heavier PAHs had low concentration and TSP loading was 0. In seasonal variation, minor loading was observed in summer. This factor was dominated by Ant, FL, Pyr and CHR, which are originated from natural gas (NG) combustion source (Yang and Chen, 2004, Li et. al., 1999, Lee et. al., 2004).

*Factor 2:* Heavy species especially BkF have moderate loadings in this factor. BkF is the indicator of diesel engines (DE) (Duval et. al.1981, Khalili et. al., 1995; Harrison et. al., 1996). But with comparison with Factor 5 (F5), this factor is determined as representative of gasoline Engines (GE). BaP, Pyr and BaA was moderate loading and these species were originated from GE (Guo et. al. 2003, Lee et. al., 2004; Li et. al. 2003, Larsen and Baker, 2003). In seasonal variation, fall 2006 and spring 2007 has the maximum contributions.

*Factor 3:* This factor was dominated by Flu, AcPy, CHR, DBA species and TSP. The loadings of total PAHs was increased in warm periods. This factor is determined as the “other group” which includes asphalt dust, evaporation of oil etc. (Harrison et. al., 1996, Lee et. al., 2004; Singh et. al., 2008).

*Factor 4:* It is determined that this factor was originated from fossil fuels because of moderate loadings of Acp, PA, Ant, DBA (Larsen and Baker, 2003, Halshall et. al., 1997). These species was coming from coal and wood combustion (CW) which were limited in the sampling location. However, indicators of coal combustion are Pyr, BaP, BaA (Harrison et. al., 1996, Simcik et. al., 1999, Wan et. al., 2006) and only BaA species have modetarely contribution in the factor. Summer periods have decreasing contributions in this factor and maximum contribution was observed in winter 2006.

*Factor 5:* The loadings of heavy PAH species were high in this factor. Maximum contribution was observed for IND, BghiP, BaA, BkF and BbF. This factor was determinated as being originated from DE (Singh et. al., 2008; Miguel and Pereira, 1989; Harrison et. al., 1996, Li et. al., 2006). Moderate contributions of BbF and BkF were also an indicator of DE (Duval et.

al., 1981, Khalili et. al. 1995; Harrison et. al., 1996; Lee et. al., 2004). In seasonal variation, maximum contribution was observed in winter 2006 and spring 2007.

*PMF results for URB2:* Five factors were selected to the station and AcPy was determined as the “weak” species.

*Factor 1:* This factor was dominated by FL, AcPy, IND and BaP. Lighter PAHs had moderate loadings. It is determined that this factor was originated from CW sources because of the moderate loadings of BaP and TSP, besides decreasing contribution in summer periods (Harrison et. al., 1996, Simcik et. al., 1999, Wan et. al., 2006).

*Factor 2:* The loadings of lighter PAHs were high for this factor. The dominant species was Ant, Pyr, Acp, FL and Nap. Minor quantities of TSP and decreasing loadings in summer were also observed. This factor was accounted for NG sources (Yang and Chen, 2004, Li et. al., 1999; Lee et. al., 2004).

*Factor 3:* DBA, AcPy, Flu, Acp and TSP have highest contributions to this factor. It is determined that this factor originated from “other” group (Harrison et. al., 1996; Lee et. al., 2004; Singh et. al., 2008).

*Factor 4:* Heavier PAHs had higher contributions and BkF, BaA, BaP and PA species had moderate loadings in this factor which originates from vehicle emissions (Ravindra 2006; Duval, et. al., 1981; Masclet et. al.1986; Fang et. al. 2004). Because of the relatively high contributions of BaP, Pyr and BaA, the origin of this factor was thought to be GE (Guo et. al., 2003; Duval et. al. 1981; Lee et. al., 2004; Li et. al., 2003, Larsen and Baker, 2003). In this factor significant seasonal variation is not observed.

*Factor 5:* The loadings of heavy species were high in this factor. Dominant species were BghiP, IND, CHR, BbF and BaA which are originated from DE, because of especially moderately contributions of BkF, IND and BghiP (Duval et. al. 1981; Ravindra 2006; Li et.al., 2006; Miguel and Pereira, 1989; Li et. al., 1993, Harrison et. al., 1996; Lee et. al., 2004, Li et. al., 2003; Singh et. al., 2008). Seasonal variation was low and maximum contribution was observed in spring 2007.

Table 4. PMF results- Source contribution (%) for URB1, URB2, RUR

| | Nap | AcPy | AcP | Flu | PA | Ant | FL | Pyr | BaA | CHR | BbF | BkF | BaP | IND | DBA | BghiP | TSP | **Source** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **URB1 (YILDIZ)** | | | | | | | | | | | | | | | | | | |
| **$R^2$** | 0.69 | 0.88 | 0.73 | 0.63 | 1 | 1 | 0.61 | 0.62 | 0.8 | 0.68 | 0.83 | 0.99 | 0.8 | 0.61 | 0.92 | 0.86 | 0.99 | - |
| **F1** | 20,6 | 8,5 | 14,9 | 0,0 | 19,7 | 87,1 | 60,6 | 37,7 | 18,8 | 31,2 | 17,4 | 1,0 | 12,8 | 13,3 | 16,9 | 0,0 | 0,0 | **NG** |
| **F2** | 19,9 | 0,0 | 16,9 | 29,4 | 21,9 | 0,0 | 12,1 | 29,3 | 9,9 | 13,6 | 15,5 | 83,0 | 36,6 | 0,4 | 10,9 | 1,3 | 0,0 | **GE** |
| **F3** | 20,9 | 39,5 | 14,9 | 65,5 | 0,0 | 0,0 | 26,9 | 22,7 | 3,8 | 31,9 | 5,7 | 0,0 | 11,8 | 0,0 | 28,7 | 11,3 | 70,4 | **Other** |
| **F4** | 0,0 | 11,0 | 31,5 | 5,1 | 25,8 | 12,9 | 0,4 | 0,0 | 10,3 | 0,0 | 9,0 | 0,0 | 4,1 | 0,0 | 11,6 | 1,8 | 19,5 | **CW** |
| **F5** | 38,6 | 41,1 | 21,8 | 0,0 | 32,7 | 0,0 | 0,0 | 10,3 | 57,2 | 23,4 | 52,3 | 16,0 | 34,8 | 86,3 | 31,9 | 85,5 | 10,2 | **DE** |
| **URB2 (DMO)** | | | | | | | | | | | | | | | | | | |
| **$R^2$** | 0.68 | 0.76 | 0.89 | 0.65 | 1 | 1 | 0.79 | 0.89 | 0.81 | 0.74 | 0.7 | 1 | 0.89 | 0.77 | 0.76 | 0.82 | 1 | |
| **F1** | 14,6 | 32,1 | 21,8 | 18,7 | 18,1 | 0,0 | 45,8 | 1,3 | 0,0 | 15,2 | 0,0 | 2,2 | 24,6 | 26,9 | 23,0 | 4,0 | 20,7 | **CW** |
| **F2** | 32,9 | 29,5 | 45,8 | 24,8 | 6,5 | 92,7 | 33,4 | 47,9 | 0,0 | 0,0 | 20,7 | 0,0 | 2,6 | 11,5 | 7,1 | 1,8 | 1,8 | **NG** |
| **F3** | 8,6 | 30,9 | 25,8 | 27,4 | 6,8 | 7,3 | 11,6 | 10,3 | 9,2 | 19,7 | 0,0 | 0,0 | 23,0 | 0,0 | 32,4 | 10,4 | 76,9 | **Other** |
| **F4** | 28,9 | 7,5 | 6,5 | 21,8 | 25,7 | 0,0 | 9,2 | 21,2 | 44,9 | 5,4 | 21,3 | 97,8 | 34,2 | 0,0 | 9,6 | 3,9 | 0,0 | **GE** |
| **F5** | 15,0 | 0,0 | 0,0 | 7,4 | 42,9 | 0,0 | 0,0 | 19,3 | 45,9 | 59,7 | 58,0 | 0,0 | 15,7 | 61,6 | 27,8 | 79,8 | 0,5 | **DE** |
| **RUR (KILYOS)** | | | | | | | | | | | | | | | | | | |
| **$R^2$** | 0.77 | 0.85 | - | - | 0.87 | 0.81 | 1 | 0.62 | 0.77 | 0.95 | 0.77 | 0.8 | 0.73 | 0.74 | 0.84 | 0.82 | 0.89 | - |
| **F1** | 71,4 | 63,4 | - | - | 19,6 | 68,1 | 4,4 | 21,7 | 2,9 | 0,0 | 2,5 | 12,1 | 0,0 | 51,5 | 56,4 | 11,5 | 68,2 | **CW** |
| **F2** | 24,9 | 24,6 | - | - | 27,2 | 27,9 | 88,7 | 19,1 | 8,3 | 20,6 | 0,0 | 6,6 | 10,3 | 18,3 | 0,0 | 7,8 | 7,9 | **NG** |
| **F3** | 1,2 | 0,0 | - | - | 20,3 | 4,1 | 0,0 | 54,4 | 70,2 | 9,1 | 89,4 | 72,3 | 89,7 | 11,4 | 0,0 | 66,9 | 3,6 | **VE** |
| **F4** | 2,5 | 12,0 | - | - | 32,9 | 0,0 | 6,9 | 4,8 | 18,6 | 70,3 | 8,1 | 9,0 | 0,0 | 18,8 | 43,6 | 13,7 | 20,3 | **Other** |

*PMF results for RUR:* In this station, 4 factors were selected. Because of the low vehicle emissions, diesel and gasoline groups were applied together. Low PAHs concentration was observed for this station resulting in high "Signal/Noise" ratios for some species. In model application AcP and Flu species were "bad" and these species were extracted from the performance.

*Factor 1:* The loadings of TSP were high in this factor. Lighter PAHs (Nap and AcPy) had moderate contributions. Major quantities of PA, Ant, Pyr and DBA were known to come from coal, wood and agricultural sources (Larsen and Baker, 2003; Halshall et. al., 1997). This station was close to agricultural areas and biomass was burned in this areas. With observing of decreasing contributions in summer, this factor was determined as CW.

*Factor 2:* Lighter PAHs had moderate contributions in this factor. The factor is dominated by FL, Ant, PA, Nap, AcPy and CHR. Because of moderate contributions of Ant and FL, it is determined that this group is NG source (Yang and Chen, 2004; Li et. al. 1999; Lee et. al., 2004). This determination was supported by low TSP contributions and decreasing loadings in summer. There is no dense urbanization near the station but the sampling site was located at the to downwind of university campus buildings in especially cold periods.

*Factor 3:* High molecular weight PAHs were the dominant species for this factor, especially BaP, BbF, BkF, BaA, BghiP and Pyr. These species originated from vehicle sources and especially from diesel emissions (Ravindra 2006; Guo et. al., 2003, Duval et. al. 1981; Harrison et. al., 1996; Lee et. al., 2004; Li et. al., 2003; Larsen and Baker, 2003; Singh et. al., 2008).

*Factor 4:* This factor was dominated by CHR, DBA, PA and IND. It is one of the important sources of TSP. This factor was evaluated as "other" group and most important component of this group is dust. (Harrison et. al., 1996; Lee et. al., 2004; Singh et. al., 2008).

**General evaluation:** For URB1 station, DE, GE, NG, CW and other factors were accounted as 30.7%, 16.6%, 25.3%, 15.1% and 12.2% of total PAHs, respectively. In URB2 station these values were 23%, 19.3%, 30.5% 11.3% and 15.9%, respectively. These stations were located in urban areas and vehicle emissions and residential heating were the most important contributors. Nevertheless these findings were compatible with what is expected.

For rural station, these contributions were 38.4% for CW, 30.7% for NG; 17.6% for VE and 13.3% for "other" groups. These results were expected for a rural station. However, vehicle emissions were relatively high for the rural site as well. These contributions were thought to be originated from ships, which are waiting to pass to strait, which connects the Black Sea to the Marmara Sea. During the sampling period, the daily number of boats waiting idle at a distance of about 3 miles off the coastline was about 20 to 30. It is known that PAH emissions from larger ships/ferries may contribute significantly to ambient PAHs concentrations depending on the geographical conditions of the local harbor and the route (Ravindra et. al., 2008), but further investigations is necessary for a more definitive explanation.

In this study source apportionment for heavier PAH (MW>200 from FL to BghiP) was also evaluated. Higher molecular weights PAHs (with four or more rings) are found mainly adsorbed in the particulate matter. This group includes all of the probable and possible carcinogenic species of PAHs (Ravindra et. al., 2008; ATSDR, 1995). Vehicle sources were determined as the most important contributor for these species with contributions of 50%, 66% and 40% for URB1, URB2 and RUR stations, respectively.

In urban stations diesel emissions were higher than gasoline emissions. In the evaluation of heavy PAHs this finding becomes clearer. It is known that diesel fueled vehicles have higher particulate emissions than gasoline fueled vehicles (Ravindra et. al., 2008). Schauer et al. (2002) found that the composition of the fuel also influences PAH emissions for diesel vehicles. For diesel vehicles, an additional source of PAHs in the exhaust emissions is the PAHs content in the fuel (Westerholm and Li, 1994; Ravindra et al., 2006). According to Turkish Statistical Institute (TUIK) diesel vehicle portion in the total vehicle fleet is 23% in 2004 in Istanbul (TUIK, 2009). This value has increased to 33% in 2006 and to 38% in 2007. This information is supporting our findings for the urban stations.

Results of our study were also compatible with studies found in the literature. Depending on the specifications of the sampling location, traffic is the major contributor in much of the source apportionment studies where the sites are located in urban areas (Li et. al., 2003; Pistikopoulos et. al., 1990; Li and Kamens, 1993; Yang and Chen 2004; Sharma et. al. 2007). By Singh et. al., 2008, vehicular emissions and diesel based processes were found as the major sources of PAHs in their source apportionment study of PAH concentrations in India’s urban atmosphere. By Samara et. al. 2003, ambient $PM_{10}$ concentrations were analyzed in an industrialized urban area in Greece which is a neighbor country of Turkey. In that study, traffic was found to be the major contributor at all three receptor sites similar to our study, and the diesel exhaust contribution was estimated to be 1.0 times greater the total gasoline exhaust contribution as an average.

## 4. CONCLUSIONS

In this study, PAHs were determined at three monitoring stations with a total of 326 airborne samples for 16 PAHs and TSP in the September 2006-December 2007 period in Istanbul, Turkey. Among the stations, the maximum PAH values were observed at the URB1, but the maximum TSP values were observed at the URB2. The RUR station had the minimum concentrations for all species, which is expected. At all the sites, the lighter compounds were the most abundant.

Carcinogenic activity of the measured PAHs species were calculated and it is determined that BaP occupied approximately a half of the activity for all the sites. Carcinogenic activity of BaP reaches elevated values in cold periods depending on its higher concentration for all of the sites. BaP equivalency results indicated that the health risk of BaP and DBA, which are markers of traffic emissions, are the highest among all the species in the urban sampling sites.

Two different source apportionment techniques were performed to the PAHs results: DR and PMF. According to DR results, measured PAH concentrations in urban stations originated mainly from traffic sources and diesel emissions were the dominant source. In rural station, it was likely that multiple PAH sources including motor vehicles may contribute to the PAH source profiles and diesel emissions were again unexpectedly the dominant source. These findings were also supported by the other source apportionment technique used; PMF.

Similarly, diesel emissions were high for urban stations in PMF results. According to TUIK, number of diesel vehicle has been increased year to year in Istanbul. In the rural site, vehicle emission contributions were determined as higher than expected. It is thought that, these elevated values originated from ships which are waiting to pass to strait which connects the Black Sea to the Marmara Sea. During the sampling period, approximately 20-30 ships were waiting idle at a distance of about 3 miles off the coastline, which may explain the diesel emissions. Results of our source apportionment studies were also in line with other studies found in the literature and CMB application, which has already been published.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
**4th International Symposium and IUAPPA Regional Conference**
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# EXPOSURE ASSESSMENT OF POLYCYCLIC AROMATIC HYDROCABONS IN LARGE CITIES OF COLOMBIA

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## ABSTRACT

We have assessed diurnal profiles of PAHs in Bogota (Colombia) using photoelectric aerosol sensor (PAS) devices. PAS instruments were located close to a congested avenue to assess exposure to pedestrians, drivers and passengers. PAS signals were found to be impacted by traffic, especially trucks and buses running on low quality diesel. Weekday PAS signals were significantly larger than weekend signals. Two PAS devices were located at different heights to assess vertical dispersion of pollutants. PAS signals at the roof experience more dilution and less short-term peaks than PAS at the ground. We found a significant correlation between PAS signals and concentrations of black carbon (BC) from an aethalometer, demonstrating that PAHs and BC are products of the same source. The effect of solar radiation was also evaluated finding that PAS signals are lower during the dry season when more solar radiation is available to degrade PAHs in the atmosphere. Our results suggest that diesel emissions constitute a significant source of PAHs in the atmosphere in Bogota and that during rush hours people are exposed to diesel combustion particles enriched with PAHs. Measures should be implemented to reduce smoky vehicles on the road in order to protect public health.

**Keywords**: PAHs, Bogota, Medellin, traffic, exposure

## 1. INTRODUCTION

Air pollution poses risks to human health, the environment and quality of life. Air pollution-related epidemiologic studies show that ambient ozone and fine particulate matter are closely associated with a wide range of adverse human health outcomes. The two air pollutants of greatest concern are ozone and $PM_{2.5}$ (particulate matter with an aerodynamic diameter less than 2.5 μm) due to their adverse human health effects. Studies have demonstrated that $PM_{2.5}$ leads to premature death, increased risks of heart attacks, adverse effects on lung function, and other health effects (Dockery et al., 1993; Pope et al., 1995; Laden et al., 2000; Peng et al., 2009; Lenters et al., 2010). $PM_{2.5}$ is composed of hundreds of compounds (carbonaceous species, metals, inorganic ions, PAHs) and originates from several sources (vehicles, industry, fugitive, erosion).

Polycyclic Aromatic Hydrocarbons (PAHs) have been recognized as carcinogenic compounds found in the particulate matter in the atmosphere (Marr et al., 2004; Li et al., 2009). PAHs are mainly emitted as incomplete products of combustion. Diurnal profiles of PAHs correspond with traffic conditions, for which PAHs have been suggested as tracers of vehicle activity (Hoshiko et al., 2011).

Elemental carbon (EC) is mainly emitted as incomplete production of combustion from mobile sources, wood burning and cigarettes (Burtscher, 2005). When EC is measured using optical absorption, EC is called black carbon (BC); EC and BC are highly correlated. Because both BC and PAHs are emitted in similar combustion conditions, relationships between PAS signals and BC concentrations from an aethalometer have been documented in several studies (Dahmann et al., 2000; Burtscher, 2005; Wallace, 2005). However, ratios between PAS signals/BC are not constant and vary between studies from 1.0 to 76.7 A/□g/m$^3$. Despite this variability, real-time PAS instruments have been identified as an expedite way to estimate concentrations of PAHs and BC.

The main sources of air pollution in Colombia are vehicles and point sources. Emission of particulate matter (PM), nitrogen oxides (NO$_x$) and carbon monoxide (CO) are predominantly from mobile sources, whereas total suspended particles (TSP) and sulfur oxides (SO$_x$) come from point sources. The large amounts of PM from mobiles sources are the result of a low diesel quality, the lack of fleet maintenance and inadequate driving patterns. Until 2008, diesel in Colombia had 1200ppm of sulfur. New legislation has improved diesel quality to 50ppm of sulfur in major urban centers, and it is expected that by 2013 all the country will consume diesel of 50ppm (Colombia., 2008). This improvement in fuel quality will permit the introduction of particle control technology in buses and trucks and a consequent improvement in the air quality. On the other hand, point sources have incomplete combustion processes and emissions of small industries can greatly contribute with large PM emissions.

## 2. METHODS

Two field campaigns were conducted in Bogota (74°4´33´´W 4°35´53´´ N) during different weather patterns: rainy season (21/11/2011-17/12/2011) and dry season (09/03/2012-17/04/2012). A photoelectric aerosol sensor (PAS 2000CE) was used to measure particle-bound PAHs in ambient air. The PAS is a portable instrument (dimensions 68mm x 175mm x 124mm) with a weight less than 3 pounds (Fig. 1). A complete description of the analytical technique and operating instructions can be found elsewhere (EcoChem, 2000). Briefly, a PAS sensor uses a UV lamp for photoionization of particles bounded with PAHs. Specific operating conditions of the PAS (irradiation energy and wavelength of the UV-lamp) guarantee that only particles with adsorbed PAH will emit photoelectrons and not other aerosols (dust, tirewear, salt). Several studies have found a good correlation between the aerosol photoemission signal and total PAHs concentrations measured by gas chromatography (GC) (EcoChem, 2000; Polidori et al., 2008) and in this way, the PAS monitor signal in amperes (A) can be translated into a total amount of PAHs in ambient air (the sum of 15 hydrocarbons).

To associate the PAS signal (in Amperes) with PAHs concentrations in ambient air, an eight-stage cascade impactor (Thermo Andersen 20-800) was placed along the PAS instrument and quartz filters were collected every 24 hours during the period 10/03/2012-10/07/2012. Filters were conditioned (@25°C, 560 mmHg) and weighted before and after the sampling campaign in the Environmental Engineering Laboratory at Universidad de La Salle in Bogota. Currently, filters are being analyzed for PAH concentrations at The University of Tokyo using a gas chromatography mass spectrometer (GC/MS) equipment.

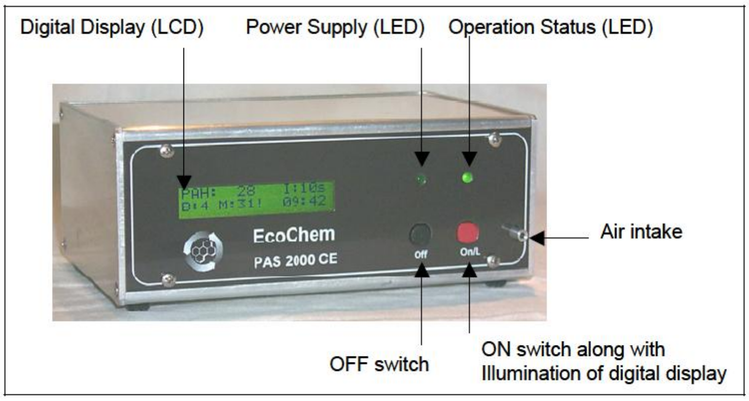

**Fig 6a: Front Panel of the PAS 2000CE / DC2000CE**

Fig 1 PAS (2000CE) front panel

## Monitoring points

In Bogota, the building of the “Ministerio de Ambiente y Desarrollo Sostenible” (from hereafter MADS) was selected for its strategic location (distance to congested avenues) and logistic conditions (security, energy supply, accessibility) to install the monitoring instruments (two PAS, one aethalometer, one cascade impactor, one portable meteorological station) (Fig 2). To assess the difference between ground and elevated locations, one of the PAS was placed at about 3 meters above the ground on the roof of a security shelter (from hereafter ground) and a second PAS was placed on the roof of the building at approximately 25 m above the ground (from hereafter roof) during 10 days (31/03/12-09/04/12) (Fig 3). The PAS instrument was placed inside a plastic box to protect from rain and humidity. A hose was connected from the air intake to the exterior passing through a desiccator. An aethalometer (MagicScientific AE42-7-ER), property of the MADS, was installed along with the PAS to evaluate the relationship between BC and PAHs. One portable meteorological station (DAVIS Vantage Pro2) was employed to record wind speed and direction, precipitation, humidity, solar radiation and temperature.

## Data collection and analysis

The PAS detected total PAHs concentrations every two minutes and recorded them for 10 days. At the end of the 10-day period, PAS signals were downloaded to a PC and the instrument was ready to record another 10 days of data. 1-hour averages were computed to construct daily PAH profiles and daily averages were then calculated to obtain weekly profiles. BC concentrations from an aethalometer were obtained every minute and averaged over the hour to estimate daily profiles.

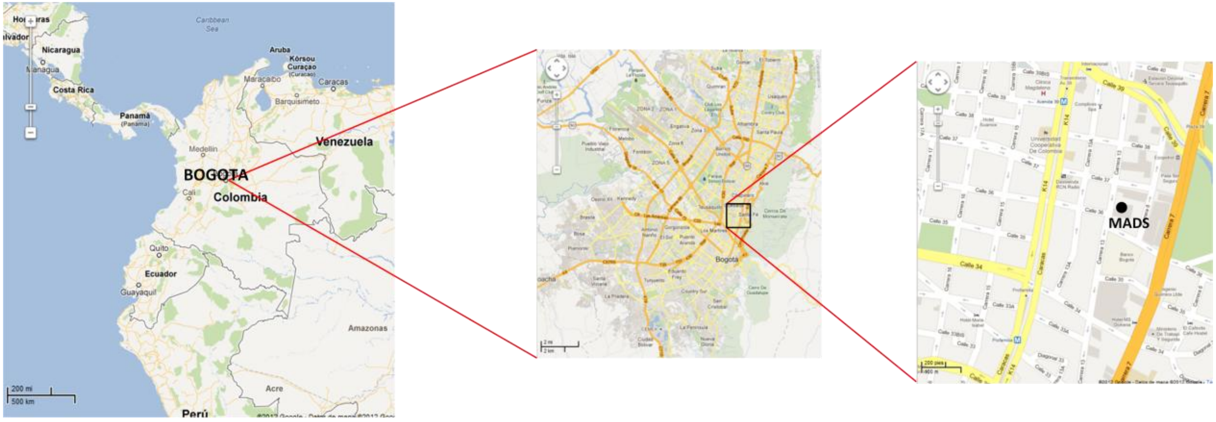

Figure 2 Location of sampling point in Bogota (Ministerio de Ambiente y Desarrollo Sostenible building, MADS)

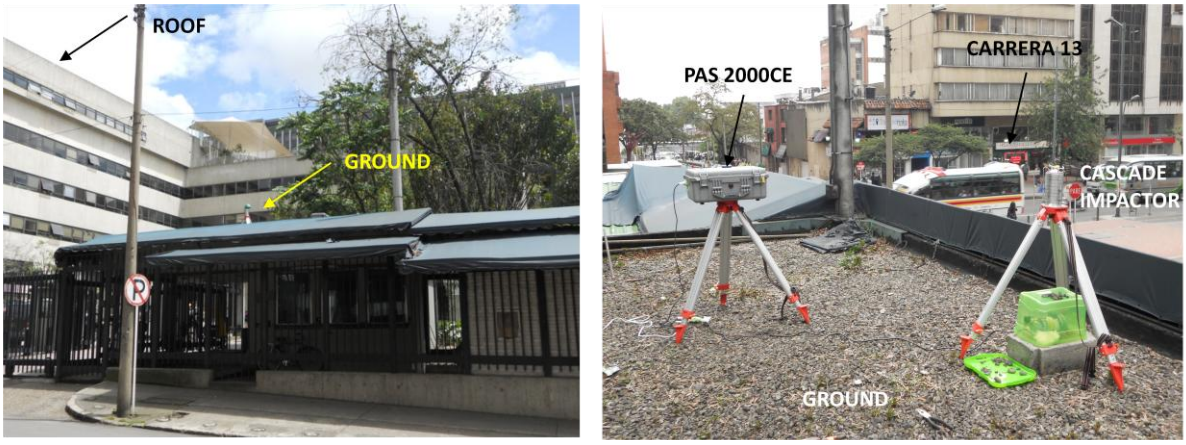

Figure 3 Location of monitoring points (ground and roof) in MADS and traffic in Carrera 13

## 3. RESULTS

Temporal and spatial variability of PAS signals were analyzed during the dry and rainy seasons. On a weekly basis, we observe larger PAS signals during weekdays than weekends, consistent with a higher impact of combustion sources during the week (Fig 4). On a weekday, PAS signal is heavily impacted by the volume of traffic, especially during morning and afternoon rush hours (from 6-9am and 5-7pm respectively). During the weekend, large signals can be observed around noon when traffic tends to increase with respect to morning and afternoon hours, but the PAS signals are significantly lower than during weekdays. Typical PAS signals observed in Bogota range 19-633 amperes (A) during weekdays and 6-135 A during the weekend. Such PAS signals are significantly higher than signals observed in other cities: 0.2-20 fA in Reston, VA (Wallace, 2005); 5-20 fA in Los Angeles, CA (Polidori et al., 2008); 5-140 in Boston, MA (Dunbar et al., 2001).

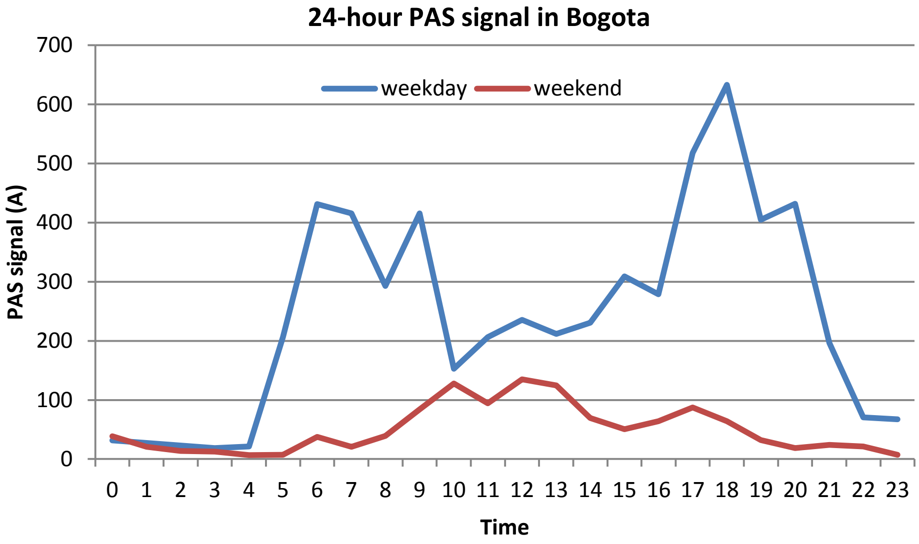

Figure 4 Typical PAS signal at the ground (approximately at 3m)

The results show the prevalence of PAHs from combustion sources, especially from mobile sources. On traffic counts from Carrera 13, the closest avenue adjacent to MADS (Fig 2), a total of 12550 vehicles were recorded during 10 non-continuous hours (6-9am, 11am-2pm, 3pm-7pm) on a typical weekday. From the total car population, 74% correspond to light vehicles and 26% to buses and trucks. Typically, private passenger vehicles in Colombia run on gasoline whereas trucks and public buses run on diesel (although recently has been an increase in the number of privately owned diesel vehicles). Currently, the bus rapid transit (BRT) system in Bogota consumes diesel with 50ppm of sulfur, while other buses are fed diesel of 450ppm sulfur. It has been shown that PAS signals are mostly impacted by buses and trucks running on diesel (Dunbar et al., 2001).

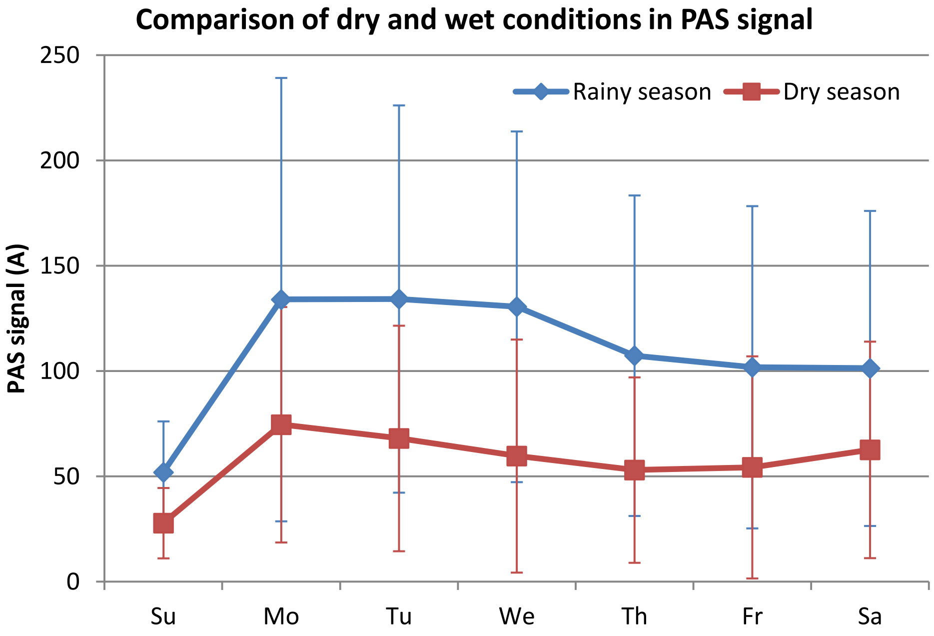

Figure 5 Comparison of dry (09/03/2012-17/04/2012) and rainy (21/11/2011-17/12/2011) periods in PAS signal

A seasonal comparison of PAS signals allows identification of higher PAS signals during the rainy season (Fig 5). This may be explained because PAHs are degraded by solar radiation (Valerio and Lazzarotto, 1985; Galarneau, 2008) and less solar radiation is present during the rainy season. On a daily basis, PAS signals are lower on Sunday because traffic is significantly lower (Fig 4). PAS signals increase on Monday and remain high until decreasing on Thursday. Saturday levels of PAS signals are in the same order of magnitude as during the week. Currently, traffic congestion in Bogota on Saturday is identified as worse than during weekdays, which may explain in part the higher level of PAS signals during this day.

Several studies have shown significant correlations between total PAH concentrations and black carbon (BC), mainly due to both being originated from combustion sources (Burtscher, 2005; Wallace, 2005; Polidori et al., 2008). To test this relationship, we installed an aethalometer (Magee Scientific Model No. AE42-7-ER) along with the PAS instrument and conducted measurements during five days (from 03/18/2012 to 03/22/2012). On the first two days (03/18 and 03/19) the number of samples taken from the PAS device and the aethalometer were different and a significant level of correlation was not obtained. For the rest of the days (March 20-22), the values of the correlation were $R^2$=0.2-0.6, demonstrating a good agreement between the PAS signal and BC concentrations (Fig 5). The results confirm our hypothesis about the predominance of diesel emissions in the PAS signals over emission from light-duty vehicles.

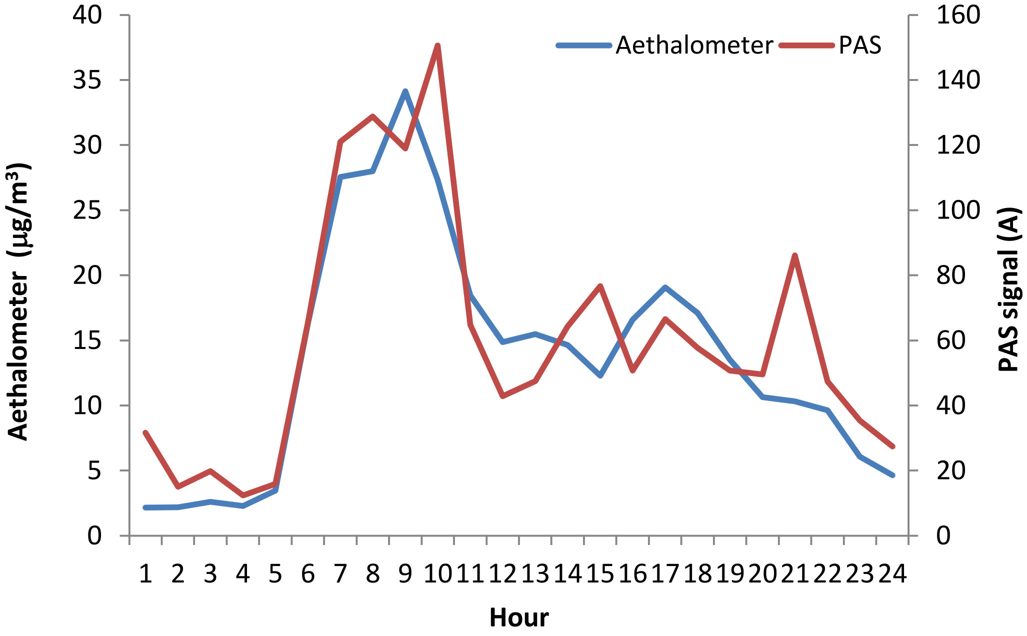

Figure 5 Diurnal trend of Aethalometer and PAS readings (averaged March 20-22)

## Comparison between roof and ground concentrations

To assess the difference in PAS signals due to monitoring height, two PAS devices were employed simultaneously during ten days (March 31-April 9), one at the ground (~3m above ground) and the second one on the roof (~25m above ground) at the MADS. As expected, we observe larger PAS signals on the ground (approximately twice) and a large number of short-term peaks in comparison with the roof signal (Fig 6). The difference in PAS signals between ground and roof locations can be explained by two factors: the closeness of the PAS device on the ground to emission sources and the greater dilution effect of the PAS device on the roof. Nonetheless, the correlation between PAS signal levels at the ground and roof in the 10-day period were between $R^2$=0.5-0.8.

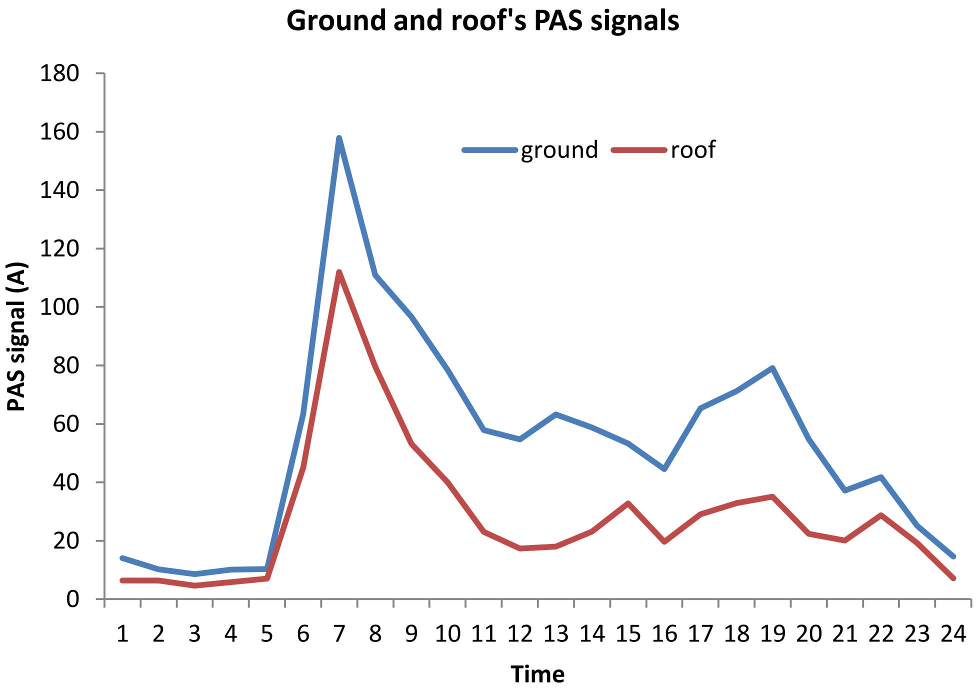

Figure 6 Ground and roof PAS signals

### Exposure assessment

Our monitoring point at the ground at MADS was 3m away from the eastern sidewalk of Carrera 13 which is constantly in use by pedestrians and bike lane users. Given the large levels of PAS signals found at the monitoring point, it can be expected that a great exposure to PAHs will be observed to pedestrians, cyclist and bus passenger and drivers who often get stuck in traffic in Carrera 13. Activities should be implemented to promote the reduction of smoky vehicles on roads in order to protect public health.

## 4. CONCLUSIONS

The PAS instrument was effective to evaluate the impact of traffic on air quality in Bogota. The PAS signals show a significant correlation with BC, a traditional tracer of diesel emissions. The effect of height on ambient concentrations was evaluated using two PAS instruments operating simultaneously. PAS signals on the ground show more short-term peaks, probably impacted by traffic, whereas PAS signals on the roof demonstrate more dilution. The effect of solar radiation was also evaluated, finding that PAS signals are lower during the dry season when more solar radiation is available to degrade PAHs in the atmosphere. Levels of particle-bound PAH in Bogota were found to be significantly higher than other cities in the world demonstrating the air quality deterioration caused by mobile sources. Exposure to PAHs is expected to be large, since the monitoring point was close to pedestrian sidewalks and bike lanes.

## ACKNOWLEDGMENTS

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# CHEMICAL CHARACTERIZATION OF AIR SAMPLES AND ROAD DUST IN A ROADWAY TUNNEL IN TURKEY: DETERMINATION OF EMISSION FACTORS FOR VEHICLES

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## ABSTRACT

A two-week sampling campaign was carried out in a rural tunnel in Bilecik, Turkey. Samples were collected simultaneously at the entrance and exit of the tunnel in the morning and afternoon periods for trace elements, volatile organic compounds (VOCs), nitrogen dioxide ($NO_2$) and ozone. Average concentrations of these compounds at the tunnel exit and entrance were determined. Emission factors for vehicle fleet were calculated using the measured concentrations at the tunnel exit and entrance. Road dust samples at 15 points along the tunnel were also collected and analyzed for trace elements. Benzene, toluene, ethylbenzene, m,p-xylene and o-xylene (BTEX), $NO_2$ and ozone concentrations were also determined by passive samplers simultaneously at the same points along the tunnel.

**Key Words:** tunnel, PM, BTEX, $NO_2$, ozone, trace elements, emission factors

## 1. INTRODUCTION

It has been known that motor vehicles are important sources of pollutants in urban environments. Quantification of the contribution of traffic emissions to ambient air concentrations is essential for developing control and management strategies to improve ambient air quality especially in congested sites in the cities. Emission inventories are useful tools for estimation of the contribution of each pollutant and sector (traffic, industry etc.) to total emissions in a certain area. Use of appropriate and realistic emission factors in emission estimations decrease the uncertainty in emission inventory calculations (Oanh et al., 2008; Shen et al., 2011).

Considering vehicular emissions, generally there are two approaches widely used to determine emission factors: dynamometer tests performed in the laboratories and real world studies carried out in the tunnels ( Pierson et al., 1996; Robinson et al., 1996; John et al., 1999).

In this study, concentrations of trace elements in particulate matter (PM), volatile organic compounds (BTEX), nitrogen dioxide ($NO_2$) and ozone were measured inside a 2470 m, two bore tunnel in Bilecik. Pollutant profile along the tunnel and real world emission factors for the pollutants were determined.

## 2. MATERIALS and METHODS

### 2.1. Tunnel Description

The study was carried out at Osmangazi Tunnel located at Bursa Mekece highway which is approximately 10 km far from Bilecik city center. The tunnel is 2470 m in length with two opposing traffic lanes aligned in east-west direction. The average speed limit is 80 km $hour^{-1}$ inside the tunnel. The ventilation of tunnel is performed by jet fans which are activated when carbon monoxide (CO) levels reach a certain level. During the study period, the jet fans were not activated either manually or automatically. The cross-sectional area of the tunnel is 73 $m^2$.

### 2.2. Sampling Strategy

Sampling was carried out at the entrance and exit of the tunnel (east tube) between 17th and 28th of August 2011. Pollutant concentrations were measured in two stations. The entrance station was set up 350 meters from the tunnel inlet and the exit station was 40 meter before the tunnel outlet. Samples were collected in the morning (9-11 am) and afternoon (14-16 pm) periods. Particulate matter, VOCs, $NO_2$ and ozone were measured during each sampling period. Road dust samples were also collected at 15 points along the tunnel to determine chemical composition of the dust samples. Concentrations of BTEX, $NO_2$ and ozone were also determined at those 15 points by passive samplers.

Particles were collected using a dichotomous sampler with a flow rate of 16.7 L $min^{-1}$. BTEX, $NO_2$ and ozone were sampled by using custom made passive samplers developed in our laboratory.

### 2.3. Sample preparation and analysis

Active carbon bed of the BTEX passive samplers were extracted with carbon disulfide ($CS_2$) and analyzed by Gas Chromatography-Mass Spectrometry (GC-MS). Nitrogen dioxide and ozone concentrations were determined after extraction of the impregnated filters of the passive samplers by deionized water and analyzed by an Ion Chromatograph equipped with a conductivity detector. Filters were acid digested in a microwave oven and analyzed for trace elements by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

## 3. RESULTS

### 3.1. Concentrations of the compounds in the tunnel

Average pollutant concentrations measured at the tunnel entrance and exit stations were given in Table 1. The highest BTEX concentrations were observed for toluene and benzene. Toluene/benzene ratios ~2.0 indicate that traffic is a pollution source in ambient atmospheres (Hansen and Palmgren, 1996; Vardoulakis et al., 2002). The average of toluene/benzene ratio was calculated for both stations in the tunnel and it was found as 1.98±0.09. Higher $NO_2$ concentrations were measured at the exit of the tunnel similar to BTEX. A reverse trend was observed for ozone concentrations being higher at the entrance station. This can be explained by the reaction between nitrogen monoxide and ozone. Trace element concentrations in the tunnel were found to be changing in a wide range. Crustal elements were found to be abundant in $PM_{10}$ samples. Highest concentrations of anthropogenic elements were measured for Sb, Zn, Co and Cu.

**Table 1.** Average pollutant concentrations measured in the tunnel (µg $m^{-3}$)

| Compound | Concentration |
|---|---|
| Benzene | 23.84±9.47 |
| Toluene | 42.87± 12.78 |
| Ethyl benzene | 11.38±7.49 |
| m,p xylene | 10.41±5.83 |
| o-xylene | 10.39±4.77 |
| $NO_2$ | 550.55±198.28 |
| Ozone | 22.26±8.22 |
| $PM_{10}$ | 313.60±144.60 |
| $PM_{2.5}$ | 129.16±79.83 |
| Sb | 4.19±1.37 |
| Zn | 0.48±0.32 |
| Co | 0.48±0.45 |
| Cu | 0.18±0.15 |

### 3.2. Emission factors (EF) of the compounds

Vehicle count data was obtained from the tunnel monitoring system. Vehicles were classified into 5 classes (car, minibus, trailer, truck, bus). Air velocity data were also available during the measurements. Contribution of different vehicle classes to the total during different time periods in a day was investigated and no significant change was observed. As it was shown in Figure 1, together with minibuses (delivery vehicles) we may assume that approximately 80% of the vehicles are diesel powered.

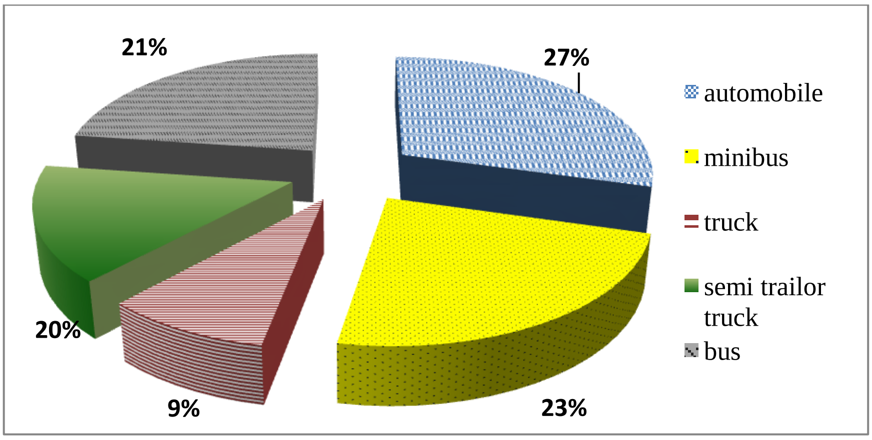

**Figure 1.** Contribution of different vehicle types to the total vehicle load

Emission factors for each pollutant were calculated using the following equation: (Weingartner et al., 1997)

(1)

where; EF is the emission factor (µg km$^{-1}$ vehicle$^{-1}$), X is the concentration of the compounds (µg m$^{-3}$), S is the cross sectional area of the tunnel (m$^2$), A is velocity of the air (m s$^{-1}$), t is the time interval (s), V is the total number of vehicles passing through the tunnel during the sampling period and L is the distance between the entrance and exit points (km). The calculated emission factors might be considered to represent a traffic flow in which almost 80% of the vehicles were diesel powered.

Average of emission factors calculated for different sampling periods were given in Table 2. In general emission factors were found to be in the range of reported values in the literature (Staehelin et al., 1998; Allen et al., 2001; Handler et al., 2008; Chiang and Huang, 2009).

**Table 2.** Emission factors (mg km$^{-1}$ vehicle$^{-1}$) of BTEX, $NO_2$ and trace elements

| Compound | Emission factor |
|---|---|
| Benzene | 12.92±7.63 |
| Toluene | 20.06±12.42 |
| Ethyl benzene | 5.32± 4.72 |
| m,p-xylene | 4.10±2.30 |
| o-xylene | 4.98±3.92 |
| $NO_2$ | 372.27±163.77 |
| Zn | 0.55±0.39 |
| Cr | 0.15±0.08 |
| Cu | 0.27±0.14 |
| Sn | 0.022±0.013 |
| Fe | 7.035±3.73 |

### 3.3. Pollutant concentration profiles along the tunnel

As it was mentioned before, road dust samples were collected at 15 points along the tunnel and were analyzed for trace elements. Passive samplers for BTEX, $NO_2$ and ozone were also deployed at the same points concurrently. There was an increasing trend observed for the BTEX and $NO_2$ concentrations from the entrance to the exit of the tunnel. A reverse trend was observed for ozone, probably due to titration of $O_3$ by the NO emitted by the vehicles. A sudden decrease in concentrations of the BTEX and $NO_2$ was observed at the point very close to exit due to dilution effect of the outside air while ozone levels increased at the same point because of the contribution of the outside atmosphere. BTEX concentrations through the tunnel were measured in the range of 18.8-21.8 µg m$^{-3}$ (benzene), 35.4-49.1 µg m$^{-3}$ (toluene), 22.3-25.0 µg m$^{-3}$ (ethyl benzene), 17.8-25.0 µg m$^{-3}$ (m+p xylene) and 13.1-17.1 µg m$^{-3}$ (o-xylene). $NO_2$ concentrations varied between 158 and 763 µg m$^{-3}$ and they were in the range of 11 and 36 µg m$^{-3}$ for ozone. The levels of the traffic related compounds such as BTEX and $NO_2$ in the tunnel were found approximately 10 times higher than the levels measured in an urban sampling site in Eskisehir (Özden, 2012) located on a street having high traffic density (~16,000 vehicles day$^{-1}$).

Enrichment factors were calculated for the trace elements measured in road dust samples by using Mason soil composition (Cyrys et al., 2003) and it was found that anthropogenic elements (Sb, Se, As, Pb Cd, Zn, Sn) in road dust samples were moderately to highly enriched in the tunnel.

## 4. CONCLUSION

Accurate and representative emission factors are essential for the assessment of ambient air quality. In this study, the real world emission factors were determined for various pollutants for the first time in Turkey. However, it should be noted that emission factors determined in this study might be different than the ones in urban tunnels where vehicle fleet composition may be different. Determination of real world emission factors in various traffic compositions and under various driving conditions are necessary to decrease uncertainty in motor vehicle emission estimations.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# RELATIONSHIP BETWEEN POLYCYCLIC AROMATIC HYDROCARBONS AND OTHER POLLUTANTS IN THE AIR OF ZAGREB, CROATIA

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## ABSTRACT

Concentrations of eight polycyclic aromatic hydrocarbons (PAHs) in $PM_{10}$ particle fraction were measured together with ozone and nitrogen dioxide concentrations at an urban site (Zagreb, Croatia) in order to find the relationship between the measured pollutants and selected meteorological parameters. Samples were collected in the period 1 January – 31 December 2009. It was found that all PAHs showed seasonal variations with high concentrations in winter and very low concentrations during the summer months. All eight PAHs also correlated well with each other. Statistically significant negative correlation was found between all PAHs and ozone and PAHs and temperature, and a positive correlation between PAHs and nitrogen dioxide and relative humidity. Multivariate regression analysis showed that ozone, temperature, relative humidity and pressure accounted for 40 to 57 % of PAH variability.

**Key Words:** meteorology, multiple linear regression, nitrogen dioxide, ozone, $PM_{10}$

## 1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are formed during incomplete combustion or pyrolysis of organic matter. As some PAHs are proven carcinogens and mutagens, it is necessary to continuously monitor their concentrations in the environment (WHO, 2000). Benzo(a)pyrene is the most commonly measured PAH and is used as an indicator of carcinogenic hazard in polluted environments. In the atmosphere, PAHs with two or three aromatic rings are stable in the gas phase, while PAHs with more aromatic rings are mostly bonded to particles (Possanzini et al., 2004). During summer, some PAHs engage in oxidation and photooxidation reactions, including reactions with ozone and nitrogen oxides. Products formed in these reactions are sometimes more dangerous than the parent compounds (Committee, 1972). Due to the complexity of aerosol chemistry, interactions of different air pollutants are still the subject of many investigations.

In this study, concentrations of eight PAHs in $PM_{10}$ particle fraction were measured together with ozone and nitrogen dioxide concentrations at an urban site. The study was carried out in order to find the relationship between the measured pollutants and some meteorological parameters.

## 2. MATERIALS AND METHODS

The measuring site was in the northern, residential part of Zagreb, Croatia, with modest traffic density. $PM_{10}$ particle fraction was collected by 24-hour sampling on quartz filters with a low volume $PM_{10}$ Sven Leckel sampler from about 50 $m^3$ of air in the period 1 January – 31 December 2009. The samples were kept frozen in aluminium foil at -18 ºC until analysis.

Filters were extracted with a solvent mixture of toluene and cyclohexane in an ultrasonic bath for one hour, separated from undissolved parts by centrifugation end evaporated to dryness in a mild stream of nitrogen at 30 ºC. They were then redissolved in acetonitrile. The analysis was performed using a Varian Pro Star high performance liquid chromatograph (HPLC) with a fluorescence detector and programmed changes in excitation and emission wavelengths (Šišović et al., 1991; Šišović et al., 2005). PAHs were separated on a Varian stainless steel Pursuit 3 PAH column (100 x 4.6 mm). The mobile phase was a mixture of acetonitrile and water, and the flow rate was 0.5 mL/min. To prepare calibration curves, a commercial PAH standard was used (Supelco EPA 610 PAHs Mix). Standard working solutions were obtained by diluting certified solutions with Merck HPLC-grade acetonitrile. Samples were analyzed for the following PAHs: fluoranthene (Flu), pyrene (Pyr), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenzo(a,h)anthracene (DahA), benzo(ghi)perylene (BghiP), and indeno(1,2,3-cd) pyrene (Ind). The detection limit varied from 0.005 ng/µL for BaP to 0.008ng/µL for BghiP. Quantification limit for PAHs in 500 µL of acetonitrile and 50 m$^3$ of air varied from 0.05 ng/m$^3$ for BaP to 0.08 ng/m$^3$ for BghiP.

Concentrations of nitrogen dioxide were measured using a HORIBA APNA-360 automatic device based on chemiluminiscence, while ozone concentrations were measured by means of UV absorption using a HORIBA APOA-360 instrument. Meteorological parameters (temperature, relative humidity and pressure) were obtained from the National Meteorological and Hydrological Service. STATISTICA 10 software package was used for statistical analyses.

## 3. RESULTS AND DISCUSSION

Summary statistics of 24-hour averages is shown in Table 1. During 2009, daily ozone mass concentrations ranged from 3 µg/m$^3$ to 98 µg/m$^3$, and the limit value for 8-hour averages (120 µg/m$^3$) set by Croatian legislation (Regulation, 2005) was exceeded only once. Concentrations in spring and summer were statistically higher than in other seasons. 24-hour averages of $NO_2$ mass concentrations ranged between 9 µg/m$^3$ and 90 µg/m$^3$ and were highest in winter.

All PAHs showed seasonal variations with high concentrations in winter and very low concentrations during the summer months. For example, daily BaP concentrations in winter ranged from 0.197 ng/m$^3$ to 8.176 ng/m$^3$, while they were between 0.004 ng/m$^3$ and 0.169 ng/m$^3$ in summer. Similar levels and seasonal variations were found at other locations in Europe (Callén et al., 2008; Caricchia, 1999; Menichini et al., 1999; Srogi, 2007).

Table 1. Summary statistics of 24-hour mass concentrations of PAHs, $O_3$ and $NO_2$ in the northern part of Zagreb (1 January – 31 December 2009)

| | | Spring | Summer | Autumn | Winter | Overall |
|---|---|---|---|---|---|---|
| Flu (ng/m$^3$) | Mean | 0.074 | 0.016 | 0.966 | 1.285 | 0.578 |
| | Range | 0.062-0.473 | 0.003-0.059 | 0.018-16.092 | 0.114-8.868 | 0.003-16.092 |
| Pyr (ng/m$^3$) | Mean | 0.135 | 0.025 | 1.138 | 2.008 | 0.818 |
| | Range | 0.004-1.123 | 0.003-0.090 | 0.016-17.628 | 0.114-12.332 | 0.003-17.628 |
| BbF (ng/m$^3$) | Mean | 0.274 | 0.068 | 1.414 | 2.117 | 0.958 |
| | Range | 0.018-2.512 | 0.010-0.193 | 0.050-6.763 | 0.261-9.526 | 0.010-9.526 |
| BkF | Mean | 0.101 | 0.028 | 0.625 | 0.855 | 0.398 |

| | | | | | | |
|---|---|---|---|---|---|---|
| (ng/m$^3$) | Range | 0.006-0.891 | 0.002-0.092 | 0.0234-3.536 | 0.123-3.792 | 0.002-3.792 |
| BaP | Mean | 0.191 | 0.045 | 1.2 | 1.539 | 0.735 |
| (ng/m$^3$) | Range | 0.007-2.562 | 0.004-0.169 | 0.041-7.345 | 0.196-8.176 | 0.004-8.176 |
| DahA | Mean | 0.016 | 0.004 | 0.050 | 0.098 | 0.042 |
| (ng/m$^3$) | Range | 0.0006-0.152 | 0.0008-0.014 | 0.002-0.278 | 0.019-0.561 | 0.0006-0.561 |
| BghiP | Mean | 0.640 | 0.159 | 3.543 | 4.693 | 2.234 |
| (ng/m$^3$) | Range | 0.031-5.826 | 0.011-0.447 | 0.142-19.384 | 0.858-16.625 | 0.011-19.384 |
| Ind | Mean | 0.236 | 0.080 | 1.415 | 1.624 | 0.829 |
| (ng/m$^3$) | Range | 0.011-1.814 | 0.005-0.417 | 0.063-7.232 | 0.237-7.554 | 0.005-7.554 |
| $O_3$ | Mean | 54.4 | 54.1 | 20.8 | 23.9 | 38.6 |
| (µg/m$^3$) | Range | 11.8-85.5 | 22.2-89.8 | 3.1-58.1 | 3.2-61.0 | 3.1-89.8 |
| $NO_2$ | Mean | 31.7 | 26.0 | 35.8 | 42.7 | 33.9 |
| (µg/m$^3$) | Range | 9.2-60.8 | 9.3-46.2 | 11.3-60.6 | 14.0-89.7 | 9.2-89.8 |

The results have shown that all eight PAHs correlate well with each other (Table 2), with linear correlation coefficients (r) between 0.79 and 0.99. Statistically significant ($p<0.01$) negative correlation was found between all PAHs and ozone (r between -0.45 and -0.65) and PAHs and temperature (r between -0.66 and -0.73). Positive linear correlation was found between PAHs and nitrogen dioxide (r between 0.45 and 0.53) and PAHs and relative humidity (r between 0.39 and 0.55) (Table 2). Similar correlation coefficients were calculated in some other studies, e.g., Yasmin et al. (2008) also found a positive linear correlation between PAHs and $NO_2$ and a negative correlation with ozone.

Due to the differences in concentrations of pollutants over the year (Table 1), data were also separated according to the season. The results showed that negative correlations between Flu and $O_3$ and Pyr and $O_3$ were not statistically significant in summer. Positive correlation between all PAHs and $NO_2$ was not statistically significant in autumn either.

In order to determine which variables ($O_3$, $NO_2$, temperature, relative humidity, atmospheric pressure) were significant in explaining the variability of individual PAHs, multivariate regression analyses was used for further investigation.

Table 2. Linear correlation coefficients (r) between PAHs, $O_3$, $NO_2$, temperature (TEMP), relative humidity (RH) and pressure (P) (1 January – 31 December 2009)

| | Pyr | BbF | BkF | BaP | DahA | BghiP | Ind | $O_3$ | $NO_2$ | TEMP | RH | P |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Flu | 0.98* | 0.85* | 0.86* | 0.83* | 0.80* | 0.81* | 0.82* | -0.47* | 0.45* | -0.67* | 0.41* | 0.12 |
| Pyr | | 0.85* | 0.86* | 0.83* | 0.81* | 0.81* | 0.81* | -0.45* | 0.46* | -0.67* | 0.39* | 0.11 |
| BbF | | | 0.97* | 0.95* | 0.89* | 0.95* | 0.96* | -0.60* | 0.50* | -0.72* | 0.50* | -0.02 |
| BkF | | | | 0.98* | 0.90* | 0.98* | 0.99* | -0.63* | 0.53* | -0.72* | 0.54* | -0.02 |
| BaP | | | | | 0.88* | 0.96* | 0.98* | -0.60* | 0.51* | -0.66* | 0.51* | -0.02 |
| DahA | | | | | | 0.88* | 0.88* | -0.58* | 0.52* | -0.69* | 0.51* | 0.03 |
| BghiP | | | | | | | 0.98* | -0.65* | 0.50* | -0.73* | 0.54* | -0.06 |
| Ind | | | | | | | | -0.65* | 0.52* | -0.70* | 0.55* | -0.04 |
| $O_3$ | | | | | | | | | -0.55* | 0.69* | -0.77* | 0.13 |
| $NO_2$ | | | | | | | | | | -0.42* | 0.36* | -0.07 |
| TEMP | | | | | | | | | | | -0.51* | 0.01 |
| RH | | | | | | | | | | | | -0.21* |

*statistically significant correlations ($p<0.01$)

Preliminary results for the whole-year period showed that variables $O_3$, $NO_2$, temperature, relative humidity and pressure may explain between 46 % (Flu) and 62 % (BkF) variability of PAHs. The results of multivariate regression analysis showed that temperature and $NO_2$ were statistically significant variables for all eight PAHs. Negative relationship of PAHs with temperature was most pronounced for Flu. Positive relationship between $NO_2$ and PAHs suggests their common source. In this model, however, ozone was found to be a significant variable only for Flu. In order to determine parameters responsible for the degradation of PAHs, variable $NO_2$ was excluded from the analysis in further investigation. Results of multivariate regression analysis, with the variables ozone, temperature, relative humidity and pressure, are presented in Tables 3-10.

Table 3. Results of multivariate regression analysis for Flu (ng/$m^3$) as the dependent variable

| Parameter | Beta | Std.Err. of Beta | B | Std.Err. of B | t | p-level | R2 |
|---|---|---|---|---|---|---|---|
| Intercept | | | -20.39 | 8.277 | -2.464 | 0.014* | 0.397 |
| $O_3$ | 0.106 | 0.077 | 0.007 | 0.005 | 1.383 | 0.168 | |
| Temperature | -0.622 | 0.057 | -0.098 | 0.009 | -10.82 | 0.000* | |
| Rel. humidity | 0.139 | 0.065 | 0.015 | 0.007 | 2.128 | 0.034* | |
| Pressure | 0.108 | 0.042 | 0.021 | 0.008 | 2.553 | 0.011* | |

*statistically significant ($p<0.05$)

Table 4. Results of multivariate regression analysis for Pyr (ng/m$^3$) as the dependent variable

| Parameter | Beta | Std.Err. of Beta | B | Std.Err. of B | t | p-level | R2 |
|---|---|---|---|---|---|---|---|
| Intercept | | | -26.16 | 10.50 | -2.491 | 0.013* | 0.443 |
| $O_3$ | 0.139 | 0.074 | 0.011 | 0.006 | 1.881 | 0.061 | |
| Temperature | -0.683 | 0.055 | -0.143 | 0.012 | -12.381 | 0.000* | |
| Rel. humidity | 0.136 | 0.063 | 0.020 | 0.009 | 2.160 | 0.031* | |
| Pressure | 0.106 | 0.041 | 0.027 | 0.010 | 2.597 | 0.010* | |

*statistically significant ($p<0.05$)

Table 5. Results of multivariate regression analysis for BbF (ng/m$^3$) as the dependent variable

| Parameter | Beta | Std.Err. of Beta | B | Std.Err. of B | t | p-level | R2 |
|---|---|---|---|---|---|---|---|
| Intercept | | | -5.271 | 7.301 | -0.722 | 0.471 | 0.549 |
| $O_3$ | -0.088 | 0.066 | -0.006 | 0.004 | -1.329 | 0.185 | |
| Temperature | -0.605 | 0.050 | -0.098 | 0.008 | -12.178 | 0.000* | |
| Rel. humidity | 0.119 | 0.057 | 0.013 | 0.006 | 2.109 | 0.036* | |
| Pressure | 0.034 | 0.037 | 0.007 | 0.007 | 0.930 | 0.353 | |

*statistically significant ($p<0.05$)

Table 6. Results of multivariate regression analysis for BkF (ng/m$^3$) as the dependent variable

| Parameter | Beta | Std.Err. of Beta | B | Std.Err. of B | t | p-level | R2 |
|---|---|---|---|---|---|---|---|
| Intercept | | | -2.449 | 3.031 | -0.808 | 0.420 | 0.562 |
| $O_3$ | -0.105 | 0.066 | -0.003 | 0.002 | -1.606 | 0.109 | |
| Temperature | -0.574 | 0.049 | -0.039 | 0.003 | -11.72 | 0.000* | |
| Rel. humidity | 0.155 | 0.056 | 0.007 | 0.003 | 2.787 | 0.006* | |
| Pressure | 0.035 | 0.036 | 0.003 | 0.003 | 0.975 | 0.330 | |

*statistically significant ($p<0.05$)

Table 7. Results of multivariate regression analysis for BaP (ng/m$^3$) as the dependent variable

| Parameter | Beta | Std.Err. of Beta | B | Std.Err. of B | t | p-level | R2 |
|---|---|---|---|---|---|---|---|
| Intercept | | | -5.243 | 6.541 | -0.801 | 0.423 | 0.488 |
| $O_3$ | -0.158 | 0.071 | -0.008 | 0.004 | -2.229 | 0.026* | |
| Temperature | -0.500 | 0.053 | -0.068 | 0.007 | -9.453 | 0.000* | |
| Rel. humidity | 0.122 | 0.060 | 0.011 | 0.006 | 2.028 | 0.043* | |
| Pressure | 0.038 | 0.039 | 0.006 | 0.006 | 0.980 | 0.328 | |

*statistically significant ($p<0.05$)

Table 8. Results of multivariate regression analysis for DahA (ng/m$^3$) as the dependent variable

| Parameter | Beta | Std.Err. of Beta | B | Std.Err. of B | t | p-level | R2 |
|---|---|---|---|---|---|---|---|
| Intercept | | | -0.723 | 0.321 | -2.250 | 0.025* | 0.523 |
| $O_3$ | -0.051 | 0.069 | 0.000 | 0.000 | -0.737 | 0.461 | |
| Temperature | -0.554 | 0.052 | -0.004 | 0.000 | -10.726 | 0.000* | |
| Rel. humidity | 0.207 | 0.059 | 0.001 | 0.000 | 3.516 | 0.000* | |
| Pressure | 0.09 | 0.038 | 0.001 | 0.000 | 2.358 | 0.019* | |

*statistically significant ($p<0.05$)

Table 9. Results of multivariate regression analysis for BghiP (ng/m$^3$) as the dependent variable

| Parameter | Beta | Std.Err. of Beta | B | Std.Err. of B | t | p-level | R2 |
|---|---|---|---|---|---|---|---|
| Intercept | | | 3.991 | 15.79 | 0.253 | 0.801 | 0.573 |
| $O_3$ | -0.163 | 0.065 | -0.023 | 0.009 | -2.518 | 0.012* | |
| Temperature | -0.561 | 0.048 | -0.202 | 0.017 | -11.61 | 0.000* | |
| Rel. humidity | 0.113 | 0.055 | 0.028 | 0.014 | 2.053 | 0.041* | |
| Pressure | -0.001 | 0.036 | 0.000 | 0.016 | -0.026 | 0.980 | |

*statistically significant ($p<0.05$)

Table 10. Results of multivariate regression analysis for Ind (ng/m$^3$) as the dependent variable

| Parameter | Beta | Std.Err. of Beta | B | Std.Err. of B | t | p-level | R2 |
|---|---|---|---|---|---|---|---|
| Intercept | | | -3.985 | 6.113 | -0.652 | 0.515 | 0.548 |
| $O_3$ | -0.194 | 0.067 | -0.010 | 0.004 | -2.917 | 0.004* | |
| Temperature | -0.500 | 0.050 | -0.067 | 0.007 | -10.05 | 0.000* | |
| Rel. humidity | 0.137 | 0.057 | 0.013 | 0.005 | 2.416 | 0.016* | |
| Pressure | 0.031 | 0.037 | 0.005 | 0.006 | 0.851 | 0.395 | |

*statistically significant ($p<0.05$)

Results given in Tables 3-10 show that ozone and meteorological parameters explain between 40 % (Flu) and 57 % (BghiP) variability of PAHs. For all PAHs, temperature and relative humidity were statistically significant variables. Lower levels of PAHs were in all cases connected with high temperature and low humidity. Ozone, however, became significant only for BaP, BghiP and Ind. Such results suggest that oxidation with ozone is less responsible for the degradation of PAHs than other processes (photooxidation, thermal decomposition or evaporation from particle to gas phase).

## 3. CONCLUSION

Measurements carried out over the one-year period in Zagreb, Croatia, have shown that PAHs have seasonal variations, with high concentrations in winter and very low concentrations during the summer months. All PAHs correlated well with each other. Statistically significant linear negative correlation was found between all PAHs and ozone and PAHs and temperature. Positive linear correlation was found between PAHs and nitrogen dioxide and PAHs and relative humidity. Multivariate regression analysis showed that ozone and meteorological parameters (temperature, relative humidity and pressure) accounted for 40 to 57 % of PAH variability. Temperature and relative humidity were significant variables for all PAHs, while ozone was significant only for BaP, BghiP and Ind.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# DETERMINATION OF GAS/PARTICLE PARTITIONING OF PCDD/Fs IN ISTANBUL ATMOSPHERE

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## ABSTRACT

In this study polychlorinated dibenzo-p-dioxins and-furans (PCDD/Fs) were sampled by using high-volume air sampler at an urban atmosphere (Istanbul, Turkey) from May 2011 to February 2012. To evaluate their gas/particle partitioning, samples were collected in both gas and particle phases. The mean concentrations were determined to be 200 fg/m$^3$ and 2189 fg/m$^3$ for gas and particle phases, respectively. The lower chlorinated congeners were found to be dominant species in gas phase and higher chlorinated ones were found dominant in particle phase. Gas phase contributions of PCDD/Fs were calculated as 1% for winter and 36% for summer sampling periods.

## 1. INTRODUCTION

PCDD/F$_s$ are semi-volatile organic compounds because of the low vapor pressures from 10$^{-2}$ to 10$^{-7}$ Pa at 298 ºK (Mackay et al., 1992). Although PCDD/Fs compounds are present both in gas and particle phases in the atmosphere, they are mainly present in the particle phase (Naitoh et al., 2005; Correa et al., 2006; Li et al., 2008). Environmental behavior and fate of PCDD/Fs are governed by their gas/particle partioning. For example, wet/dry depositon mechanisms, photolytic reactions and hydroxyl radical reactions have distinct effects on gas and particle phases. Gas phase PCDD/Fs compounds are depleted from the atmosphere by photochemical degradation (Brubaker and Hites, 1997) and hydroxyl radical reactions, while particle-bound PCDD/Fs are transported to long distances from sources (Lohmann and Jones, 1998; Welsch-Pausch and McLachlan, 1998) and have considerable effects on human health and ecosystem. Distribution of semi-volatile organic compounds in gas and-particle phases depends on subcooled liquid vapor pressure, Henry’s constant, octanol-air coefficient, properties of particle (size distribution, organic and elemental carbon content), atmospheric conditions (ambient temperature, relative humudity) (Esen et al., 2008a; Vardar et al., 2008). Vapor pressure and ambient temperature are the main physical properties influencing gas/particle partitioning of PCDD/F compounds (Foreman and Bidleman, 1987; Pankow, 1987, Lee et al., 2008). Molecular weight is another property which affects the gas/particle partitioning of PCDD/Fs and higher chlorination level is the cause of higher particle phase concentration.

In this study, gas/particle partitioning of PCDD/Fs was investigated at three different areas. In addition, the effects of TSP concentration and meteorological conditions (temperature, relative humudity) on gas/particle partitioning of PCDD/Fs were also investigated.

## 2. MATERIAL AND METHOD

### 2.1 Sampling locations

Samples were collected from three different areas in Istanbul (Figure 1). Davutpasa sampling station has a mixed source groups such as industry, traffic, residential. Yildiz sampling station is located in a city center and surrounded by main roads. Therefore public transportation vehicles and cars are considered as principal air pollutant sources in this area. Fenertepe sampling station is located out of the city center which is characterized by semi-urban caharacteristics. However, medical and hazardous waste incinerators (located at 8 km norheast and 12 km southeast of this station), use of fossil fuels for domestic heating during colder months, biological sources due to surrounding large forests are the principal sources of air pollutants at this area.

Figure 1. Location of sampling sites.

## 2.2 Sampling and Analyses

Monthly samples were collected at the stations of Dasvutpaşa, Yıldız and Fenertepe in Istanbul during May 2011 to February 2012. High volume samplers (TCR TECORA- Echo, ITALY) were used for sampling and operated approximately at 225 Lt/min flow rates. Particle and gaseous phases of PCDD/Fs were sampled by using glass fiber filter (GFF, diameter 9 cm) and polyurethane foam (PUF, 6x4.5 cm) plugs, respectively. After sampling, extraction, clean up and fractionation were applied for all samples. Finally, qualitative and quantitative analysis were made by using high resolution gas chromatograf and high resolution mass spectrometer (HRGC/HRMS). Sampling standard solutions (3 ng $^{37}$Cl-2,3,7,8 T$_4$CDD) and extraction standart solutions (0.2 ng $^{13}$C$_{12}$–labeled internal standart) were used to determine the efficiency of sampling and extraction processes. Recovery values of $^{13}$C$_{12}$ and $^{37}$Cl-2,3,7,8 T$_4$CDD were determined to be in the ranges of 61-91% and 61-87% respectively. These values meet the sample recoveries of EPA Method TO 9A. Meteorological parameters were measured by wireless weather station (Davis Vantage Proplus 2) (Table 1).

Table 1. Results of the measurements and meteorological parameters

| | **Davutpasa** | **Yildiz** | **Fenertepe** |
|---|---|---|---|
| Sampling date | 05/2011-01/2012 | 05/2011-01/2012 | 05/2011-01/2012 |
| Air volume (m$^3$) | 1715 (645-2228) | 1455 (645-1952) | 1706 (948-2248) |
| Temperature (°C) | 15 (4-25) | 14 (3-25) | 13 (1-25) |
| Relative humudity | 76 | 78 | 83 |
| Rain (mm) | 0 | 0.03 | 0.05 |
| TSP (µg/m$^3$) | 77 (45-122) | 71 (27-115) | 42 (18-108) |

# 3. RESULTS AND DISCUSSION

## 3.1 Gas/particle partitioning

Gas phase concentrations of PCDD/Fs were ranged between 9.5-20 fg I-TEQ/m$^3$ with an average of 14 fg I-TEQ/m$^3$. Particle phase concentrations were range of 38-198 fg I-TEQ /m$^3$ with an average of 102 fg I-TEQ/m$^3$. Mass concentrations for gas phase were determined 212 fg/m$^3$ (185-222 fg/m$^3$) while for particle phase were determined 2189 fg/m$^3$ (916-4116 fg/m$^3$). The highest gas phase concentrations were observed at Fenertepe during summer months while the highest concentration for particle phase were observed at Davutpasa during the winter months (Figure 2). Percentages of the particle phase was determined as 96%, 89%, 80% for Davutpasa, Yildiz and Fenertepe stations respectively. Percentages of the gas phase was found to be 4%, 11% and 20% for Davutasa, Yildiz and Fenertepe stations respectively.

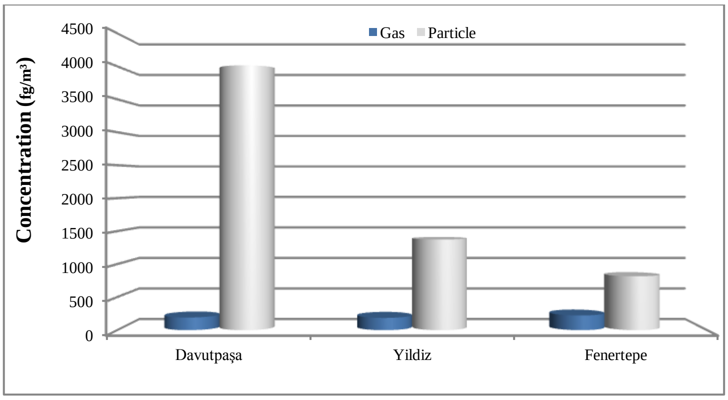

Figure 2. Gas/particle distribution of the sampling areas.

In addition, higher chlorinated dioxin/furan congeners were found in particle phase while the lower chlorinated congeners were found in gas phase. These results are in accordance with the results of previous studies (Eitzer and Hites, 1989). Gas and particle participation of ∑PCDF and ∑PCDD were found to be 71%, 64% and 29% and 36% respectively. Particle fraction of PCDD congeners was higher than PCDF congeners. This result is also in accordance with the results of previous studies (Lee and Jones, 1999; Chao et al., 2004; Correa et al., 2004; Li et al., 2008a). This situation complies with the fact that vapor pressures of PCDD congeners are lower than PCDF congeners (Rordorf, 1989).

## 3.2 Effect of molecular weight

Gas/particle ratio of PCDD/F depends on their molecular weight and particle fraction increases with increasing chlorination level. The average particle fractions of homolog groups were determined as 4% for 4-Cl-PCDD/F, 8% for 5-Cl-PCDD/F, 8% for 6-Cl-PCDD/F, 39% for 7-Cl-PCDD/F and 41% for 8-Cl-PCDD/F. The average gas fraction of PCDD/F were determined as 28% for 4-Cl-PCDD/F, 15% for 5-Cl-PCDD/F, 10% for 6-Cl-PCDD/F, 19% for 7-Cl-PCDD/F and 28% for 8-Cl-PCDD/F (Figure 3). Similar results have been reported by other researchers (Eitzer and Hites,1989; Lee and Jones, 1999; Lohmann et al., 2000a; Lohmann et al., 2000b, 2007; Oh et al., 2001; Park and Kim, 2002; Chao et al., 2004; Correa et al., 2004; Kadowaki and Naitoh, 2005; Li et al., 2007).

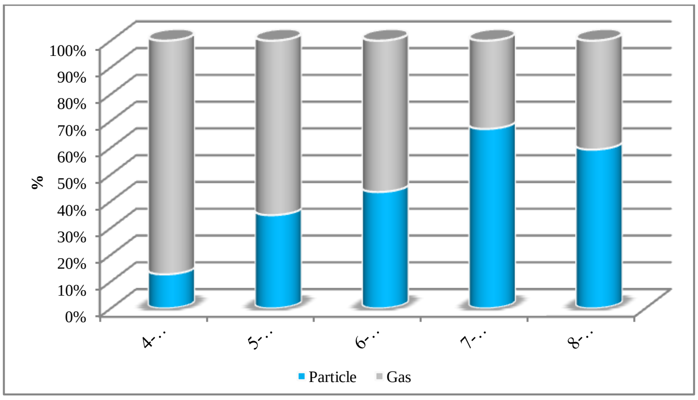

Figure 3. Gas/particle distribution of homolog groups.

### 3.3 Effect of molecular structure

Lower chlorinated congeners were found primarily in the gas phase while higher chlorinated congeners were found in particle phase in this study (Figure 4). For example, contribution of 2,3,7,8-TCDD congener for gas and particle phases were 3% and 0% while contribution of OCDD congener were 9% and 20%. Similarly, contribution of 2,3,7,8-TCDF and OCDF congeners were 17%, 2% and 11% and 8% for gas and particle phases respectively. The highest concentrations for gas phase were determined in summer months (Figure 4). These results are in accordance with previous studies (Eitzer and Hites., 1989; Lee and Jones., 1999; Chang et al., 2004). The average concentrations were found as 176 fg/m$^3$ (gas phase), 14975 fg/m$^3$ (particle phase) in summer and 167 fg/m$^3$ (gas phase), 299 fg/m$^3$ (particle phase) in winter respectively. The highest gas phase concentration (268 fg/m$^3$) was measured at Fenertepe sampling station in summer while the highest particle phase concentration (9763 fg/m$^3$) was found at Davutpasa sampling station in winter. Therefore it was considered that Fenertepe sampling station can be affected by other sources (medical and hazardous waste incinerators, biological sources, products of chlorinated cehemicals) except for traffic emissions.

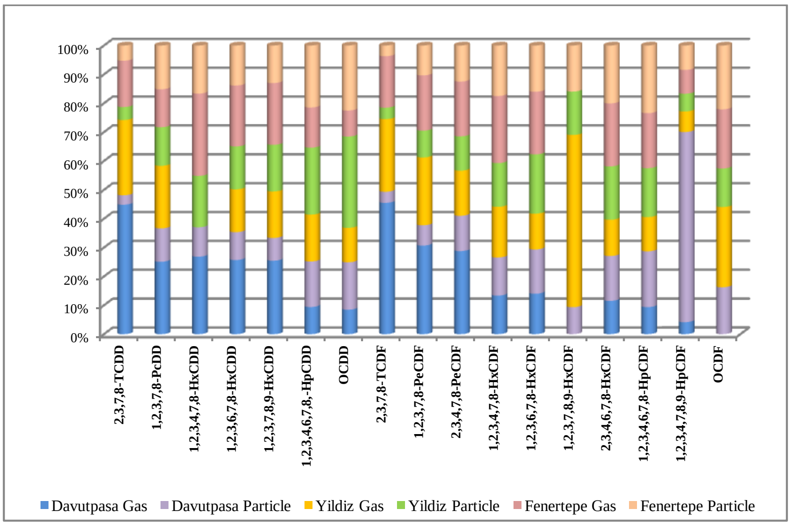

Figure 4. Gas/partititoning of congeners at sampling areas.

Davutpasa sampling station is affected by fossil fuel combustion sources for domestic and commercial heating in winter therefore it was considered that particle phase PCDD/Fs concentrations increased significantly at this sampling station during colder months. In additon, particle phase concentrations significantly increased at all sampling stations in winter (Figure 5).

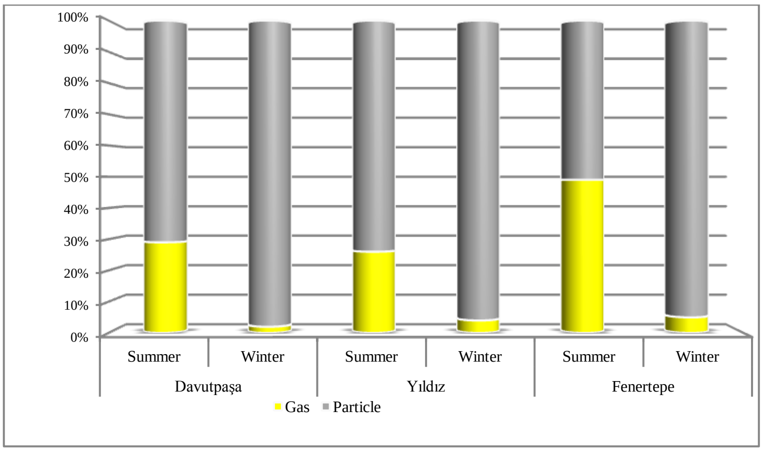

Figure 5. Seasonality of the gas/particle distribution of the PCDD/F.

Therefore, use of fossil fuels for domestic and commercial heating is considered as the principal source of PCDD/Fs compounds in Istanbul during colder months. Gas phase contribution of PCDD/Fs were calculated as 1% for winter and 36% for summer sampling periods. Increase in gas phase contribution in winter can be explained by a few reasons; For example, i) desorption of PCDD/F compounds from solid surface to the atmosphere because of high ambient air temperature. ii) decrease in adsorption rate: Adsorption is an exothermic reaction, therefore rate of adsorption mechanism decreases with increasing temperature. iii) vapor pressure: Vapor pressure is the main physical property influencing gas/particle distribution of PCDD/Fs compounds, a property strongly related to temperature (Foreman and Bidleman, 1987; Pankow, 1987). Vapor pressure of lower chlorinated congeners are higher than higher chlorinated congeners and vapor pressure increases with increasing temperature. Therefore gas phase concentration of 2,3,7,8 TCDD/F in summer was higher than particle phase concentration in this study (Table 2).

Table 2. Average concentrations of lower and higher chlorinated congeners in winter and summer.

| **Average concentration (fg/m$^3$)** | **Summer (mean 23°C)** | | **Winter (mean 6°C)** | |
|---|---|---|---|---|
| | Gas | Particle | Gas | Particle |
| 2,3,7,8-TCDD | 3 | 0 | 8,3 | 33 |
| 2,3,7,8-TCDF | 23 | 7 | 55 | 263 |
| OCDD | 21 | 76 | 17 | 2873 |
| OCDF | 21 | 51 | nd | 1075 |

Gas/particle partitioning of lower chlorinated congeners were shown seasonal variation due to the variation of ambient air temperature. The lower chlorinated congeners were found primarily in gas phase during summer. Similar results have been reported by other researchers (Eitzer and Hites, 1989; Oh et al., 2001; Kadowaki and Naitoh, 2005; Li et al., 2007).

## 3.4 Effect of TSP concentration

Average TSP concentrations were determined as 77 µg/m$^3$, 71 µg/m$^3$ and 42 µg/m$^3$ at Davutpasa, Yildiz and Fenertepe stations respectively. Motor vehicles are considered to be the principal source of high TSP concentration at Davutpasa and Yildiz. Similar results have been reported by Aristizábal et al., 2011; Velasco, 2006; Echeverri and Maya, 2008 for locations which are characterized by high traffic density. Average TSP concentration and particle phase PCDD/Fs concentrations were determined as 72 µg/m$^3$ and 4959 fg/m$^3$ in winter while average concentrations were determined as 65 µg/m$^3$ and 278 fg/m$^3$ in summer. Interestingly, the average TSP concentrations for winter and summer sampling period were very close to each other while particle phase PCDD/Fs concentrations were found significantly higher in winter (Table 3). Combustion of fossil fuels for domestic heating are considered as primarily cause of high particle phase PCDD/Fs concentration in winter. Correlation coefficients (r) for TSP and particle phase PCDD/Fs were calculated as 0.35, 0.48 and 0.47 in this study. Regression coefficients ($r^2$) were calculated as 0.14, 0.017 and 0.47 for Davutpasa, Yildiz and Fenertepe stations respectively. Multiply regression coefficients between PCDD/Fs and temperature, relative humudity were calculated as $r^2$=0.68 (p=0.06), $r^2$=0.38 (p=0.37), $r^2$=0.87 (p=0.004) for Davutpasa, Yildiz and Fenertepe respectively. According to these results, particle phase PCDD/Fs concentration was affected by a few factors such as TSP concentration, temperature, relative humudity and formation sources and mechanisms of these compounds. It was considered that formation sources of TSP is more important than total particle matter concentration according to measurement results in this study. Similar results have been reported by Li et al., 2008; Lee et al., 2007; Ghim et al., 2003. In contrast to this situation, Chi and Chang (2006) reported that particle phase PCDD/Fs concentration increases with increasing TSP concentration at Taiwan.

Table 3. Seasonal variations of TSP and particle phase PCDD/Fs concentrations

| | **Winter** | | **Summer** | |
|---|---|---|---|---|
| | TSP (µg/m$^3$) | PCDD/F (fg/m$^3$) | TSP (µg/m$^3$) | PCDD/F (fg/m$^3$) |
| **Davutpasa** | 85 | 9763 | 78 | 331 |
| **Yildiz** | 70 | 3234 | 73 | 245 |
| **Fenertepe** | 61 | 1881 | 44 | 257 |
| **Average** | 72 | 4959 | 65 | 278 |

## 4. CONCLUSION

Average concentrations of gas and particle phases were determined as 200 fg/m$^3$ and 2063 fg/m$^3$ according to the results of all measurements. Percentage fractionations of particle phase were calculated as 98% for Davutpasa, 88% for Yildiz and 79% for Fenertepe sampling stations. Lower chlorinated congeners (2,3,7,8-TCDD/F) were found primarily in gas phase while higher chlorinated ones (1,2,3,4,6,7,8-HpCDD/F and OCDD, OCDF) were found in particle phase. Similarly, lower chlorinated homolog groups (4 Cl-PCDD/F) were found in gas phase while higher chlorinated homolog groups (7-8 Cl-PCDD/F) were found in particle phase. Gas phase concentrations were found almost similar for summer and winter seasons while particle phase concentrations in winter were significantly higher than summer. Therefore it was considered that particle phase PCDD/Fs concentrations are affected by some factors such as TSP concentration, temperature, relative humudity according to the results of multiply regression analysis.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# EVALUATION OF THREE INTERPOLATION METHODS FOR PARTICULATE MATTER POLLUTION DISTRIBUTION UNDER THE INFLUENCE OF INVERSION AS A CASE STUDY FOR ISTANBUL AND IZMIT

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## ABSTRACT

In this case study, we examined the dispersion of air pollution by means of particulate matter, namely PM10 for the Boshporus-Izmit Bay band, under meteorological conditions of inversion, high pressure and calm wind. The study area includes the industrial regions of Istanbul and Izmit. Our aim was to understand the efficiency of Geographic Information System's chosen interpolation methods, which were Inverse Distance Weighted, Spline and Kriging for modeling the concentrations of the pollutant. 12 stations were considered for the data and 2 other were assessed as control stations. In general, Kriging gave the best results, but Spline had a significant performance of prediction.

**Key Words:** Particulate Matter, Inversion, Kriging, Spline, Inverse Distance Weighted

## 1. INTRODUCTION

Air quality is influenced by meteorological factors such as temperature, humidity, solar radiation, wind speed and direction, turbulence, precipitation, and the characteristics of pressure gradient. Topography also affects the quality of air. In the study represented by this paper, we examined particulate matter having diameter less than 10 micrometers (PM10) as the air quality parameter.

Turkey has a high potential for pollution regarding PM10 (Chen et al., 2008). One of the predominant reasons of the PM10 pollution profile is the Sahara Desert. Winds can transport thick sheets of sand and dust from desert regions which are one of the largest sources of particles (Incecik, 1994). The Sahara Dust is transported to Turkey by southerly winds from Africa, therefore contribute to high PM10 concentrations.

Air quality is crucial to public health. So it needs to be observed, managed and predicted constantly. To accomplish this task, Geographic Information System (GIS) technology along with air quality modeling systems is frequently used, in order to store the gathered data, assimilate/manipulate the data with celerity for modeling and prediction. GIS is equipped with effective tools for spatial and statistical analysis. For this reason, we chose to work with ArcGIS 10's ArcINFO module (by ESRI).

Interpolation methods are frequently used in atmospheric sciences. There are 3 main interpolation techniques commonly used in studies for air quality management. These are Inverse Distance Weighted (IDW), Spline and Kriging. The studies and reports are generally focused on pollutants such as CO2, SO2, NOX or dispersion and concentration of O3 (Thepanondh & Toruksa, 2011; Horálek et al., 2008; Horálek et al., 2010). There are also studies on PM pollution (Wu et al., 2006). While some of these studies determine that IDW is the most suitable interpolation method (Jha et al., 2011), some come to the conclusion that it is Kriging that approximates the measurements with higher accuracy (Thepanondh & Toruksa, 2011).

In this very case study for the Boshporus-Izmit Bay or Istanbul-Izmit (Kocaeli) band, we evaluated these three interpolations techniques (IDW, Spline and Kriging) using PM10 data. Interpolation is not a dynamic model which includes some meteorological data. Since these techniques are statistical models and meteorological parameters do not affect their results. In order to resolve this problem, we chose the interval from 05.11.2010 00:00 to 08.11.2010 00:00 where meteorological parameters are mostly homogenous with the presence of a continuous temperature inversion. There was a continuous high pressure influence as well.

## 2. MATERIAL and METHODS

### 2.1. Data and Region

This study was conducted taking into account the meteorological conditions that directly affect air quality. For this reason, suitable meteorological conditions were observed over the study region between 05.11.2010 00:00 and 08.11.2010 00:00.

The study area (Figure 1) is located in northwestern Turkey and the north-east of Marmara Region. The study area, the Istanbul-Izmit Band, has high population density and widespread industrial areas. Industrial areas are concentrated at west and east of Istanbul and coastal areas of Izmit.

Currently, The Ministry of Environment and Urbanization has been monitoring air quality with more than 100 stations in Turkey. This study was conducted with 73-hours PM10 observations of the specified data range.

Data for 12 air quality stations were considered while two other were assessed as control stations. Kocaeli, Kocaeli-OSB and Umraniye stations had the highest PM10 concentration in study period. Additionally, seasonality was observed especially in Esenler, Kartal, Yenibosna and Umraniye Air Quality (AQ) Stations. The lowest PM10 concentrations were measured at Aksaray, Beşiktaş and Yenibosna AQ Stations. According to EU Air Quality standards, average PM10 measurements of 24 hours should not exceed 50 $\mu g/m^3$. However hourly average measurements were above the standards for the study period (Figure 2) (EU, 2012).

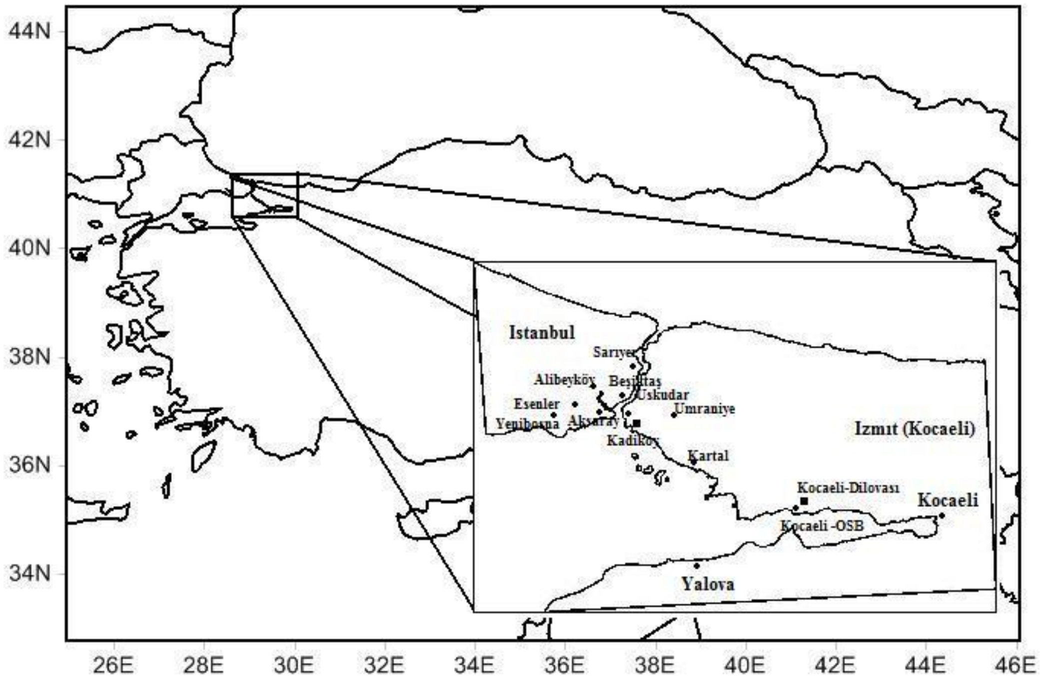

Figure 1. The study area

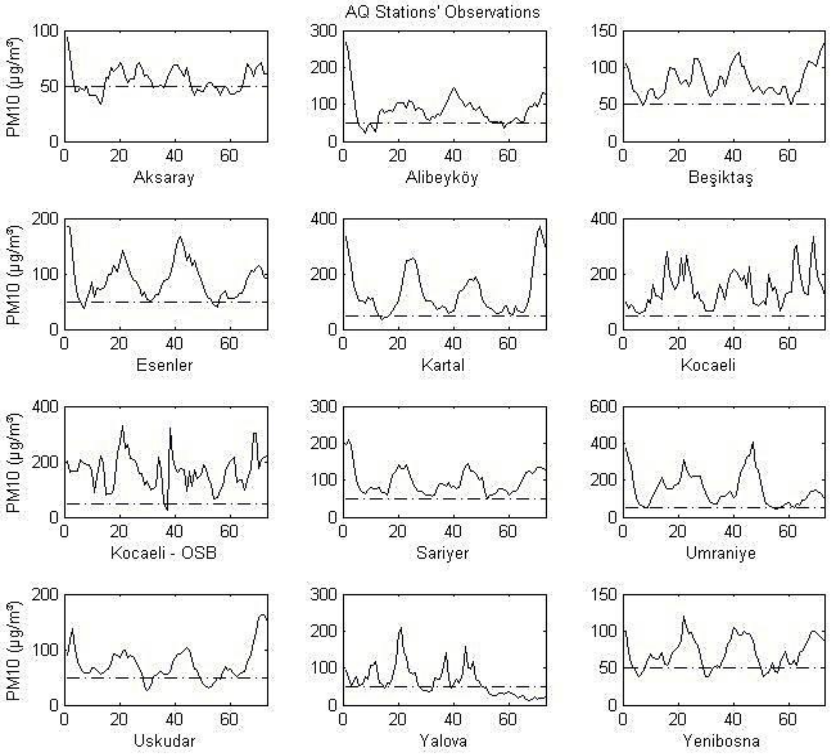

Figure 2. Air quality observations and EU standard for PM10 in study area.

## 2.2. Methods

In this study, data from 12 stations were used. Kocaeli-Dilovası and Kadıkoy Air Quality (AQ) Stations were designated as control stations. Study period was chosen according to atmospheric conditions that affect air quality. The presence of high pressure prevents wind formation. Pollutants emitted into the atmosphere where the wind is calm are suspended. Temperature inversion in lower atmosphere prevents the air from rising and mixing due to turbulence. Besides, presence of inversion within a high pressure system generates a sinking area (Figure 3). Therefore, polluted air is trapped near the surface.

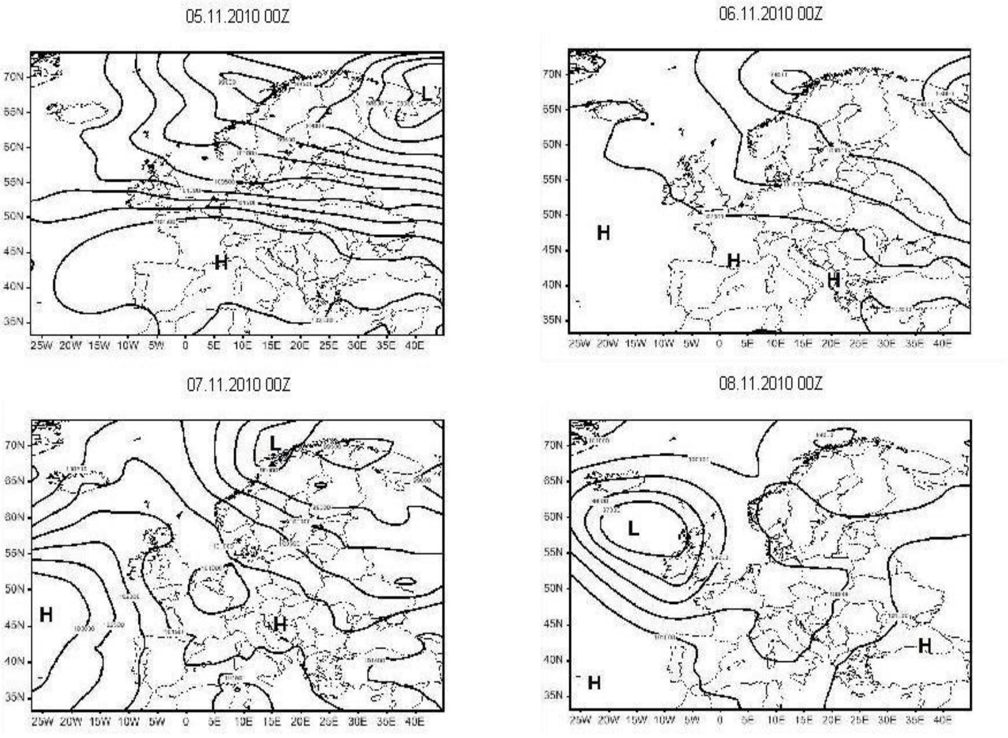

Figure 3. High Pressure System over Europe and Turkey in Study Period

According to these criteria, continuous temperature inversion and high pressure were observed between 05.11.2010 00:00 and 08.11.2010 00:00. The database was prepared with the 73-hours measurement data which was obtained using ArcCATALOG, module of ArcINFO. Prediction maps for 73-hours were created with the three interpolation methods of ArcMAP, using this database.

First, we utilized IDW for interpolation. IDW makes a prediction for all cells of the raster maps, using the means of data points. For smaller distances, the weight on prediction process is higher (Bratt & Booth, 2000). IDW has two main parameters to build up prediction process: First and the most important one is the power. In this study, the default value used for power was 2. However, higher values of power cause smoother surfaces. Secondly, the radius type was selected as fixed to evaluating the distance between stations automatically.

After this, we used Spline which evaluates the prediction values with two distinct methods due to the smoothness. First one is Regularized Spline which allows regulating the smoothness of the surface. Tension Spline is the second method and it generates less smooth surfaces (Bratt & Booth, 2000). And it causes more prediction error. For this reason, we applied Regularized Spline. Weight affects the degree of smoothness in Spline. Therefore the weight value of 0.1 was preferred to make a better prediction. The number of points defines how many data stations were used in calculation.

Kriging was the last method that we used to create prediction maps. It is not completely different from IDW. The only difference is that the weight does not only depend on the distance between points but also on the whole spatial border (Bratt & Booth, 2000). In order to utilize from the spatial border to building up the model, Ordinary Kriging (OK) was considered as the appropriate Kriging method. Semivariagram model type was selected as spherical. Because it gave the best fitting with the measured values. And the radius type was selected as fixed, like it was in IDW.

These prediction maps were then divided into grids using the multidimension tool of ArcGIS 10. Thus, predicted values were produced using these grids for the control stations, Kadıköy and Kocaeli-Dilovası.

## 3. RESULTS and DISCUSSION

Three interpolation methods were applied to 12 stations for Istanbul-Izmit band. Kadıköy and Kocaeli-Dilovası AQ Stations were allocated for validation and they were compared with the methods used.

As a result, predicted values have a high correlation (0.708) with observed values for Kadıköy AQ Station. However, the correlation is lower (0.341) at Kocaeli-Dilovası AQ Station. Therefore Kriging, for both control stations, gives results closer to reality than other interpolation methods. Additionally, IDW and Kriging have similarities. Spline is slightly different (Figure 4).

Coefficient of Correlation (R) is the insufficiency to differentiate two variables. A degree of model predictions' error defines the Index of Agreement (IOA). The operating range of the test is between 0 and 1. When the result of test for IOA is 1, it means that predictions and observations are overlapping (Willmott, 1981). In addition to correlation coefficient, we analyzed the study according to IOA (d).

Kriging gave the best results (0.896) when analyzed with IOA. However, when the results were examined on the basis of stations, Spline had the best performance (0.799) at Kadikoy AQ Station. Also, OK gave satisfactory results at Kocaeli-Dilovası AQ Station (0.896).

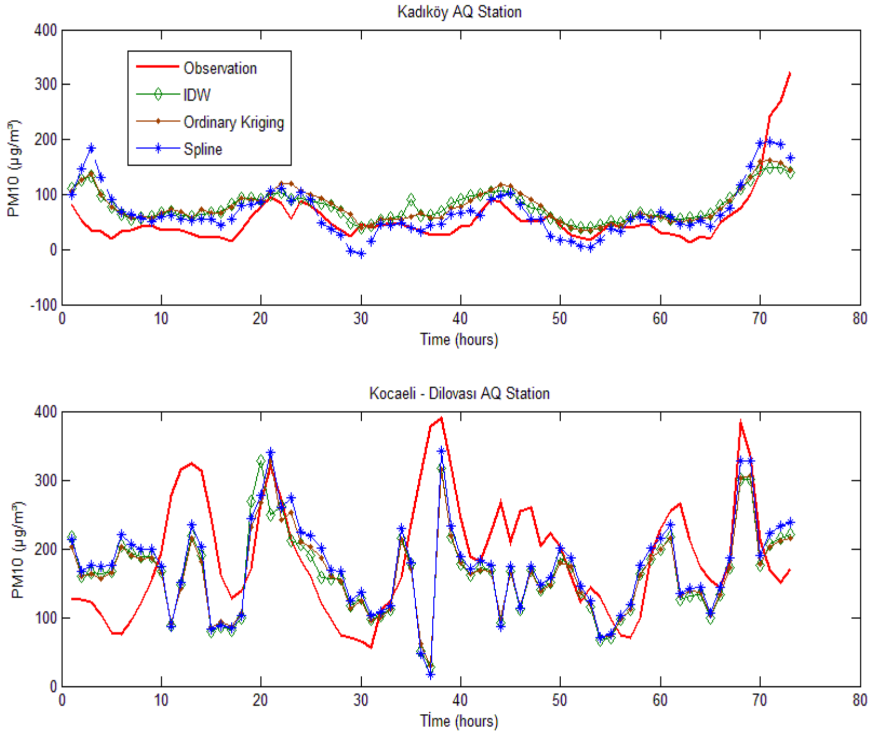

Figure 4. The correlation of observation and predicted values for (a) Kadıköy and (b) Kocaeli-Dilovası AQ Stations

For the results to be more distinctive and significant, two more statistical analyses were applied to the study: Normalized Mean Square Error (NMSE) and Normalized Root Mean Square Error (NRMSE). For NMSE, if the value of NMSE is close to zero, the model is working better. Generally, NMSE is expected as 0.5 and less for a good performance (Silva et al., 2010; Kumar et al., 1993).

For NRMSE, when the calculated value is equal to zero, it means the prediction is considered complete. If the calculated value is equal to or near to 1, then the prediction is only equal to the average value (Itoh, 1995). For Eq. (1), $x_i$ and $y_i$ are observed and predicted values, respectively, and $\sigma$ is the standard deviation of $x_i$. Also N is the number of observations. Both NMSE and NRMSE results support the IOA (Table 1).

(1)

Table 1. Results of statistical analysis of IDW, Spline and Kriging for Kadıköy and Dilovası AQ Stations

| | **IDW** | | **Spline** | | **Kriging** | |
|---|---|---|---|---|---|---|
| | Kadiköy | Dilovası | Kadiköy | Dilovası | Kadiköy | Dilovası |
| **NMSE** | 0.450 | 0.256 | 0.434 | 1.976 | 0.438 | 0.243 |
| **R** | 0.700 | 0.346 | 0.688 | 0.341 | 0.708 | 0.373 |
| **IOA** | 0.703 | 0.803 | 0.799 | 0.632 | 0.728 | 0.896 |
| **NRMSE** | 0.862 | 1.065 | 0.804 | 1.070 | 0.855 | 1.040 |

Interpolation methods, especially Kriging, were used widely in both theoretical and practical studies for air quality (Sertelet al., 2007; Bayraktar & Turalioglu, 2005; Malherbe et al., 2012). Interpolation methods were also used for different studies in meteorology other than air quality, such as temperature, precipitation as climate indicators (Tsanis & Gad, 2001; Vincete-Serrano et al., 2003).

Jha et al. (2011) achieved remarkable results according to IOA in his study of comparison of interpolation techniques. Also, Wu et al. (2006) indicated that IDW mostly gives better results than Kriging for particulate matter. In contrast, Theponandh et al. (2011) and Horálek et al. (2008) took better results from air quality studies with OK. Besides, OK was utilized for temperature as a climate indicator and has represented good performances (Chuanyan et al., 2005; Eldrandaly & Abu-Zaid, 2011). In addition to these methods, Tsanis et.al (2001) applied the Spline Interpolation Method to storm kinematics analysis with other interpolation methods. The analysis gives an idea about the storms movement, using Spline and others. However, the performance for air quality studies using Spline was generally low. Therefore, the studies are focused on IDW and Kriging.

Although OK generally showed good results in our study, Spline gave positive results on basis of stations. In our study, Kadikoy AQ Station was selected for it represented a high density of station and Kocaeli-Dilovası AQ station symbolized a low density. As the result of the analysis in basis of stations, Spline had the best performance for the area with high density of stations which refers to Kadiköy AQ Station, though studies generally contradict this result. In addition, Ordinary Kriging Interpolation Method as a statistical model had a significant performance to predict PM10 values at Kocaeli-Dilovası AQ Station. While OK gives high accuracy, Kriging's other methods could be better than OK. It recommended trying the other Kriging methods to PM10 data.

## 4. CONCLUSION

Interpolation is an advantageous implementation due to its simplicity and speed. But it still has differences from the observed because it is a statistical method. This means that interpolation is an error resource for any study. So, in this study, a comparison between three interpolation methods was made to discover which leads to the least errors.

To sum up, three interpolation methods as a tool of GIS were applied for PM10 on the influence of temperature inversion and high pressure at Istanbul–Izmit Band. PM10 remained concentrated at a lower atmospheric level and did not disperse under meteorological conditions of inversion and high pressure. As a result of the study, two methods came forth: Ordinary Kriging and Spline. In general, Ordinary Kriging Method showed higher consistency. Regarding the density of stations, Spline was the best for higher density.

Kadiköy AQ Station was a proper validation point where Kocaeli-Dilovası AQ Station was not. OK gave better results at lower density of stations.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# EFFECTS OF METEOROLOGICAL CONDITIONS, BUILDING DENSITY AND EDGE VEGETATION ON THE PM CONCENTRATIONS AT A HIGH POLLUTED TRAFFIC ROAD

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## ABSTRACT

Stuttgart-Neckartor is the traffic monitoring station with the highest exceedances of $PM_{10}$ 24h limit values in Germany. At this site and for comparison at the same road but at a site with edge vegetation (bushes and trees) and at a nearby background site in a park PM investigations have been carried out. By analysis of size, morphology, composition, and mineralogy the main potential PM sources at the traffic site could be identified. The great influence of meteorological conditions could be determined by correlating the results with wind speed, number of rainfall days and inversion resp. mixing heights. Beside these influences it could be observed that roadside vegetation reduces the $PM_{10}$ load.

**Keywords:** PM at high traffic roads, PM size distribution, meteorological effects, influence of edge vegetation

## 1. INTRODUCTION

Stuttgart-Neckartor is the traffic monitoring station with the highest exceedances of the $PM_{10}$ 24h limit values in Germany. Transport can be considered as one of the most important sources of PM, and is largely involved in major urban air pollution issues, e.g. Colvile (2001). At the heavily trafficked site of Stuttgart Neckartor with 75 000 vehicles per day the 24 h average limit value of 50 µg/m³ for $PM_{10}$ prescribed by the European legislation was exceeded 89 and 112 times in 2008 and 2009 respectively. During the winter season, the basin area of Stuttgart is exposed to weather conditions such as high atmospheric pressure and little wind which often result in the formation of temperature inversions. In the past, these special weather conditions resulted in extensive PM episodes in the ambient air. During the particular $PM_{10}$ pollution episode in January to February 2006, approximately 54 % of the $PM_{10}$ in Neckartor originated from traffic (LUBW 2006). This traffic-related $PM_{10}$ proportion was among the highest compared to other ambient air monitoring stations in the state of Baden-Württemberg. The main causes for these high $PM_{10}$ exceedances can be summarized as follows:

- strong traffic-related emission sources: soot emissions from diesel exhaust gases and re-suspended road dust
- poor local dispersion conditions caused by building density with the extreme of street canyons (Kukkonen et al. 2005)
- poor regional atmospheric synoptic weather conditions that favour long-range transport of particles (e.g. calm winds, temperature inversions, etc.)
- natural sources of coarse particles that are not easily controllable (e.g. windblown dust, sea salt, etc.) (Bruckmann et al. 2008; Kocak et al. 2009).

At this site and for comparison at the same road but at a site with roadside vegetation (bushes and trees) intensive PM investigations have been carried out. The two traffic sites were characterized by the same exposure to traffic emissions but different roadside conditions. After PM sampling, the size, morphology, composition, and mineralogy of particles were individually analyzed. Thus, it was possible to identify three main potential PM sources at the traffic site. The influence of meteorological conditions had been investigated by correlating PM measurement results with wind speed, number of rainfall days and inversion resp. mixing heights. By means of the two monitoring stations, the influence of vegetation could be investigated.

## 2. $PM_{10}$ COMPOSITION AT THE HIGH TRAFFIC ROAD

In a first campaign PM samplings had been carried out by means of eight stage non-viable cascade impactors and $PM_{10}$ samplers. Three main groups of potential PM sources could be identified at this site with a method of size-fractionated PM samplings coupled with Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX) analyses (Baumbach et al. 2006). The PM coarse fractions of 2.1 to 10.0 µm, which accounted for 44 % of the $PM_{10}$, were identified as re-suspended road dust. The PM fractions of 0.7 to 2.1 µm, which accounted for 38 % of the $PM_{10}$, were identified as background and agglomerated particles with N and S containing crystals. The finer PM fractions smaller than 0.7 µm, which accounted for 18 % of the $PM_{10}$, were identified as agglomerated diesel soot particles with traces of S. The results from these cascade impactor samplings and single particle analyses with SEM/EDX at Neckartor during high PM concentrations ($PM_{10,\ 24h} > 80\ \mu g/m^3$) were averaged and depicted in a summarizing diagram in Figure 1.

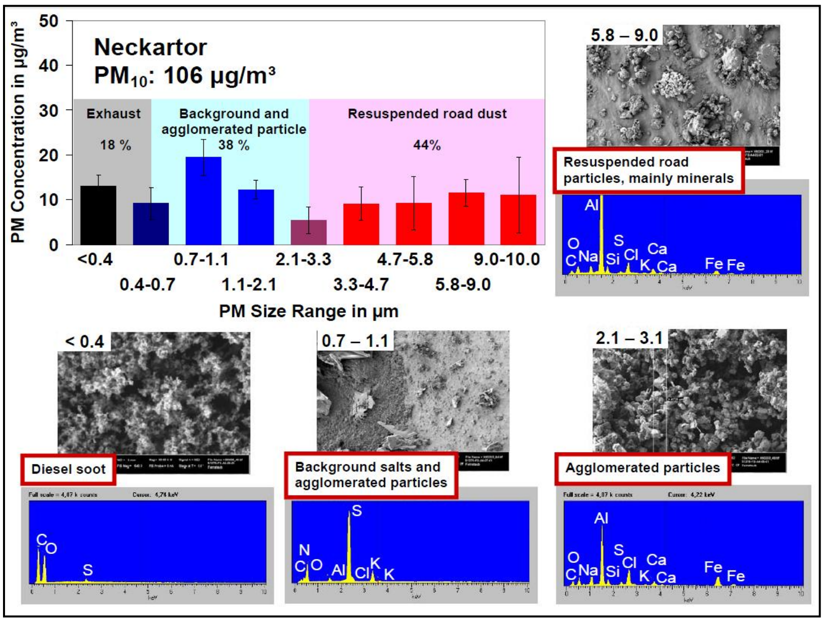


**Figure 1.** Single particle analyses of size fractionated PM at Stuttgart Neckartor during high PM concen-trations ($PM_{10,\ 24h} > 80\ \mu g/m^3$) (Baumbach et al. 2006)

## 3. DEPENDENCY ON METEOROLOGICAL CONDITIONS

### 3.1 Influence of great weather types

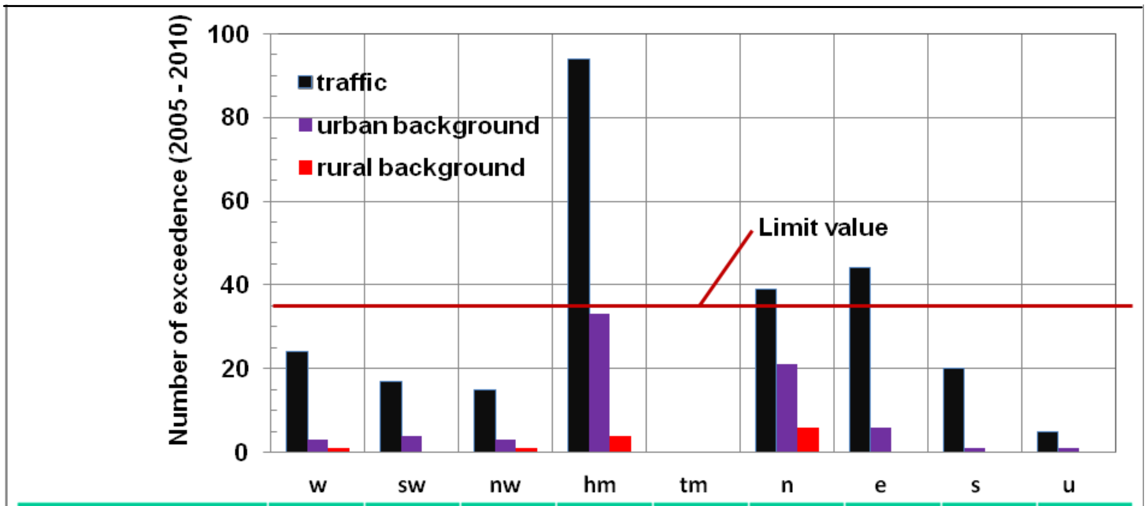
It has been investigated whether and how the $PM_{10}$ concentrations depend on different weather situations. For that the measured $PM_{10}$ concentrations at several monitoring stations in and around the city of Stuttgart and in the state of Baden-Wuerttemberg have been correlated to Great Weather Types (GWT). Major weather events which primarily form the circulation and the direction of air supply are grouped in majority of the cases of statistical studies. These groups of related weather situations form the major type of weather. In this way all western locations form a large weather-type-west, all north locations form a large weather-type-north and so on etc.. Table 1 shows the GWT according to the catalogue of Hess and Brezowsky in Werner and Gerstengarbe (2010). An evaluation of the frequency distribution of these Great Weather Types over the years 1961 to 1990 is given in Table 1. It can be seen that the weather events in Central Europe over these 30 years are determined primarily by maritime air masses: w (27%), sw (7%), nw (7%). But winds from north and east which transport continental air occur also relative frequently: n (15%), e (14.3%). During the years of this weather statistics no continuous PM measurements had been carried out at traffic sites. To correlate PM data from different site categories, especially from traffic sites with such Great Weather Types situations a newer period had to be selected. For the period from 2005 to 2010 enough $PM_{10}$ data were available for the correlation. To compare the frequency of the GWT situations during this period (2005 to 2010) with the long term period of 1961 to 1990 the relative frequencies are also shown in Table 1. There are some differences between the short and long term distribution but the main distribution is comparable. So, an evaluation over this shorter period may be considered to be representative.

**Table 1.** Great Weather Types (GWT) over Europe, their abbreviations and their frequencies in the years 1960 to 1990 and 2005 to 2010 (Ene 2012)

| **Circulation form** | **Great weather type (GWT)** | **Abbre-viation** | **Relative Frequency 1961 - 1990 in %** | **Relative Frequency 2005 - 2010 in %** |
|---|---|---|---|---|
| Zonal | West | w | 27.0 | 21,0 |
| Mixed | Southwest | sw | 7,0 | 10,0 |
| | Northwest | nw | 7,0 | 8,0 |
| | Central European high | hm | 15,9 | 19,0 |
| | Central European low | tm | 2,4 | 1,0 |
| Meridional | North | n | 15,0 | 19,0 |
| | East | e | 14,3 | 11,0 |
| | South | s | 9,9 | 10,1 |
| | Unknown | u | 1,5 | 1,0 |

To determine the impact of the Great Weather Type situations, the $PM_{10}$ daily mean values of all the stations according to the three categories – traffic, urban and rural background - for every type of weather, were averaged and the number of exceedances of 50 $\mu g/m^3$ calculated.

These exceedances are shown in Figure 2 for each Great Weather Type and each station category.



| | w | sw | nw | hm | tm | n | e | s | u |
|---|---|---|---|---|---|---|---|---|---|
| Rel. Freq. % | 21 | 10 | 8 | 19 | 1 | 19 | 11 | 10,1 | 1 |
| Wind Speed average m/s | 1,2 | 1,04 | 1,5 | 1,2 | 1,07 | 1,13 | 1,35 | 1,14 | 1,38 |
| Precipitation average l/m² | 0,03 | 0,05 | 0,02 | 0,04 | 0,04 | 0,04 | 0,03 | 0,05 | 0,08 |

**Figure 2.** Number of $PM_{10}$ exceedences of 50µg/$m^3$(as daily average) under the influence of great weather types (2005 - 2010) for 5 traffic, 7 urban and 3 rural backgroud monitoring stations in and around Stuttgart; windspeed and precipitation are averages of the 7 urban background monitoring stations (Ene (2012); data from LUBW (2012) and DWD (2012))

It is evident that the central European high (hm) gives significantly the highest concentrations and exceedances while the central European low type (tm) has much lower concentrations and exceedances than the average. The high pressure area over central Europe (hm) brings stable stratification conditions, that hinder the vertical exchange of air and the dilution of pollutant concentration. The west (w), southwest (sw) types bring their moisture content, reaching Europe by air masses with their unstable conditions and associated precipitation tendency as well as good mixing of the surface air layer. Thus, dilution of the emissions on the ground leads to lower concentrations and lower number of exceedances. The north and east types bring continental air which results in higher $PM_{10}$ values. The diagram shows that all violations of the limit value of 35 times were recorded at the traffic monitoring stations for the great weather types high pressure over central Europe (hm), north (n) and east (e). The highest recorded violation was during the high pressure over central Europe (hm) weather type especially at the traffic monitoring stations with 94 times and also at the urban background some violations up to 33 times were recorded.

So, it can be concluded that the high $PM_{10}$ values and the number of exceedances occur under special Great Weather Type situations, especially during high pressure over central Europe and northerly and easterly wind situations.

### 3.2 Wind speed influence

The dependency of $PM_{10}$ concentrations at the traffic site Stuttgart-Neckartor on wind speed had been evaluated for one and a half year measurements (01.2004 to 05.2005). In Figure 3 the average concentrations are depicted over wind speed classes. It can be seen that with increasing wind speed the concentrations are decreasing. Up to wind speeds of < 3 m/s the 24h limit value of 50 µg/m$^3$ was exceeded. The highest concentrations of 65 µg/m$^3$ occur during calms and wind speeds < 1 m/s

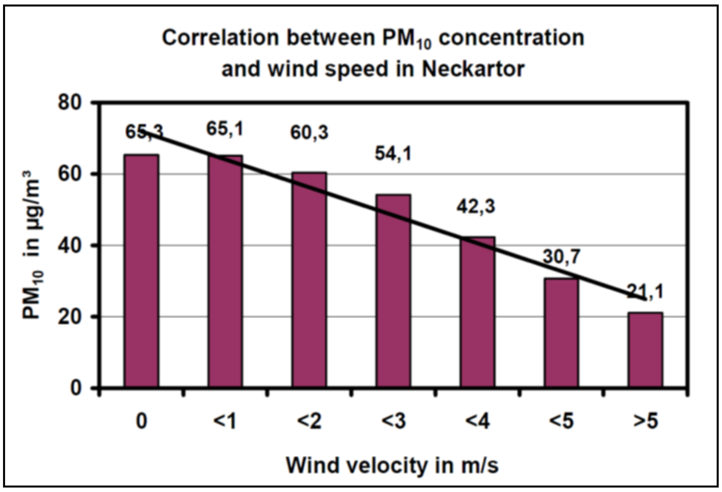


**Figure 3.** Dependency of PM$_{10}$ concentrations on wind speed at Stuttgart-Neckartor; evaluation from 01.2004 to 05.2005 (Zeng 2005)

### 3.3 Dependency on rain

In Figure 4 the influence of rain on the PM$_{10}$ concentrations at the traffic site is shown.The more rainy days are existing the lower the PM$_{10}$ concentrations are becoming. It is evident that during dry situations the highest concentrations are occuring.

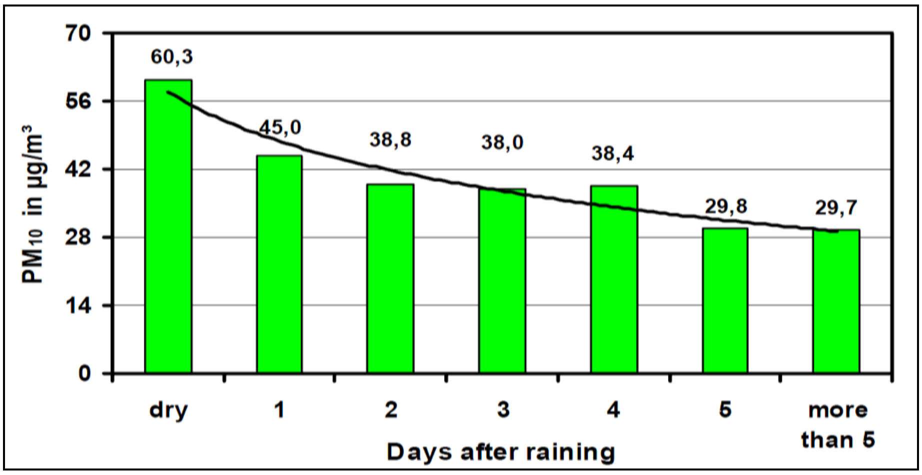


**Figure 4.** Dependency of PM$_{10}$ concentrations on number of rainy days at Stuttgart-Neckartor; evaluation from 01.2004 to 05.2005 (Zeng 2005)

## 3.4 Influence of mixing height

In winter months strong surface inversions are frequently occurring. Especially the city of Stuttgart is affected by such inversions since it is located in a valley and surrounded by hills. From these hills the cold air flows into the valley where Stuttgart-Neckartor is located. In Figure 5 the correlation between $PM_{10}$ concentrations and mixing heights is depicted. The mixing height is per definition the height between the ground and the first inversion layer. It has been determined by evaluation of balloon soundings carried out by the Deutsche Wetterdienst, Stuttgart, at midnight and at noon (DWD 2005). Mixing height 0 (zero) stands for the surface inversion beginning at ground.

Figure 5 is separated in night time (9 pm to 3 am) and day time (9 am to 3 pm) mixing heights.

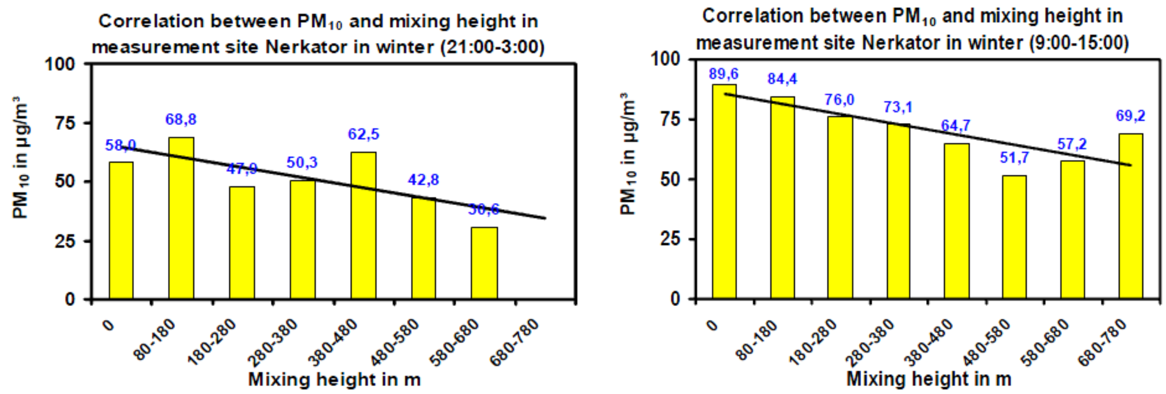


**Figure 5.** Influence of mixing heights on the $PM_{10}$ concentrations at Stuttgart-Neckartor; 01.2004 to 05.2005 (Zeng 2005)

In Figure 5 (left part) it can be seen that during night the highest concentrations occur with mixing heights of 80 to 180 m and 380 to 480 m above ground. That indicates that during night the high traffic road at which the monitoring station is located is not the main source for $PM_{10}$. That is obvious since during night only a very low traffic volume is existing.

If surface inversions are occuring during day time (right part of Figure 5) then relativly high $PM_{10}$ concentrations are occurring. Even during elevated inversion layers (mixing heights up to 380 to 480 m) the concentrations are increased. Compared to wind and rain influence the mixing height has the greatest importance for the $PM_{10}$ concentrations. Of course, the low mixing heights occur only during weak wind speeds and no rain. Thus, it can be stated that low wind speed and no rain are necessary but not only adequate conditions for high $PM_{10}$ concentrations. The limited mixing height has the strongest influence. That may be well known, but here it could be quantifieded.

## 4. ROADSIDE VEGETATION

During a measurement campaign to investigate the possibility of reducing the $PM_{10}$ load by street cleaning a second monitoring station had been installed at the same high traffic road where the Neckartor monitoring station is located. But since the Neckartor station is bordered by a high building (one-sided street canyon) the additional station (Cannstatter Straße) was located at the same road at a side wall with bushes and trees. The results of these measurements are shown in Figure 6: During no street cleaning the $PM_{10}$ concentrations at Neckartor are 1,64 times higher than at Cannstatter Straße. That means that the vegetation at the roadside leads to around 40% lower $PM_{10}$ concentrations than the roadside bordered with buildings at Neckartor. In general, both sites have low wind speeds due to their location in the valley and due to roadside buildings on the one hand (Neckartor) and vegetation on the other hand (Cannstatter Straße). So, it can be concluded that it is better to have vegetation (bushes and trees) at the roadside than a direct bordering by buildings.

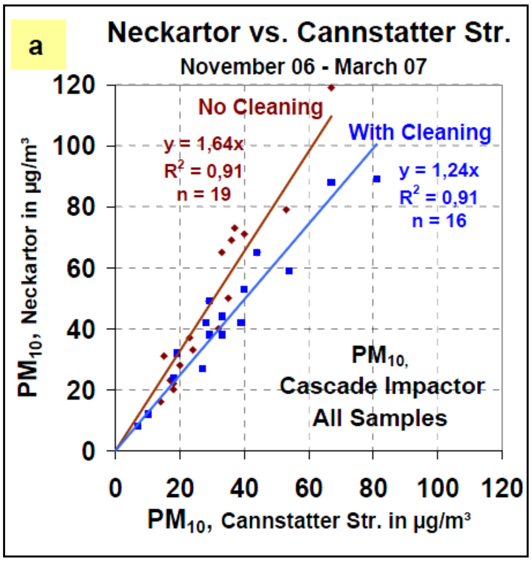


Figure 6. Comparison of $PM_{10}$ measurement results at Neckartor (bordered by buildings) and Cannstatter Straße with roadside vegetation (Hu 2007)

## 5. CONCLUSIONS

Iit can be concluded that at high traffic roads high $PM_{10}$ concentrations and high number of exceedances occur under special Great Weather Type situations, especially during high pressure over central Europe and northerly and easterly wind situations. Low wind speeds and no rain are necessary but not only adequate conditions for high $PM_{10}$ concentrations. Low mixing heights have the strongest influence. That may be well known, but here it could be quantifieded. Furthermore, it could be shown that that roadside vegetation (bushes and trees) improves the air quality compared to direct bordering by buildings.

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# DETERMINATION of WET DEPOSITION FLUXES and WASHOUT RATIOS of PAHs in BURSA/TURKEY

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## ABSTRACT

Ambient air and wet deposition samples of polyaromatic hydrocarbons (PAHs) were collected from an urban sampling site in the Yavuzselim (YS) sampling site of Bursa, Turkey. Annual average PAH concentration was 185±275 ng/m$^3$ at the YS. On the other hand, total average rainwater PAH concentration was 1345±1310 ng/L for YS sampling site. Wet deposition fluxes of particle and dissolved phases were determined 36060±35550 and 7730±5780 ng/m$^2$-day, respectively. Wet deposition is a function of the atmospheric particle characteristics and meteorological conditions. Our results were higher than the reported values in literature. This was mainly because we used exact precipitation durations in our calculations rather than considering a bulk sampling periods. Average gas and particle phase washout ratios, calculated by considering the ambient air and rain water PAH concentrations, were $9.5\times10^5$ and $4.1\times10^5$, respectively. The sources of PAHs in the air were estimated by principal component analysis (PCA) and molecular diagnostic ratios. PCA results showed that pyrolytic sources affected PAH concentrations at the sampling site.

**Key Words:** Ambient air concentration, Precipitation, PCA, Diagnostic Ratio, Flux.

## 1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a group of semi-volatile organic compounds and consisting of two or more fused benzene rings. They can be products of incomplete combustion from both natural and anthropogenic sources. Some PAHs are known to be mutagenic and potentially carcinogenic, thus, they could pose adverse health effects to higher organisms (IARC, 2010). PAHs in air, soil and water can be transported from one medium to another by volatilization, evaporation, dissolution, dry/wet deposition and gas adsorption processes (Lohmann and Lammel, 2004, Birgul et al., 2011). Natural and anthropogenic compounds are deposited from the atmosphere to the earth's surface by numerous processes. They are washed out by precipitation, resulting in wet deposition, or deposited by direct impaction of particles and gaseous molecules on land and water surfaces, resulting in dry deposition. The estimation of washout ratio demands a quite deliberate task because it is influenced by many factors (Bodnár and Hlavay, 2005). Furthermore, precipitation scavenges both gas-phase and particle-associated PAHs from the atmosphere, and concentrations in wet deposition reflect those in air (Poster and Baker, 1996 a,b, Gunindi and Tasdemir, 2011). The efficiencies of gas and particle washout from the atmosphere by precipitation are empirically defined as:

$$W_g=C_{d,rain}/C_{v,atm} \qquad (1)$$

$$W_p=C_{p,rain}/C_{p,atm} \qquad (2)$$

where $C_{d,rain}$ and $C_{p,rain}$ are the dissolved and particle associated concentrations of the precipitated PAH, respectively, and $C_{g,atm}$ and $C_{p,atm}$ are the gas and particle phase concentrations of PAHs in the atmosphere, respectively (Simcik, 2004).

In this study, the objectives of the research were to determine wet deposition fluxes, and to calculate the washout ratios of PAHs at the urban sampling site.

## 2. MATERIALS AND METHODS

### 2.1. Sampling Program

Rainwater and ambient air samples (before the rain) were taken between June 2008 and June 2009 from an urban sampling site, called Yavuzselim (YS) (40°11'48.40"N-29°5'46.80"E). It was located 500 m away from the nearest major road. The samplers were placed on the roof of a 3-storey building. One high volume air sampler (HVAS) and one wet and dry deposition sampler (WDDS) were deployed during the sampling campaign. Details of the WDDS have been previously described (Birgul et al., 2011, Gunindi and Tasdemir, 2011). The mean flow rate and sampling volume for each sampling were about 0.20 $m^3$/min and 260 $m^3$, respectively. Field blanks were generated by equipping the sampler with GFF and PUFs without switching on. There was a meteorology station at the sampling site in order to provide the meteorological data.

### 2.2. Extraction and Analysis

Extraction, clean-up, analytical method and GC-MS oven programme had recently been described (Birgul et al., 2011 and reference therein). All samples and blanks were spiked with PAH surrogate standards prior to extraction. Moreover, pyrene-$d_{10}$ was used as internal standard to determine exact sample volume and was spiked into the extract just prior to injection.

### 2.3. Quality Control and Quality Assurance (QC/QA)

When the surrogate recoveries were between 50 and 120% in a sample, the corresponding PAH compounds were considered in the calculations. The limit of detection (LOD) was determined as the mean blank mass plus three standard deviations (Tasdemir and Holsen, 2005). In general, PAH amounts in the samples were substantially higher than LODs. PAH quantities exceeding the LOD in the samples were quantified and blank corrected. Concentration and flux values were corrected with field blanks in order to eliminate the background contamination and artifacts by subtracting the average blank amount from the sample values (Odabasi et al., 1999).

## 3. RESULTS AND DISCUSSION

### 3.1. PAHs in Wet Precipitation

Average total (gas+particle) PAH concentration was measured 185±275 ng/$m^3$ for the YS sampling site. Average gas and particle phase total PAH ($\Sigma_{12}$PAH) concentrations were 140±205 ng/$m^3$ and 55±85 ng/$m^3$, respectively. Lower molecular weight (MW) PAHs (Phe and Ant) were primarily present in the gas-phase while the higher MW PAHs (Pyr, BaA, Chr, BbF, BkF, BaP and BghiP) were primarily present in the particulate phase. Phe and Flt had the highest concentrations. The gas/particle phase distributions indicated that about 77% of $\Sigma_{12}$PAHs were in the gas phase. Ambient air PAH concentrations are presented in Table 1.

**Table 1.** Ambient air concentrations (ng/m$^3$), rainwater concentrations (ng/L) and wet deposition fluxes (ng/m$^2$-day) of PAHs at the YS sampling sites

| Compounds | YS (Yavuzselim) | | | | | |
|---|---|---|---|---|---|---|
| | Urban Site | | | | | |
| | Particle Phase | | | Dissolved Phase | | |
| | Ambient Air Concentration | Rainwater Concentraion | Flux | Ambient Air Concentration | Rainwater Concentraion | Flux |
| Phe | 0.96 | 207.50 | 6205 | 78.63 | 221.43 | 3724 |
| Ant | 0.15 | 17.11 | 488 | 12.44 | 21.70 | 498 |
| Flt | 3.66 | 362.36 | 9074 | 36.96 | 114.38 | 2543 |
| Pyr | 3.85 | 309.63 | 9945 | 26.09 | 89.00 | 2308 |
| BaA | 7.59 | 54.52 | 1589 | 2.35 | 9.67 | 237 |
| Chr | 7.91 | 92.69 | 3666 | 2.87 | 15.88 | 457 |
| BbF | 8.70 | 58.57 | 2842 | 0.11 | 7.04 | 173 |
| BkF | 6.50 | 34.15 | 1734 | 0.08 | 8.93 | 202 |
| BaP | 6.51 | 28.09 | 1368 | 0.01 | 4.61 | 214 |
| IcdP | 4.67 | 33.42 | 1811 | 0.01 | 2.97 | 87 |
| DahA | 0.80 | 5.11 | 280 | 0.002 | 0.57 | 25 |
| BghiP | 4.29 | 32.67 | 2027 | 0.01 | 2.75 | 72 |
| | | | | | | |
| Total | 55.61 | 1067.56 | 36060 | 141.68 | 359.02 | 7730 |

Annual average total rainwater PAH concentration was determined to be 1345±1310 ng/L while particle and dissolved phase PAH concentrations in rainwater were 1070±1140 ng/L and 360±305 ng/L, respectively. Phe, Flt, and Pyr were predominant compounds in the rainwater samples. The seasonal mean concentrations of total PAHs in precipitation were found as 2845 ng/L, 1010 ng/L , 585 ng/L and 560 ng/L for winter, spring, summer and fall, respectively. Seasonal variations of rainwater PAH concentrations are shown in Figure 1a. Different factors, such as increase in source intensity, traffic intensity, lower mixing height and decrease in solar flux are thought to act in the favour of the atmospheric seasonal PAH concentrations. Because PAHs in the gas phase are degraded by hydroxyl radical attack (Halsall et al., 2001), the atmospheric abundance of OH radicals was likely an important factor in determining PAH concentrations. A lower solar flux could result in a smaller OH radical concentration (Leuenberger et al., 1988) and less extensive degradation of PAHs.

## 3.2. Wet Deposition Flux of PAHs

Particle and dissolved phases wet deposition fluxes of PAHs were determined 36060±35550 and 7730±5780 ng/m$^2$-day, respectively (Table 1). Seasonal fluctuations of PAH flux values were investigated and maximum wet deposition flux values for particle and dissolved phase were obtained in the winter season as observed for the concentration variations. Seasonal fluctuations of wet deposition fluxes were shown in Figure 1b. Particle phase flux values were in order of summer>winter>fall>spring and for dissolved phase the order was winter>spring>fall>summer. Wet deposition fluxes of PAHs were determined by considering real rainy time periods recorded by the timer on the WDDS. This means they only refer to the rainy periods. Our reported values are higher than the ones reported in literature. This is mainly because the bulk sampling periods are used instead of net rain periods in the literature. Moreover, the sampling site, sampling period, meteorological conditions, sampler type etc. can also affect the wet deposition flux values.

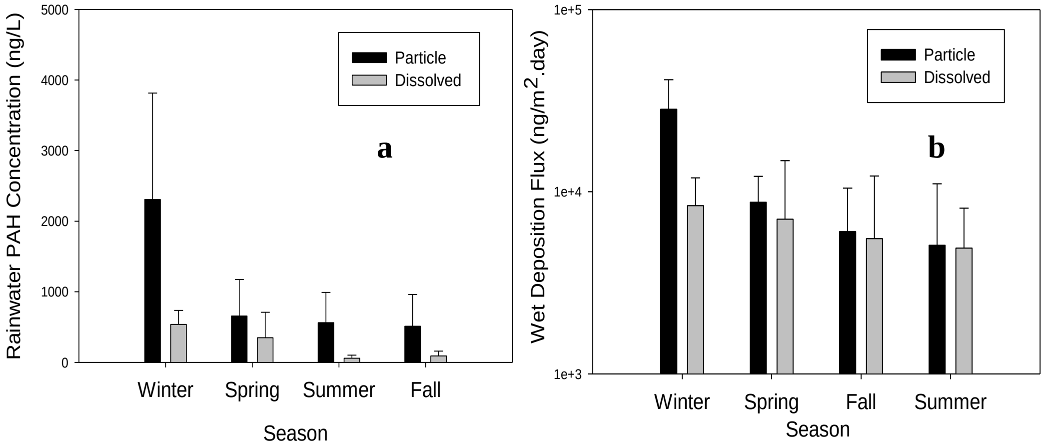

Figure 1. Seasonal variations of (a) rainwater concentrations, (b) wet deposition fluxes

### 3.3. Washout Ratios of PAHs

Average washout ratios of $\Sigma_{12}$PAH compounds for particle and dissolved phase were determined to be $9.5\times10^5$ and $4.1\times10^5$, respectively. Bidleman (1988) presented a rigorous evaluation of literature data and concluded that one could expect a range from $2\times10^3$ to $1\times10^6$ for the particle phase washout ratios for semi-volatile organic compounds. Poster and Baker (1996) reported total suspended particulate matter in both air and rain for samples from the Chesapeake Bay atmosphere and the resulting particle mass washout ratio ranged from $0.43\times10^5$ to $1.3\times10^5$. Washout ratios of PAHs determined in this study are shown in Figure 2. Dissolved phase washout ratios of higher MW PAHs were greater than the lower MW PAHs. The most abundant compounds were Pyr (particle phase) and BghiP (dissolved phase). The highest washout ratios were determined at spring and winter seasons for particle and dissolved phase, respectively. Further characterization of the meteorological parameters, including the intensity of precipitation and the size distribution of the raindrops, as well as better measurements of the particle-size distributions and compositions, is required to more accurately describe the removal of the organic contaminant from the atmosphere by precipitation (Li et al., 2009).

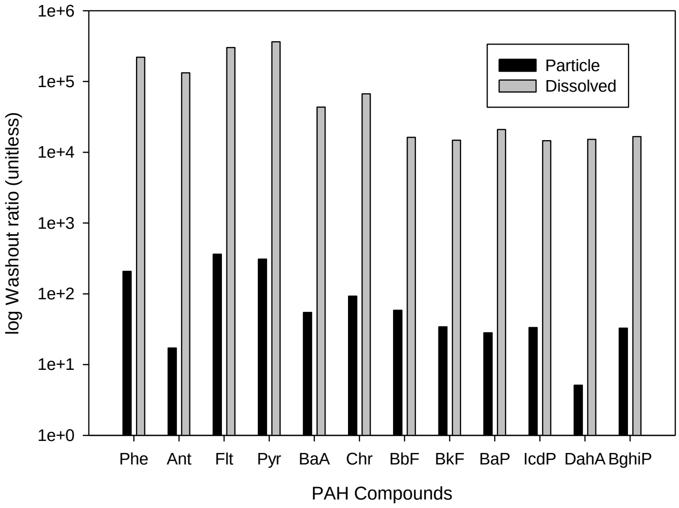

Figure 2. Washout ratios of PAH compounds at the sampling site

### 3.4. Source Estimates from Principal Components Analysis

Principal component analysis (PCA) is a useful data analysis technique for examining factors to reveal relationships and patterns within datasets. PCA has been widely used to identify the origins of organic compounds (Li et al., 2006). The statistical analysis of PCA was performed using SPSS statistical software packages (IBM SPSS 20). PCA was performed with varimax rotation and principal components (factors) having eigenvalues>1 were used to extract the possible sources. Factor analysis was conducted for 12 PAHs. Two principal factors were identified for particle phase concentration values, explaining 97% of the total variance in the data. Factor 1, accounting for the majority of the total variance (53%), was highly loaded with Phe, Flt, Pyr and Ant. Factor 2, which accounted for 44% of total variance, was highly loaded with BaA, Chr, BbF, BkF, DahA, BaP and IcdP. Furthermore, 3 principal factors were identified for gas phase concentration values, explaining 93% of the total variance in the data. Factor 1, accounting for the majority of the total variance (35%), was presented with Ant, Phe, BaP and IcdP. The second factor was composed of the total variance (35%), was highly loaded with Pyr, BbF, Flt, BaA, DahA and BghiP. Factor 3 constituted of 23% of total variance and highly loaded with Chr and BkF. At the YS sampling point, PCA results indicated that coal combustion was an important PAH source. Distribution patterns of PAHs at the YS sampling site was presented in Figure 3.

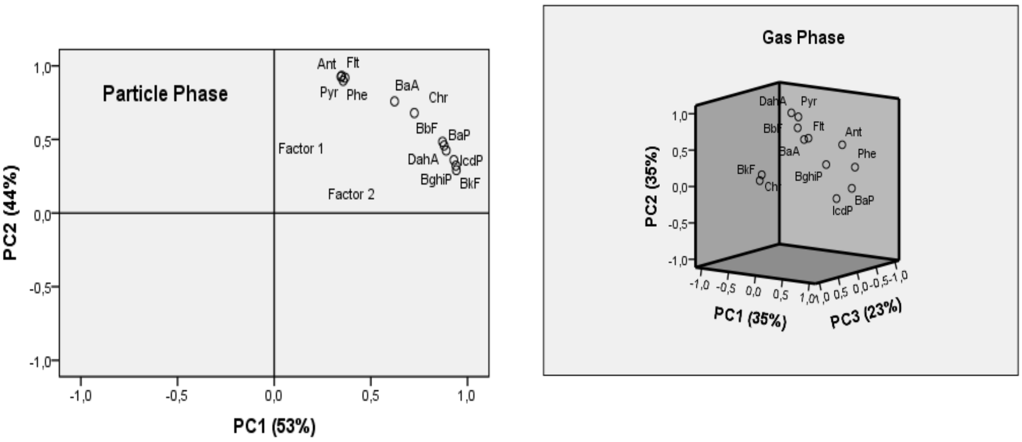

Figure 3. Distribution patterns of PAHs the sampling site.

### 3.5. PAH Compound Diagnostic Ratios for Source Identification

In addition to PCA values, molecular diagnostic ratios have been applied to the data to identify sources of PAHs. Molecular ratios of some marker PAHs have been used to identify the sources of PAHs in the environment (Guo et al., 2003; Katsoyiannis et al., 2011). The Flt/Pyr ratio allows to separate the pyrolytic (combustion origin) and petrogenic (unburned petroleum products) PAH sources. For example, if Flt/Pyr ratio is higher than 1, it is assumed to be of a pyrolytic origin, whereas a value lower than 1 it is assumed to be of petrogenic origin (Sicre et al., 1987). In this study, Flt/Pyr ratio was determined as 1.1 for the sampling site. This result indicates the influence of pyrolytic PAHs. Another considered ratio was Phe/(Phe+Ant). The ratio of Phe/(Phe+Ant) was identified as 0.65 for diesel, 0.50 for gasoline and 0.76 for coal combustion emissions by Khalili et al. (1995). In this study, the ratios were calculated 0.84 for the heating period (November to March) and 0.90 for the non-heating period (April to October). For the 4-ring PAH isomer indicator of BaA/(BaA+Chr), a ratio higher than 0.35 indicates pyrolytic sources, lower than 0.2 indicates petrogenic sources and between 0.2 and 0.35 could be either petrogenic or pyrolytic sources (Socio et al. 2000). The BaA/(BaA+Chr) ratios were determined for heating period 0.48, non-heating period 0.31, respectively. Overall, these ratios indicate the dominance of pyrolitic sources of PAHs at the YS sampling site. Galarneau (2008) reported that it was not possible to say that PAHs directly stems from a particular source. Despite the different sources, PAH compound ratios were determined very close to each other and consulted compilations were determined relatively sparse and the corresponding confidence intervals on the mean ratios were large. Source variability and similarity suggest that PAH ratios were not specific to generic source types.

## 4. CONCLUSIONS

Wet deposition fluxes and washout ratios of PAHs were determined between June 2008 and June 2009 at urban site of Bursa. Particle and dissolved phase rainwater concentrations and wet deposition fluxes of PAH compounds were determined successfully. It was found that 77% of the total PAH concentration was in the gas phase. Phe and Flt had the highest concentrations at the sampling site.

Source identification studies revealed that pyrolytic sources were the dominant factors.

Precipitation levels in particle and dissolved phases were determined separately. The total PAH concentrations in particle phase 1070±1140 ng/L and 360±305 ng/L in dissolved phase at the YS sampling site. Wet deposition fluxes of PAHs were determined by considering exact rainy time periods. Wet deposition fluxes for particle and dissolved phases were determined 36060±35550 and 7730±5780 ng/m$^2$-day, respectively. Atmospheric concentrations and rain water concentrations were used to calculate washout ratios of PAHs and it was found that the washout ratios of higher MW PAHs were greater than the lower MW PAHs.

Bursa is one of the industrial and commercial centres of Turkey, and may represent the typical environmental status of most industrialized cities. Similarly, this situation may also exist in other developing countries with similar climatic, geographical and socio-economic conditions. More studies are needed to understand the impact of PAHs on the environment. A higher level of environmental vigilance will be required for the Bursa and Marmara region.

## ACKNOWLEDGEMENTS

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# MASS CONCENTRATIONS OF PM1 PARTICLE FRACTION IN ZAGREB AIR

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## ABSTRACT

Main purpose of this investigation was to provide samples for chemical analyses of particle content in accumulation mode, skipping that way the bias caused by coarse particle fraction. Daily samples of PM1 airborne particle fraction were collected in Zagreb at two measuring sites (city centre and urban background) during 3-years period 2009-2011. Concentrations measured show seasonal dependence and their distribution could be approximated to the lognormal distribution. Difference in PM1 concentration levels between two sampling sites show slightly elevated values measured at town centre compared to those measured at urban background site, although these differences are less pronounced than for PM10 and PM2.5 particle fractions.

**Key Words:** air pollution, PM1 particle fraction, mass concentration ratios, Zagreb

## INTRODUCTION

Airborne particle fraction PM1, opposite to fractions PM2.5 and PM10, is not defined on the basis of particle penetration and deposition characteristics into the human respiratory tract and related conventions, so it is not used in health related studies and it is not probable that it would be adopted as an ambient standard. In studies performed in urban environments of Australia (Keywood et al. 1999), Helsinki, Finland (Vallius et al. 2000) and the Pittsburgh,USA (Cabada et al. 2004) the relationship between PM1 and PM2.5 was explored. On the other hand, Lundgren et al. (1996), claimed that PM1is a better indicator for a roadside microenvironment than PM2.5, because, compared with PM2.5 and PM10, it minimizes interference from natural sources. The main conclusion was that majority of mass in both fractions originate from the same sources and that measurement of PM1 did not yield significant new information. Main purpose of PM1 (FP fine particles) investigation is to provide samples of the "aged" aerosol for chemical analyses of particle content in accumulation mode, skipping that way the bias caused by inter-modal (PM2.5-PM1) and coarse (PM10-PM2.5) particle fractions (Haller et al., 1999).

## MATERIALS AND METHODS

Daily samples of PM1 airborne particle fraction were collected in Zagreb, Croatia at two measuring sites (city centre and urban background) during 3-years period 2009-2011 by means of low volume LVS3 and sequential samplers SEQ47/50 (Sven Leckel, Germany). Since no reference method is prescribed for PM1 mass concentration determination, accredited gravimetric method following EN14907 was used. Samples were collected on quartz microfibre filters (Whatman) at the flow rate of 2.3 $m^3$ $h^{-1}$from approximately 55 $m^3$. Filters were conditioned at air temperature in the range between 20±1°C and relative air humidity in the range between 50±5% and weighed after 48 and again after 24 hours prior and after sampling. Mettler TOLEDO MX5 Microbalance with resolution of 1 μg was used for mass determination. Average daily and yearly extended uncertainties (k=2) of PM1 mass concentrations were 2.05μg $m^{-3}$ and 0.71μg $m^{-3}$ respectively.

## RESULTS AND DISCUSSION

Time series of PM1 concentrations show strong seasonal dependence at both measuring sites, with low concentration levels during warm and elevated concentrations values during cold period of the year. In Figure 1 PM1 concentrations measured at urban background site over 2009-2011 three-year period are presented.

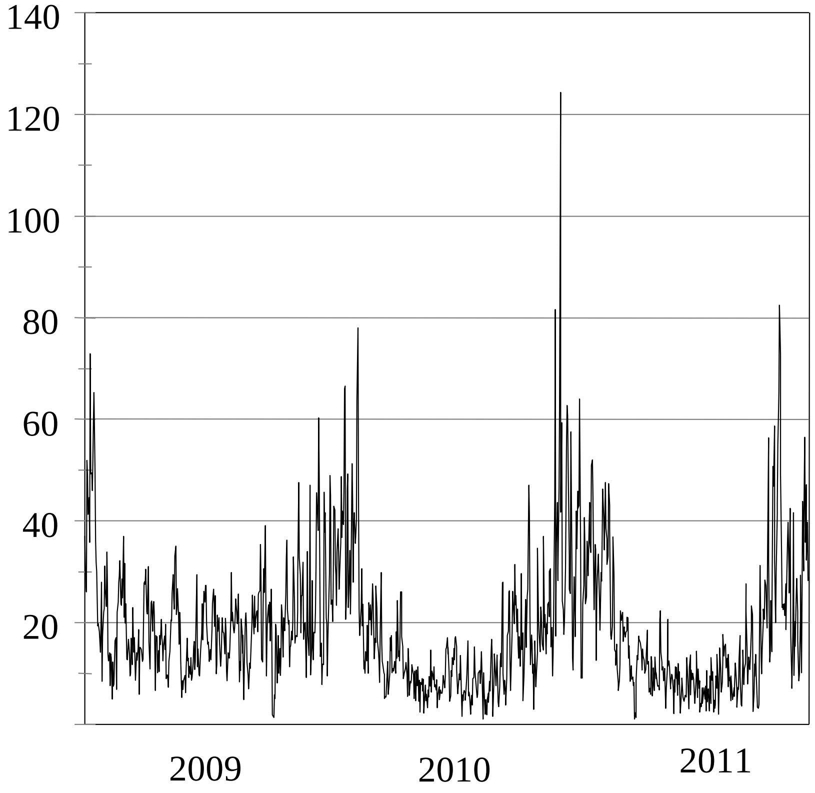

Figure 1. Time series of PM1 mass concentrations (μg m$^{-3}$) at urban background site

Yearly sets of PM1 concentration distributions for both measuring sites could be approximated to lognormal distribution. In Figure 2 distribution of PM1 mass concentrations at urban background site is shown.

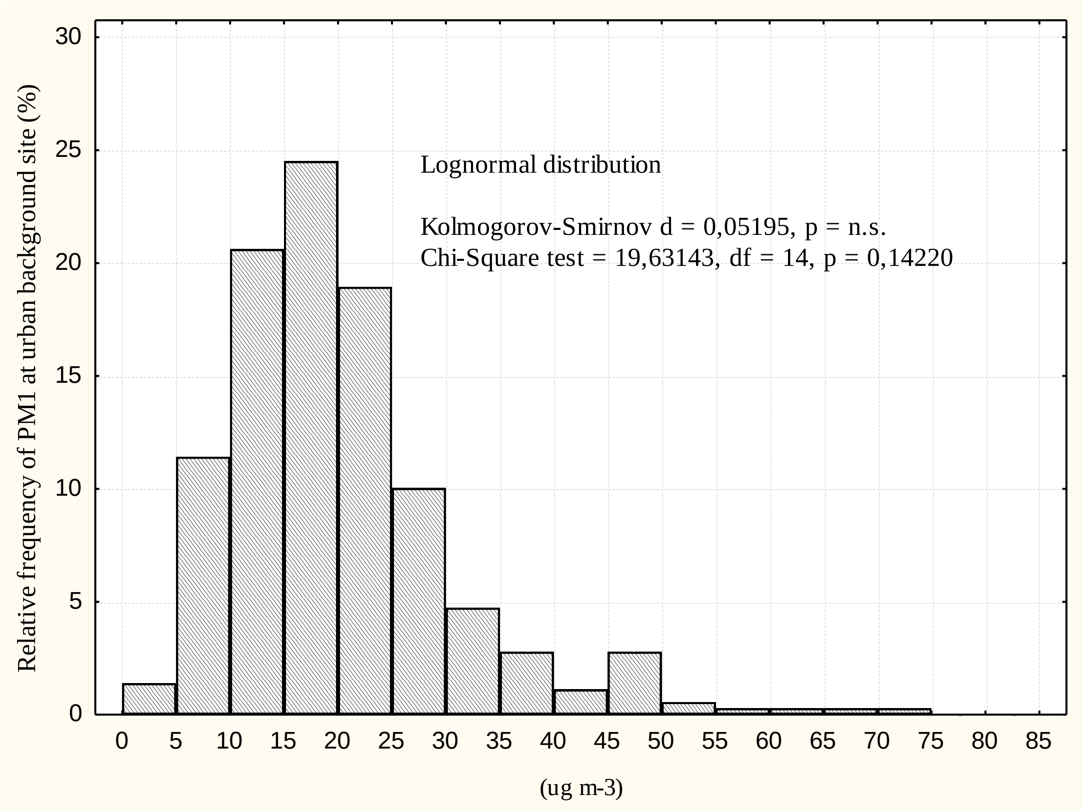

Figure 2. Distribution of PM1 mass concentrations at urban background site

Statistical parameters of PM1 concentrations for both measuring sites are presented in Table 1. Median concentration values in 2009, for both measuring sites, were higher compared to the rest of the measuring period.

Table 1. PM1 mass concentrations (μg $m^{-3}$) and number of samples

| | **Urban background** | | | | **City centre** | | | |
|---|---|---|---|---|---|---|---|---|
| **Period** | **2009** | **2010** | **2011** | **2009-11** | **2009** | **2010** | **2011** | **2009-11** |
| **N** | 359 | 363 | 356 | 1078 | 352 | 310 | 208 | 870 |
| **Mean** | 20.2 | 17.9 | 18.6 | 18.9 | 22.3 | 19.4 | 18.1 | 20.3 |
| **Std.Dev.** | 10.5 | 14.6 | 14.0 | 13.2 | 14.4 | 14.2 | 13.7 | 14.2 |
| **Median** | 18.3 | 13.9 | 13.3 | 15.6 | 18.2 | 14.7 | 14.9 | 16.6 |
| **Minimum** | 1.3 | 1.0 | 1.1 | 1.0 | 3.3 | 2.5 | 2.3 | 2.3 |
| **Maximum** | 72.9 | 124.3 | 82.4 | 124.3 | 110.6 | 99.4 | 84.5 | 110.6 |

High correlations between concentrations of different particle fractions (PM10, PM2.5 and PM1) were found for both measuring sites (Table 2) suggesting that all fractions originate from the same particle sources.

Table 2. Correlations between mass concentrations of different particle fractions

| | **r** | **$r^2$** | **N** |
|---|---|---|---|
| | **Urban background** | | |
| **PM10 - PM2.5** | 0.964 | 0.930 | 356 |
| **PM10 - PM1** | 0.926 | 0.858 | 359 |
| **PM2.5 - PM1** | 0.929 | 0.862 | 352 |
| | **City centre** | | |
| **PM10 - PM2.5** | 0.969 | 0.939 | 233 |
| **PM10 - PM1** | 0.936 | 0.875 | 242 |
| **PM2.5 - PM1** | 0.969 | 0.938 | 334 |

Mass concentration ratios PM1/PM2.5, PM1/PM10 and PM2.5/PM10 presented in Table 3 are higher for urban background site showing that particle distribution is shipped towards smaller particle sizes, presumably representing an “aged” aerosol.

Table 3. PM1/PM10 and PM1/PM2.5 mass ratios for both sampling sites

| | **Urban background** | | | | **City centre** | | | |
|---|---|---|---|---|---|---|---|---|
| **PM1/PM10** | | | | | | | | |
| | **2009** | **2010** | **2011** | **2009-11** | **2009** | **2010** | **2011** | **2009-11** |
| **N** | 359 | 361 | 355 | 1075 | 242 | 304 | 206 | 752 |
| **Mean** | 0.63 | 0.56 | 0.53 | 0.57 | 0.55 | 0.49 | 0.37 | 0.48 |
| **Std.Dev.** | 0.12 | 0.13 | 0.13 | 0.13 | 0.10 | 0.10 | 0.10 | 0.12 |
| **Median** | 0.64 | 0.57 | 0.54 | 0.58 | 0.54 | 0.48 | 0.36 | 0.48 |
| **PM1/PM2.5** | | | | | | | | |
| **N** | 358 | 357 | 343 | 1058 | 233 | 291 | 207 | 731 |
| **Mean** | 0.76 | 0.77 | 0.75 | 0.76 | 0.72 | 0.67 | 0.59 | 0.67 |
| **Std.Dev.** | 0.14 | 0.15 | 0.16 | 0.15 | 0.13 | 0.12 | 0.15 | 0.14 |
| **Median** | 0.75 | 0.77 | 0.78 | 0.76 | 0.71 | 0.65 | 0.62 | 0.66 |

These ratios were lower for city centre indicating the fresh influence of particle sources. Although no limit values for PM1 particle fraction exists, comparison to PM2.5 limit values lead us to the conclusion that PM1 concentration levels are elevated and that they could cause possible health effects.

## CONCLUSIONS

High correlations between concentrations of different particle fractions suggest that all fractions originate from the common particle sources.

Difference in concentration ratios of different particle fractions between measuring sites implies active particle sources in city centre and more stable, aged, aerosol at urban background site.

Comparisons of PM1 to PM2.5 concentrations lead us to the conclusion that PM1 concentration levels are elevated and that they could cause possible health effects in humans.

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# SPATIO-TEMPORAL ANALYSIS OF $PM_{10}$ CONCENTRATION IN TURKEY

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## ABSTRACT

$PM_{10}$ measurements from 2008 to 2010 at 118 air quality monitoring stations of Ministry of Environment and Urbanization, was used to determine air pollution levels in Turkey. Spatial and temporal analysis was conducted to identify clusters of high $PM_{10}$ concentration and to identify possible trends in the data. K-means clustering method was performed for spatial analysis suggested that 81 cities in Turkey can be divided into five groups. The eastern regions; belong to two most polluted clusters with means of 126.2 and 91.5 $\mu g/m^3$, which are more polluted than industrial and populated western regions with cluster means of 69.5 and 53.4 $\mu g/m^3$ mean values. This paper will present the findings of the spatio-temporal analysis of $PM_{10}$ levels as well as possible reasons causing the spatial variance.

**Keywords:** $PM_{10}$, Spatio-temporal analysis, K-means, Turkey

## 1. INTRODUCTION

Particulate matter pollution is one of the major concerns in the developing countries, due to its harmful effect on human health. Many study results show that particulate matter pollution cause various diseases on short term and long-term exposure. In a study conducted by Atkinson *et al.* [2001], 10 µg increase of $PM_{10}$concentrations causes %0.6 increase in overall deaths on short term exposure. In other study, hospital admissions for asthma and COPD were observed to be increased by 1 percent per 10$\mu g/m^3$ increase in $PM_{10}$ among older people (65+) [Katsouyanni *et al.*, 2001]. Avol *et al.*, [2001] concluded that changes in air pollution exposure have a significant impact on lung function growth and performance. EU established limit values to prevent the harmful effects of the pollutants on human health. It is suggested that 24 h mean concentration of 50 $\mu g/m^3$ should not to be exceeded more than 35 times during a year.

Emission of industrial, traffic, agriculture activities as well as topographical conditions, meteorological factors and natural sources are the main causes of the particulate pollution in Turkey. There are some studies on air quality in Turkey that focuses on particulate matter pollution sources in large cities. In a study conducted by Kindap et al., (2006), particulate matter transport from Eastern European countries to Turkey was examined via meteorological and air quality model. High $PM_{10}$ winter episodes over Istanbul in 2002 related to long-range transport of particles from Eastern Europe were investigated. Im *et al.,* 2010, analyzed $PM_{10}$ level in Istanbul with WRF and CMAQ models using a regional emissions inventory. In another study conducted by Tayanc (2000), increase in SO2 concentrations during 1980s and 1990s were identified to be caused by fossil fuel heating and industrial emissions from 1980s to 1990s. Currently, there are not many studies focusing on the spatio-temporal distribution of particulate matter in Turkey. Such an analysis is critical to understand possible sources of air pollution so that necessary mitigation methods can be developed.

K-means is a simple tool that enables spatial analysis. In a study, Lu *et al.*, 2005, evaluate $PM_{10}$ concentrations over Taiwan. They have divided monitoring stations data into five groups using three different clustering methods; hierarchical clustering (Ward's method), non-hierarchical clustering (K-means) and two-level approach (self-organizing maps neural network, then K-means clustering). In another study, K-means algorithm is used to group back trajectories arrived to the Belfast and Harwell city in UK. [Abdalmogith *et al.*, 2005]. Rodriguez *et al.*, 2003, use K-means and principal component analysis to evaluate the chemical profiles of the different PM episodes in Eastern Spain. In another study Austin *et al.*, 2012, the classification of gaseous and particulate air pollution evaluated by K-means method.

In this study the main objectives are: i) to determine the level of $PM_{10}$ in Turkey, ii) to develop temporal analysis of $PM_{10}$ levels, and iii) to develop a spatial analysis to understand if there are clusters of high $PM_{10}$ levels. For this purpose, we have utilized the air quality data provided by the Turkish Ministry of Environment and Urbanization.

## 2. METHODOLOGY AND RESULTS

The air quality network operated by the Turkish Ministry of Environment and Urbanization has over 118 sites throughout Turkey (since 2008), which are used to monitor air pollution. Out of 81 cities, 12 of them have more than one station. Marmara region (Northwestern part of Turkey) hosts 22 stations of which 10 of them are located in Istanbul and Kocaeli have 3 air quality monitoring stations. In the Aegean region (Western part of Turkey) there are 15 stations where 6 of them are located in İzmir and Denizli and Mugla have 2 stations each. Mediterrenean region (Southern part of Turkey) has 13 stations where only Adana and Kahramanmaras has multiple stations (4 and 2 respectively). Central Anatolia (Inner Anatolia) has 25 stations with Ankara having 10 stations and Kayseri and Konya have 3 and 2 stations. Black Sea region (Northern part of Turkey) has 20 stations where Trabzon and Samsun have 2 stations each. Eastern Anatolia has 14 and Southeastern Anatolia has 8 stations. In these regions every city has only one station. The location of the 118 monitoring stations are shown in Figure 1.

The observations used in this study are hourly $PM_{10}$ concentrations in $\mu g/m^3$ from January 2008 to December 2010. For the cities that multiple stations, average values were estimated. For example, there are 10 stations in Istanbul; the mean values of the 10 stations at each hour computed and then they were used for the data analysis as a single station. Daily averages of $PM_{10}$ concentration at 81 cities were calculated from hourly data over 3 years period.

Analysis showed that annual averages of $PM_{10}$ in Turkey is 78.2, 69.6, 69.2 $\mu g/m^3$ for 2008, 2009 and 2010 respectively. It should be noted that all these values are above the EU limit value of 40 $\mu g/m^3$.

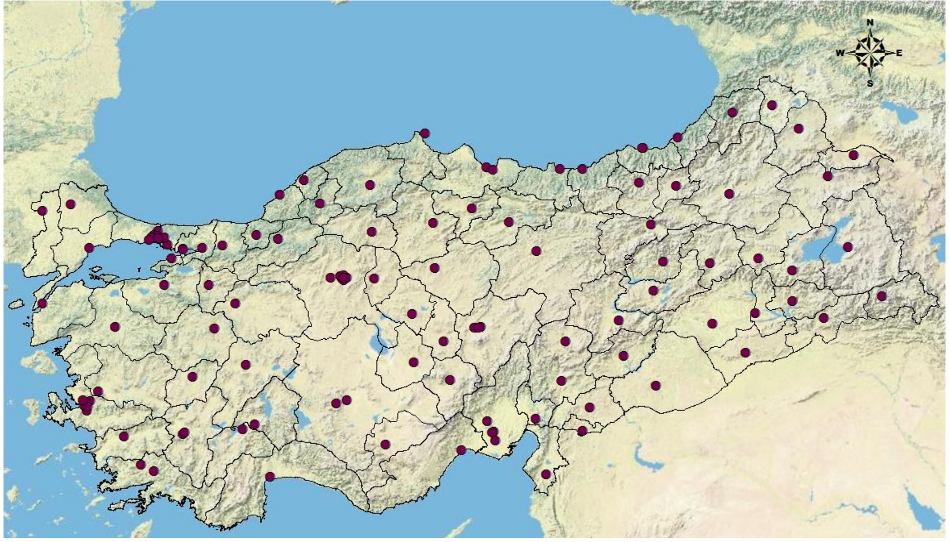


Figure 1 : Location of the air quality monitoring stations in Turkey.

Although the annual averages suggest a decreasing trend, in order to fully answer this question we have conducted a temporal analysis. For this purpose, we have utilized daily $PM_{10}$ data averaged over 118 stations. Figure 2 presents these daily data. As seen in the Figure, daily averages ranges between 22 and and 174 $\mu g/m^3$. It should be noted that only 25 percent of the data have $PM_{10}$ values lower than 50 $\mu g/m^3$, and 75 percent of the data are less than 87 $\mu g/m^3$. As expected, there is a strong seasonality in the data as highest values occur during winter period and the lowest values occur during summer. We have conducted a time series regression using time values as the independent variable. We have also included sine and cosine cycles to capture the seasonality (Blue line in Figure 2 presents the result of this time series regression). We should note that regression equation has a slope almost zero with a r-square value less than 20 percent. Based on this analysis it is concluded that there is no increasing or decreasing trend in the daily $PM_{10}$ values.

Spatial analysis of the $PM_{10}$ data were conducted using K-means method. K-means clustering method is the most widely used nonhierarchical clustering method to grouping the datasets. The method divides the data in to a number of clusters, which is defined ahead of the analysis. Clusters must be determined iteratively with an initial guess (xi=2,3,….n). The centroids, mean values of the vector, computed of each cluster for the first guess. Then Euclidian distance (Eq.1) is calculated between the each point of the current data and the centroids. Each point of the data, assigned to the clusters by the closest distance from the centroids. [Wilks, 2006]. The algorithm repeated until minimize the distance to obtain no more changes of partitioning of the data points. In this study, sum of squares within-clusters were utilized to obtain the clusters.

$$\|x-y\| = \sqrt{\sum_{k=1}^{K} (x_k - x_k)^2} \qquad \text{(Eq. 1)}$$

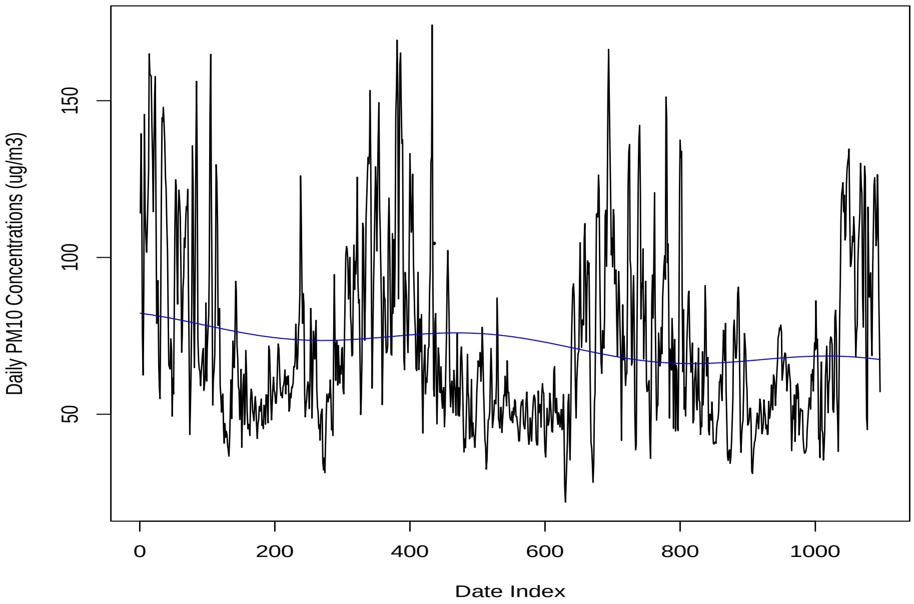


Figure 2: Time series plot of three years data

In this analysis, optimum number of cluster was identified by Bayesian Information Criterion (BIC) method, where within-cluster sum of squares is reduced for the given number of cluster. The result of the BIC suggested that 5 is the optimum number.

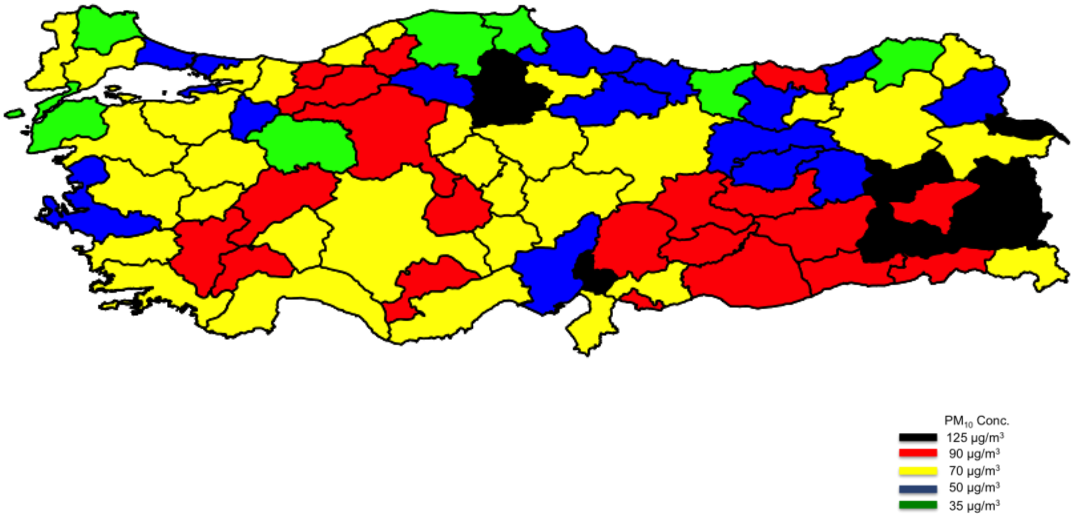
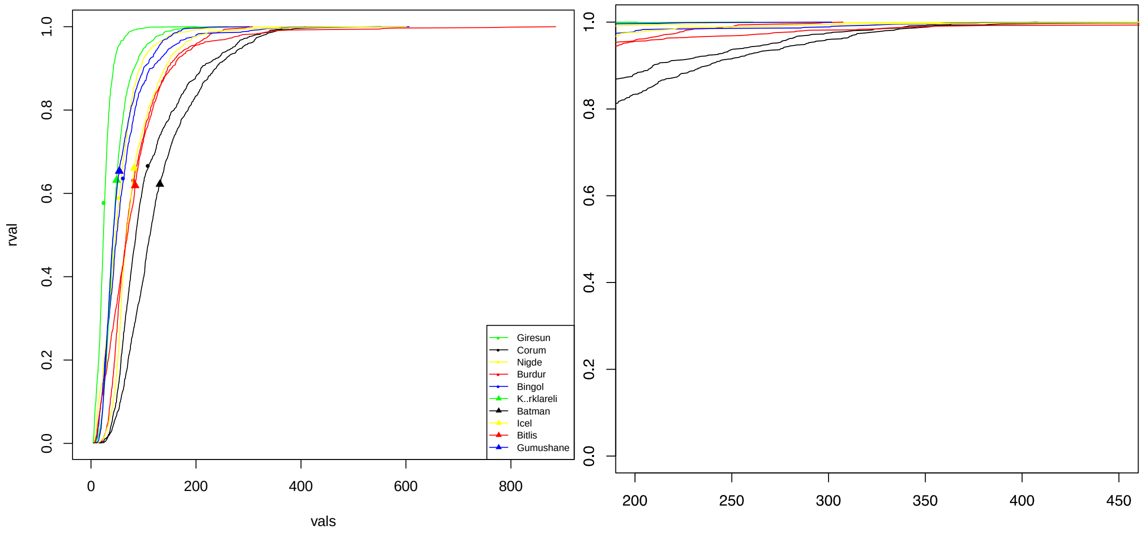


Figure 3: K-means clustering colored map of three years mean values in Turkey.

In the first step we have utilized mean values as the main parameter. Three years K- means clusters for the mean values is shown in Figure 3. The colors, black, red, blue, yellow and green respectively, represent the highest $PM_{10}$ values of the cluster to lowest $PM_{10}$ values. The highest centroid in 5 cluster is 126.24 $\mu g/m^3$, represented by the black color and the lowest centroid is 35.74 $\mu g/m^3$, represented by the green. There are only seven city; Çanakkale and Kırklareli in the

Marmara region, Kastamonu, Sinop, Giresun and Artvin in the Black Sea region and only Eskişehir in the Central Anatolia, below the EU $PM_{10}$ limit value (shown with the green color). As it is clear from Figure 3, there is not a homogen distribution of the cities to the clusters. East and South East Anatolia region have the highest and 2nd highest $PM_{10}$ levels and Çorum in the Black Sea region has 111.4 $\mu g/m^3$ and Osmaniye in the Mediterranean region has 127 $\mu g/m^3$ $PM_{10}$ concentrations. Central Anatolia, Aegean and a part of Mediteranean region of the country are yellow colored, around 70 $\mu g/m^3$ $PM_{10}$ concentration. The megacities Istanbul and Izmir in the blue colored clustered with 50.8 and 48.6 $\mu g/m^3$ $PM_{10}$ concentrations respectively. However, Ankara in 2nd highest $PM_{10}$ level with 94.01 $\mu g/m^3$ $PM_{10}$ concentrations.

In order to understand whether using mean as the parameter is effective in defining the clusters, we have plotted Cumulative Distribution Functions (CDFs) for some of the selected clusters (Presented in Figure 4a). The colors used in the Figure 4 are black, red, blue, yellow and green refers the highest $PM_{10}$ level to the lowest respectively. Each cluster have 2 cities, one is the city which have minimum $PM_{10}$ concentrations at the cluster and the other one is the maximum. Mean values of the cities are shown on the CDFs' with a circular shape for the city have minimum $PM_{10}$ concentration and a triangle for the maximum. Çorum and Batman in the highest $PM_{10}$ cluster with black color. Çorum is the minimum of the cluster with 111 $\mu g/m^3$ and Batman is the maximum of the cluster with 145 $\mu g/m^3$ $PM_{10}$ concentrations. Giresun and the Kırklareli in the lowest cluster, only cluster below the EU standats, with green color. Giresun is the minimum of the cluster with 29 $\mu g/m^3$ and Kırklareli is the maximum of the cluster with 43 $\mu g/m^3$ $PM_{10}$ concentrations. A zoom of the region towards the higher is also provided in Figure 4b. As seen in the Figure, although the clusters are distinct for the lower end (for example, green color is siginificantly lower as compared to red), towards the higher end the difference reduces signficantly. For example, the difference between the green and red colors is almost non-existent for the values over 200 $\mu g/m^3$. This might suggest that clustering method used is not effective to differentiate high $PM_{10}$ values. In order to overcome this problem we have conducted K-Means clustering using 4 parameters (mean, median, 2.5th percentile and 97.5th percentile). The results for this analysis is given in Figure 5.



a) b)

Figure 4: a) Cumulative distribution functions (CDFs) of the k-means clusters with only mean values. b) Zoom to the CDFs above 200 µg/m$^3$.

The East and Southeast Anatolia regions also have the highest and 2nd highest $PM_{10}$ level with more cities in the region. The results shown that only three cities, Sinop, Giresun and Artvin in the Black Sea region below the EU annual limit value. Central Anatolia in the 3rd highest $PM_{10}$ level as in the k-means result with only mean values. When we compare results in Figure 3 and Figure 5, there are similarities. Two of megacities Istanbul, Izmir are in the 4th highest $PM_{10}$ level cluster. Another megacity Bursa is also in the same cluster (3rd highest $PM_{10}$ level) result of the two analysis. Antalya, Mersin in the Mediteranean Region, Sivas, Kayseri and Tokat in the Central Anatolia Region, Artvin, Giresun and Samsun in the Black Sea Region are some of the other cities whose clusters did not change. Çanakkale, Kırklareli, Kastamonu and Eskişehir cluster changed from the lowest $PM_{10}$ levels to 4th highest $PM_{10}$ level. The results of K-means with mean values, Afyon and Isparta in the Aegean region, Karabük, Bolu and Düzce in the Black Sea region are in the 3rd $PM_{10}$ level. However, these cities are in the highest $PM_{10}$ level with 4 parameter K-means results. Hakkari in the Southeast Anatolian Region, Kars and Erzincan in the East Anatolian Region have significant changes where Hakkari is in the highest $PM_{10}$ level cluster with 4 parameter K-means results from the 3rd highest $PM_{10}$ level clusterfor mean analysis. Kars and Erzincan have changed from the 4th highest $PM_{10}$ level to 2nd highest $PM_{10}$ level.

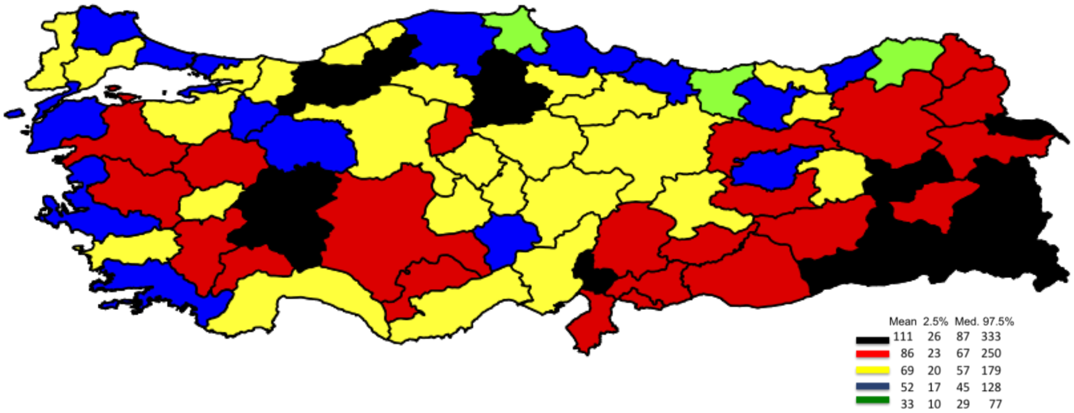


Figure 5: K-means clustering colored map of three years with 4 parameters; mean,median, 2.5% and 97.5%.

Cumulative Distribution Functions (CDFs) fort he 4-parameter case is shown in Figure 6a. Isparta and Van in the highest $PM_{10}$ cluster with black color. Isparta is the minimum of the cluster with 84 μg/m$^3$ mean and 339 μg/m$^3$ for 97.5th percentile and Van is the maximum of the cluster with 135 μg/m$^3$ and 294 μg/m$^3$ for 97.5th percentile. Giresun and the Sinop in the lowest cluster with green color. Giresun is the minimum of the cluster with 25 μg/m$^3$ mean and 64 μg/m$^3$ for 97.5th percentile and Sinop is the maximum of the cluster with 36 μg/m$^3$ mean and 82 μg/m$^3$ for 97.5th percentile $PM_{10}$ concentrations. Figure 6b show that the differences between clusters are also reduce at the towards the higher end. It should be noted that the difference is more distinctive in the 4 parameter K-means results for the values over 200 μg/m$^3$.

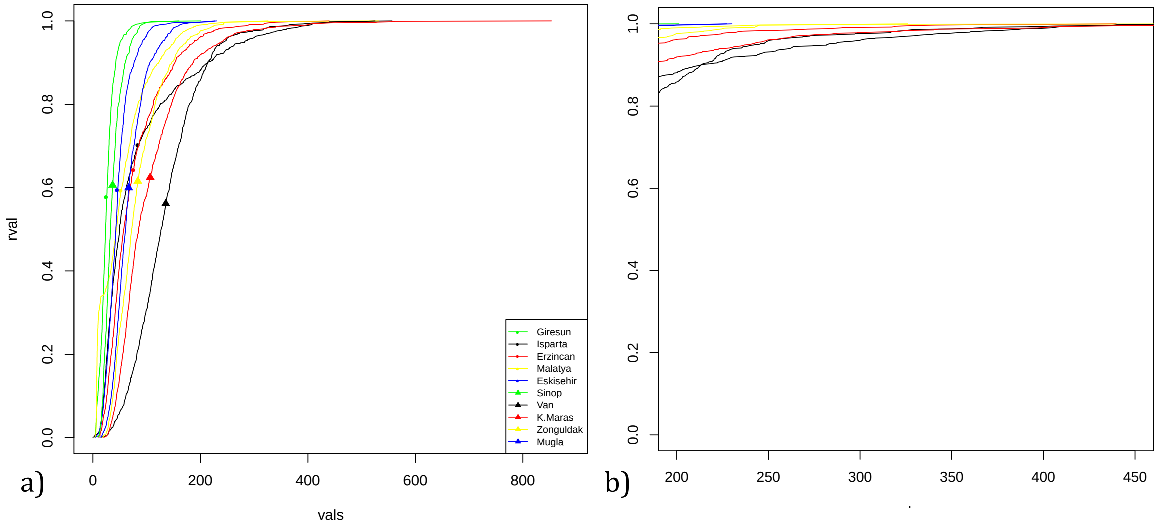


Figure 6: a) Cumulative distribution functions (CDFs) of the k-means clusters with four parameters (mean, median, 2.5%, 97.5%). b) Zoom to the CDFs above 200 μg/m$^3$.

## 3. CONCLUSION

In this study $PM_{10}$ level in Turkey was evaluated by spatio-temporal analysis. Determination of $PM_{10}$ level is important due to the harmful health effects of particulate pollution. $PM_{10}$ measurements of 118 monitoring stations of the Turkish Ministry of Environment and Urban Planning over three years (2008-2010) were used for this study. Temporal analysis revealed that daily average $PM_{10}$ values do not have a decreasing or increasing trend between 2008 and 2010. For spatial analysis, BIC method result suggested that the $PM_{10}$ data can be divided into five clusters. The K-means analysis began with three years mean values. The results shown that distribution of the cities are not homogeneous. The East and Southeast Anatolian Region have the highest $PM_{10}$ level and only 7 of the 81 cities are below the EU standards. CDFs of the selected cities in the clusters have plotted to examine the mean is the correct parameter to identify the clusters. The differences above the 200 $\mu g/m^3$ are reduce significantly. Four different parameters (mean, 2.5%, median, 97.5%) were used for K-means algorithm to overcome this reduction. Mostly, there are similarities between two datasets clustering results. However, the assessment of the CDFs shown that 4 parameter K-means is more effective than the K-means with only mean.

Although local emission source is important for the $PM_{10}$ level, topographic and meteorological conditions have significant effects. The western part of the country, more populated and industrilized region, (Marmara, Aegean and also Black Sea region) have lower $PM_{10}$ levels than the eastern part. Meteorological and topographic conditions, and poor economical standarts might be the main causes of the East and Southeast Anatolia Regions air pollution.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
**4th International Symposium and IUAPPA Regional Conference**
**10-13 September 2012 Istanbul -Turkey**

# FRACTIONAL ANALYSIS OF $PM_{10}$, $PM_{2.5}$ AND $PM_1$ CONCENTRATIONS AND THEIR CORRELATION AT A KOREAN EASTERN COASTAL CITY UNDER THE DUST TRANSPORTATION FROM THE NORTHERN CHINA IN MAY OF 2007

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## ABSTRACT

Using hourly concentrations of $PM_{10}$, $PM_{2.5}$ and $PM_1$ measured by a GRIMM aerosol sampler in Gangneung city in the eastern Korea, fractional analysis and correlation coefficients of $PM_{10}$, $PM_{2.5}$ and $PM_1$ were invested from May 6 to 10, 2007. Before dust transportation from Nei-Mongo in the northern China to the Korean eastern coast, correlation coefficients of $PM_{2.5}$ to $PM_{10}$, $PM_1$ to $PM_{2.5}$ and $PM_1$ to $PM_{10}$ were 0.91, 1.00 and 0.90. The fractions of $(PM_{10}-PM_{2.5})/PM_{2.5}$ and $(PM_{2.5}-PM_1)/PM_1$ showed 0.32 and 0.35, which implied generally fine particulate matter (< 2.5μm) rather than coarse particulate (10~2.5μm) matter to make a great contribution to the distribution of $PM_{10}$ concentration in the Korean coastal city. On the other hand, during the dust transportation from May 7~8, correlation coefficients of $PM_{2.5}$ to $PM_{10}$, $PM_1$ to $PM_{2.5}$ and $PM_1$ to $PM_{10}$ concentrations were 0.65, 0.93 and 0.35. The fractional ratios of $(PM_{10}-PM_{2.5})/PM_{2.5}$ and $(PM_{2.5}-PM_1)/PM_1$ were 3.88 and 0.88, which implied coarse particulate matter (10~2.5μm) rather than fine particulate matter (< 2.5μm) to make a great contribution to the formation of high PM concentrations at this city. Coarse particulates transported from the northern China could cause mainly the increase of $PM_{10}$ concentration at the coastal city. Correlation coefficients after the dust storm period, similarly to ones before the dust period, were 0.82, 1.00 and 0.81. For this study, MTSAT-IR satellite picture, HYSPLIT-backward trajectory model and TOMS aerosol index were used. This work was funded by the Korea Meteorological Administration Research and Development Program under Grant CATER 2006-2308-"Generation mechanism and prediction of windstorm in the mountainous coast" and continued in 2012.

**Keywords:** $PM_1$, $PM_{2.5}$, $PM_1$, coarse particulate matter, fine particulate matter cyclonic air flow, nocturnal surface inversion layer, thermal internal boundary layer

# CAMPAIGN OF PARTICULATE MATTER AND POLLEN MEASUREMENTS IN BERLIN

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## ABSTRACT

A six week pilot study campaign of parallel measurements of $PM_{10}$ and pollen has been carried out during the pollination season of grass pollen in May/June 2011 in the city of Berlin. The measurements run as 24h daily samplings at three monitoring sites, characterized as inner-city, suburban and traffic locations with different vegetation influences. First study results show the highest burden for urban public health at the traffic hot-spot, both for $PM_{10}$ and grass pollen. On several days grass pollen concentration in densely populated parts of the city reached health relevant levels able to induce allergy symptoms.

**Key Words:** Parallel Measurement Campaign, Particulate Matter, Pollen, Spatial Distribution, Health Relevance.

## 1. INTRODUCTION

Pollen allergy currently affects nearly a fifth of the German and European population. Recent studies indicated that pollinosis is found more frequently in urban areas than in rural environments. Exposure to pollen allergen loaded fine particles is related to allergic airway response in pollen-sensitized children and adults suffering on rhinitis and/or asthma bronchiale. Recent reports indicated links between global climate change and altered local pollen productions. From public health perspective a warmer climate will lead to an earlier and longer pollination season and more days with peak pollen counts. Furthermore it will increase the risk of proliferation of neophytes with well-known allergenic pollen grains, such as ragweed, which would increase the number of vulnerable people suffered by this burden (Bergmann and Jäger, 2010). Burkard pollen traps are used in network of 45 monitoring sites distributed all over Germany to sample and analyze qualitative and quantitative data on pollen flight. This pollen network is operated by the Foundation German Pollen Information Service (http://www.pollenstiftung.de ), which provides measurement data for pollen broadcast, clinical studies and other scientific projects.

Pollen are transferred into the atmosphere without change in its chemical composition. In rural areas the formation of primary bioaerosols (pollen) is prevalent, while the situation in urban agglomerations is less investigated so far. Pollen measurements are not part of continuous ambient air measurements provided by the responsible air quality monitoring networks in Germany. Some model calculations derived that a contribution of aeroallergens may comprise 5% to $PM_{10}$ mass in ambient air in periods when vegetation is partly active (Winiwater et al., 2009). Because information on pollen at the city level is missing, there is a need to improve the understanding on small scale distribution and variation of pollen and their contribution to fine particulate matter in a city, as well as to ameliorate assessments of exposure and health impacts of aeroallergens in an urban population.

Thus, a comparative pilot study was planned and conducted by the Federal Environment Agency (Umweltbundesamt/UBA) in co-operation with the Foundation German Pollen Information Service (Stiftung Deutscher Polleninformationsdienst/PID) to investigate the spatial distribution and burden of fine particulate matter ($PM_{10}$) and various pollen species (during the grass pollen season) in ambient air of Berlin.

## 2. METHODS

$PM_{10}$ and pollen measurements took place as 24h daily samplings carried out in parallel during a period of six weeks between 12 May and 23 June 2011 at three monitoring sites in the city of Berlin. They are characterized as inner-city park (*'Tiergarten'*), suburban (*'Adlershof'*) and traffic-related hot spot located nearby residences (*'Stadtautobahn'*). All three sites are influenced by different vegetation conditions (Figure 1).

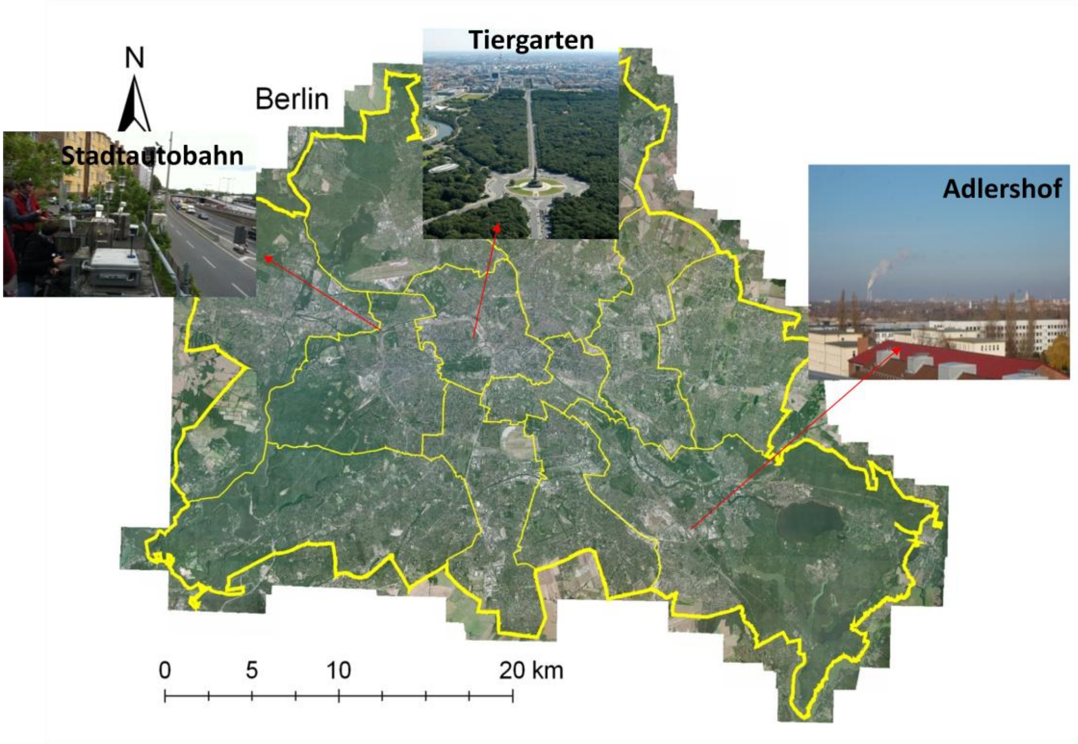

Figure 1. Sampling site locations in the city of Berlin

$PM_{10}$ was daily sampled by UBA with three low-volume samplers (Kleinfiltergerät LVS3.1 Derenda; flow rate of 2.3 $m^3/h$). Particles were collected on glass fiber filters (Pallflex, Tissuquartz 2500QAT-UP, 47 mm) and gravimetrically determined at UBA laboratory.

Pollen were sampled by PID with three Burkard pollen traps. The concentration was optically determined at Charité laboratory according the national guidelines for pollen analytic (Hecht and Winkler, 1994). The samples were analyzed by an experienced co-worker and stored for further analyses.

## 3. RESULTS

Table 1 shows $PM_{10}$ concentrations measured during the six week period at the respective three monitoring sites in the city of Berlin, with highest concentration at station *'Stadtautobahn'* (appr. 155.000 vehicles per day passing this section of inner city motor highway ‘BAB 100’), medium at the inner-city park site *‘Tiergarten’* (around 34.000 vehicles per day), and lowest in the suburban area *‘Adlershof’* (around 4.500 vehicles per day).

Table 1. $PM_{10}$ concentrations [µg/m³] measured in May/June 2011 in Berlin

| Stations (type) | Mean | Std.dev. | Max. |
|---|---|---|---|
| *Adlershof* (suburban) | 15.2 | 5.2 | 29.5 |
| *Tiergarten* (city, park) | 18.9 | 6.6 | 34.4 |
| *Stadtautobahn* (traffic) | 22.6 | 7.5 | 35.5 |

Comparing UBA $PM_{10}$ measurement results with the mean values of the regional air quality network ‘BLUME’ of the city administration of Berlin for the same measurement period, the concentrations show very good accordance to following three sites: ‘Friedrichshagen’ (suburban): 15.0 µg/m³; ‘Innenstadt-Mitte’ (city-centre): 20.0 µg/m³; ‘Schildhornstraße’ (traffic): 21.0 µg/m³.

As expected, May/June 2011 appeared as peak season for emissions of grass pollen in the North-Eastern region of Germany, to which Berlin belongs. Table 2 shows the results of daily grass pollen counts measured in parallel during the six week period at the same three monitoring sites in the city of Berlin, with -again and surprisingly- highest concentration at station *‘Stadtautobahn’*, medium in the suburban area *‘Adlershof’*, and unexpected lowest in the inner-city central park *‘Tiergarten’*.

Table 2. Concentrations of grass pollen and total pollen counts [pollen counts/m³ air per 24h] measured in May/June 2011 (43 daily samplings per station) in Berlin

| Stations (type) | Mean | Std.dev. | Max. |
|---|---|---|---|
| *Tiergarten* (city, park) - grass | 7.9 | 7.9 | 33 |
| - total pollen | 62.1 | 34.3 | 136 |
| *Adlershof* (suburban) - grass | 11.8 | 15.6 | 65 |
| - total pollen | 55.8 | 41.6 | 185 |
| *Stadtautobahn* (traffic) - grass | 17.2 | 18.2 | 83 |
| - total pollen | 72.3 | 36.9 | 163 |

During the 43 comparative measurement days the meteorology was dominated predominantly by a stable high pressure condition with sunshine durations above the long-term average (1961-1990). The temperature increased significantly in Berlin (e.g. at the meteorological station Berlin-Dahlem: mean temperature from 10.8 to 27.1 °C; maximum temperature from 14.9 to 33.3 °C). Parametric (Pearson) correlations coefficient was calculated for the six week sampling campaign to assess the relationship between the temperature measured at Berlin-Dahlem and the three monitoring sites, for both $PM_{10}$ and grass pollen. No correlations have been found for the mean temperature. But the correlations are highly significant between daily maximum temperature and daily grass pollen concentration, and partly significant between maximum temperature and $PM_{10}$ (Table 3).

Table 3. Pearson correlations coefficient for the relationship between maximum temperature with $PM_{10}$ and grass pollen; (** $p < 0.01$)

| r | $PM_{10}$ | grass pollen |
|---|---|---|
| *B-Dahlem* - *Tiergarten* | 0.41* | 0.57** |
| *B-Dahlem* - *Stadtautobahn* | 0.41** | 0.47** |
| *B-Dahlem* - *Adlershof* | 0.31 | 0.33** |

Further parametric (Pearson) correlation coefficients have been calculated to assess the relationship of concentration distribution within this measurement period between the three monitoring sites, for both $PM_{10}$ and grass pollen. Table 4 shows highly significant correlations (** $p < 0.01$) between the measurements at the three monitoring sites were found for both parameters.

Table 4. Pearson correlations coefficient for $PM_{10}$ and grass pollen; (** $p < 0.01$)

| r | $PM_{10}$ | grass pollen |
|---|---|---|
| *Adlershof – Tiergarten* | 0.87** | 0.84** |
| *Tiergarten – Stadtautobahn* | 0.81** | 0.82** |
| *Adlershof – Stadtautobahn* | 0.77** | 0.81** |

## 4. DISCUSSION AND CONCLUSION

The presented pilot study has been planned as a comparison campaign of parallel measurements of particulate matter and pollen at three sampling site locations to get an idea of pollen concentration variations and their spatial distribution in an urban agglomeration. Therefore, measurements have been carried out during a six week campaign (from 12 May to 23 June 2011) in the city of Berlin. The results show that high grass pollen concentration levels are measured in the city centre, particularly with peak concentrations close to residences (site *'Stadtautobahn'*), which could have health impacts to the urban population. Such concentrations exceeded in some cases the clinically relevant threshold value (30 grass pollen grains/$m^3$) (Behrendt et al., 2007) to induce allergy symptoms of hay fever and/or pollen asthma. Because no grass grows in the vicinity of this site, it can be concluded that such burden of peak grass pollen counts can be explained by re-suspension of sedimented pollen from frequent passing highway traffic, and by long-range ambient air transport. The study may explain also earlier data on a higher prevalence of pollen allergies in children living in cities near to streets with high traffic in comparison with the same population living in the same city but near to streets with lower traffic (Morgenstern et al., 2008). A study analysis of a continental-scale pollen data set reveals an increasing trend in the annual amount of airborne pollen for many taxa in Europe, which is more pronounced in urban than semi-rural/rural areas (Ziello et al., 2012). Climate change may contribute to such findings, however increased temperatures do not appear to be the only influencing factor. Anthropogenic rise of atmospheric $CO_2$ levels are discussed to be influential. Regarding human exposure to allergenic pollen a comparison study conducted in France concluded that the burden is higher in rural than in urban areas; the most abundant pollen in each area did not originated from the same taxa (Bosch-Cano et al., 2011). Considering this particularly for urban areas, until now, there have been no recommendations (e.g. in Germany) to new planting of trees and shrubs in public spaces that takes the needs of people suffering from pollen allergy into account. In order to prevent a further increase of allergenic tree pollen in cities, recently Bergmann et al. (2012) proposed a list of tree species that municipalities should avoid planting, and a second one of allergologically safe trees that are suitable for cultivation.

Further laboratory analyses of the pilot study samples will be performed to quantify and assess the primary biological aerosol particles contribution, particularly pollen, to $PM_{10}$ concentration in order to provide detailed urban-relevant information and to improve the understanding on small scale distribution and variation of pollen and their contribution to fine particles in a city, as well as to ameliorate assessments of health impacts of aeroallergens for urban public health. Such results could supplement those of e.g. Winiwater et al. (2009) and Wagener et al. (2012), indicating a contribution of primary biological aerosol particles, including pollen, to $PM_{10}$ concentrations. They found a maximum during the summer half-year or increased concentrations in late summer and autumn, respectively, when $PM_{10}$ levels are generally lower compared to the winter months.

Finally, within forthcoming decades climate change will lead to an increasing temperature which prolongs pollen season and more days with high pollen counts. In addition, a warmer climate increases the risk of proliferation of new plants with well-known allergenic pollens like ragweed and parietaria judaica which have not caused allergy in Northern-Europe so far. Long distance transport of pollen like ragweed or birch is another phenomenon, which seems to be in relation to climate changes. The pattern of change will vary regionally depending on different factors such as altitude, latitude, as well as weather factors such as precipitation and storms, but also urbanization (Bergmann and Jäger, 2010).

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# SIZE DEPENDENT SOLUBILITIES OF ELEMENTS IN EASTERN MEDITERRANEAN AEROSOL

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## ABSTRACT

Large amounts of atmospheric aerosol wet or dry-deposit to world oceans every year. Fates of these particles in water depend on their physicochemical characteristics, particularly their solubility. Elements that enter to sea water in soluble form can be taken up by the living organism. However, elements that enter to sea in particulate form are likely to end up in sediments, which can be a permanent sink for them. Solubility of Fe attracted particular attention in last years, because soluble Fe is a nutrient in most oceans and addition of soluble Fe to sea, which is known as “iron fertilization” can significantly increase primary productivity, which in turn can have far-reaching consequences, such as sequestration of $CO_2$ from atmosphere. Because of all these reasons it is important to know solubility of trace elements associated with atmospheric aerosol. In this study, solubility tests were performed on impactor samples collected many years at a rural station, which is located approximately 20 km to the west of at Antalya city. Impactor samples were collected and analyzed in 1993 and size distributions of elements and their dry deposition fluxes were discussed in an earlier publication[1]. One-quarter of impactor substrates from nine impactor sets are dissolved to find the percent solubility of Al, Fe, Pb, Zn, Cd, Na, Mg, Mn, Ni, Cr, K, Ca and V. Solubility of these elements was investigated by a number of researchers in the past. They all demonstrated that anthropogenic contribution is an important parameter affecting solubility. Advantage of impactor stages is that in there is nicely separated crustal, marine and anthropogenic particles in each impactor set. A clear relation was established between solubility of elements and their enrichment factors. Most of the elements have low solubility in coarse fraction, but their solubility decrease with their aerodynamic diameter. However, solubility behaviors of non-crustal elements were not the same. For example, Cd has high solubility in all stages. Solubility in sub-micron fraction is only slightly higher than its percent solubility in other stages. Solubility of Pb, on the other hand, was less than 10% in first three impactor stages, but increase to 80% in stage four and five. This is important for dry deposition fluxes, because, contribution of coarse particles on deposition is higher than contribution of fine fraction particles. Results also demonstrated that solubility of Al and Fe, which are crustal markers, are less than 10% in stages 1-5, but solubility of Fe in stage 6 were as high as 40% in some of the impactor sets, suggesting the existence of anthropogenic, fine fraction Fe in the aerosol population.

**Keywords:** Eastern Mediterranean, aerosol, trace elements, impactor, solubility

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AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES
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# MASS CONCENTRATIONS OF MAYOR ACIDIC SPECIES IN $PM_{10}$ PARTICLE FRACTION MEASURED AT TWO DIFFERENT SAMPLING SITES IN ZAGREB, CROATIA

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## ABSTRACT

This investigation focuses on the influence of the sampling site and the season of the year on mass concentrations and relative contribution of measured acidic species chlorides, nitrates, and sulphates to $PM_{10}$ mass. Daily $PM_{10}$ samples were taken continuously throughout 2011 at two sampling sites. Annual average $PM_{10}$ mass concentrations were: 34.2 $\mu g\ m^{-3}$ at site A and 36.0 $\mu g\ m^{-3}$ at site B. The annual average mass concentrations of the investigated anions followed the order chloride < nitrate < sulphate at the both sites, respectively. Mass concentrations of the investigated pollutants were significantly influenced by the season, reaching their high values in the winter. We also observed significant correlations between mass concentrations of $PM_{10}$ and investigated anions.

**Key Words:** Chlorides, Nitrates, Sulphates, Seasonal Influence

## 1. INTRODUCTION

Airborne particulate matter is a complex mixture of solid particles and liquid droplets suspended in the air. They vary in size, chemical composition and origin. Airborne particles with an aerodynamic diameter of less than 10 μm ($PM_{10}$) have been found widely associated with health problems. They can also influence many atmospheric processes including visibility variations and cloud formation, and play a major rule in acidification of rainfalls and affect climate (Bourotte et al. 2007, Wang and Shooter 2001).

The analyses of the aqueous extract of the aerosols shows that the chemicals originating from motor vehicle exhausts, soil dust re-suspension and industry emission, mainly occur in an easily water-soluble form (Fernandez Espinosa et al. 2002, Kyotani and Iwatsuki 2002) where sulphate ($SO_4^{2-}$), nitrate ($NO_3^-$), ammonium ($NH_4^+$) and water-soluble organic carbon are the dominant chemical species of water-soluble matter in aerosol particles (Kumagai et al. 2009, Khoder and Hassan 2008, Bourotte et al. 2007, Wang and Shooter 2001, Fosco and Schmeling 2006, Wang et al. 2006, Xiao and Liu 2004).

This investigation focuses on the influence of the sampling site and the season of the year on mass concentrations and relative contribution of measured acidic species chlorides, nitrates, and sulphates to $PM_{10}$ mass in Zagreb air measured at two different sampling sites.

## 2. MATERIALS AND METHODS

Daily $PM_{10}$ samples were collected continuously throughout 2011 in the northern residential part of Zagreb, with moderate to high traffic density (site A) and in the southern part of the city centre near a busy crossroads with high traffic density, offices, parking lots and garage (site B).

Samples of $PM_{10}$ were collected on quartz filters from approximately 50 $m^3$ of ambient air on site A using referent Sven Leckel (LVS3) low volume sampler and from 720 $m^3$ of ambient air on site B using Automatic HVS, DA 80 HTD Digitel sampler. Mass concentrations of $PM_{10}$ fraction were determined by gravimetry.

The samples were analysed for mass and content of water soluble ions, chlorides, nitrates, and sulphates using ion chromatography. Dionex DX-120 ion chromatograph equiped with suppressed conductivity detection, Dionex AS14: 4mm analytical column + AG14: 4mm guard column was used.

## 3. RESULTS AND DISCUSSION

Table 1 summarises the statistical parameters: number of samples (N), mean values, medians, and maximum values of mass concentrations of measured pollutants over the entire measuring period at sampling sites A and B.

Table 1. Mass concentration of pollutants (μg/$m^3$)

| Sampling site | Statistical parameters | $PM_{10}$ | $Cl^-$ | $NO_3^-$ | $SO_4^{2-}$ |
|---|---|---|---|---|---|
| A | N | 364 | 364 | 363 | 363 |
| | Mean | 34.2 | 0.16 | 2.73 | 4.99 |
| | Median | 25.9 | 0.08 | 1.30 | 2.79 |
| | Maximum | 182.7 | 2.12 | 22.54 | 43.8 |
| B | N | 363 | 350 | 348 | 350 |
| | Mean | 36.0 | 0.10 | 2.52 | 3.71 |
| | Median | 26.5 | 0.03 | 1.13 | 2.46 |
| | Maximum | 182.0 | 1.41 | 16.11 | 24.94 |

Figure 1 shows monthly average $PM_{10}$ mass concentrations measured at sampling sites A and B. The same parameters for chloride mass concentrations are shown in Figure 2, for nitrate in Figure 3, and for sulphates in Figure 4.

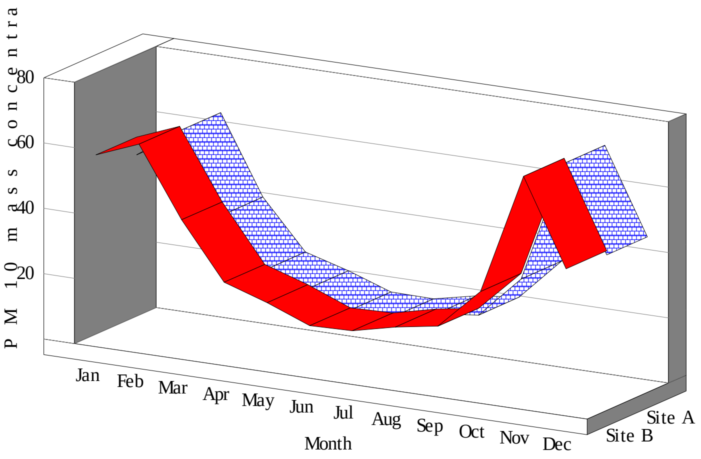

Figure 1. Monthly average $PM_{10}$ mass concentration measured at sites A and B

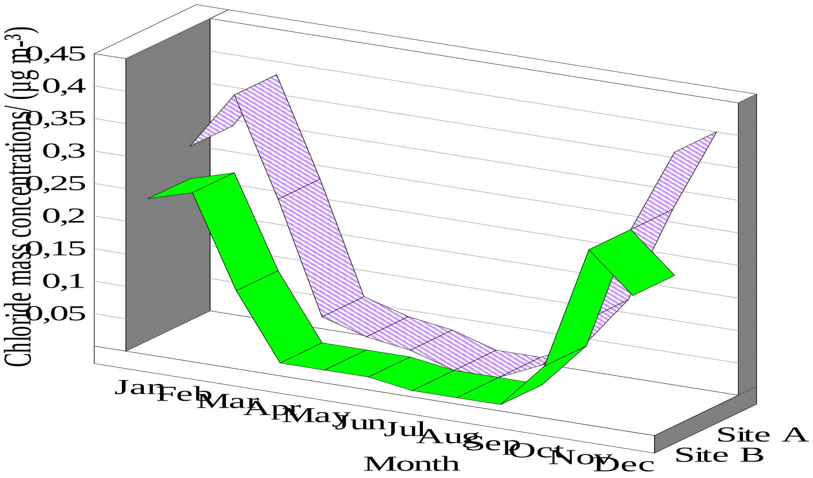

Figure 2. Monthly average chloride mass concentrations measured at sites A and B

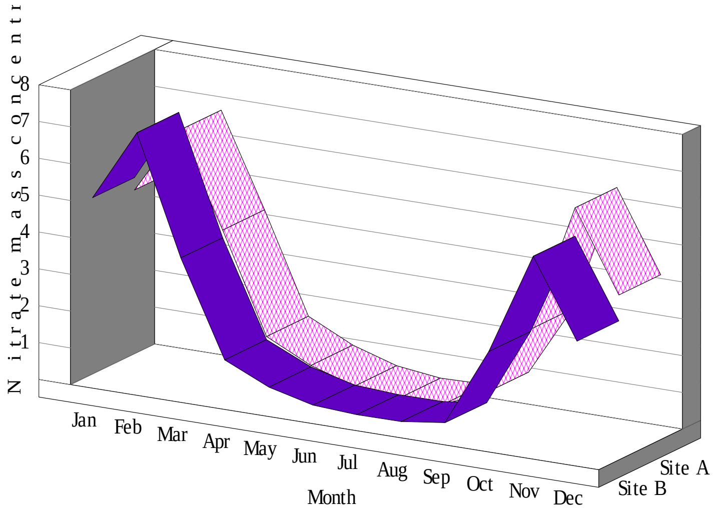

Figure 3. Monthly average nitrate mass concentration in $PM_{10}$ measured at sites A and B

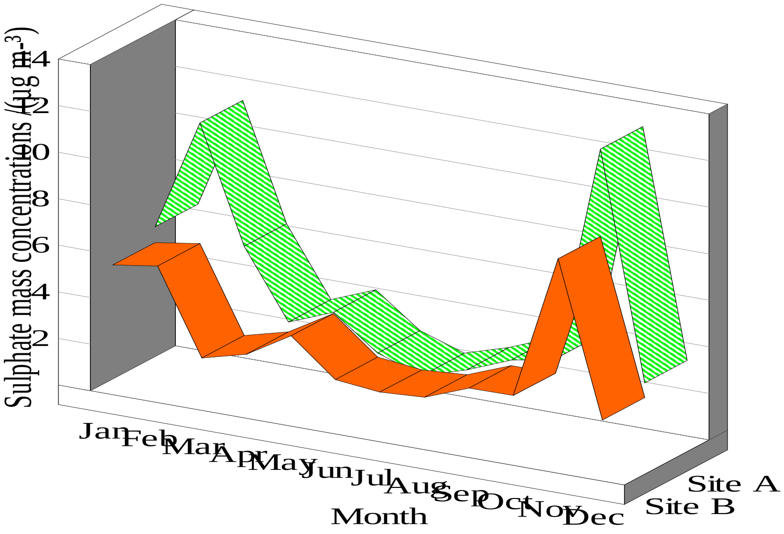

Figure 4. Monthly average sulphate mass concentrations in $PM_{10}$ measured at sites A and B

Table 2 shows the correlation coefficients between pollutant mass concentrations in $PM_{10}$ particle fraction for entire year measured at site A. The same parameters for site B are presented in Table 3.

Table 2. Correlation coefficients between pollutant mass concentrations in $PM_{10}$ particle fraction at site A

| Correlated components | $Cl^-$ | $NO_3^-$ | $SO_4^{2-}$ |
|---|---|---|---|
| $PM_{10}$ | 0.579** | 0.809** | 0.734** |
| $Cl^-$ | | 0.577** | 0.118 |
| $NO_3^-$ | | | 0.378** |

** $P < 0.01$

Table 3. Correlation coefficients between pollutant mass concentrations in $PM_{10}$ particle fraction at site B

| Correlated components | $Cl^-$ | $NO_3^-$ | $SO_4^{2-}$ |
|---|---|---|---|
| $PM_{10}$ | 0.811** | 0.844** | 0.599** |
| $Cl^-$ | | 0.691** | 0.306** |
| $NO_3^-$ | | | 0.459** |

** $P < 0.01$

Figure 5 shows monthly average anion mass contributions (%) to overall $PM_{10}$ mass measured at site A. The same parameters for site B are shown in Figures 6. Figure 7 shows annual average anion mass contribution (%) to overall $PM_{10}$ mass measured at sites A and B.

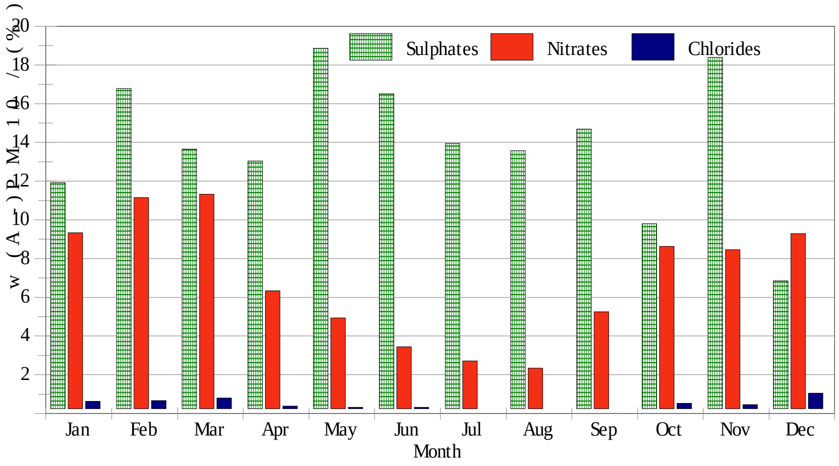

Figure 5. Monthly average anion mass contributions (%) to overall $PM_{10}$ mass measured at site A

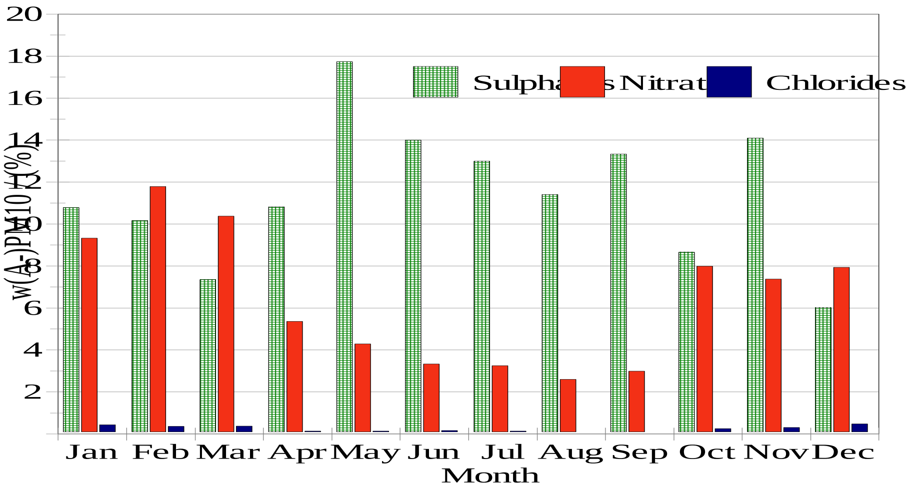

Figure 6. Monthly average anion mass contributions (%) to overall $PM_{10}$ mass measured at site B

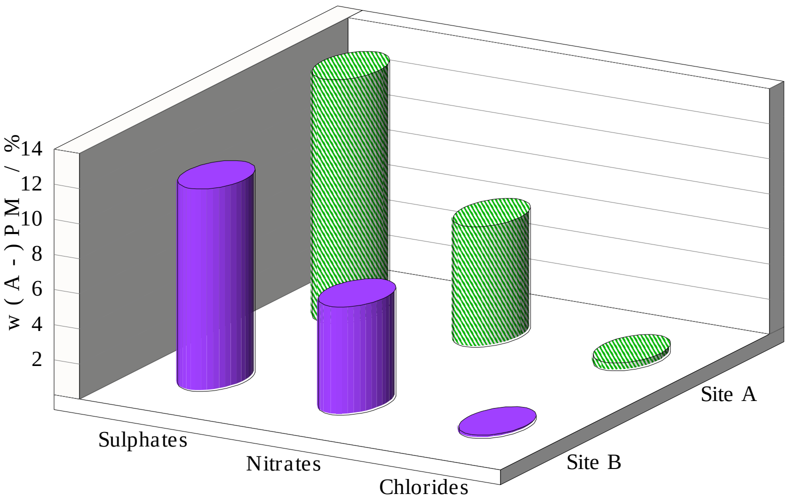

Figure 7. Annual average anion mass contribution (%) to overall $PM_{10}$ mass measured at sites A and B

The results of measurements of $PM_{10}$ particle fraction and acidic components (chlorides, nitrates, and sulphates) in $PM_{10}$ particle fraction at two sampling sites in Zagreb air show that the annual average $PM_{10}$ mass concentrations were higher at site B (36.0 μg $m^{-3}$ ) compared to the site A (34.2 μg $m^{-3}$ ), and the difference was not significant ($P>0.05$).

The annual average mass concentrations of the investigated anions followed the order chloride < nitrate < sulphate at both sampling sites reaching higher values at site A. The significant differences between anion mass concentrations measured at sites A and B were obtained for chlorides and sulphates ($P<0.05$), while for nitrate difference was not significant.

Mass concentrations of the investigated pollutants at both sites were significantly influenced by the season, reaching their high values in cooler period. Higher mass concentrations of all pollutants measured in cooler period may be due to great emissions of pollutants and their precursors from anthropogenic sources, combustion of fossil fuels, motor vehicle exhaust and meteorological conditions.

Anion mass contributions to the overall $PM_{10}$ mass were significantly influenced by the season, reaching the lower values for chloride and for nitrate at both sites in the warm period, while sulphate contributed less in the cooler period.

Marked seasonal variations of chloride and nitrate contribution to the overall $PM_{10}$ mass measured at both sampling sites could be attributed to the variation in the volatility of ammonium and sodium salts leading to lower summertime values. The high sulphate content in the warm period may be due to strong solar radiation, and photochemical gas-phase oxidation of gas precursor pollutants. During the winter aqueous-phase oxidation of gas precursor pollutant to secondary aerosols is common (Khoder 2002).

The annual average anion mass contributions to the overall $PM_{10}$ mass followed the order chloride < nitrate < sulphate, and accounted for about 0.44%, 6.84% and 13.87% of total $PM_{10}$ mass at the site A, respectively. At site B the annual average anion mass contribution to the overall $PM_{10}$ mass also followed the order chloride < nitrate < sulphate, and accounted for about 0.20%, 6.15% and 11.52% of total $PM_{10}$ mass, respectively.

Significant correlations were obtained between $PM_{10}$ and investigated anions at both sampling sites indicating that pollutants may have originated from the same sources or that the intensity of the pollutant source is relatively constant. No significant correlation was found between chlorides and sulphates at site A.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# INVESTIGATION OF TEMPORAL AND SPATIAL VARIATIONS IN ATMOSPHERIC CONCENTRATIONS OF PCDDs and PCDFs IN ISTANBUL

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## ABSTRACT

In this study, temporal and spatial variations of the atmospheric concentrations of polychlorinated-p-dibenzo dioxin (PCDDs) and polychlorinated dibenzofuran (PCDFs) congeners were investigated in Istanbul at three different locations. The highest average concentration (3481 fg/m$^3$) was observed at the sampling location which is characterized by mixed source groups during colder months. The lowest average concentration (749 fg/m$^3$) was observed at sampling station which is characterized by semi-urban characteristics. ∑PCDD/F concentration showed seasonal variation in this study. The highest concentration was determined to be 4373 fg/m$^3$ in winter while the lowest concentration was determined to be 498 fg/m$^3$ in summer.

**Key words:** Polichlorinated dibenzodioxins, polychlorinated dibenzofurans, persistent organic pollutants, toxic air pollutants, air quality.

## 1. INTRODUCTION

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are ubiquitous persistent organic pollutants (POPs) (Jones and de Voogt, 1999; UNEP, 2009). They are produced as unwanted byproducts from the natural and antropogenic processes (UNEP, 2002) such as solid waste incinerators (Olie et al., 1977), metallurgic processes (Buekens et al., 2001; Anderson and Fisher, 2002; Quaß et al., 2004), iron and steel factories (Anderson and Fisher, 2002; Wang et al., 2003; Aries et al., 2006), automobile emissions (Marklund et al., 1987), steel mills (Tsyklind et al., 1989) and chemical production processes (Hutzinger et al., 1985). They can be transported over long distances in the atmosphere and stored by wet/dry deposition mechanisms in all environmental systems such as surface water sources, soil, sediment, biota urban/rural areas, remote areas and polar regions (Hutzinger, 1985; Jones and de Voogt, 1999; Lohmann and Jones, 1998; Lohmann et al., 1999; Baker and Hites, 1999; Sclabach et al., 1996; Lee and Jones, 1999; Jimenez et al., 2000; Cohen et al., 2002; Corsolini et al., 2002; Hilscherova et al., 2003; Minh et al., 2003). They can bioaccumulate in the food chains (van der Oost et al., 2003) and cause serious health effects in humans and wildlife (WHO, 1997) due to their resistant structre against photolitic, chemical and biological degradation processes. Therefore, ambient air monitoring studies were carried out by several researchers to determine their atmospheric concentrations and worldwide environmental behaviour. According to these studies, atmospheric concentrations of PCDD/F compounds fluctuate largely for urban areas (Aristizábal et al., 2011; Li et al. 2008; Menichini et al., 2007; Lee et al., 2007). Several factors such as meteorology, topography, climate, source characteristics, degradation processes affect PCDD/F concentrations in the atmosphere (Alcock ve Jones, 1996; Abad vd., 1997; Wevers vd., 1993). In addition, in this study, very fluctuating concentrations of PCDDs and PCDFs were observed for different locations of Istanbul.

## 2. MATERIAL AND METHOD

### 2.1 Sampling Site and Stations

Three sampling locations were chosen to determine atmospheric PCDD/F concentrations (Figure 1). Davutpaşa sampling station is characterized by mixed source groups such as industrial, residential and traffic. Yildiz sampling station is located almost in city center which receives high traffic emissions. Fenertepe sampling station is located out of the city center and surrounded by forest areas and rural settlements. Although there is no industrial activities in this area, the medical and hazardous waste inicneration plants are located about 8 km northeast and about 12 km southeast from the sampling station, respectively.

Figure 1. Sampling domain and stations.

Ambient air samples were collected monthly between May 2011 and January 2012 by using high volume samplers (TCR TECORA- Echo, ITALY). Ambient air volumes in the range of 645 to 1900 $m^3$ were collected from the each sampling station. Meteorological parameters (temperature, wind velocity/direction, relative humudity etc.) were measured by wireless weather stations (Davis Vantage Pro 2) at each sampling station.

### 2.2 Analytical procedure

Sampling and analyses were conducted in accordance with the reference method of EPA TO-9A. Before sampling, filters were conditioned at 450°C for 5h and PUFs were precleaned with asetone in soxhlet extractor for 16 h. Extraction, clean up and fractionation were applied after sampling to all filter and PUF samples. Sampling standard solutions (3 ng $^{37}$Cl-2,3,7,8 $T_4$CDD) and extraction standard solutions (0.2 ng $^{13}C_{12}$–labeled internal standart) were used to determine the recovery eficiency of sampling and extraction processes. Recovery values were determined in the ranges of 61% to 91% and 60% to 118% for $^{13}C_{12}$ and $^{37}$Cl-2,3,7,8 $T_4$CDD respectively. These values meet the sample recoveries of the EPA Method TO 9A.

## 3. RESULTS AND DISCUSSION

### 3.1 Spatial variations of PCDD/F concentrations

Average concentration of $\sum_{17}$PCDD/F ranged from 749 to 3481 fg/$m^3$ with an average value of 1746 fg/$m^3$. Toxicity equivalency of $\sum_{17}$PCDD/F range from 32 fg I-TEQ/$m^3$ to 165 fg I-TEQ/$m^3$ with an average value of 82 fg I-TEQ/$m^3$. Similar results have been reported in previous studies by Lohmann et al., (2000) and Li et al., (2010). Mean concentrations for each sampling station were shown in Figure 2. The highest concentrations were found at

Davutpasa sampling station. Concentrations ranged from 190 to 15297 fg/m$^3$ (mean 3481 fg/m$^3$) and 1.7 to 460 fg I-TEQ/m$^3$ (mean 165 fg I-TEQ/m$^3$) in this station. This region is affected by mixed source groups being industrial, residential and traffic sources. The intercity bus terminal (approximately at 1.5 km NE), the foundry industry area (approximately at 9 km NW), other industrial activities (metal, metal coating, automotive, glass, iron-steel products, textile, casting etc.) and the use of fossil fuels for domestic heating purposes are considered as the cause of high level of PCDD/Fs. The lowest concentrations were measured at Fenertepe (semi rural station) sampling station which is located at out of the city center and the values of concentrations ranged from 98 to 2093 fg/m$^3$ (mean 749 fg/m$^3$) and from 7 to 121 fg I-TEQ/m$^3$ (mean 32 fg I-TEQ/m$^3$). The values of the PCDD/F concentrations and I-TEQs for Yıldız sampling station ranged from 89 to 3075 fg/m$^3$ (mean 1007 fg/m$^3$) and from 0 to 186 fg I-TEQ/m$^3$ (mean 48 I-TEQ fg/m$^3$) respectively. This station is surrounded by the main traffic arteries therefore traffic emissions are considered as principal source of the PCDD/F compounds in this area.

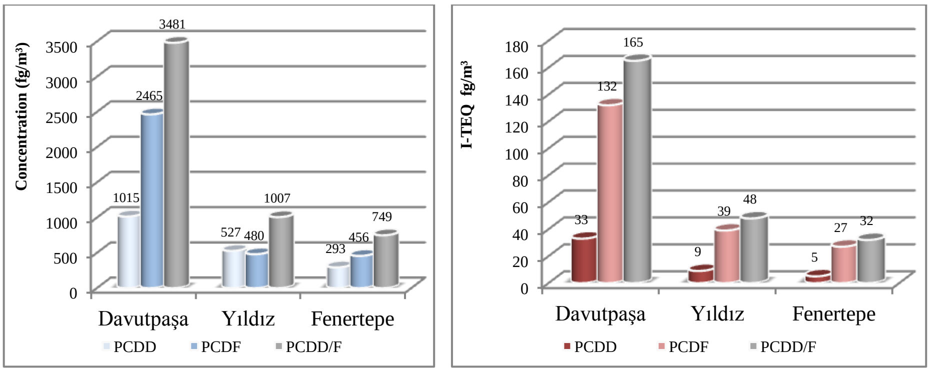
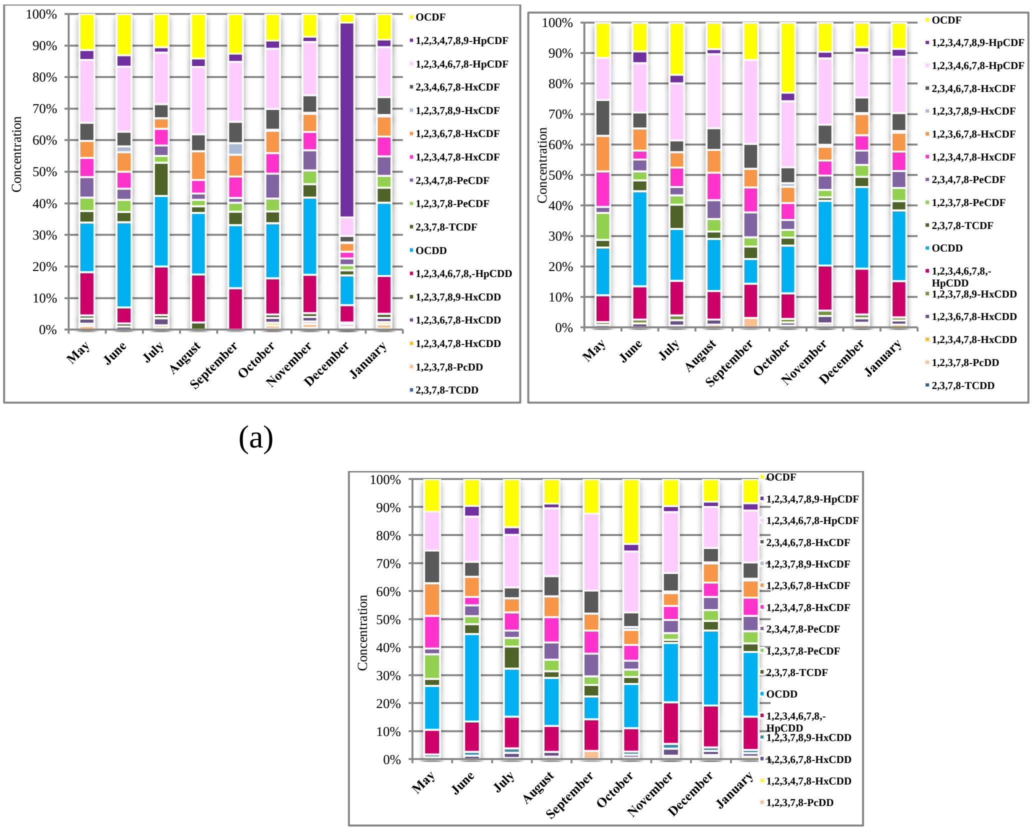


Figure 2. Average PCDD/F level of ambient air samples at different sampling stations.

### 3.2 Congener profiles

Congener profiles for each sampling station were shown in Figure 3. In this study, OCDD, 1,2,3,4,6,7,8 HpCDD/F and OCDF were found as the most abundant congeners at all sampling stations. This result is in accordance with previous studies which have been reported by Abad et al. (2007), Assuncao et al. (2005) and Aristizábal et al. (2011). The combustion sources such as solid waste incinerators, motor vehicles, combustion of fossil fuels for domestic and industrial purposes are reported to be principal sources of these congeners (Cleverly et al., 1997). Interestingly, the concentration of 1,2,3,4,7,8,9-HpCDF was found higher during December sampling period than other sampling periods at all sampling stations. Especially, the highest concentration level was observed at Davutpasa sampling station as 9471 fg/m$^3$. Secondary aluminum smelters, solid waste incinerators and industrial/utility coal combustors have been reported as the most important emission sources of this congener by Cleverly et al. (1997). Due to increased 1,2,3,4,7,8,9-HpCDF concentrations especially in winter months, (increase in coal consumption for domestic heating), domestic heating is considered as the main source for the 1,2,3,4,7,8,9-HpCDF congener in this study. 1,2,3,4,7,8,9-HpCDF (31%), OCDD (15%), 1,2,3,4,6,7,8-HpCDF (11%), 1,2,3,4,6,7,8-HpCDD (9%), and OCDF (6%) were found as the main contributors for ∑PCDD/F concentrations at Davutpasa sampling station. OCDD (34%), 1,2,3,4,6,7,8-HpCDD (15%), 1,2,3,4,6,7,8-HpCDD (13%), OCDF (7%) were found as the principal congeners for Yildiz sampling station. The congener profile at Fenertepe was similar to congener patterns at Davutpasa sampling station that OCDD (22%), 1,2,3,4,6,7,8-HpCDF (18%), 1,2,3,4,6,7,8-HpCDD (13%) and OCDF (11%) were the principal congeners (Figure 3). Although the abundant congeners are similar to all sampling stations, concentrations of PCDD congeners at

Yildiz sampling station are higher than other sampling stations. 2,3,4,7,8-PeCDF (42%), 1,2,3,6,7,8,-HxCDF (9%), 1,2,3,4,7,8-HxCDF (9%), 2,3,4,6,7,8-HxCDF (8%) were determined as the main contributors of the I-TEQ concentration according to the average of all samples. Contribution of 2,3,4,7,8-PeCDF to the total PCDD/F was calculated as 43%, 40% and 38% for Davutpasa, Yildiz and Fenertepe sampling stations, respectively. 2,3,4,7,8-PeCDF was found to be the most important congener at all sampling stations which accounted for 43%, 40% and 38% of ∑PCDD/F for Davutpasa, Yildiz and Fenertepe sampling stations, respectively. We found that the congener profiles of all samples did not change considerably over time in general.



(a) (b)

(c)

Figure 3. The congener profiles for the sampling locations a) Davutpasa sampling station b) Yildiz sampling station c) Fenertepe sampling station.

### 3.3 PCDD/PCDF Ratio

The relative contribution of PCDD and PCDF conegeners to ∑PCDD/F concentration are determined by PCDD to PCDF ratio. This ratio gives information about the sources and degradation processes of these compounds (Lohmann and Jones, 1998). The mean ratios were calculated as 0.5 (0.2-0.7), 1.0 (0.6-1.7), 0.5 (0.3-0.9) for Davutpasa, Yildiz and Fenertepe sampling stations, respectively. Similarly, I-TEQ values were calculated as 0.25, 0.22, 0.17 for Davutpasa, Yildiz and Fenertepe sampling stations, respectively. According to these results, concentrations of PCDF congeners were higher than PCDD congeners at Davutpasa and Fenertepe sampling stations while concentrations of PCDD and PCDF congeners are almost equal at Yıldız sampling station. Traffic emissions are principal emissions sources at Yıldız sampling station, therefore ratio of PCDD congeners higher than other sampling stations. Concentration of OCDD was found higher than OCDF during summer months. It has been reported that unleaded gasoline vehicles and diesel trucks (tailpipe emissions) are the most important sources especially for PCDD congeners (Cleverly et al., 1997). Except for motor vehicles, other combustion sources such as industrial combustion processes (at Davutpasa), residential and commercial heating processes and solid waste incineration processes (at Fenertepe) affected ambient air quality at Davutpasa and Fenertepe sampling stations. The mean ratio for three sampling stations was found to be 0.7, therefore PCDD/F congener profile is dominated by PCDD congeners in İstanbul ambient air. This ratio agrees with the ratios which were reported by Yu et al. (2006), Li et al. *(*2008), while is disagrees with the ratio which was reported by Raun et al. (2005) for Houston ambient air. The congener profiles which are characterized by PCDF congeners are related to the urban sources *(*Oh vd., 2002; Lee vd., 2006; Lee vd., 2007). PCDD and PCDF congeners concentrations were accounted for 34% and 66% of the total 2,3,7,8-substituted congeners. Contribution of the I-TEQ values to the ∑PCDD/F were calculated as 19% and 81% for PCDD and PCDF respectively. It has been reported that the concentration of the PCDF congeners is more than 50% of the total PCDD/F concentration (Lohmann and Jones, 1998).

## 3.4. Temporal variations of the PCDD/F concentrations

Temporal variability of the ambient air concentrations of PCDD/Fs are affected by many factors such as source strengths of PCDD/Fs (combustion of fossil fuels for domestic and commercial heating) and/or changes in long range air mass transport over sites of study and meteorological conditions (temperature inversion, lower mixing height, solar radiation, UV) (Wallenhorst et al., 1997 Sin et al., 2002; Hippelein et al1996; Duarte-Davidson et al., 1997; Lee et al., 1999; Lohmann and Jones, 1998; Hiester et al., 1995). Therefore, ambient air PCDD/Fs concentration is higher in winter than in summer which is explained as winter effect (Hippelein et al., 1996; Duarte et al., 1997; Lee et al., 1999; Lohmann et al., 1999). Temporal variation of the PCDD/Fs concentration was shown in Figure 4. The lowest concentrations were observed in September as 156 fg/m$^3$ (3fg I-TEQ/m$^3$) while the highest concentration were observed in December as 6822 fg/m$^3$ (245 fg I-TEQ/m$^3$) according to the average of all samples. Similar results were reported by several researchers in the literature (Krauthacker et al., 2006; Coutinho et al., 2007; Lohmann and Jones, 1998). Increasing PCDD/Fs concentrations during winter months were observed especially in particle phase. Mean particle phase concentrations for three sampling stations were found to be 304 fg/m$^3$ and 4202 fg/m$^3$ in summer and winter (December, January), respectively. Mean gas phase concentrations were found to be 194 fg/m$^3$ and 171 fg/m$^3$ in summer and winter months, respectively. Therefore, combustion of fossil fuels for residential/ commercial heating during winter period is considered as the most important emission source of PCDD/F compounds in Istanbul. Interestingly, the concentrations of PCDD/Fs and total suspended particulate (TSP) in January decreased significantly. Observed heavy rainfall/snowfall during this sampling period is considered as the cause of decreasing TSP and PCDD/F concentration in winter. It has been reported that a wet deposition mechanism is an important removal mechanisms for most suspended organic pollutants in the atmosphere (Assunção et al., 2005) that rainfall is a cause of low levels of PCDD/F concentrations in the atmosphere (Chang et al., 2003). Higher deposition fluxes have been reported for winter than for summer. Duarte-Davidson et al. (1994), Halsall et al., (1997a,b), Wallenhorst et al. (1997) reported a positive relationship between total deposition flux (wet and dry) and rainfall. In this study, the lowest mean concentrations for three sampling stations were determined for Fenertepe sampling station. Possible reasons for this situation: i) medical and hazardous waste incineration plants which are located about 8 km NE and 12 km ESE from this sampling station respectively. The prevailing wind directions were determined as N and NE for this sampling period. ii) biochemical and photolitic reaction products of chlorinated chemicals such as pentachlorophenol, insecticide, fungicide, herbicide. iii) biological sources due to surrounding forests. Leaf waxes, microbial degradation and herbal odds have been reported as dioxin/furan sources by Rogge et al. (1993c).

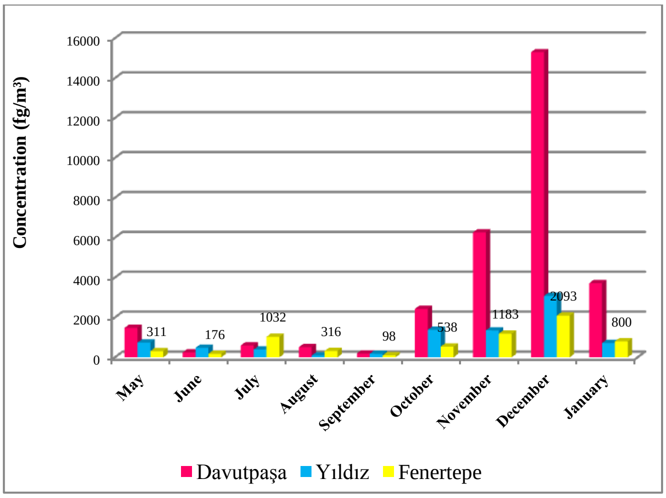


Figure 4. Temporal variation of the PCDD/F concentration

## 4. CONCLUSION

In this study, the mean concentration of the PCDD/F compounds were determined as 1746 fg/m$^3$ and 82 I-TEQ fg/m$^3$ for Istanbul ambient air. The highest concentration was determined as 3481 fg/m$^3$ (190-15297 fg/m$^3$) for residential/industrial sampling station whereas the lowest concentration was determined as 749 fg/m$^3$ (98-2093 fg/m$^3$) for semi-rural sampling station. Concentrations of dioxin congeners were higher than furan congeners, therefore the congener profiles of Istanbul ambient air are dominated by PCDF congeners. OCDD, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,6,7,8-HpCDD and OCDF were found to be common congeners for all sampling stations and all sampling periods. In addition, the highest concentration level of 1,2,3,4,7,8,9-HpCDF was found only during December sampling period at Davutpaşa sampling station. It was also found that the concentration of PCDD/F compounds showed seasonal variation in Istanbul ambient air. Mean concentration for winter months was found to be approximately 10 times higher than summer months. Therefore, seasonality of PCDD/Fs in the Istanbul atmosphere could be said to be affected by heating and temperature inversion in winter, or photodegradation and $OH^-$ radical reactions in summer.

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# MIGRATION OF PAHs IN FOOD INDUSTRY SLUDGE TO THE AIR DURING REMOVAL BY UV AND $TiO_2$

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## ABSTRACT

This study was carried out to investigate the removal rates of polycyclic aromatic hydrocarbons (PAHs) from treatment sludge of a food industry and evaporation rates of PAHs to air. The impacts of temperature, UV application and titanium dioxide ($TiO_2$) addition were studied in a controlled apparatus which was specifically designed for this study. Air in the apparatus was vacuumed in order to collect the evaporated PAHs. The total PAH content reduced by 69% in the sludge samples that were kept in the apparatus for 24 hours at 35 $^oC$. This removal rate increased to 95% through UV application at 40 $^oC$. 91% of the PAHs in the sludge were evaporated into the air as a result of UV application. A PAH removal rate of 95% was attained with the addition of $TiO_2$ at the rate of 5% of the dry weight of the sludge in UV-$TiO_2$ experiments where the PAH content released into the air did not exceed 25%. The application of UV-$TiO_2$ was considered as an alternative PAH removal method which restricts transportation of pollutants since it removes PAHs at a rate of 95% and reduces the PAH content that is released into the air.

**Keywords:** Treatment sludge, Photo-catalyst, Evaporation, Temperature

## 1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are of hazardous organic pollutants which are released into the environment through incomplete combustion of fossil fuels. These pollutants are released into the environment mainly via natural or anthropogenic sources such as power and heat generation, fires and vehicle exhaust emissions. They may cause mutagenic/carcinogenic effects when they enter the human body via the food chain (IARC, 1986). Thus PAH compounds must be removed from environmental media as well as from waste matrices. One of these matrices is the treatment sludge which is an undesired byproduct resulting from wastewater treatment. Treatment sludge contains semi-volatile organic compounds such as PAHs, as well as numerous other pollutants with different characteristics (Salihoglu et al., 2012).

An important issue that needs to be observed during the process of PAH removal is to minimize transportation of the PAHs into the air from the waste matrix. PAH compounds have high tendency to migrate to air due to their volatility properties (Wang et al., 2005). While the PAH content in the sludge is reduced on one hand, the PAH content in the air will increase on the other hand and the process will result in transportation of pollutants rather than removal. Consequently the resulting increase in atmospheric PAH concentrations will magnify pollution at a global scale and expose all living organisms to higher levels of PAH pollution.

In this study, migration of PAHs in treatment sludge to the air during removal with UV technology was investigated. The impact of the temperature, UV and the use of $TiO_2$ on the removal of PAHs and migration of PAHs from the sludge to the air were determined. PAH removal mechanisms were assessed on the basis of PAH content and removal rates with a view to demonstrating the most favorable experimental conditions that restrict PAH migration.

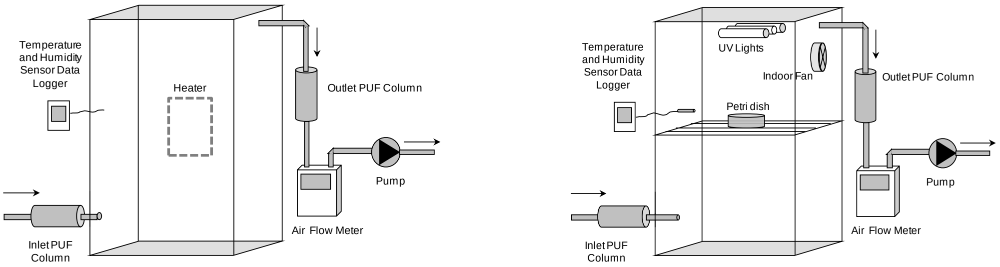
## 2. MATERIALS AND METHODS

### 2.1. Sludge Sampling

Sludge samples were collected at the belt filter press outlet. Characterization of the sludge and the other details can be found elsewhere (Salihoglu et al. 2012).

### 2.2. UV Apparatus

The apparatus used in UV experiments is fully insulated from external environmental conditions. The intake air is totally purified from PAH compounds with the PUF columns placed at the inlet of the apparatus. Thus interference between the PAHs that evaporate from the sludge and PAHs in the airborne air is prevented (Figure 1). Details of the apparatus are explained in the study by Karaca and Tasdemir (2011).



a) Exterior View b) Interior View

Figure 1. Apparatus (Salihoglu et al., 2012; Karaca and Tasdemir, 2011)

### 2.3.PAH Removal Experiments

#### 2.3.1. UV and UV - $TiO_2$ Applications

UV and UV-$TiO_2$ applications were carried out at 40°C. Additionally, UV-$TiO_2$ experiments were carried out at 20 °C with a view to verifying the usability of $TiO_2$ at low temperatures. Degussa P25 series $TiO_2$ with surface area ≈50 $m^2/g$ and average diameter of 20 nm was used in the UV-$TiO_2$ experiments. $TiO_2$ was dosed to the sludge at the rate of 5% and 20% of dry sludge weight, respectively. Preliminary analyses were conducted following PAH removal experiments and PAH concentrations were measured by using a GC-MS. All experimental studies were repeated 3 times and details such as measuring the luminous intensity and positioning of sludge samples in the apparatus etc. were explained in the study by Karaca and Tasdemir (2011).

#### 2.3.2. Sampling of the Evaporated PAHs from the Sludge

The air inside the apparatus was vacuumed through steel columns containing polyurethane foam (PUF) at a flow rate of 0,8 $m^3$/hour with a view to determine the amount of PAH content evaporating from the sludge (Figure 1). The PUFs that are placed at the inlet of the apparatus are used to capture airborne PAH compounds. Extraction procedure and PAH analysis of the PUF samples were explained in Salihoglu et al. (2012).

### 2.4. PAH Extraction, Cleanup and Determination

The PAH content in the sludge and in the air prior to and after performing PAH removal processes were measured in this study. Targeted PAHs were chosen from the priority pollutants list issued by the USEPA. The properties of the chemicals used in the experimental studies and details regarding extraction and PAH analysis processes are as described in the study by Salihoglu et al. (2012).

### 2.5.Quality Assurance / Quality Control

Field blanks at the rate of 10% of the number of sludge samples were taken to determine any contamination during the experimental process. The PAH tests that were applied to the sludge samples were also applied to the field blanks containing 5 g of $Na_2SO_4$. Details of the blank sample handling can be found elsewhere in detail (Karaca and Tasdemir, 2010, Salihoglu et al., 2012).

## 3.RESULTS AND DISCUSSION

### 3.1. Temperature Applications

The PAH content migrating to the air from the sludge following PAH removal studies that were carried out at 20 $^{o}$C and 40 $^{o}$C is provided in Figure 2. The mean values of PAH content measured before and after the removal processes (UV and UV-$TiO_2$) at 20 $^{o}$C and 40 $^{o}$C were calculated to determine the PAH content that was migrated to the air and the influence of temperature on the migration of PAHs from the sludge to the air was demonstrated. Additionally, the distribution of PAH species that have migrated to the air following UV and UV-$TiO_2$ applications are analyzed in detail at the end of this section.

As provided in Figure 2, more than 90% of the PAHs that have migrated to the air comprise 3 ring species. It is known that 3 ring species have higher tendency to evaporate due to high levels of vapor pressures (Huang et al., 2004). The higher content of these species in the air indicates that they have evaporated more from the sludge.

Increasing the average temperature from 20$^{o}$C to 40$^{o}$C increased the amount of 3 ring PAH compounds in the air by 100 ng on the average and the amount of 4 ring PAH species by 20 ng. Under the light of this finding, it is arrived at a conclusion that the amount of PAHs that migrate to the air increases depending on temperature. Studies investigating the change in atmospheric PAH concentrations with respect to temperature have demonstrated that a raise in the temperature has increased the PAH concentrations that migrate to the air, which is in line with the data obtained in this study (Chen et al., 2011).

An analysis of the PAH species in the air has demonstrated that light species migrate to air at higher levels than heavy species both with or without the presence of UV. 92% of PAHs that migrate to air from the sludge without the presence of UV comprises 3 ring Phe and Ant compounds. The remaining 8% comprises 4 ring species. An analysis of the PAHs in the air following UV application has demonstrated that 70% comprises 3 ring species and the remaining 30 % comprises 4 ring species. It is an expected result for the 3 ring species which have a higher tendency to evaporate due to high levels of vapor pressure, to migrate to the air from the sludge at higher levels. It was observed that the light species dominate as a result of UV-$TiO_2$ applications at 20 $^{o}$C and 40 $^{o}$C, as was the case in UV applications. The 3 and 4 ring species were present in the air samples at the rate of 91% and 9 %, respectively at 20 $^{o}$C and the 3 and 4 ring species were present in the air samples at the rate of 96% and 4 %, respectively at 40 $^{o}$C. It was observed that the amount of Phe and Ant species which have a higher tendency to evaporate was increased with an increase in the temperature.

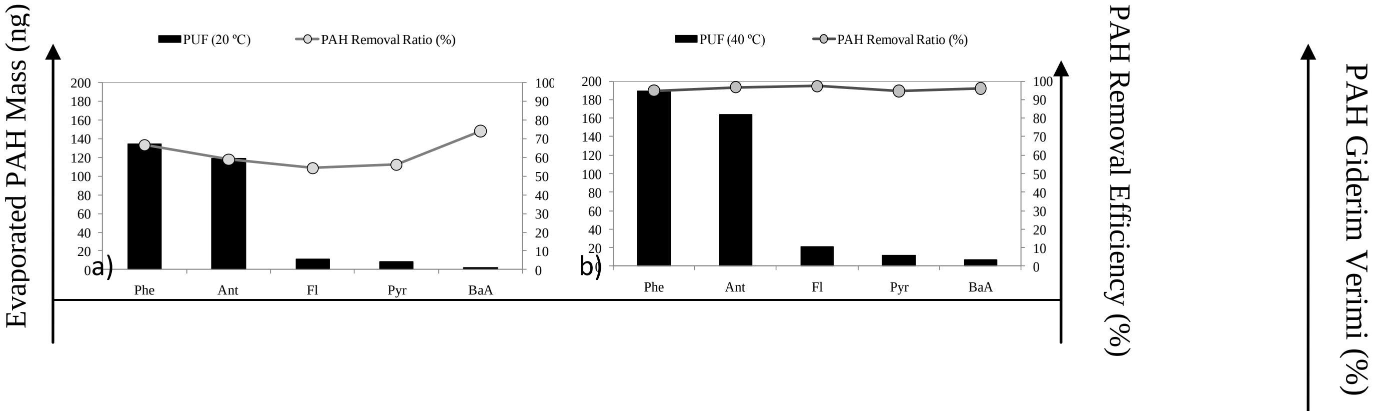


Figure 2. The influence of temperature on the amount of PAHs that migrate to thehe air a) 20 $^{o}$C b) 40 $^{o}$C

## 3.2.UV Applications

The concentration of $\Sigma_5$PAH species in the food industry sludge was measured as 440 ng/g dry matter. The $\Sigma_5$ PAH content was reduced by 69% when the samples were kept in the apparatus at 35 $^{o}$C for 24 hours. However the removal rate reached 95% following the UV application (40$^{o}$C) (Figure 3). Present study have demonstrated that the UV application increases removal of PAHs through photo-degredation by 26% as a minimum. It is known that UV rays increase PAH removal rate in solid matrices, thus the data obtained from this study is in compliance with the literature (Karaca and Tasdemir 2011; Zhang et al., 2008).

The amount of PAHs that have migrated from the sludge to the air following PAH removal experiments was calculated as 93 ng in the absence of UV and 395 ng in the presence of UV. In other words it was seen that 21% and 91% of the total PAH content in the sludge has migrated to the air, respectively. It is known that two main mechanisms, namely photo-degradation and evaporation play an effective role in the PAH removal process. It was showed that a 5 $^{o}$C raise in the average temperature increased the evaporation rate (Wang et al., 2005). The fact that, 95% of the PAH content was removed through photo-degradation and 91% of the PAH content in the sludge migrated to the air, indicates that PAHs that were removed during UV application migrated from the sludge to the air. As a matter of fact, in addition to the increase in the removal rate, the PAH content in the air also increased for the 5 species that were mentioned previously following the UV application. It was believed that some of the 4 ring species were first transformed to 3 ring species through photo-degradation (Guieysse et al., 2004) and then evaporated during this process. This also explained the increase in the Ant amount (ng) following the UV application, compared to the initial value.

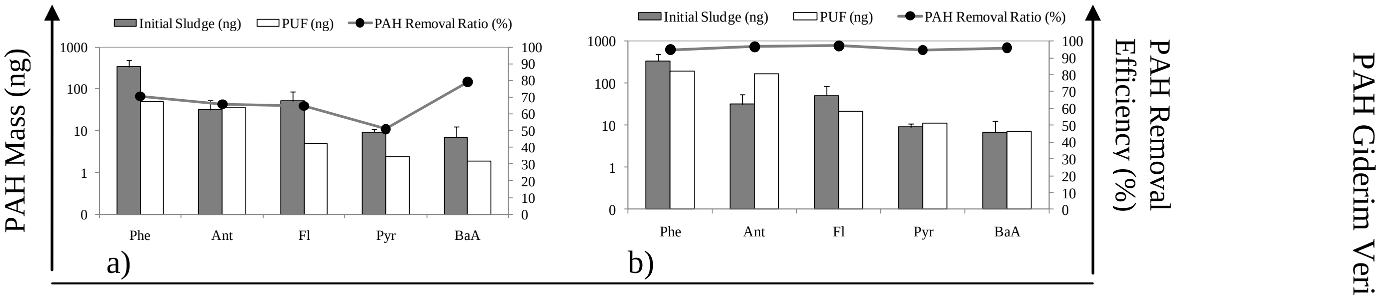


Figure 3. The influence of UV on the removal of PAHs from treatment sludge and on the migration of PAHs to the Air a)35 °C b) UV, 40 °C

### 3.3.UV-$TiO_2$ Applications

PAHs were tried to be removed by applying UV to the sludge samples to which $TiO_2$ was dosed at the rate of 5% and 20% of dry sludge weight respectively, for a period of 24 hours. PAH removal ratios attained by applying UV-$TiO_2$ and the amount of PAHs that were migrated to the air by the end of 24 hours are provided in Figure 4. PAH removal ratios were 87% and 72%, respectively at 20 $^oC$ in the samples containing $TiO_2$ at the rate of 5% and 20%, and the PAH removal ratios at 40 $^oC$ were 95% and 71%, respectively. It was observed that a rise in the temperature increased the removal rate of 4 ring Pyr compound in particular. Photo-degradation reactions are expected to accelerate under high temperatures (Zhang et al., 2010). Accordingly it was reasonable for the PAH removal efficiency to increase for all PAH species and for the 4 ring species, to which the UV rays penetrate more easily, in particular.

The rate of PAH removal from the sludge was lower when a high dosage of $TiO_2$, at the rate 20% was used. Similarly, the study by Zhang et al., (2006) demonstrated that $TiO_2$ dosage at the rate of 0.5% is sufficient for PAH removal from the soil, and that an increase in the dosage did not increase the removal rate (Zhang et al., 2006). In the present study, increasing the dosage of the catalyst from 5% to 20%, in other words increasing the number of $TiO_2$ particles in the environment might have caused scattering of UV rays, reducing penetration of the UV rays to the sludge, resulting in a decrease in the PAH removal rate.

In the samples containing $TiO_2$ at the rate of 5% of dry sludge weight, the rates of migration of the PAHs from the sludge to the air were 78% at 20 $^oC$ and 25% at 40 $^oC$ when they were exposed to the UV rays for 24 hours. On the other hand, the rates of migration of the PAHs to the air were 25% at 20 $^oC$ and 32% at 40 $^oC$ as a result of UV experiments with samples containing $TiO_2$ at the rate of 20% of dry sludge weight. It was observed that the PAH removal efficiency was higher and the rate of migration of PAHs to the air was lower at higher temperatures (40$^oC$). Although it was expected for the PAH content in the air to increase with a rise in the temperature, the actual result was to the contrary. This indicates that the photo-degradation mechanism was more effective than the evaporation mechanism. It was believed that PAH compounds were transformed to intermediate compounds as a result of photo-degradation reactions initiated by absorption of UV rays by $TiO_2$, where the OH* radicals that were generated break of the PAHs (Wang et al., 2009). Otherwise, it was normally expected for the PAHs to be transformed to light compounds as a result of photo-degradation and to evaporate under the heat and migrate to the air.

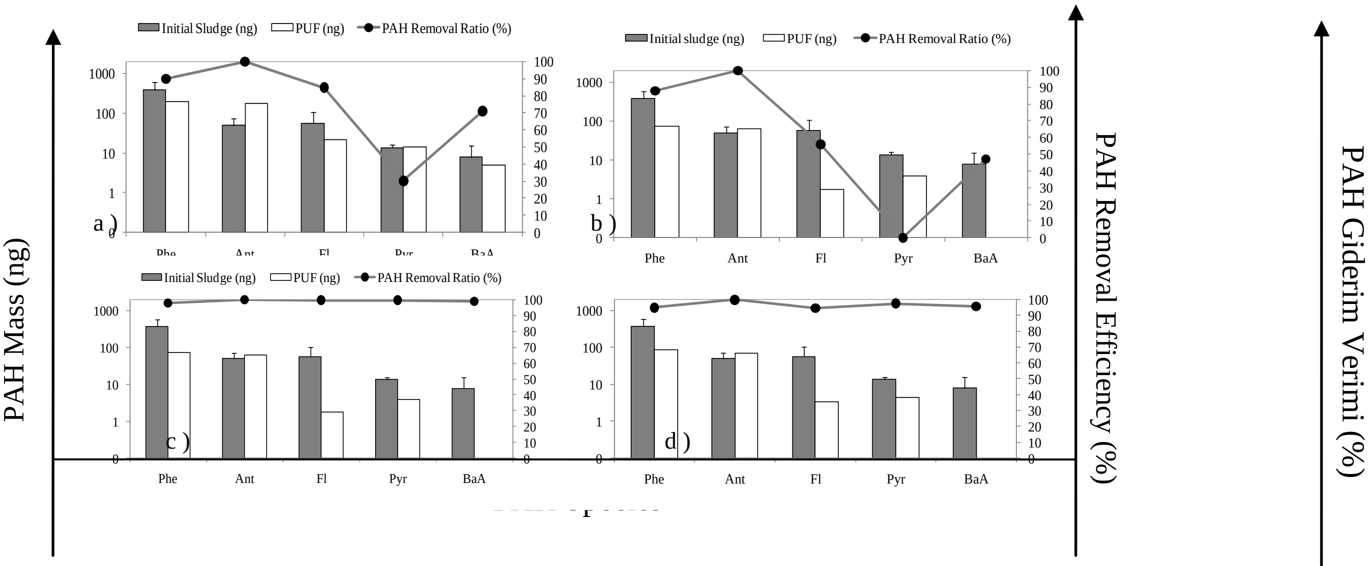


Figure 4.The influence of UV-TiO$_2$ applications under different levels of temperature, on the removal of PAHs from municipal treatment sludge and migration of PAHs to the air

a) 5% TiO$_2$, 20°C b) 20% TiO$_2$, 20°C c) 5% TiO$_2$, 40°C d) 20% TiO$_2$, 40°C

The PAHs in the food industry sludge were removed at the rate of 95% both under the UV and UV-TiO$_2$ applications. Although the removal efficiency of both applications was the same, there was a huge difference in the total amount of PAHs which were migrated from the sludge to the air by the end of 24 hours. While 395 ng of PAH was migrated to the air as a result of the UV application, only 145 ng of PAH was migrated to the air as a result of the UV-TiO$_2$ application. It was observed that if TiO$_2$ is not dosed to the sludge, heavy PAH species are transformed to light PAH species and then evaporate as a result of photo-degradation reactions (Guieysse et al., 2004) thus balancing the removal rate and the amount of PAHs that are migrated to the air. It was thought that, hydroxylation reactions occured with OH* radicals during the photo-degradation process in UV applications where TiO$_2$ was dosed, reducing the PAH content in the sludge and in the air by the end of 24 hours. The UV-TiO$_2$ study by Wen et al., (2003) on photo-degradation of PAHs demonstrated that Phe and Pyr were transformed to phenanthrenedialdehyde and 1,6-pyrenedione compounds (Wen et al., 2003). Another study demonstrated that 3-5 ring PAH species were transformed to PAH-dione compounds as a result of UV-TiO$_2$ applications and the samples did not have toxic properties according to EC$_{50}$ toxicity tests (Woo et al., 2009). In addition, various researchers stated that byproducts generated as a result of photo-degradation of PAHs might also have toxic properties such as PAHs (Kot-Wasik et al., 2004).

On the basis of the data obtained as a result of experiments, it was concluded that UV-TiO$_2$ application might have been a good alternative for PAH removal which ensures a high rate of removal of PAHs from the sludge and reduces the PAH content that was released into the air, thus restricting transportation of pollutants.

## 4.DISCUSSION

In this study while removal of PAH pollution was investigated, the rates of migration of the pollutants to the air environment were also measured. Under this framework, the influence of UV rays, temperature and use of $TiO_2$ as a photo-catalyst on the migration of PAHs from the food industry sludge to the air was also assessed.

Since the food production facility which was taken as the target indusry in this study generates 50 tons of dry treatment sludge per year, the amount of $\sum_5$PAH that is released to the air as a result of the UV application will be 24 g/year. This value will not exceed 7 g/ year as a result of UV-$TiO_2$ application. These figures reflect the amount of PAHs released to the air from one food production facility only. The total amount of treatment sludge generated in Bursa is around 1.600 dry tons /day according to 2008 data (Filibeli and Ayol, 2008). In other words, the total amount of sludge that needs to be disposed of on an annual basis is 584.000 dry tons. When the scenario regarding the food industry treatment sludge is applied to the entire amount of treatment sludge generated in Bursa, annual amount of PAHs that migrate to the air from treatment sludge for the $\sum_5$ PAH species will be 270 kg/year as a result of UV applications and 75 kg/year as a result of UV-$TiO_2$ applications. Release of PAHs to the air in an uncontrolled manner shall be prevented with a view to avoiding problems on a global scale due to atmospheric PAH concentrations. The importance of studies using alternative methods that restrict transportation of pollution during removal of PAHs from the sludge is emphasized once more under the light of this study. Otherwise treatment sludge will serve as a resource for atmospheric PAHs.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
**4th International Symposium and IUAPPA Regional Conference**
**10-13 September 2012 Istanbul -Turkey**

# VARIATIONS IN CHEMICAL COMPOSITIONS OF THE AEROSOLS IN ISTANBUL

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## ABSTRACT

Atmospheric aerosol samples were collected in accordance with ASTM-G140 standard method during April-October 2011 period at the sampling stations located in the coastal lines and some inland points of İstanbul. Aerosol samples were analyzed for various ions and trace elements (anthropogenic or crustal originated) via Ion chromatography and ICP-OES analyses. Effects of marine and land originated species were investigated on the composition of aerosols. Especially mass fluxes of sodium and chloride ions were estimated and evaluated in order to determine the effect of marine-originated aerosols. Statistical analyses of the concentrations of aerosol compositions showed that considerably narrower variations in the concentrations of coastal line sample compositions than in the inland samples become apparent due to the dominant effects of marine originated species. During the transportations of marine aerosols toward inland areas, various anthropogenic and naturally occurring land originated aerosols become considerable and cause larger variations in the compositions of inland aerosols.

**Keywords:** Atmospheric aerosol, Marine aerosol, Terrestrial aerosol, ASTM-G140, trace metal

## 1. INTRODUCTION

İstanbul metropolitan city is heavily affected by aerosols due to being surrounded by Marmara Sea, Black Sea and Bosphorous, and involving anthropogenic sources primarily traffic and industrial activities, On the other hand, the city is also affected by regional and continental pressure systems and located along the transport routes of air parcels coming primarily from Europe, Black Sea and Russia during winter and autumn seasons, and from the Mediterranean and Africa during spring and summer (Uygur et. al., 2010). For this reason, various studies which concentrated on aerosol chemical sturucture investigated the effects of local (Koulouri et. al., 2008) or long range transportation on aerosol compositions. Local and global contributions, mathematical model approaches (Foltescu, 2005), statistical methods hav been extensively used in order to determine source of components of complex aerosols in the atmospheres of developing cities. Goegraphical location of Istanbul and urbanization are likely to change the natural structure of Istanbul. Rapid grow of İstanbul is also effective mechanism on dominant wind directions (Karaca, 2005). When the effects of long range transport and local source contributions are compared, long range transport is effective on aerosol composition in rural and suburban areas because of low local emission sources (Niemi et al., 2009; Tecer et al., 2008; Karaca et al., 2008). Local and global emissions may comprise of natural and anthropogenic source contributions. Marine aerosols which are present throughout coastal settlements are the most important part of total atmospheric aerosols. An estimated 3300 Tg of sea salt is injected into the atmosphere annually as a result of the agitation of ocean surface by wind (IPCC, 2001). Generally these aerosol groups turn into sea salt solution or sea salt as a result of the effect of air temperature after emitted into the atmosphere. Sea salt aerosol (SSA) produced by surface winds, is an important component of atmospheric aerosols over the oceans.

İstanbul city is also under the influence of this type of mechanism. Beside this, anthroppogenic source contributions are also effective and should be mentioned. Especially, heavy metal concentrations of aerosol compositions are getting greater in the regions of dense industrial activities and traffic.

## 2. EXPERIMENTAL

### 2.1. Sampling Locations, Apparatus and Analyses

Monthly aerosol samplings were carried out in Istanbul in a total of 13 stations most of which being along the coastal lines of Marmara Sea, Black Sea and the Bosphorus (names of the stations are Silivri, Avcılar, Bakırköy, Yenikapı, Bostancı, Maltepe, Rumeli Feneri, Kabataş, Sarıyer), and the rest being the inner part stations at Yildiz Technical University (YTU) Maslak Campus, Levent İşbank Tower, YTU Yildiz Campus, Büyükçamlıca hill. Figure 1 shows these stations. Coastal sampling stations have distinct properties because of fluctuating natural and anthropogenic source contributions while inner part stations are under the prevailing effects of traffic, industrial activity, and marine aerosols the effects of which is being dependent upon the distance from the sea. Sampling campaign was carried out during the period of March to October of 2011 in accordance with the standard method ASTM-G140 the apparatus of which is shown in Figure 2.

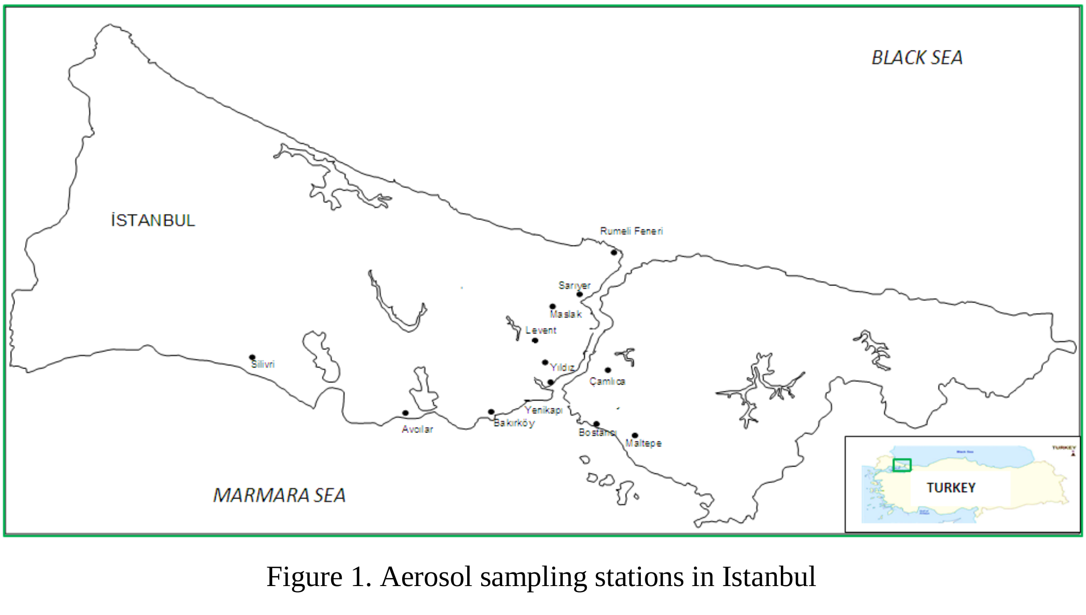


Figure 1. Aerosol sampling stations in Istanbul

The apparatus is a kind of passive sampling tool which is open to wind circulation in the atmosphere. Prevailing wind currents from sea side that carry sea aerosols will impact and leave aerosols on the wet surface of the apparatus while passing over it. The details of the apparatus can be found in the related standard.

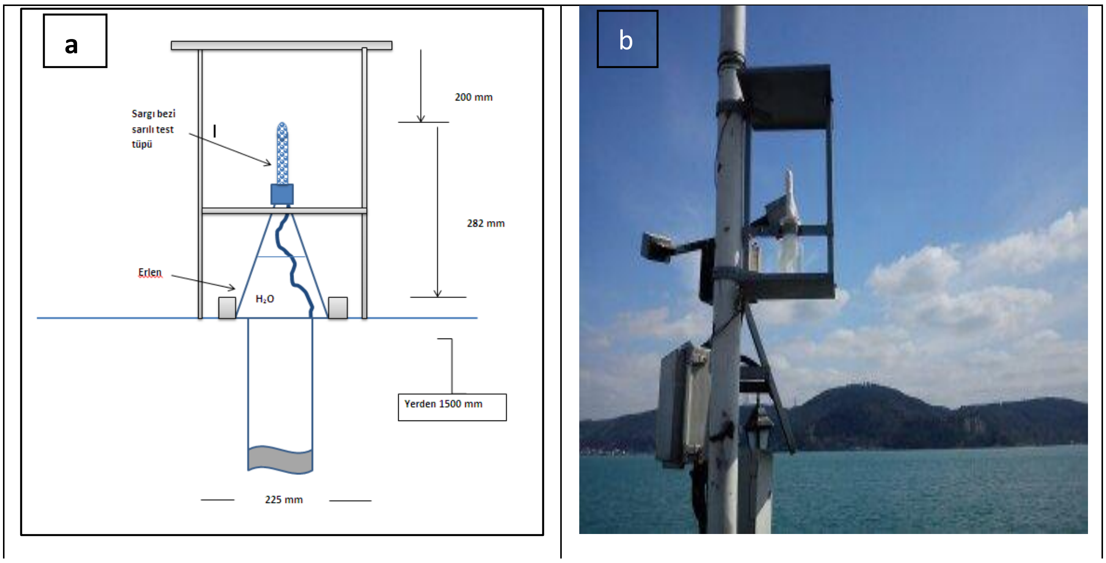


Figure 2. a. Schematic of ASTM-G140 Wet Candle sampling apparatus and b. a picture of a sampling station.

The collected aerosol samples during a one month sampling period were analyzed for ions ($F^-$, $Cl^-$, $NO^-_2$, $Br^-$, $NO^-_3$, $SO^-_4$, $PO^{-2}_4$, $Li^+$, $Na^+$, $NH^+_4$, $K^+$, $Mg^{+2}$, $Ca^{+2}$) and trace elements (Al, Fe, Ca, Zn, Co, Pb, Ca, Ni, Fe, Mn, Cr, V, Cu, Al, B) by Ion Chromatography and ICP instruments, respectively.

## 2.2.Data analysis

Mass fluxes of major ions were calculated according to Eqn (1) representing the amount of a specific matter in aerosols carried by wind through a unit atmospheric area in a unit time.

$$Mass\ Flux\ \left(\frac{mg}{m^2 \cdot day}\right) = \frac{sample\ concentration\,(mg/l)\ x\ samplevolume}{sampling\ period\,(day)\ x\ candle\ surface\ area} \quad (1)$$

Variations in spatial and temporal scales of collected aerosol samples were evaluated by means of basic descriptive statistical tools (box-and-whisker plots) in accordance with their chemical compositions during all study period and with respect to regional differences of sampling stations. Meteorological conditions (DMI, 2012) were also considered while analyzing the variations and differences in the chemical compositions of aerosols.

# 3. RESULTS AND DISCUSSION

## 3.1. Mass fluxes of aerosol constituents

Mass fluxes of aerosol constituents were shown for selected stations in Fig. 3. Nitrate ion flux is close to sulfate for all stations. Nitrate and sulfate flux values varied from 1 to 15 $mg/m^2$.day and 5 to 40 $mg/m^2$.day respectively during the entire sampling period. Only nitrate was found to be 67 $mg/m^2$.day at Avcılar station in September and this situation is thought to be related to traffic density. Sulfate ion flux showed an increase up to 50 $mg/m^2$.day in October in Rumeli Feneri. Formation of dimethylsulphite (DMS) as a result of biological activity in the sea and NNE wind direction from sea to land are thought to be effective on this increase.

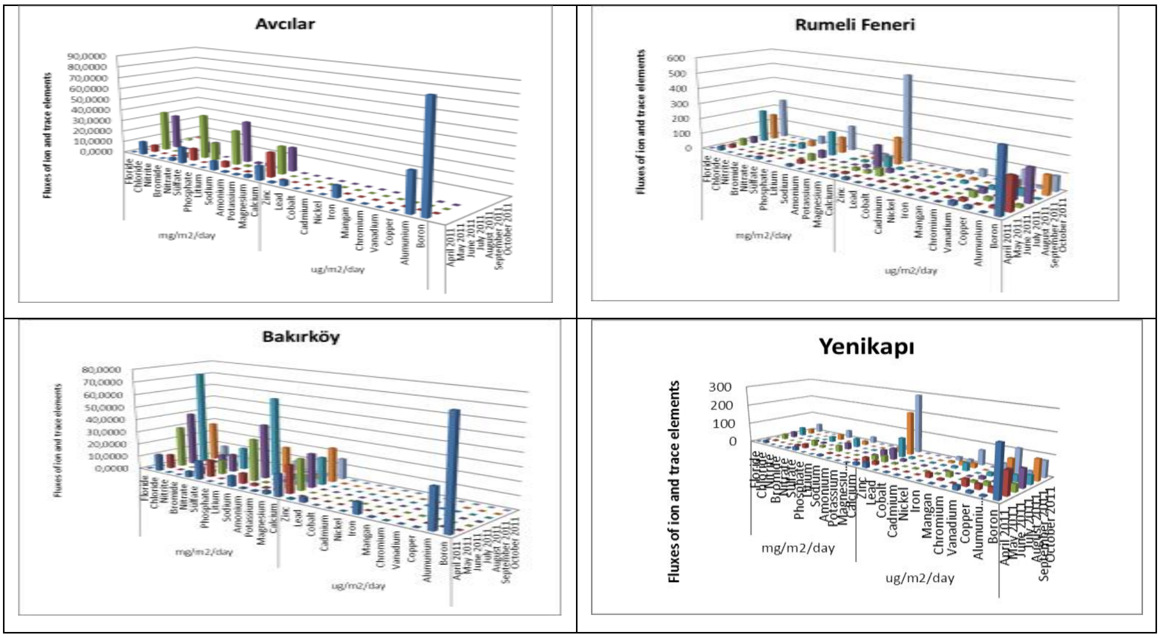


Figure 3. Examples of mass fluxes of species in selected stations

Ca ion flux values varied between 10-25 mg/m$^2$.day during the entire sampling period. Ca is found to exist mostly in larger fractions of PM and originated from soil structure (Karaca, 2005). In parallel, the fluxes of Mn, Cr, Cu, and Zn followed the same trends at Bakırköy and Avcılar in April and September. These findings imply an anthropogenic effect in September along the coastal line of European side of İstanbul. This situation may be explained by the contribution of long range transportation because of long period sampling.

### 3.2. Spatial and temporal variations in compositions of aerosols.

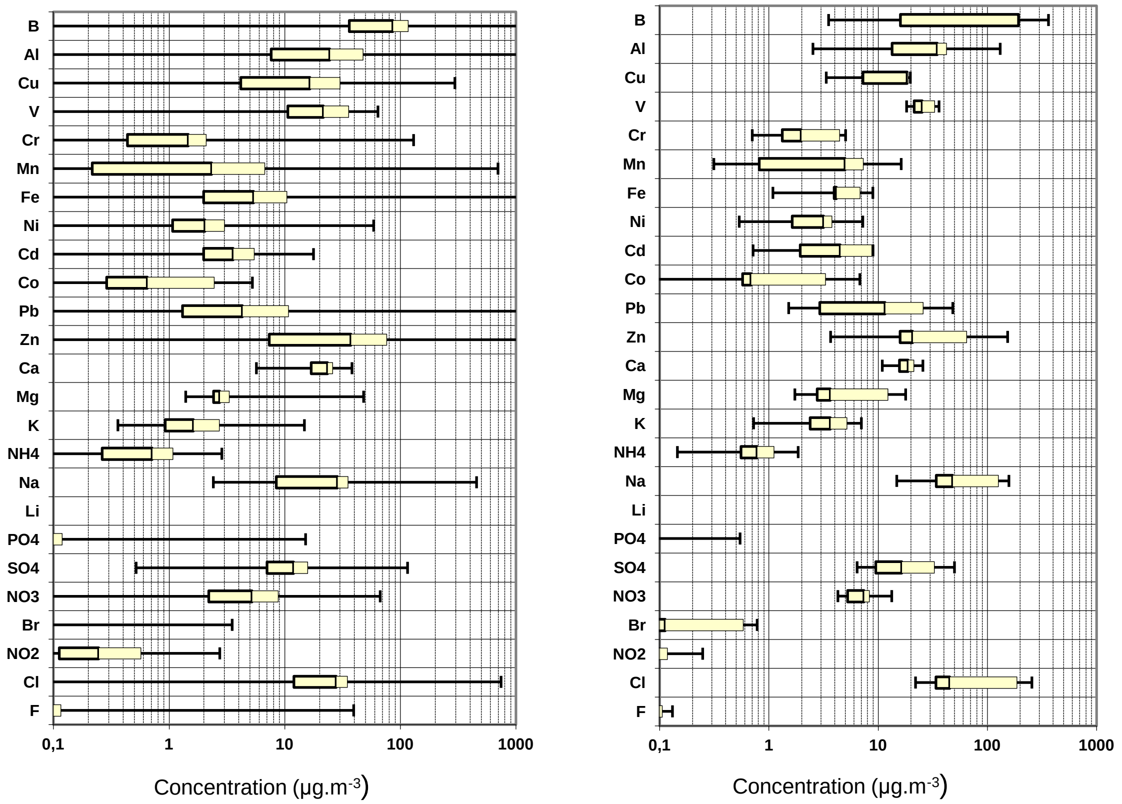
Spatial variations of aerosol constituents were analyzed by whisker plots as shown in Fig. 4. In this Figure, the graph of Marmara Sea stations (Silivri, Avcılar, Bakırköy, Yenikapı, Maltepe, Bostancı) represents the variations of aerosol constituents of all stations along the coastal line of Marmara Sea during the whole sampling period. In the same way, the graph of Black Sea represents the situation for Black sea stations (only Rumeli Feneri), the Bosphorus graph represents the situation for the stations along the Bosphorus (Kabataş, Sarıyer, Kadıköy).

An overall evaluation of the variations of species shows a general situation that Na and Cl ion concentrations of Marmara stations fluctuated in the narrowest range. This situation may be explained by dominant unique source of Na and Cl ions in aerosol compositions which is sea. That means all Marmara coastal line stations were under the dominant effect of marine aerosols originating from Marmara Sea.

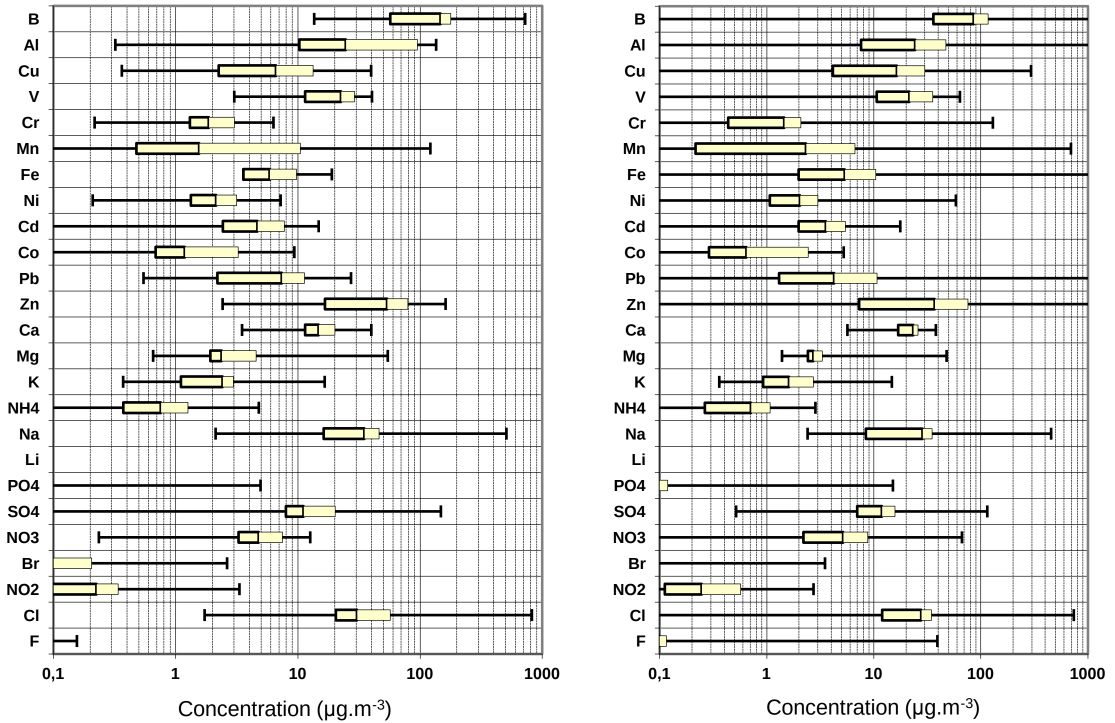
Another fact for dominat Na and Cl ion fluxes is the denser marine traffic. Most of the stations in Marmara shoreline and all stations in the Bosphorus were influenced by marine traffic. Marine traffic cause wider wavings on sea surfaces that generate marine aerosols via whitecap mechanism.

Na and Cl ion fluxes showed fluctuating trends at relatively higher values as 152.5, 101.2, 158.5 mg/m$^2$.day being Na fluxes, and 207.8, 167.9, 257.4 mg/m$^2$.day being Cl fluxes in Rumeli Feneri in August, September and October. This station may be explained by Black Sea aerosols that NNE winds were dominant in those sampling periods.

In the inner part stations, concentrations of aerosol constituents showed relatively wider variations. This is because varying antropogenic sources become considerable as the aerosols are transported toward inland areas. Consequently, the effcet of sea originated aerosol contributions decreases as moving toward inland regions.



**Marmara Sea Stations** **Black Sea Station**



**Bosphorus stations** **Inner side stations**

Figure 4. Variations of concentrations of species as the groups of sampling stations

## 4. CONCLUSIONS

In this study, an investigation was carried out on the variation of aerosol compositions in Istanbul. The effects of anthropogenic and natural sources were inversitager through a sampling campaign at stations located along coastal lines (Marnara Sea, Black Sea and the Bosphorus strait) and some iner parts of Istanbul.

Cities surrounded by seas like Istanbul were apparently affected by sea originated aerosols. This situation was observed for Istanbul as seen on the aerosol samples collected during this study. Aerosols samples collected at coastal line stations apparently showed dominant marine aerosol effect on the aerosol compositions while inner part aerosols are influenced by varying antropopgenic sources.

## ACKNOWLEDGEMENT

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AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES
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# TEMPORAL VARIATION IN CHEMICAL COMPOSITION OF LOWER TROPOSPHERIC AEROSOLS AT NORTHWESTERN TURKEY

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## ABSTRACT

In this study daily particulate matter (PM) samples was collected at a rural area, which is approximately 30 km away from the Kırklareli, a city located in northwestern Turkey. Distance of the sampling location to Bulgarian-Turkish border is 5 km. Approximately 350 daily PM samples were collected, between April 2006 and May 2008, using a high volume sampler. Collected samples were analyzed for 55 major, minor and trace elements using ICP-MS and major ions (Cl-, NO3-, SO42-, Na+, NH4+, K+, Mg2+ and Ca2+) by Ion Chromatography and black carbon by Optical Transmissometer. Interspecies correlations between measured species were determined. Aluminum showed good correlation with Mg2+ (r= 0.70, $p<0.05$) and Ca2+ (r=0.76, $p<0.05$) indicating that sources of these ions is earth's crust. Magnesium ion were also correlated with Na+ (r=0.33, $p<0.05$) and Cl- (r=0.24), this implied that sea-salt emissions contributed to observed Mg2+ concentrations. Potassium ion, which is a well-known marker of biomass burning, were correlated with NH4+ (r=0.56, $p<0.05$), SO42- (r=0.46, $p<0.05$) and Cl- (r=0.23, $p<0.05$). This indicated that besides K+, NH4+, SO42- and Cl- could also be emitted by biomass burning activities in/around the region. Correlations between the major ions showed that (NH4)2SO4, NH4HSO4, NH4NO3, NH4Cl, NaNO3, Ca(NO3)2, KCl and NaCl were the main ionic species found in the samples.

**Key Words**: ions, interspecies correlation, long-range transport, aerosol

## INTRODUCTION

Aerosol composition in Eastern Mediterranean part of Turkey is well documented (Rodriguez, Querol et al. 2002; Bardouki, Liakakou et al. 2003; Gullu, Dogan et al. 2005; Sciare, Oikonomou et al. 2005; Kocak, Mihalopoulos et al. 2007; Glavas, Nikolakis et al. 2008; Querol, Alastuey et al. 2008; Theodosi, Markaki et al. 2010; Nicolas, Chiari et al. 2011; Perrone, Piazzalunga et al. 2011). However studies conducted in northwestern part of Turkey is less and limited to İstanbul which is the most populated city and one of the major industrial centers of Turkey. Therefore even conducted in rural sides of İstanbul, these studies are affected from local sources. In this study, aerosol chemical composition in northwestern Turkey is determined in a rural station in where long range transport is the major factor determines the aerosol composition. Comparison of pollutant concentrations measured in this study with those reported at other parts of Turkey will be a novel study to differentiate pollution originated from Turkey's own emissions and from other countries. The aim of this study is to compare measured aerosol composition with those reported at other parts of Turkey, and using correlation and simple regression analyses to determine the major sources and chemical forms of aerosols.

## MATERIALS AND METHODS

The sampling point is located in a rural area which is approximately 30 km away from the Kırklareli ($41^{o}$ 57.996´N and $27^{o}$ 23.670´E), a city located at the northwestern Turkey. Location of sampling point is depicted in Figure 1 along with the prevailing wind direction (measured at 10 m above ground) of the location. As seen in Figure 1, the dominant wind direction is from NE, while Kırklareli city is located in the south of the station. Air flow climatology of the region (using synoptic scale meteorology) is also investigated and found that air masses arriving the sampling station spent 80% and 65% of its total time in W, NW, N and NE directions in winter and summer seasons, respectively. Surface meteorology together with synoptic scale meteorology of the region emphasizes that sampling location in this study is not affected from the local sources, but under the influence of long range and/or regional transport of pollution.

Particulate matter (PM) samples were collected daily by High Volume Air Sampler (SIERRA-ANDERSEN Model SAUV-1H) on 20x25 cm Whatman®41 (Whatman Inc., Clifton, NJ) cellulose filters. Filters were conditioned before and after sampling in a constant temperature (25±5)$^o$C and humidity (26±4)% chamber before they were weighted using a four digit analytical balance. All filter handling were performed under twice HEPA filtered air in a clean area. Field blanks were collected nearly once in each weak by operating the sampler for 5 minutes.

Daily PM samples collected between April 2006 and May 2008. A total of 350 samples were collected. Samples were cut into 8 parts. The first part was used for ICP-MS analysis, the second part was used for IC analysis, the third part was used for BC analyses, remaining parts were archived in case of reanalysis of the sample or for analysis of a different parameters in the same samples. Samples were analyzed for 55 major, minor and trace elements by ICP-MS, major ions (Cl-, NO3-, SO42-, Na+, NH4+, K+, Mg2+ and Ca2+) by Ion Chromatography and black carbon by Optical Transmissometer. Samples, which were collected for trace element analysis were digested using a microwave, prior the ICP-MS analysis, with a mixture of 6.0 ml HNO3 and 1.0 ml HF. NIST-SRM 1648 urban particulate matter was used for quality control of ICP-MS measurements in this study. For IC analyses, samples were dissolved in 50 mL of nanopure water (18.2 MΩ.cm) assisted by supersonic shaker and agitated for an hour. The accuracy of the IC measurements was tested by dissolution of high purity salts (NaCl, K2SO4, NaNO3, KCl, CaCl2 and NH4Cl) in nanopure water. Although H+ ion and carbonates were not measured, ionic balance may be used as a quality control of IC measurements. For this reason total equivalents of cations versus total equivalents of anions were plotted in Figure 2. The slope of the regression line is 1.08 which is close to 1.0 and indicates that all major anions and cations were determined in samples.

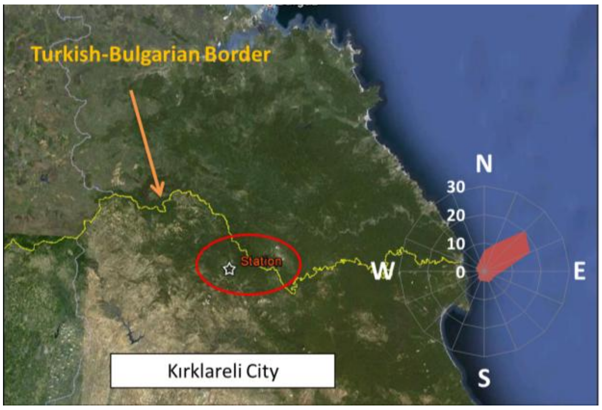


Figure 1.Location of sampling point and prevailing wind direction

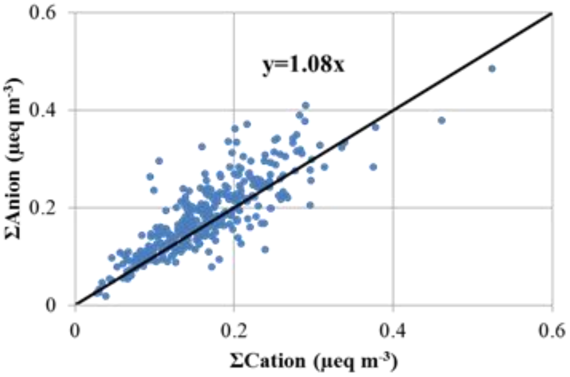


Figure 2. Quality control of IC analyses

## RESULTS AND DISCUSSION

Statistical summary of elements (in this paper only Al is reported) and ions measured between April 2006 and May 2008 is given in Table 1. For most of the parameters in the table, standard deviations are comparable to their corresponding mean concentrations, and mean concentrations are higher than corresponding median concentrations. This implies that these species show right skewed distribution which is also supported by calculated positive skewness values for most of the elements and ions measured (not reported in Table 2).

Concentrations of ions reported for various locations in Turkey are depicted in Figure 2. Sea-salt species, namely Na+ and Cl- measured in our station have lower concentration than those measured in coastal sites in Turkey, i.e, Eastern Mediterrenean coast of Turkey (Gullu, Olmez et al. 1998; Kocak, Kubilay et al. 2004; Mihalopoulos et al. 2007; Öztürk and Tuncel 2009) and those measured in İstanbul (Theodosi, Im et al. 2010; Szigeti, Mihucz et al. 2012). This difference is probably due to larger distance between the Kırklareli station and the Black Sea coast, which is approximately 50 km. Fairly similar concentrations of sea salt elements were also reported for anoter Black Sea station, which is also not at the immediate vicinity of the coast (Karakaş and Tuncel 1997).

Crustal species, including Ca2+ and Mg2+ exhibeted lower concentrations among the all studies given in this paper. This is interesting and unexpected because bulk PM is collected in this study, hence contribution of crustal source is expected to be predominant (Hien, Binh et al. 2001). We have used soluble concentrations for comparison as only soluble forms of these elements are reported in the literature. Total Na, K, Mg and Ca concentrations determined by ICP-MS are compared with water soluble fractions of these elements determined by IC (Figure 4). Total Na and water soluble Na+ are strongly correlated with a slope of approximately unity, indicating that Na associated with particles in our samples is highly soluble. However total-to-soluble fraction ratio is 3.5 for Mg, 2.2 for K and 1.6 for Ca, indicating that they are not entirely soluble. Crustal enrichment factor (EFc) values are 1.8, 2.6 and 3.3 for K, Mg and Ca, respectively. Elevated total concentrations of

Table 2. Summary statistics of the species (ng m-3)

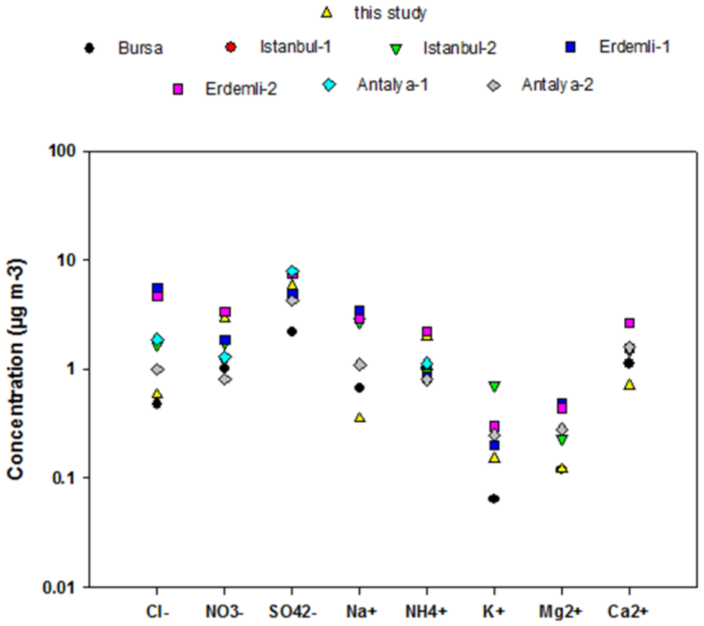
| | N[a] | Mean | STD[b] | Median | Min[c] | Max[d] |
|---|---|---|---|---|---|---|
| PM | 334 | 66000 | 75000 | 49000 | 1100 | 920000 |
| SO42- | 349 | 5800 | 2600 | 5600 | 340 | 16650 |
| NO3- | 348 | 2900 | 1800 | 2500 | 160 | 12000 |
| NH4+ | 350 | 2000 | 1300 | 1700 | 242 | 19220 |
| Al | 348 | 920 | 1050 | 520 | 4 | 6500 |
| Ca2+ | 349 | 700 | 620 | 520 | 40 | 5820 |
| Cl- | 333 | 580 | 770 | 320 | 1 | 8850 |
| Na+ | 349 | 350 | 450 | 180 | 2 | 4540 |
| K+ | 350 | 150 | 120 | 125 | 17 | 1330 |
| Mg2+ | 344 | 120 | 100 | 95 | 3 | 830 |

N[a] represents number of samples

STD[b] represents standard deviation

Min[c] represents minimum measured value

Max[d] represents maximum measured value



Bursa (Karakaş and Tuncel 1997), İstanbul-1 (Szigeti, Mihucz et al. 2012), İstanbul-2 (Theodosi, Im et al. 2010), Erdemli-1 (Kocak, Kubilay et al. 2007), Erdemli-2 (Kocak, Kubilay et al. 2004), Antalya-1 (Öztürk and Tuncel 2009) and Antalya-2 (Gullu, Olmez et al. 1998)

Figure 3. Comparison of measured ion concentration with other studies in Turkey

K, Mg and Ca and low EF values shows that these elements are mainly from crustal sources while soluble forms of these elements are not abundant in the geological profile of the region (Almeida, Freitas et al. 2006).

Levels of secondary pollutants, namely NO3-, SO42- and NH4+ are comparable and even higher than those reported at Eastern Mediterrenaean coast of Turkey and İstanbul. This is a very important finding of this study and indicates that our sampling station is under the influence of longe range/regional transport of these pollutants. As stated earlier our sampling station is located in a rural area very close to Turkish-Bulgarian border, there is no antropogenic sources in the immediate vicinity of the station and synoptic scale air flows arriving the station is mostly from N, NE and NW sectors. These sectors cover nearly all eastern and northern European countries that have numerous anthropogenic sources, e.g., power plants and industries.

Correlations between selected elements and ions are given in Figure 5. Sodium ion and Cl- have the highest correlation coefficient (r=0.86) between one another pointing to the sea salt source of these elements. This is also supported by the Cl-to-Na mass ratio, which, on the average, is 2.1 in our samples. Similarity of this value to Cl-to-Na ratio in bulk sea water, which is 1.8 (Seinfeld and Pandis 2006) also suggest a sea salt source for $Na^+$ and $Cl^-$ concentrations measured at our station.

Statistically significant correlations of Al with Mg2+ (r= 0.70), Ca2+ (r=0.76) and $K^+$ (r=0.36) shows that sources of these ions are mainly crust. However, Mg2+ also shows statistical significant correlation with Na+ (r=0.35) and Cl- (r=0.24) at 95% confidence level, suggesting that Mg2+ concentrations at Kırklareli are contributed by both sea salt and crustal material. Contribution of sea salt to observed Mg2+ is high in winter season when bubble bursting process is enhanced and less in summer, due to dominant influence of soil-related material in summer season because of the dry soil in this season. Potassium ion shows statistically significant correlation with Al due to its well-documented soil source. However, K is correlated with NH4+ (r=0.56), SO4 (r=0.46), NO3- (r=0.38) and Cl- (r=0.23), which have anthropogenic sources. Potassium is a well-known marker of biomass burning (Sciare, Bardouki et al. 2003), hence correlation between K+ and Cl- and these secondary pollutants implies that biomass burning activities contributes to observed NH4, NO3-, SO4 and Cl- concentration. Contribution of biogenic emissions on concentrations of these species are also reported in literature (Alves, Goncalves et al. 2010).

To determine the chemical forms of major ionic species exist in PM, simple regression between equivalent weights of significantly related ions are used. Regression equations are given in Table 3 with their corresponding spearman correlation coefficients at 95% confidence level. The high correlation between NH4 and SO4 with a slope of 0.68 indicates a high but incomplete neutralization of SO4 by NH4. Therefore major species formed by SO4 and NH4 are expected to be (NH4)2SO4 and NH4HSO4. Relatively small correlation with a slope of 0.13 between SO4 and Ca$^{+2}$ implies partial neutralization of SO4 by Ca$^{2+}$, and suggests that CaSO4 is also one of the species found in PM. NO3 is found in the form of (NH4)NO3 and NaNO3, while it is also partially neutralized by Ca$^{2+}$ and found as Ca(NO3)2. Na ion is existed mostly in the form of NaCl and NaNO3.

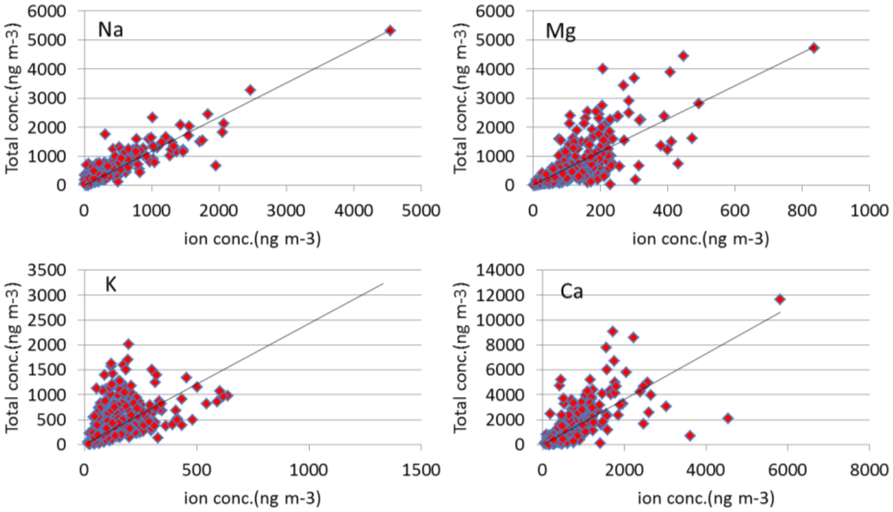


Figure 4. Relationship between total and water soluble elements of sodium, potassium, magnesium and calcium in PM

| | **PM** | **Al** | **Cl-** | **NO3-** | **SO4** | **Na+** | **NH4+** | **K+** | **Mg2+** | **Ca2+** |
|---|---|---|---|---|---|---|---|---|---|---|
| **PM** | 1.00 | | | | | | | | | |
| **Al** | 0.57 | 1.00 | | | | | | | | |
| **Cl-** | | | 1.00 | | | | | | | |
| **NO3-** | 0.21 | 0.19 | 0.47 | 1.00 | | | | | | |
| **SO4** | 0.12 | 0.20 | | 0.40 | 1.00 | | | | | |
| **Na+** | | | 0.86 | 0.51 | 0.11 | 1.00 | | | | |
| **NH4+** | 0.12 | 0.17 | | 0.50 | 0.82 | 0.11 | 1.00 | | | |
| **K+** | 0.11 | 0.36 | 0.23 | 0.38 | 0.46 | 0.22 | 0.56 | 1.00 | | |
| **Mg2+** | 0.47 | 0.70 | 0.24 | 0.30 | 0.35 | 0.35 | 0.34 | 0.38 | 1.00 | |
| **Ca2+** | 0.53 | 0.76 | | 0.36 | 0.36 | 0.20 | 0.40 | 0.38 | 0.79 | 1.00 |

Figure 5. Matrix of Spearman correlation coefficients (r) (n=309 complete cases) Note that only p values < 0.05 are showed

Table 3. Simple regression between ions with corresponding correlation coefficients

| **Regression equation** | **Spearman correlation coefficient (r)** |
|---|---|
| $NH_4^+ = 0.02679 + 0.6819 \times SO_4^{2-}$ | 0.82 |
| $NH_4^+ = 0.02679 + 0.3410 \times HSO_4^-$ | 0.82 |
| $NH_4^+ = 0.0506 + 1.2379 \times NO_3^-$ | 0.50 |
| $Na^+ = 0.0037 + 0.2475 \times NO_3^-$ | 0.51 |
| $Na^+ = 0.0017 + 0.8653 \times Cl^-$ | 0.86 |
| $Ca^{2+} = 0.01973 + 0.1270 \times SO_4^{2-}$ | 0.36 |
| $Ca^{2+} = 0.01465 + 0.4220 \times NO_3^-$ | 0.36 |
| $\sum \left( NH_4^+ + Ca^{2+} \right) = 0.04621 + 0.8110 \times SO_4^{2-}$ | 0.78 |
| $\sum \left( NH_4^+ + Ca^{2+} \right) = 0.06506 + 1.6623 \times NO_3^-$ | 0.52 |

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# CHEMICAL COMPOSITION OF EASTERN BLACK SEA AEROSOL – PRELIMINARY RESULTS

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## ABSTRACT

In this study, trace element composition of atmospheric particles collected at a high altitude site on the Black Sea coast of Turkey were investigated to understand atmospheric transport of pollutants to this semi-closed basin. Aerosol samples were collected at a Ministry of Forestry storage area located at approximately 5 km to the southwest of the Torul village. Daily coarse ($PM_{2.5-10}$) and fine ($PM_{2.5}$) aerosol samples were collected in 2011 using a "stacked filter unit". Collected samples were shipped to the Middle East Technical University at Ankara, where Na, Mg, Al, Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Ba, Pb and elemental carbon are measured. Comparison of measured concentrations of elements with corresponding data generated at other parts of Turkey demonstrated that concentrations of pollution derived elements are higher at Eastern Black Sea than their corresponding concentrations measured at other parts of Turkey. Trajectory analysis showed that these high concentrations are due to frequent transport of pollutants from north wind sector. A multivariate analysis was applied to understand types of sources affecting eastern Black Sea and trajectory statistics was used to understand locations of emission sources affecting our sampling point.

**Keywords:** Eastern Black Sea, Trace elements, atmospheric transport, aerosol

## 1. INTRODUCTION

Atmospheric particulate matter (PM) is composed of a mixture of solid and aqueous species which are emitted into the atmosphere both by human activity (anthropogenic) and natural sources. Since they interact with solar radiation and affect micro-meteorological processes, aerosols may affect radiative transfer and affect Earth's energy balance and hence climate (Cunningham and Zoller, 1981; Charsol et al., 1992). Due to the large number of natural and anthropogenic sources, aerosols may present diverse physical (size, surface, area, density, number) and chemical characteristics in different regions.

Therefore, identification of the sources of these is an important first step for air quality management. A receptor oriented multivariate statistical tool, namely, Positive Matrix Factorization (PMF), has been widely used in last two decades to identify the sources of atmospheric aerosol at receptors. (for example; Lee et al., 1999; Kim et al., 2004; Tecer et at.,2012)

There are very few studies (Hacisalihoğlu et al., 1992; Karakas et al., 2004; Tecer et al., 2012) related to chemical composition of Black Sea aerosol. In this study, we determined elemental composition of $PM_{2.5}$ and $PM_{2.5-10}$ aerosol size fractions at the eastern Black Sea region and applied statistical tools identify their possible sources.

## 2. MATERIALS AND METHODS

Coarse ($PM_{2.5-10}$) and fine ($PM_{2.5}$) aerosol samples were collected on polycarbonate (Nuclepore) filters using Gent Stacked Filter Unit (SFU) (Hopke et al., 1997) at a Ministry of Forestry, log storage area located at approximately 5 km to southwest of the Torul village, which is a small town with 12000 population (40°32’34”N 39°16’57”E) at the eastern Black Sea coast. The station is approximately 50 km from the coastline. The loading and unloading of the filters were done under twice HEPA filtered air in a clean area.

Collected samples were shipped to the Middle East Technical University at Ankara, where they were first re-weighted, using a Sartorius MC-5 microbalance, to determine $PM_{2.5}$ and $PM_{2.5-10}$ mass concentrations then analyzed for elemental carbon using a Magee Scientific, Model OT21 Transmissometer. Trace elements in samples, including Na, Mg, Al, Si, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Ba and Pb were analyzed by XRF using an Oxford ED–2000 energy dispersive X-Ray Spectrometer at Sarayköy research center of the Turkish Atomic Energy Agency (TAEK). The EDXRF was calibrated with spiked synthetic standards and accuracy of results were tested by running NIST SRM 2783 (Air Particulate Matter on Filter Media) along with samples.

## 3. RESULTS AND DISCUSSION

Average concentrations of measured 17 elements in the coarse ($PM_{2.5-10}$) and fine ($PM_{2.5}$) fractions are given in Table 1. Concentrations varied between approximately 1 ng $m^{-3}$ for As and 1800 $ng^{-3}$ for $SO_4^{2-}$. All parameters have right-skewed distributions. Chi square test demonstrated that most but not all are log-normally distributed.

Concentration of Na which is a good marker element for sea salt is fairly low due to 50 km distance between the station and coastline. Its concentration is higher in the coarse fraction as expected. Concentrations of soil-derived elements, including Al, Si, K, Ca, Ti, V and Fe are higher in the coarse fraction as soil particles have mass median diameter of approximately 3.0 to 3.5 μm (Kuloglu and Tuncel, 2005).

Concentrations of elements with mixed natural and anthropogenic sources, such as, Ti, V, Cr, Mn and Ni have generally higher concentrations in coarse fraction, which is understandable because part of their concentrations are due to presence of coarse soil particles.

Pollution-derived elements depicted interesting variations in terms of their coarse and fine fraction concentrations. Sulfate ion has higher concentration in the fine fraction, which is expected behavior for a secondary specie. However, other anthropogenic elements, including Cu, Zn, As and Pb have higher concentrations in coarse fraction. The reason for this unexpected behavior of anthropogenic elements is not known for the time being.

Table 1.Elemental average concentrations in the Black Sea PM (concentrations are in ng $m^{-3}$)

| | Average±SD | |
|---|---|---|
| | Coarse ($PM_{2.5-10}$) | Fine ($PM_{2.5}$) |
| Na | 88.0 ± 131.6 | 36.7 ± 30.7 |
| Mg | 225 ±611.6 | 69.9 ± 103.2 |
| Al | 695.3 ±1659.7 | 337.3 ± 347 |
| Si | 2063.4 ± 6026.4 | 630.7 ± 1081 |
| $SO_4$ | 274.3 ± 372.7 | 1809.5 ± 2509 |

| | | |
|---|---|---|
| K | 170.5 ± 273.9 | 123.5 ± 93.4 |
| Ca | 940.3 ± 2073.6 | 550.9 ± 781.8 |
| Ti | 915.2 ± 5759.6 | 96.6 ± 143.9 |
| V | 43.5 ± 211.5 | 4.4 ± 5.2 |
| Cr | 57.7 ± 202.9 | 39.4 ± 172.3 |
| Mn | 48.5 ± 160.6 | 14.5 ± 20.6 |
| Fe | 2435 ± 6385.7 | 1126.5 ± 1687.9 |
| Ni | 8.4 ± 7.2 | 8.6 ± 5.1 |
| Cu | 22.6 ± 32.2 | 14.6 ± 21.9 |
| Zn | 71.9 ± 315.4 | 28.4 ± 37.6 |
| As | 0.9 ± 0.4 | 1 ± 0.1 |
| Pb | 118.8 ± 5.16.4 | 13.1 ± 9 |

Seasonal variations in concentrations of measured elements are given in Table 2. Crustal elements like Al, Fe, Ca have higher concentrations in summer, due to easier resuspension of soil particles during dry summer season. Since soil is damp or ice covered in winter resuspension of local soil is less likely. This scenario results in higher concentrations of soil-related elements in winter. Similar seasonal pattern of crustal elements was also observed in most of the studies in the eastern Mediterranean region.

Sodium which is a marine element in most of the coastal studies has also higher concentrations in summer, suggesting a strong crustal contribution to its observed levels at our station.

Anthropogenic elements As, Pb, Cu and Zn have either comparable concentrations in both seasons, or have slightly higher concentrations in summer. Although concentrations of $SO_4^{2-}$, Cu and Zn are higher in summer the difference between their summer and winter concentrations are not as large as the difference observed in crustal elements.

Table 2.Seasonal average concentrations of elements (concentrations are in ng m$^{-3}$)

| | Coarse ($PM_{2.5-10}$) Average | | Fine ($PM_{2.5}$) Average | |
|---|---|---|---|---|
| | Summer | Winter | Summer | Winter |
| Na | 105.1 | 48.5 | 41.3 | 19.0 |
| Mg | 247.1 | 150.6 | 76.1 | 40.7 |
| Al | 754.9 | 484.0 | 371.0 | 188.9 |
| Si | 2521.5 | 829.9 | 711.0 | 283.7 |
| $SO_4$ | 311.8 | 210.5 | 1944.7 | 1671.6 |
| K | 181.8 | 132.6 | 133.4 | 100.1 |
| Ca | 1085.9 | 639.5 | 633.0 | 374.9 |
| Ti | 1139.5 | 85.2 | 108.9 | 55.0 |
| V | 60.7 | 8.3 | 5.8 | 3.0 |
| Cr | 114.5 | 11.7 | 75.5 | 10.2 |

| | | | | |
|---|---|---|---|---|
| Mn | 89.8 | 13.1 | 21.6 | 8.4 |
| Fe | 3635.8 | 1005.6 | 1702.7 | 632.7 |
| Ni | 9.6 | 6.8 | 10.2 | 5.4 |
| Cu | 26.1 | 18.6 | 18.9 | 9.8 |
| Zn | 95.0 | 23.7 | 34.8 | 17.7 |
| As | 1.1 | 0.7 | 1.0 | 0.0 |
| Pb | 13.3 | 435.3 | 13.7 | 10.4 |

Concentrations of $SO_4^{2-}$ and other elements measured in this study are compared with corresponding levels reported for other locations in the Eastern Mediterranean atmosphere. This comparison depicts some interesting features of the Eastern Black Sea aerosol. Sodium concentration at our station is the lowest in all studies shown in the table. Concentrations of sea salt elements at any site depend heavily on the distance of the station to coastline. In all studies shown in the table sampling location is very close to the sea, but our station in this work is 50 km from the Black Sea. This difference is the main reason for observed difference in Na concentrations in the table.

One interesting point in the table is unexpectedly high concentrations of crustal elements at the Eastern Black Sea (this work). Most of the stations in the Eastern Mediterranean (also in the Western Mediterranean) are under strong influence of dust transport from North Africa and thus expected to have higher levels of soil-related elements than sites in the Black Sea. Interestingly, concentrations of crustal elements like Al, Si, and Fe are among the highest in Table 3. At this point, sources of high concentrations of crustal elements are not clear. Transport from distant sources, like Sahara, or in this case, from Asian deserts can result in observed concentrations of crustal elements. Analysis of air mass Backtrajectories, which is not performed for the time being, will provide some information for the observed high levels of these elements.

Although our station is far from strong anthropogenic emission sources (nearest densely populated town is approximately 50 km away, strong industrial emissions are even further away), concentrations of pollution-derived elements, such as, Cu,

Table 3. Concentrations of trace elements and $SO_4^{2-}$ reported for different locations in the Eastern Mediterranean and Black Sea (concentrations are in ng $m^{-3}$)

| | THIS WORK | Bolu Turkey | Kirklareli Turkey | Antalya Turkey | Cyprus | Ashdod (Israel) | Beirut Lebanon | Northern Greece | Crete, Greece | Erdemli Turkey |
|---|---|---|---|---|---|---|---|---|---|---|
| Sampling Year | 2011 | 2011 | 2011 | 2001 | 2003 | 2005 | 2005 | 2001 | 2001 | 1999 |
| Na | 125 | 333 | 285 | 1476 | 1357 | 40172 | | | 2000 | 2900 |
| Mg | 400 | 218 | 470 | 371 | 189 | 692 | | 280 | 300 | 440 |
| Al | 1000 | 664 | 825 | 511 | 471 | 776 | | 667 | | 7500 |
| Si | 2700 | 1571 | 1835 | | 693 | 2300 | 4100 | 1604 | | |
| SO4 | 2100 | 7289 | 4194 | 6624 | 4500 | 1320 | 7700 | 2700 | 6900 | 7500 |
| K | 290 | 510 | 349 | 267 | 353 | 630 | 530 | 521 | 290 | 300 |
| Ca | 1500 | 2615 | 1203 | 968 | 1780 | 4655 | 6600 | 6775 | 1500 | 2700 |
| Ti | 1012 | 83 | 119 | 29 | 108 | 113 | 170 | 89.6 | | |
| V | 47.9 | 8 | 9 | 3 | | 38.5 | 174 | 5.5 | | |
| Cr | 98 | 37 | 35 | 4 | 6 | 21.8 | | 17.22 | | |
| Mn | 62 | 47 | 48 | 7 | 36 | 38 | 44 | 33.4 | | |
| Fe | 3566 | 1645 | 2370 | 297 | 470 | 1210 | 2200 | 1389 | | |
| Ni | 17 | 12 | 12 | 3 | | 14.5 | | 12.17 | | |
| Cu | 38 | 26 | 33 | | 6 | 14.2 | 61 | 36.2 | | |
| Zn | 100 | 95 | 92 | 10 | 12 | 165 | | 40.8 | | |
| As | 1.9 | 2 | 1 | 1 | | 0 | | 7.85 | | |
| Ba | 0 | 26 | 54 | | 19 | 0 | | | | |
| Pb | 132 | 44 | 23 | 19 | 26 | 49 | 170 | 20.37 | | |
| | | Tuncel unpublished data | | Öztürk et al 2012 | Bari et al 2009 | Mamane et al 2008 | Saliba et al 2007 | Samara et al 2005 | Bardouki et la 2003 | Koçak et al 2004 |

Zn, As, Pb, Ni, Cr are among the highest in the table, indicating that Eastern Black Sea atmosphere are under strong influence of pollution sources.

Concentrations of $SO_4^{2-}$ measured in the Eastern Mediterranean is on the average 2100 ± 2800 ng $m^{-3}$. This average value is smaller than $SO_4^{2-}$ concentrations reported for other sites in the table. It should be noted that, $SO_4^{2-}$ concentrations depends on the year samples were collected. This may be partly responsible for the low $SO_4^{2-}$ measured at our site in the year 2011.

### 3.1. Positive Matrix Factorization

Receptor-modeling techniques that incorporate the concentrations of aerosol components at a receptor site have been proved to be effective in resolving aerosol sources. Positive Matrix Factorization, PMF has been extensively used in source apportionment studies (Reff et al., 2007).

Positive Matrix Factorization (PMF) uses a weighted least-squares fit with the known error estimates of the elements of the data matrix used to derive the weights. PMF provides a solution that minimizes an object function, Q, based on uncertainties for each observation. With unknown source profiles, PMF minimizes the Q value, where $x_{ij}$ is the ambient concentration of species *j* in sample *i*, $f_{jk}$ is the factor loading of species *j* in source *k*, $g_{ik}$ is the factor score of source *k* in sample *i*, and $\sigma_{ij}$ is the uncertainty of ambient concentration of species *j* in sample *i (*Paatero and Tapper, 1994).

$$Q = \sum_{i=1}^{m} \sum_{j=1}^{n} \left( \frac{x_{ij} - \sum_{k=1}^{N} g_{ik} f_{jk}}{\sigma_{ij}} \right)^2$$

In this study, the uncertainties were estimated using the approach developed by Polissar et al. (2001) wherein the error estimates were set to 10% of the measured concentration plus the DL. Values below the DL were replaced by half of the DL, and their overall uncertainties were set at 5/6 of the DL values (Begum et al., 2005; Hammond et al., 2008). In this study PMF was applied to fine fraction aerosols and results shown in Figure 1.

Factor 1 explains approximately 80% of the variance for Fe and 40%-80% of the variances of anthropogenic elements such as, V, Mn, Ni, Cu and Zn. Although the profile factor is dominated by Fe and Ca, the source represented by Factor 1 is in anthropogenic nature. Anthropogenic sources of Fe can be associated with iron and steel industry (Gurzau et al., 2003; Ledoux et al., 2006; Moreno et al., 2006; Tsai et al., 2007). Factor scores for this factor showed that a clear seasonality, higher during winter months and lower towards summer. This indicates that sources should be close to the sampling site. Particles transported over long distances will removed from the atmosphere by wet scavenging during winter and hence, their concentrations are expected to be higher during dry summer season.

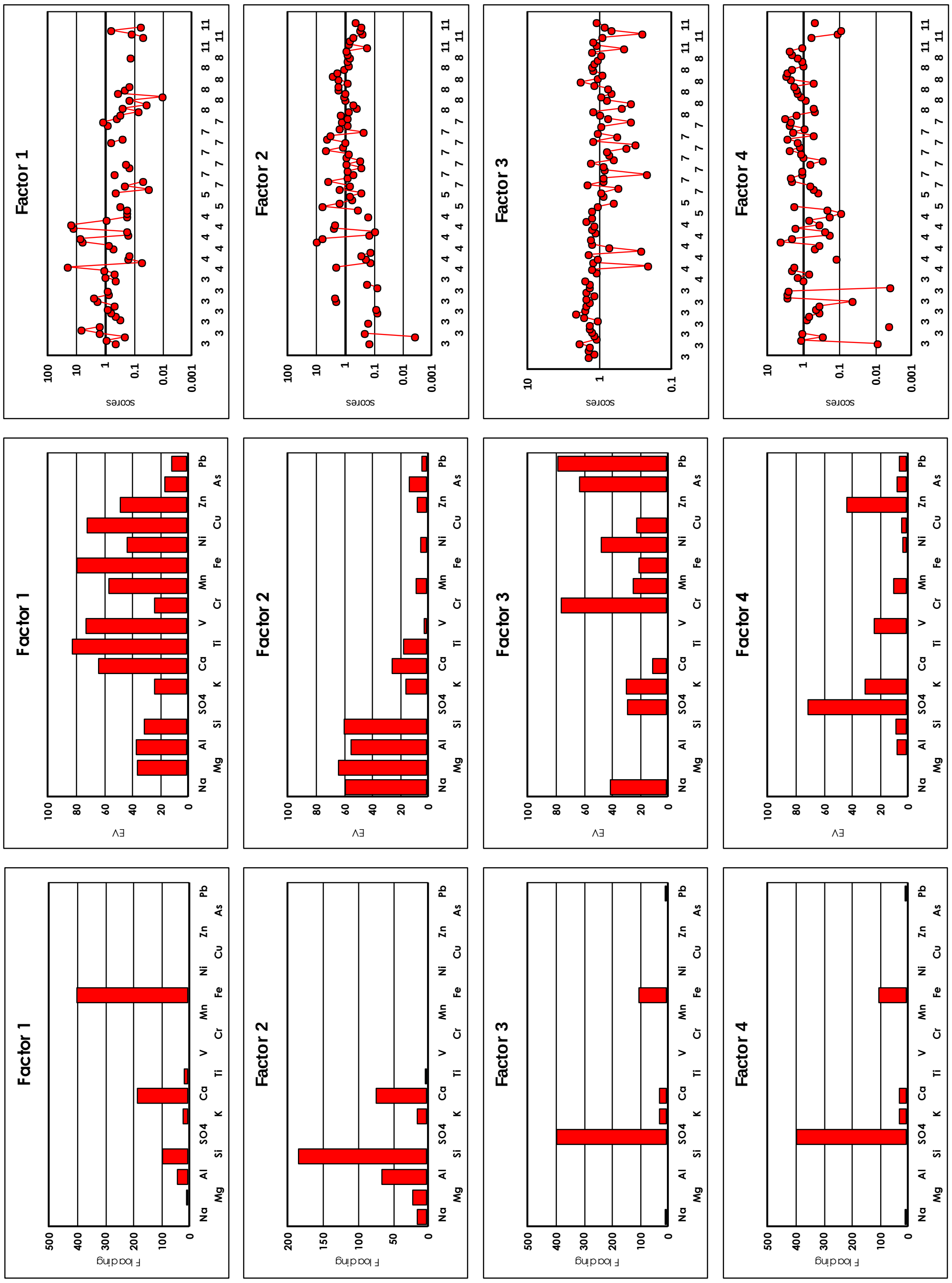

Figure 1.Factor-(F loading), explained variances (EV) ,g-scores in each factor with PMF

Factor 2 is a typical crustal factor. It accounts for most of the variance of lithophilic elements such as, Al and Si. Factor scores are higher at summer months. This is a mostly seen seasonal variation in crustal factors. Formation of crustal aerosol is only possible when the soil is not covered with ice or snow. Thus, during summer period, higher crustal dust contribution in the atmosphere is more likely as the soil is dry.

Factor 3 is seems like metallurgy industry. Most of the variances of Cr, Ni, As and Pb explained by Factor 3. Factor scores indicate high $SO_4$ concentrations but it is not accounted for variance of $SO_4$. Factor scores are slightly higher during summer months. Dzubay et al. (1984) indicated that this region is affected from metallurgy industries located in central part of Russia.

Factor 4 is identified as secondary $SO_4$ factor. $SO_4$ is the most important specie in Factor 4 profile as concentration. It explains almost approximately 70 % of the variance. Although less part of the variances of other species explained in this factor, presence of other anthropogenic elements reminiscent that they are formed from mixture of emissions from different sources during long range transport. There isn’t any distinct difference between summer and winter factor scores of this factor.

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# CHEMICAL-PHYSICAL CHARACTERIZATION OF URBAN PARTICULATE MATTER RANGING BETWEEN 10 NM AND 10 MM

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## ABSTRACT

This communication shows a complete chemical-physical characterization of the particulate matter in the range 10 nm to 10 µm. This task is important for understanding the effects of new technological processes on the evaluation of the air quality; simultaneously, it is not trivial considering the relative analytical implications. We will show how the main fraction of the aerosol average size distributions during different events in Rome both in winter and summer periods, is characterized by significant levels of PM2.5, especially in summertime, when the atmospheric stability conditions are numerically more than those in other period causing a pollutant accumulation: almost 75% of total PM10 fraction is PM2.5. A particular attention has been devoted to investigate the contribution of Ultrafine Particles (UFPs) on aerosol number concentration and their dynamic of formation: the trends of UFPs vs. NOx and of UFPs vs. total PAH show the primary origin of this pollutant and the narrow relationship between combustion processes and their presence in urban atmosphere. Particle formation in the nucleation mode was favoured in periods with high radical oxidative activity
About the chemical characterization we determined almost 30 elements in PM10, PM2.5 and PM1; after, we analyzed 4 different granulometric size below 100 nm for investigating the element distribution in particles extremely dangerous for the human health. An important issue of this communication regards the comparison of these data with previous measurements performed by the authors. In particular, the concentration level comparisons of OC/EC and PM2.5 (over the last two decades) and, mainly, of PM10 (over the 4 last decades) will be shown. All the samples were collected in downtown Rome; the UFPs were investigated by SMPS and FMPS analyzers (TSI, Shoreview, MN, USA) whereas the elements were determined by mean of Instrumental Nuclear Activation Analysis (INAA).

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# SPATIAL AND TEMPORAL VARIATIONS OF TRACE ELEMENT DEPOSITION FLUXES IN ALIAGA INDUSTRIAL REGION, TURKEY

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## ABSTRACT

The objective of the study was to determine the spatial and temporal variations of atmospheric bulk deposition and trace element deposition fluxes in Aliaga industrial region, Turkey. Sampling campaigns were conducted during four seasons at ten sampling sites between June 2009 and April 2010. The average sampling time was 30 day periods. The particular matter (PM) mass fluxes were determined by gravimetric analysis. Samples were analyzed for trace elements (Ag, Al, As, Ba, Ca, Cd, Cr, Co, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, V and Zn) using ICP-MS. Bulk deposition fluxes for all sampling periods and sites ranged from 53 to 1 761 mg $m^{-2}$ $day^{-1}$. The mean deposition rates of all areas were 403, 223, 306 and 352 mg $m^{-2}$ $day^{-1}$ for summer, autumn, winter and spring, respectively. Similar to mass fluxes, anthropogenic trace element fluxes were also higher at sites close to industrial activities. The highest elemental deposition fluxes measured in the study area were 31.9 (Ag), 19.3 (As), 72.2 (Cd), 308 (Cr), 13.5 (Co), 616 (Cu), 88 451 (Fe), 22.9 (Mo), 101 (Ni), 3 372 (Pb), 21.8 (Sb), 1.2 (Se), 61.9 (Sn), 51.1 (V) and 14 751 (Zn) µg $m^{-2}$ $day^{-1}$. The high fluxes observed for marker elements (i.e., Zn, Pb and Fe) of steel plants indicated their influence on the air quality in the area.

**Key Words:** Bulk deposition, trace elements, industrial region, Aliaga

## 1. INTRODUCTION

Atmospheric deposition is an important transfer process for atmospheric trace elements onto terrestrial surfaces. Studies on the atmospheric deposition of particulate matter and trace elements indicate two main sources; wind entrained soil and anthropogenic sources, i.e., fossil fuel combustion (V, Cr, Mo, Ni), traffic and road emissions (Cr, Mn, Fe, Co, Cu, Zn, Ba, Sb, Pb), metal production (Ag, As, Cd, Cu, Pb, Fe, Mn, Sn, Zn), non-ferrous metal production (Cu, Zn, Cd) and residential heating (As, K, Sb, Se) (Schauer et al., 1996; Pacyna and Pacyna, 2001; Bilos et al., 2001; Kara et al., 2011). Trace elements are widely dispersed in the environment (air, water and soil compartments) and their interaction with different natural components may result in harmful effects on the biosphere.

The magnitude of atmospheric deposition and the ratio of wet to dry deposition are controlled by emission sources, distance of emission sources to receptor site and meteorological conditions, e.g. prevailing wind directions, wind speed, frequency and amount of precipitation. Since both wet and dry deposition may contribute significantly to total deposition, it appears essential to include both wet and dry deposition in loading estimates by atmospheric deposition. The characterization of bulk deposition is important for identifying the variability and sources of the atmospheric pollutants (Odabasi et al, 2002; Avila and Rodrigo, 2004; Azimi et al, 2005; Motelay-Massei et al., 2005). During the past few decades, many studies on bulk (wet and dry) deposition of trace elements in urban or industrial areas have been widely used to estimate the influence of atmospheric inputs of trace elements to the environments compartments (Wong et al., 2003; Dundar, 2006; Naddafi et al, 2006; Papaefthymiou and Anousis, 2006; Sharma et al., 2008; Balakrishna and Pervez, 2009; Wang et al, 2009; Mizij et al, 2010).

The objective of this study was to investigate the spatial and seasonal variations of the deposition fluxes of particulate matter and trace elements (Ag, Al, As, Ba, Ca, Cd, Cr, Co, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, V and Zn) in Aliaga industrial region in Turkey.

## 2. MATERIALS and METHODS

### 2.1. Study Area

The study area of the present work (Aliaga industrial region, Izmir, Turkey, located ~50 km north of Izmir) contains several pollutant sources including a large petroleum refinery and a petrochemical complex, scrap processing iron-steel plants with electric arc furnaces (EAFs), scrap storage and classification sites, steel rolling mills, a natural gas-fired power plant, a very dense transportation activity of ferrous scrap trucks, heavy road and rail traffic, a ship dismantling area, and busy ports with scrap iron dockyards. The monthly average temperature in the area ranged between 2.6-6.2 °C in winter and between 23.2-25.4 °C in summer. The annual average precipitation is 676 mm. The prevailing winds are north and easterly. Aliaga has a typical Mediterranean climate characterized by hot, dry summers and cool, wet winters. General view of the region and locations of the sampling sites are shown in Figure 1.

### 2.2. Sample Collection and Analysis

The bulk deposition samples were collected using open polyethylene cylinder samplers (26 cm diameter and 30 cm height) with collecting chamber fitted on a stand at about 2 m above the ground. Both dry and wet particulate depositions were collected continuously for 30 day periods. Sampling campaigns were conducted during four seasons at ten sampling sites in Aliaga between June 2009 and April 2010. After the sampling, the samplers were rinsed with to complete transfer of PM from collecting chamber. The particulate matter mass fluxes were determined by gravimetric analysis after the water content in the sample was evaporated in the laboratory.

The samples were acid digested using a nitric acid ($HNO_3$) and hydrochloric acid (HCl) mixture. Digested samples were diluted to 100 ml with deionized water and filtered through a 0.45 µm PTFE filter. Samples were analyzed for trace elements (Ag, Al, As, Ba, Ca, Cd, Cr, Co, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, V and Zn) using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS).

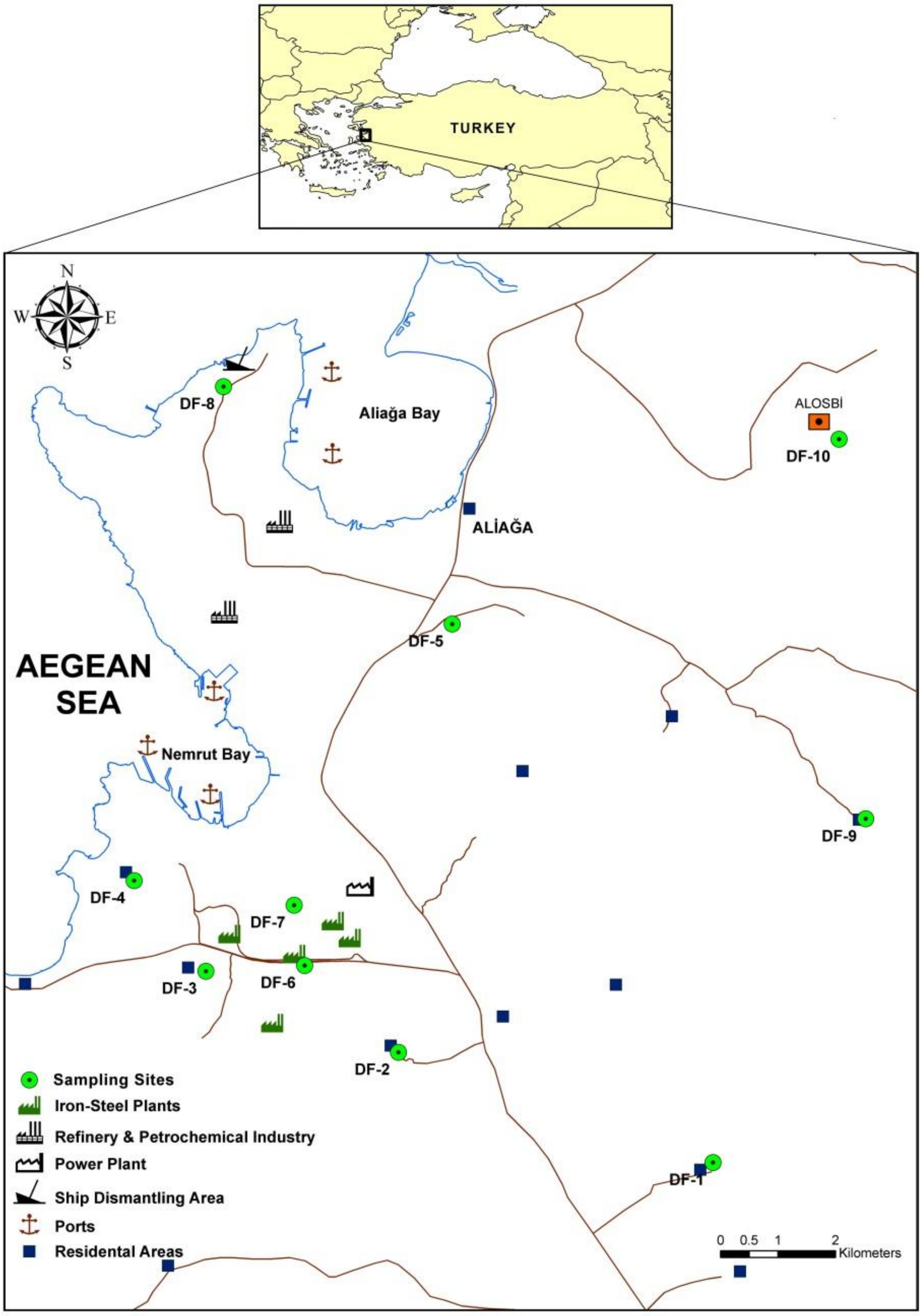

**Figure 1.** General view of Aliaga industrial region and sampling sites

## 3. RESULTS

Atmospheric deposition samples were collected from June 2009 to April 2010 at four seasons (summer, autumn, winter and spring) at ten sites in Aliaga region (city center, ship dismantling area, steel production area, organized industrial zone, coal plants area, and four villages in the region). Samples were analyzed for trace elements (Ag, Al, As, Ba, Ca, Cd, Cr, Co, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, V and Zn) and their bulk deposition fluxes were determined.

### 3.1. Atmospheric Bulk Deposition Fluxes

The seasonal bulk deposition fluxes for all sampling sites measured in this study are presented in Table 1 and the spatial variations of deposition fluxes are given in Figure 2. Spatial deposition fluxes at the sampling sites varied widely. This may be attributed mainly to variations of pollutant sources, distances of emissions sources to sampling sites, and meteorological parameters (i.e., temperature, wind direction and speed, mixing height). The bulk deposition fluxes of the sites within the industrial region such as steel production area, coal plants area, Horozgedigi and ship dismantling area ranged between 241 and 1 761 mg $m^{-2}$ $day^{-1}$ as the highest values were measured at steel production area. The average deposition fluxes were measured as 219, 214, 204 and 169 mg $m^{-2}$ $day^{-1}$ at Helvacı, Aliaga city center, Bozkoy and Cakmaklı villages, respectively. The smallest values were observed at Citak site that could be defined as a background sites which was not affected from industrial source.

**Table 1.** The seasonal variations of PM bulk deposition fluxes (mg $m^{-2}$ $day^{-1}$) at all sites

| | | **PM bulk deposition fluxes** | | | |
|---|---|---|---|---|---|
| **Code** | **Name** | **Summer** | **Autumn** | **Winter** | **Spring** |
| DF-1 | Helvacı | 256 | 198 | 147 | 275 |
| DF-2 | Bozkoy | 195 | 169 | 207 | 244 |
| DF-3 | Horozgedigi | 307 | 287 | 354 | 572 |
| DF-4 | Cakmakli | 156 | 108 | 195 | 217 |
| DF-5 | Aliaga city center | 216 | 175 | 152 | 311 |
| DF-6 | Steel Production Area | 687 | 520 | 646 | 823 |
| DF-7 | Coal plants area | 1 761 | 395 | 705 | 384 |
| DF-8 | Ship dismantling area | 258 | 241 | 370 | 385 |
| DF-9 | Cıtak | 97 | 86 | 95 | 95 |
| DF-10 | Aliaga OIZ | 100 | 53 | 186 | 210 |

### 3.2. Elemental Deposition Fluxes

The average daily trace elements deposition fluxes (µg $m^{-2}$ $day^{-1}$) for all sampling sites showed that the most abundant element was Ca (26 431), followed by Fe (14 974), Na (5 205), Mg (3 536), Al (2 968), K (2 359), Zn (2 189), Mn (632), Pb (467), Ba (133), Cu (113), Sr (64), Cr (58), Ni (25), V (17), Cd (10), Sn (10), As (5), Ag (4.9), Co (3.8), Mo (3.7), Sb (3.2) and Se (0.4). This order of elemental abundance is similar to those already obtained for bulk deposition in other studies (Sandroni and Migon, 2002; Wong et al., 2003; Motelay-Massei et al., 2005; Sharma et al., 2008). Average daily trace elemental deposition fluxes for all sampling sites are given in Table 2.

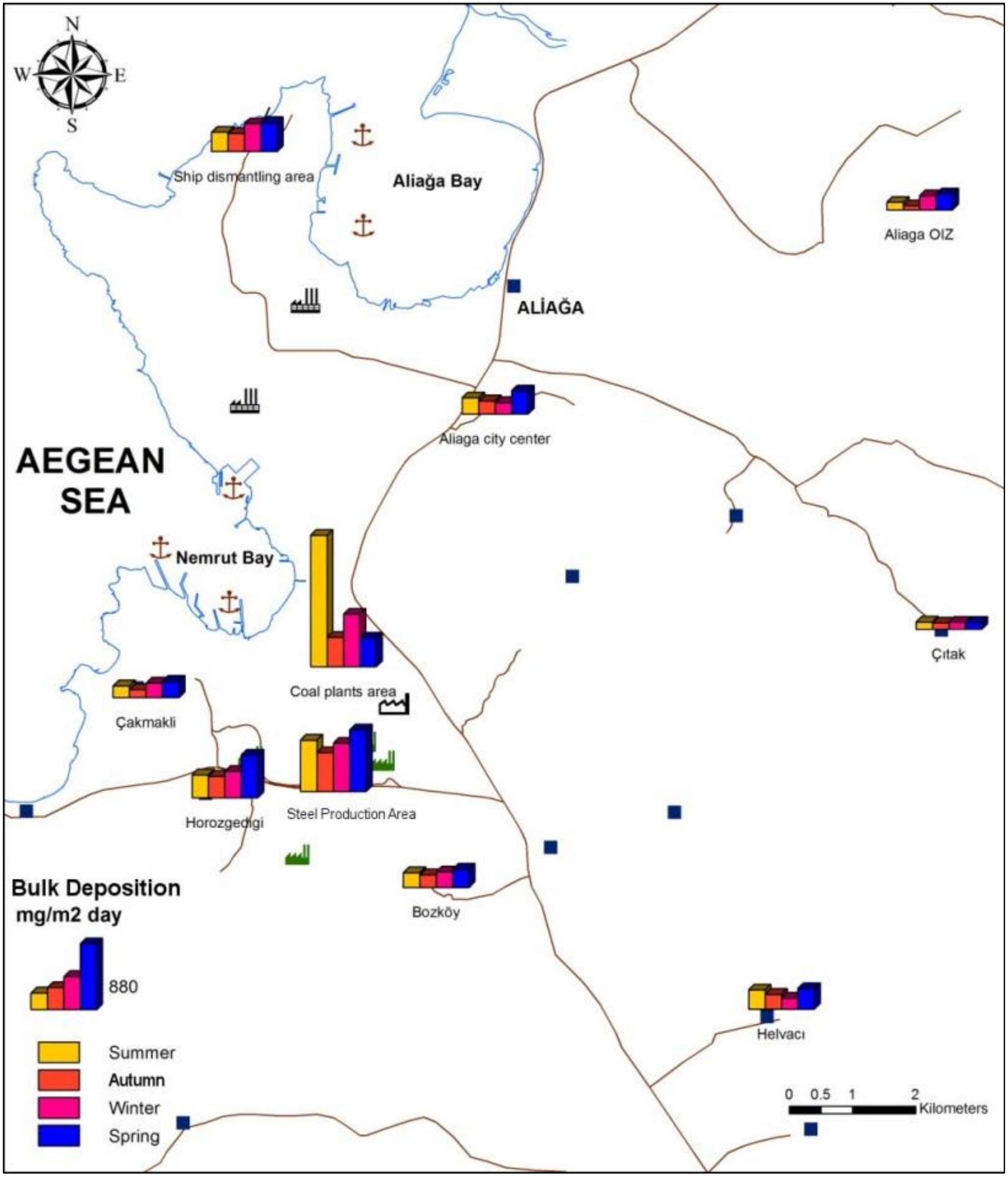

**Figure 2.** The spatial variations of PM deposition fluxes at all sampling sites

In general, trace element deposition fluxes (µg m$^{-2}$ day$^{-1}$) showed large variations between different sampling locations due to differences in source distances, wind speed and direction and presence of local sources. As expected the deposition values were highest at the steel production site, being 88 451, 14 570, 3 125, 2 018, 616, 308, 101, 72, 62, 14, 32 and 22 µg m$^{-2}$ day$^{-1}$ for Fe, Zn, Mn, Pb, Cu, Cr, Ni, Cd, Sn, Co, Ag and Sb, respectively. High deposition values of Fe, Mn, Zn, Pb, Cu, Cd, Sn and Ag in samples at this site could be attributed the emissions from the electric arc furnaces of steel production and steel rolling mills. The most significant correlations between elements ($p<0.05$) were Pb-Zn ($r=0.99$), Ag-Zn ($r=0.99$), Pb-Sn ($r=0.99$), Pb-Ag ($r=0.98$) and Ag-Sn (0.99) since these are marker elements of steel production from ferrous scrap.

The different trends in the maximum fluxes were found among the 23 trace elements, but for most of the elements the maximum values were observed in winter (January) and spring (April). The minimum values for most of the elements were measured during summer (July) or autumn (October). In general, seasonal variations of trace elements in bulk deposition fluxes are associated with the nature of the sites, so seasonal trends showed differences for each element. Specially, when the significant alterations are not observed in elemental fluxes at sampling sites within the industrial sources, the element deposition flux values at other sites significantly depended on the seasons.

**Table 2.** Average daily trace elements deposition fluxes (µg m$^{-2}$ day$^{-1}$) for all sampling sites

| **Location** | **Ca** | **Mg** | **Na** | **Fe** | **K** | **Al** | **Zn** | **Mn** | **Pb** | **Ba** |
|---|---|---|---|---|---|---|---|---|---|---|
| Helvacı | 15 021 | 3 288 | 5 874 | 2 153 | 5 940 | 1 061 | 353 | 95 | 61 | 39 |
| Bozköy | 17 931 | 2 188 | 6 582 | 6 920 | 2 146 | 1 800 | 1193 | 336 | 228 | 91 |
| Horozgediği | 38 128 | 5 439 | 4 171 | 17 412 | 1 903 | 4 635 | 3090 | 972 | 609 | 179 |
| Çakmaklı | 15 249 | 1 497 | 3 308 | 5 739 | 1 051 | 1 480 | 572 | 212 | 109 | 70 |
| Aliaga City | 15 171 | 3 185 | 5 437 | 3 719 | 4 591 | 1 749 | 208 | 105 | 41 | 44 |
| Steel Prod. | 65 151 | 8 847 | 6 575 | 66 561 | 2 553 | 7 607 | 10 380 | 2 786 | 2 319 | 384 |
| Coal Plants | 56 380 | 6 345 | 7 971 | 27 876 | 2 240 | 6 331 | 4 744 | 1 425 | 1 039 | 276 |
| Ship Dismant. | 27 853 | 2 545 | 5 186 | 15 925 | 1 170 | 3 335 | 645 | 276 | 164 | 192 |
| Çıtak | 6 110 | 850 | 2 706 | 1 215 | 957 | 764 | 116 | 30 | 24 | 22 |
| Aliaga OIZ | 7 321 | 1 179 | 4 238 | 2 224 | 1 043 | 915 | 590 | 83 | 79 | 36 |

| **Location** | **Sr** | **Cu** | **Cr** | **V** | **Ni** | **Cd** | **Sn** | **As** | **Co** | **Mo** | **Ag** | **Sb** | **Se** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Helvacı | 73 | 19 | 8.3 | 5.5 | 7.0 | 1.3 | 1.6 | 2.2 | 3.9 | 0.8 | 0.8 | 0.5 | 0.2 |
| Bozköy | 40 | 49 | 29.4 | 9.4 | 13.1 | 4.9 | 5.7 | 3.2 | 1.9 | 2.4 | 2.2 | 2.0 | 0.3 |
| Horozgediği | 67 | 135 | 75.8 | 21.2 | 44.6 | 13.4 | 12.2 | 6.5 | 4.4 | 4.4 | 5.8 | 3.9 | 0.6 |
| Çakmaklı | 36 | 38 | 18.6 | 11.0 | 13.8 | 2.2 | 3.8 | 3.1 | 1.9 | 1.8 | 1.2 | 1.9 | 0.2 |
| Aliaga City | 53 | 30 | 10.0 | 11.9 | 18.2 | 0.8 | 1.9 | 3.2 | 2.0 | 1.3 | 0.6 | 0.5 | 0.2 |
| Steel Prod. | 131 | 424 | 266 | 44.2 | 78.2 | 52.2 | 46.2 | 12.3 | 10.5 | 17.1 | 22.2 | 14.4 | 1.1 |
| Coal Plants | 127 | 161 | 125 | 35.2 | 40.9 | 21.3 | 19.1 | 12.4 | 7.0 | 5.2 | 11.4 | 4.5 | 0.7 |
| Ship Dismant. | 64 | 234 | 24.5 | 21.0 | 21.0 | 3.0 | 7.4 | 4.4 | 4.3 | 2.8 | 3.0 | 3.0 | 0.2 |
| Çıtak | 23 | 19 | 4.7 | 3.6 | 2.4 | 0.4 | 0.5 | 1.2 | 0.7 | 0.4 | 0.3 | 0.3 | 0.2 |
| Aliaga OIZ | 27 | 19 | 15.4 | 4.7 | 7.3 | 2.6 | 1.7 | 1.3 | 1.0 | 0.7 | 0.9 | 0.5 | 0.2 |

The annual trace element deposition fluxes averaged for all sampling sites in this study compared with element deposition fluxes reported by the previous studies in Table 3. In general, for most of the elements, the average fluxes measured in the present study were higher than those reported previously for urban and rural areas. The marker elements of steel production (Fe, Zn, Mn, Pb) were significantly higher in this study. Also, fluxes (Cu, Cr, V, Ni, Cd) trace elements of anthropogenic origin were 2-3 times higher than those reported for different regions. The results for As, Co and Mo were similar to those measured in Xi'an, an important industrial center of the central-northwest region, China (Cao et al., 2011).

**Table 3.** Annual trace element deposition fluxes (mg $m^{-2}$ $year^{-1}$) in different regions

| | **Xi'an, China** [a] | **Belgrade, Serbia** [b] | **Pearl River Delta, China** [c] | **Nice, France** [d] | **Nagasaki, Japan** [e] | **Zemaitija, Lithuania** [f] | **Aliaga, Turkey** |
|---|---|---|---|---|---|---|---|
| Fe | | 594 | 555 | | | 98 | 5 466 |
| Al | | 329 | | 141 | 166 | | 1 083 |
| Zn | 51 | 41 | 104 | 41 | | 37 | 799 |
| Mn | 47 | 26 | 9.0 | | 14 | 7.6 | 231 |
| Pb | 18 | 22 | 13 | | 7.7 | 8.1 | 171 |
| Cu | 7.7 | 35 | 19 | 1.3 | 4.2 | 6.0 | 41 |
| Cr | | 1.6 | 6.4 | 0.60 | 4.6 | 0.50 | 21 |
| V | 6.9 | 20 | 2.1 | | 1.2 | | 6.1 |
| Ni | 4.4 | 11 | 8.4 | 1.1 | 4.5 | 2.6 | 9.0 |
| Cd | | 0.22 | 0.07 | 0.06 | 0.29 | 0.21 | 3.7 |
| As | 2.6 | | | | 1.3 | 0.34 | 1.8 |
| Co | 1.5 | | 0.19 | | | | 1.4 |
| Mo | 1.4 | | | | | | 1.3 |

[a] Cao et al., 2011

[b] Mijic et al., 2010

[c] Wong et al., 2003

[d] Sandroni and Migon, 2002

[e] Sakata and Asakura, 2011

[f] Kvietkus et al., 2011

## 4. CONCLUSION

The present study aimed to characterize the atmospheric fluxes of PM and trace elements (Ag, Al, As, Ba, Ca, Cd, Cr, Co, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, V and Zn) in Aliaga region for four seasons between June 2009 and April 2010. Annual bulk deposition fluxes of trace elements were significantly higher than those measured in the other studies around the world, reflecting the strong anthropogenic inputs by industrial activities in the Aliaga region. These results showed that the elemental pollution is significant in the region and that the monitoring of elemental levels is needed.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# INFLUENCE OF ENVIRONMENTAL PARAMETERS; THERMAL, IRRADIANCE, AND DUST ON SOME INORGANIC SOLAR CELL

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## ABSTRACT

This study conducted a series of systematic experimental measurements to investigate the irradiance and temperature performance of CdS/$Cu_2S$ solar cell and to determine the influence of dust on the efficiency of crystalline silicon solar cell. The decrease in short circuit current and open circuit voltage with variation in irradiance (9953-117100 Lux) of a clear summer day and temperature (31-36°C) was 90% and 19%, respectively. The decrease of output power with variation of irradiance and temperature is 92%. The accumulation of dust on the surface of crystal Si solar cell at a heavy commercial activities street is investigated. Results show that the presence of dust has a considerable effect on the performance of crystalline silicon solar cell.

**Keywords:** Photovoltaic, irradiance, temperature, dust

## INTRODUCTION

In recent decades, air quality at the local, regional, and even worldwide level has received great attention from scientists, policy makers, and the general public alike (Panis et al., 2006). The increased industrialization and economic activity as well as the high population density constitute the prime causes for the increased levels of air pollution. The two most commonly observed types of air pollutants; high concentrations of particulate matter and gaseous pollutants are mainly deriving from the combustion of fossil fuels and industrial processes (Nastos et al., 2006).

In this regard, renewable energy resources appear to be the one of the most efficient and effective solutions. Among the many types of renewable energy solar energy is considered promising, since it is comparatively more evenly distributed geographically (George et al., 1999). A branch of solar energy research that has received worldwide attention is photovoltaic (PV). Solar photovoltaic (PV) modules convert solar energy directly into electricity and bring about environmental benefits such as greenhouse gas and air pollution reduction, all with minimal maintenance requirements (Tsoutsos et al., 2005). Residential, vehicular, space and aircraft are the main fields of solar energy applications (Khaligh and Onar, 2010). In order to establish PVs as a commercially competitive technology, high attention should be paid to the factors which affect their energy performance (Gan, 2009). In this context, a part from the variation of the solar radiation intensity, which is the main factor affecting the PV-modules' output, reductions up to 15% on PVs' energy production may also be the result of several other parameters such as; temperature, angle of incidence, ageing, soil, snow, and partial shading (Thevenard, 2005).

In addition, the dust accumulate on the surface of the solar cell can cause a significant degradation in the efficiency of the solar cell and may considerably reduce the amount of solar energy absorbed by the panels mainly due to the increased reflection which leads to the reduction of the incident solar irradiance on the PV-cell (Biryukov, 1998**)**. Furthermore, the dust accumulation may indirectly influence the rate of heat transfer between the PV and the environment through convection in a negative way (Kappos et al., 1996). Although dust effects depend on local conditions such as the presence of air pollution, frequency of rain, wind speed, humidity, as well as the panels' orientation and inclination, certain attempts have been made to determine the influence of dust on the performance of PV-panels (Al-Hasan and Ghoneim, 2005).

In this context, investigation of the dust effects on the performance of PV modules becomes of special interest, especially in the case of an urban environment heavily aggravated from air pollution. The temperature is another significant factor that strongly affects the PV cell efficiency and performance (Mattei et al., 2006). The physical properties that change with temperature are the band gap, the minority-carrier life time, built-in voltage drop, the potential barrier of the p-n junction of the solar cell, and the separation ability of the junction (Radziemska and Klugmann, 2002). Therefore, the present study focuses on the influence of some environmental parameters such as; irradiance, temperature, and dust on the characteristics and performance of some inorganic solar cells.

## EXPERIMENTAL METHODOLOGY

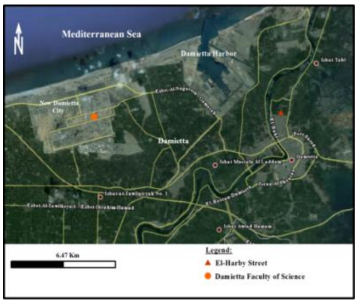
In this study, the influence of some air pollutants, namely; dust, temperature, and humidity on the characteristics of $CdS/Cu_2S$ and crystalline Si solar cell was investigated.

### Irradiance and Temperature Performance of $CdS/Cu_2S$ Solar Cell and (In/c-Si/Al)

In this study, the current-voltage (I-V) characteristics of cadmium sulfide/copper sulfide ($CdS/Cu_2S$) solar cell with area of $5cm^2$ was investigated in dark and under different light intensities from 462 to 5600 Lux in a clean laboratory environment. Stabilized power supply and high impedance electrometers (Keithley 617) were used, while the illumination source was an ordinary tungsten filament lamp. The intensity of the light was recorded using a calibrated digital light meter (Lutron-Model LX-107). In addition, the variation of $CdS/Cu_2S$ characteristics with change in irradiance and temperature during the time period of a day of 25/7/2010 and of three months (June, July, and August) was investigated under field conditions on the roof of the Faculty of Science, New Damietta, Egypt (Map1). The cell was mounted horizontally on a designed stand and placed on the roof. The current-voltage (I-V) characteristics of $CdS/Cu_2S$ solar cell were measured every two hours throughout the day to establish a base line for daily irradiance, later measurements were limited to the time of peak irradiance (1PM) through one day of the three months. The temperature was measured using Chromel-Alumel thermocouple connected to a thermometer.

### Investigate the Influence of Dust on Crystalline Si Solar Cell at Al-Harby Street

The influence of dust on characteristics of crystalline silicon solar cell was investigated at Al-Harby Street in Damietta city, Egypt (Map 1), from January to March 2011. It is characterized by heavy commercial activities, furniture workshops, and heavy traffic flow. The crystalline Si solar cell with an area of $2.83cm^2$ was mounted in a cubic glass test box with dimensions of $15 \times 15 \times 15$ $cm^3$, and was placed at 6 ±2 m height at rooftop level subjected to the atmosphere of Al-Harby street. The cubic box was designed with a configuration which allowed the entry of dust into the box using a suction pump. The concentration of dust accumulate on the surface of the solar cell is measured in microgram per cubic meter ($\mu g/m^3$). The dust samples were collected on a membrane filter (0.45µm), using an open face holder connected to the sampling pump operating for 24hr. The flow rate of the pumps was calibrated to 4 L/min (Katz, 1986). The humidity and the temperature of the atmosphere were recorded during all tests.



**Map 1** Location map of the study

## EXPERIMENTAL RESULTS ANALYSIS AND DISCUSSION

### Effect of Irradiance on $CdS/Cu_2S$ Solar Cell at the laboratory

The current–voltage characteristics of $CdS/Cu_2S$ solar cell in the dark and under different light intensity conditions are shown in fig.(1). The current value at a given voltage for $CdS/Cu_2S$ solar cell under illumination is higher than that in the dark. This indicates that the light generates carrier-contributing photocurrent due to the production of electron-hole pairs as a result of the light absorption (El-Nahass et al., 2005). In spite that the forward current was greater than the reverse current, the effect of solar irradiation on the reverse current was much more pronounced than that on the forward current. The $I_{sc}$ is proportional to the illumination intensity and the applied voltage. In reverse, bias region, $I_{sc}$ is independent of applied voltage. Increasing light intensity from 462 to 5600 Lux, the open circuit voltage and short circuit current in $CdS/Cu_2S$ solar cell increased from 0.39 to 0.48V and from 7 to 73.97mA, respectively, as shown in fig.(2). However, Gupta et al. (2002) investigated the effect of illumination intensity on the I-V characteristics of n-C/p-Si heterojunction solar cell. The $I_{sc}$ was found to be proportional to the illumination intensity and was independent of the applied voltage. Figure (3) illustrates a linear increase in short circuit current density ($J_{sc}$) of the $CdS/Cu_2S$ solar cell with the increase in light intensity. This is due to the increase in the number of photo-generated carriers occurring in a semiconductor with the increase of light intensity. The relationship between light intensity ($P_{in}$) and short circuit current density for $CdS/Cu_2S$ may be expressed by the following equation:

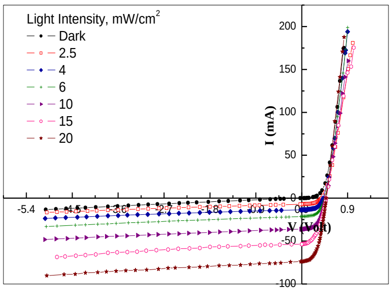


**Fig.1** I–V characteristics of $CdS/Cu_2S$ solar cell at different illumination intensities.

$$J_{sc}\,(CdS/Cu_2S \text{ solar cell}) = 0.34+0.003\,P_{in} \qquad (1)$$

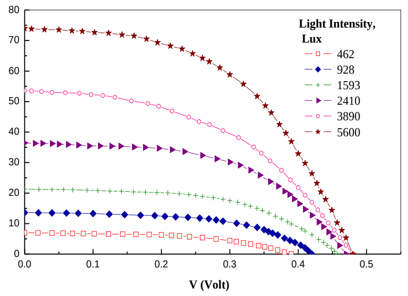


**Fig.2** Current-voltage curves of maximum power region for CdS/$Cu_2S$ solar cell under different illumination intensities

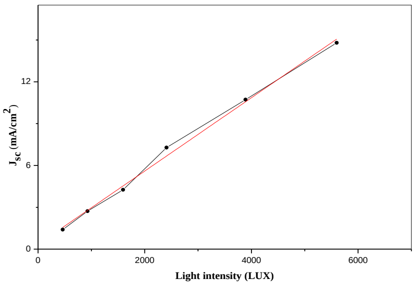


**Fig.3** Variation of $J_{sc}$ with light intensity for CdS/$Cu_2S$ solar cell under different illumination intensities

This is in agreement with Anuforom et al. (1987) who reported that the short-circuit current of silicon solar cells exposed to changes in intensity of solar radiation under tropical atmospheric conditions in Nigeria increases non-linearly with intensity of solar radiation. Figure (4) shows that $V_{oc}$ of the CdS/$Cu_2S$ solar cell increases non-linearity with increasing light intensity. The maximum power $P_m$ of CdS/$Cu_2S$ solar cell increases from 1.36 to 17.77mW with the increase of light intensity (Fig.5). Whereas, fig.(6) illustrates a linear increase in maximum power ($P_m$) of the CdS/$Cu_2S$ solar cell with increase light intensity ($P_{in}$), the relationship may be expressed by the following equation:

$$P_m(\text{CdS/Cu}_2\text{S solar cell}) = 0.05 + 6.46\times10^{-4}\, P_{in} \tag{2}$$

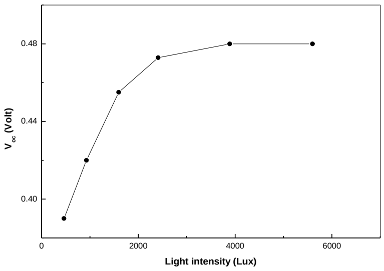


**Fig.4** $V_{oc}$ versus light intensity for CdS/$Cu_2S$ solar cell under different illumination intensities

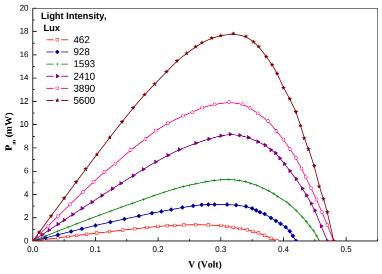


**Fig.5** Output power versus voltage of CdS/$Cu_2S$ solar cell under different illumination intensities

This finding is in agreement with Tian et al. (2007) who observed that the dimming of solar radiation in the urban environment was the main reason for the decrease of PV module output using the climatic data of urban and rural sites in Mexico City for year 2003. Moreover, Amin et al. (2009) investigated the effects of irradiance level change on the output power of monocrystalline silicon solar cells and observed that the output power of these cells increased with solar irradiance.

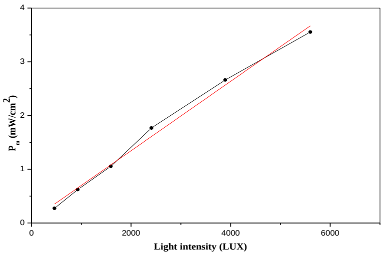


**Fig.6** $P_m$ versus light intensity for CdS/$Cu_2S$ solar cell under different illumination intensities

### Effect of Irradiance and Temperature on CdS/Cu$_2$S Cell on Roof of the Faculty

Figure (7) shows the variation of I-V characteristics curves of CdS/Cu$_2$S solar cell under the influence of irradiance (9953-117100 Lux) on a clear summer day and solar cell temperature in the range (31-36°C). The influence of irradiance and temperature on short circuit current was much more remarkable than an open circuit voltage. The decrease in short circuit current and open circuit voltage with variation in irradiance and temperature was 90% and 19%, respectively. The variation of short circuit current and open circuit voltage with irradiance and temperature influenced the output power of a solar cell. The output power of a solar cell varied along the hours of a day depending on irradiance and temperature as shown in fig.(8). The highest output power was attained at 1PM. The decrease of output power with variation of irradiance and temperature was 92%.

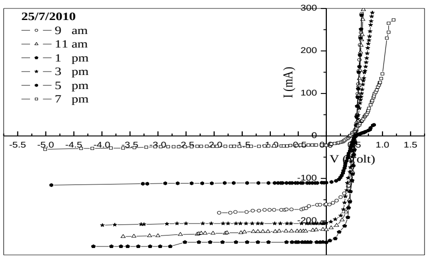


**Fig.7** I-V characteristics of CdS/Cu$_2$S solar cell under different irradiance and temperature of a clear summer day (25/7/2010)

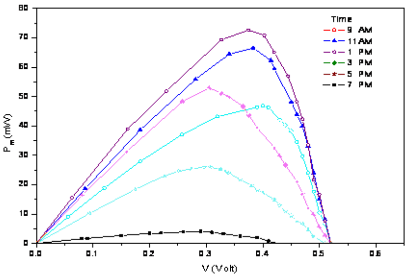


**Fig.8** Output power versus voltage of CdS/Cu$_2$S solar cell under different irradiance and temperature of a clear summer day (25/7/2010)

Figure (9) shows the influence of irradiance and temperature on (I-V) characteristics of CdS/Cu$_2$S solar cell through the study period (Table 1). The temperature was constant at 32°C and the irradiance showed a little variation during the test at the 15th of June (1PM) and July. Table (1) and fig.(9) show stability of the characteristics under these conditions. At 1PM of the 4th of August; the temperature increased to 35°C and irradiance decreased to 113300Lux, the short circuit current and maximum power was observed to decrease while open circuit voltage had no variation. The decrease in maximum output power was ~40% (Fig.10).

**Table 1** Effect of variation of irradiance and temperature on CdS/Cu$_2$S solar cell parameters at different months.

| Date | Irradiance (Lux) | T (°C) | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | $V_m$ (V) | $I_m$ (mA) | $P_m$(mW/cm$^2$) |
|---|---|---|---|---|---|---|---|
| 15/6/2010 | 115120 | 32 | 46.65 | 0.52 | 0.37 | 194.52 | 14.59 |
| 15/7/2010 | 116800 | 32 | 47.76 | 0.53 | 0.39 | 185.38 | 14.64 |
| 4/8/2010 | 113300 | 35 | 35.4 | 0.52 | 0.3 | 147.76 | 8.83 |

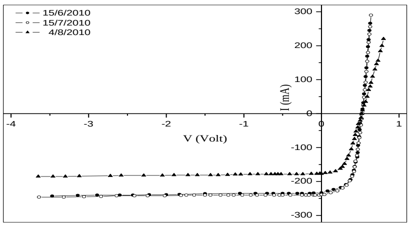


**Fig.9** Variation of irradiance and temperature on the (I-V) characteristics of CdS/$Cu_2S$ solar cell through the study period

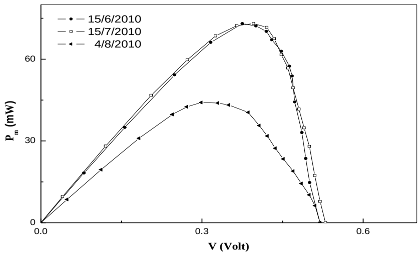


**Fig.10** Output power versus voltage of CdS/$Cu_2S$ solar cell through the study period

## Influence of Dust on Crystalline Si Solar Cell at Al-Harby Street

The average concentrations of dust accumulate on the surface of the solar cell at Al-Harby Street was 322.72µg/$m^3$ (Fig.11). This concentration is about 4.6 times the maximum allowable concentration given by the Egyptian Environmental Law No. 4, 1994 (70 µg/$m^3$ 24 hr). The high concentrations of PM at this site may be attributed to the heavy commercial activity, furniture work-shops, coupled with the high concentration of particulate matter emitted from traffic **(El-Henawy, 2011)**. Figure (12) presents the current-voltage characteristics curve of maximum power region for crystalline Si solar cell. The short circuit current and open circuit voltage decreased with the increase of exposure time. The decrease of short circuit current was much more remarkable than that of open circuit voltage.

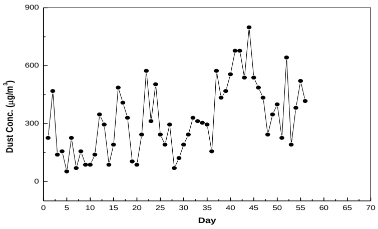


**Fig.11** The daily concentrations of dust (µg/$m^3$) through the study period

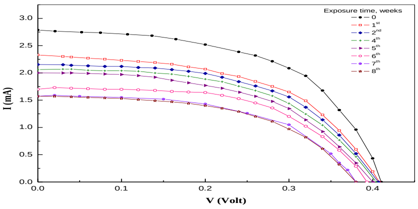


**Fig.12** Current-voltage curves of maximum power region for crystalline Si solar cell under various concentrations of air pollutants.

Figure (12) implies that with further dust accumulation beyond (1701µg/$m^3$) the short circuit current decreased less steeply, i.e., it becomes less sensitive to dust accumulation. A quantitative estimation of the dependence of short circuit current density and open circuit voltage on accumulated dust concentration is depicted in fig.(13). $J_{sc}$ and $V_{oc}$ decreased non-linearly with the increase in accumulated dust concentration and they arrived to least constant values in the seventh week where accumulated dust concentration was (2200 µg/$m^3$). The reduction in the short circuit current and the open circuit voltage after exposure for seven weeks was 43% and 7%, respectively. El-Shobokshy et al. (1985) concluded that the change in I-V characteristics due to dust accumulation per unit area was more dominant than the exposure time. For dust accumulation higher than (2200 µg/$m^3$), the short circuit current density and the open circuit voltage arrived to approximately constant values. The particles tend to accumulate on the surface of a solar cell forming a homogenous dust thickness. The reduction in short circuit current density and open circuit voltage was attributed to the decrease in the light transmittance. This opinion is supported by Al-Hasan and Ghonein (2005) whom found that the short circuit current increased as the incident power increases for both clean and dusty modules.

The reduction in $J_{sc}$ and $V_{oc}$ with accumulated dust reflected on the output power versus voltage curve of crystalline Si solar cell under various concentrations of air pollutants (Fig.14).

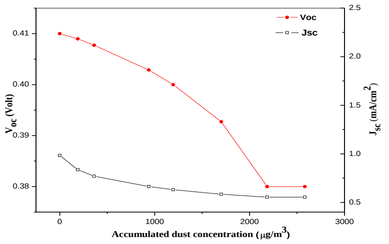


**Fig.13** Variation of $V_{oc}$ and $J_{sc}$ with different concentrations of dust

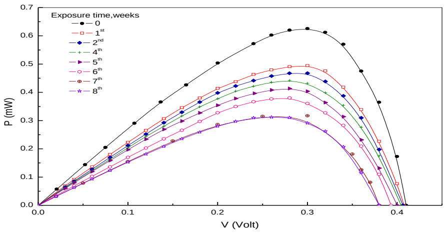


**Fig.14** Output power versus voltage of crystalline Si solar cell under various concentrations of air pollutants

The output power decreased with the increase of exposure time. The output power decreased less steeply after the sixth week of exposure. The maximum output power decreased non-linearly with the increase the concentration of accumulated dust and it had a constant value at dust concentration of (2200 μg/m$^3$) (Fig.15). These results indicate that the short circuit current is the dominant factor influencing the output power of a solar cell. The observed degradation of output power can also be attributed to the fact that the dust particles scatter and absorb some of the sunlight resulting in a decrease of sunlight reaching the solar cell. The changes of $J_{sc}$ and $V_{oc}$ with time reflected on the solar cell parameters with small changes in temperature and humidity were not regular (Table 2). Therefore, the changes in solar cell parameters may be attributed to accumulation of particulates.

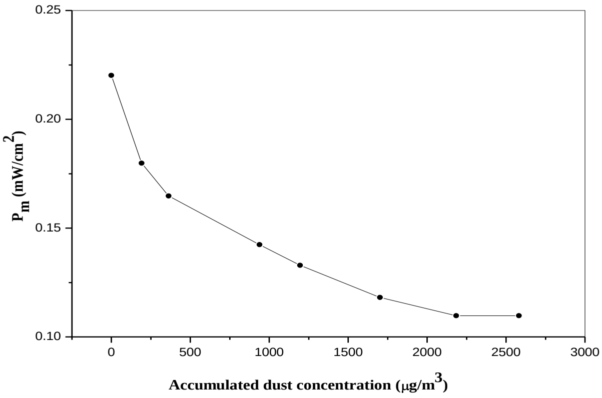


**Fig.15** Maximum power versus accumulated dust concentration

**Table 2** Effects of temperature and humidity on crystalline Si solar cell parameters.

| **Time** | **Before exposure** | **after 1 week** | **after 2weeks** | **after 4weeks** | **after 5weeks** | **after 6weeks** | **after 7weeks** | **fter 8weeks** |
|---|---|---|---|---|---|---|---|---|
| **Mean of Temp.,°C** | 15 | 16 | 15.75 | 16.75 | 16.5 | 17.11 | 16.87 | 14.87 |
| **Mean of Humidity** | 75 | 75 | 84 | 78 | 72 | 72 | 74 | 70 |

## CONCLUSION

The obtained results demonstrate that the short circuit current, open circuit voltage and maximum power of $CdS/Cu_2S$ solar cell increase with increasing irradiance level. However, under field conditions the output power of the solar cell varies along the hours of the day depending on irradiance and temperature. Moreover, dust has a significant effect on the performance of crystalline Si solar cell. A decrease in short circuit current, open circuit voltage and maximum power were observed.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
**4th International Symposium and IUAPPA Regional Conference**
**10-13 September 2012 Istanbul - Turkey**

# SIMULATION OF FUEL PROCESSORS TO PRODUCE HYDROGEN IN FUEL CELL APPLICATIONS

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## ABSTRACT

Current energy production systems should be replaced with cleaner and more efficient technologies due to the environmental concerns. Fuel cell technology is recognised as a quiet, reliable and low environmental impact technology, and this makes it suitable for residential and commercial applications. Although it is an environmentally friendly technology, hydrogen production, transportation and storage issues limit its application. On-site hydrogen production is one of the solutions to this problem. Natural gas is cost effective, relatively more abundant in nature and easily deliverable to individual houses via avaliable and extensive pipeline infrastructure. Hydrogen production from natural gas through autothermal reforming is considered as the most efficient method, and involves critical steps such as fuel processor (FP), CO elimination and a burner, all of which are important in emission control. In this work, hydrogen rich fuel processor requirements were determined by steady state simulation by using Aspen HYSYS® (aspentech). Effects of the process conditions, equipment selection, placement, and process design alternatives on the electrical efficiency were evaluated to produce 1 kWe energy with high temperature polymer electrolite membrane (HTPEM). Production alternatives were tested, and optimum conditions were determined.

**Keywords:** autothermal reforming, hydrogen production system, fuel cell technology

**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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**10-13 September 2012 Istanbul -Turkey**

# THE SCENARIO ANALYSIS ON $CO_2$ EMISSION MITIGATION POTENTIAL IN TURKISH ELECTRICITY SECTOR: 2006-2030

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## ABSTRACT

The purpose of this study is to evaluate the future $CO_2$ emission mitigation potential of Turkey’s electricity sector. A scenario analysis method based on the Long range Energy Alternatives Planning system (LEAP) model has been used for this study. The results imply that electricity demand and associated $CO_2$ emissions in Turkey will rise in two scenarios named as Business As Usual (BAU) and Mitigation due to the economic growth until 2030. However, through structural adjustments in Turkey’s electricity sector varying degrees of $CO_2$ abatement can be achieved. Compared with the BAU in the Mitigation Scenario 17.5% mitigation ratio is achieved through all time horizon of the study.

**Keywords**: Turkish electricity sector, $CO_2$ mitigation potential, LEAP

## 1. INTRODUCTION

Scientifically proved anthropogenic climate change is assumed to be one of the major global environmental problems of our century (İncecik, 2007). Since industrial revolution due to the increasing use of fossil fuels for electricity production and industrial processes, land use change and deforestation all cause fast increasing of greenhouse gas emissions. All these and the contribution of the urbanization result strengthening of natural greenhouse gas effect that cause the increase of world’s surface temperature. In Turkey, as in all over the world, annual growth rates and the share of $CO_2$ emissions from electricity generation have the most important place in total greenhouse gasses. As being a part of Kyoto Protocol (KP) since 2009, Turkey will have obligation to mitigate greenhouse gasses (GHGs). Before setting an applicable countrywide mitigation target for $CO_2$ emissions, sectoral emission mitigation potential should be determined. Thus determination of $CO_2$ emissions mitigation potential in Turkish electricity generation sector, is getting more importance.

Increasing $CO_2$ emissions in the electricity sector, is mainly due to the increasing electricity demand and the composition of the electricity generation. As Turkey has not completed her development, electricity demand continues to rise that mainly causes increasing emissions. Therefore long term electricity demand projections are essential for the emission mitigation options determination.

In electricity generation $CO_2$ emissions are caused by combustion of fossil fuels. In Turkey 74% of total electricity generation belongs to fossil fuels and lignite is the major domestic energy resource for electricity generation (TEİAS; 2010a).

As a result of all these data electricity generation should be planned according to meet increasing demand and reduce corresponding $CO_2$ emissions in Turkey. All mitigating options should be evaluated and corresponding action plans should be established. As technical and economic applicability of all options should be proved during policy making, model simulations get importance.

Therefore, the aim of this study is to evaluate the future $CO_2$ emission reduction potential of Turkey’s electricity sector. The results present the outputs for Turkey’s future policies those will be compatible with the international agreements for preventing climate change and especially contribute to determination of electricity production policy.

For this purpose, total electricity demand is estimated till 2030. . Correspondingly, electricity production scenarios were built. In this paper, two scenarios named as Business as Usual (BAU) and Mitigation (Mt) Scenario, are employed for electricity generation with the Long-Range Energy Alternatives Planning systems (LEAP) model.

## 2. METHODOLOGY

This study has used an integrated energy–environment and scenario based accounting model LEAP 2008, (SEI, 2010). to generate scenarios for Turkish electricity sector. Scenarios are based on bottom-up approach including the electricity demand and sectoral production with different energy resources and energy intensities of each power plant. Time horizon of the study is 2006-2030, setting 2006 as base year.

Electricity demand projections are mainly based on Gross Domestic Product (GDP) and population growth with taken into consideration of below 6 sectors:

- Residential,
- industrial,
- transport,
- commercial,
- agricultural, and
- services.

Annual growth rates and the proportion of each demand sector in total electricity demand are taken into consideration for demand projections. Demand projections from 2011 to 2030 are given in Table 1 (Özer, 2012).

Table 1. Net electricity demand projections (Özer, 2012).

| Year | 2011 | 2012 | 2013 | 2014 | 2015 | 2016 | 2017 | 2018 | 2019 | 2020 | 2021 | 2022 | 2023 | 2024 | 2025 | 2026 | 2027 | 2028 | 2029 | 2030 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TWh | 184 | 198 | 212 | 228 | 244 | 261 | 280 | 300 | 320 | 341 | 364 | 388 | 414 | 447 | 476 | 509 | 545 | 588 | 640 | 696 |

Fuel specific carbon emission factors (CEFs) of lignite, hard and import coal, and the oxidation fraction of lignite and hard coal fuelled thermal power plants are calculated from each thermal power plant data supplied from EUAS (2011) and given with Table 2. For international fuels such as natural gas, fuel oil, diesel, naphtha IPCC (1996) values are used.

Table 2. Fuel spesific CEFs and oxidation fractions (Özer, 2012).

| Fuel | CEF, ton C/TJ | Oksidation fraction, % |
|---|---|---|
| Lignite | 29.504 | 89.13 |
| Hard coal | 30.62 | 95 |
| Import Coal | 24.25 | 98* |
| Natural gas | 15.3* | 99.5* |
| Fuel Oil | 21.1* | 99* |
| Diesel | 20.2* | 99* |
| Naphtha | 20.0* | 99* |

*: IPCC (1996)

CEFs and oxidation fractions of each fuel are input data of LEAP for $CO_2$ emissions, where fuel specific installed capacities, maximum capacity factors, internal uses and thermal efficiencies of each thermal power plant were used for electricity generation input data of LEAP.

Annual gross electricity demands were calculated by adding internal uses of power plants, transmission and distribution losses of the system to the annual net electricity demand.

## 2.1 Scenarios

BAU and Mt Scenarios are generated in LEAP. Scenarios differ from each other with different installed capacities, internal uses, actual capacity factors of power plants and distribution losses of the system. Mainly the share of the renewable energy resources for electricity generation which represents the $CO_2$ emission mitigation potential is essential for the scenarios.

Common assumptions for the scenarios are given below:

- Total electricity demand is assumed to be supplied by domestic energy resources.
- The fuel specific emission factors of all renewable energy resources are accepted as zero.
- Thermal efficiencies of power plants are assumed to be same for both scenarios.
- Net electricity demands are same for both scenarios.
- Gross electricity production was taken into consideration for $CO_2$ emissions.

### BAU Scenario

BAU scenario considers electricity supply rather than climate change. Current electricity composition is assumed to be continued through all time horizon of the study. Installed capacities by fuel type are given with Table.3.

### Mt Scenario

Mt scenario is established due to the increased share of the renewable energy sources, such as hydropower, wind, biomass and geothermal. And all potential of renewable domestic energy resources are used through time horizon of the study. For deciding installed capacities, Turkey’s 2023 year targets given by Ministry of Energy and Natural Resources (ETKB, 2009) are taken into consideration with the values also given by Turkish Electricity Transmission Company (TEIAS, 2010b; TEIAS, 2004). This scenario is mainly based on obtaining maximum benefit of installed capacities and using all renewable domestic energy resources except solar for electricity generation. Mt Scenario installed capacities by fuel type are given with Table.4.

Gross electricity demand of this scenario is lower than BAU Scenario, as internal uses of the power plants and distribution losses of the system assumed to decrease compared with BAU. The annual internal use of the system is 4.2% and distribution losses of the system is 12.2% all over the study period in BAU Scenario, where in Mt Scenario internal use is assumed to decrease from 4.2% in 2011 to 3.9% from 2016 to 2030, and distribution losses of the system is assumed to decrease from 12.2% in 2011 to 8% from 2023 to 2030.

Annual percentage distributions of the renewable energy sources in electricity generation for both scenarios are given with Table 5. The mean value through time horizon of the study for BAU and Mt Scenarios are %24 and %36 respectively.

## 3. RESULTS

This study presents the $CO_2$ emission mitigation potential of Turkish electricity generation sector via LEAP model results. Electricity production and corresponding $CO_2$ emissions are projected through BAU and Mt Scenarios with the model. The results imply that electricity demand and associated $CO_2$ emissions in Turkey will rise in the two scenarios due to the economic growth until 2030. $CO_2$ emissions and the mitigation potential of Turkish electricity sector from year 2006 to 2030 are given with Table 6.

Table 3: BAU Scenario Installed Capacities, MW.

| Year | Natural Gas | Lignite | Hydro | Import Coal | Fuel Oil | Hard Coal | Wind | Biomass | Geothermal | Diesel | Naphtha | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **2006** | 14.315 | 8.682 | 13.063 | 1.686 | 2.123 | 300 | 67 | 41 | 15 | 252 | 21 | **40.565** |
| **2007** | 14.560 | 8.682 | 13.395 | 1.686 | 1.772 | 300 | 154 | 43 | 15 | 206 | 21 | **40.836** |
| **2008** | 15.055 | 8.676 | 13.829 | 1.686 | 1.771 | 300 | 364 | 60 | 30 | 26 | 21 | **41.817** |
| **2009** | 16.548 | 8.615 | 14.553 | 1.956 | 1.651 | 435 | 792 | 87 | 77 | 26 | 21 | **44.761** |
| **2010** | 17.641 | 8.691 | 15.522 | 3.316 | 1.483 | 435 | 1.266 | 97 | 94 | 26 | 17 | **48.588** |
| **2011** | 17.996 | 8.691 | 18.081 | 3.316 | 1.794 | 435 | 1.548 | 97 | 94 | 26 | 17 | **52.096** |
| **2012** | 19.110 | 8.691 | 19.363 | 4.529 | 1.794 | 435 | 1.548 | 97 | 94 | 26 | 17 | **55.705** |
| **2013** | 20.159 | 8.691 | 20.462 | 5.137 | 1.794 | 435 | 1.548 | 97 | 94 | 26 | 17 | **58.461** |
| **2014** | 20.770 | 8.691 | 21.335 | 5.413 | 1.794 | 714 | 1.548 | 97 | 94 | 26 | 17 | **60.500** |
| **2015** | 20.770 | 8.691 | 22.535 | 5.413 | 1.794 | 714 | 1.548 | 97 | 94 | 26 | 17 | **61.700** |
| **2016** | 20.770 | 8.691 | 23.476 | 5.413 | 1.794 | 714 | 1.548 | 97 | 94 | 26 | 17 | **62.641** |
| **2017** | 20.770 | 8.691 | 23.476 | 5.413 | 1.794 | 714 | 1.548 | 97 | 94 | 26 | 17 | **62.641** |
| **2018** | 21.489 | 9.042 | 24.187 | 5.573 | 1.866 | 733 | 1.590 | 100 | 98 | 30 | 18 | **64.726** |
| **2019** | 23.354 | 9.952 | 26.035 | 5.938 | 2.053 | 782 | 1.698 | 109 | 104 | 36 | 20 | **70.081** |
| **2020** | 24.344 | 10.436 | 27.016 | 6.132 | 2.152 | 808 | 1.755 | 113 | 108 | 40 | 21 | **72.925** |
| **2021** | 25.958 | 11.223 | 28.613 | 6.448 | 2.314 | 851 | 1.848 | 120 | 114 | 46 | 22 | **77.557** |
| **2022** | 27.945 | 12.073 | 30.337 | 6.789 | 2.489 | 897 | 1.949 | 128 | 121 | 53 | 24 | **82.805** |
| **2023** | 29.924 | 13.025 | 32.270 | 7.171 | 2.684 | 949 | 2.062 | 137 | 129 | 61 | 26 | **88.438** |
| **2024** | 32.235 | 14.036 | 34.775 | 7.765 | 2.892 | 1.023 | 2.222 | 148 | 139 | 66 | 28 | **95.329** |
| **2025** | 34.318 | 14.950 | 37.038 | 8.231 | 3.081 | 1.089 | 2.370 | 157 | 148 | 70 | 30 | **101.482** |
| **2026** | 36.691 | 16.000 | 39.600 | 8.800 | 3.300 | 1.165 | 2.531 | 170 | 160 | 75 | 32 | **108.524** |
| **2027** | 39.427 | 17.097 | 42.360 | 9.413 | 3.523 | 1.250 | 2.700 | 180 | 170 | 75 | 34 | **116.229** |
| **2028** | 42.485 | 18.506 | 45.851 | 10.190 | 3.815 | 1.350 | 2.931 | 195 | 185 | 90 | 40 | **125.638** |
| **2029** | 46.211 | 20.130 | 49.875 | 11.085 | 4.148 | 1.470 | 3.190 | 212 | 200 | 94 | 40 | **136.655** |
| **2030** | 50.275 | 21.900 | 54.260 | 12.060 | 4.515 | 1.600 | 3.470 | 230 | 220 | 105 | 45 | **148.680** |

Table 4: Mitigation Scenario Installed Capacities, MW.

| Year | Natural Gas | Lignite | Hydro | Import Coal | Fuel Oil | Hard Coal | Wind | Biomass | Geothermal | Diesel | Naphtha | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2006 | 14.315 | 8.682 | 13.063 | 1.686 | 2.123 | 300 | 67 | 41 | 15 | 252 | 21 | **40.565** |
| 2007 | 14.560 | 8.682 | 13.395 | 1.686 | 1.772 | 300 | 154 | 43 | 15 | 206 | 21 | **40.836** |
| 2008 | 15.055 | 8.676 | 13.829 | 1.686 | 1.771 | 300 | 364 | 60 | 30 | 26 | 21 | **41.817** |
| 2009 | 16.548 | 8.615 | 14.553 | 1.956 | 1.651 | 435 | 792 | 87 | 77 | 26 | 21 | **44.761** |
| 2010 | 17.641 | 8.691 | 15.522 | 3.316 | 1.483 | 435 | 1.266 | 97 | 94 | 26 | 17 | **48.588** |
| 2011 | 17.641 | 8.691 | 15.522 | 3.316 | 1.496 | 435 | 1.555 | 97 | 94 | 30 | 17 | **48.894** |
| 2012 | 17.641 | 8.691 | 15.522 | 3.316 | 1.496 | 435 | 1.555 | 97 | 94 | 30 | 17 | **48.894** |
| 2013 | 17.641 | 8.691 | 15.522 | 3.316 | 1.496 | 435 | 1.555 | 97 | 94 | 30 | 17 | **48.894** |
| 2014 | 17.641 | 8.691 | 15.522 | 3.316 | 1.496 | 435 | 1.555 | 97 | 94 | 30 | 17 | **48.894** |
| 2015 | 17.641 | 8.691 | 18.081 | 3.316 | 1.496 | 435 | 1.555 | 97 | 94 | 30 | 17 | **51.453** |
| 2016 | 17.641 | 8.691 | 19.500 | 3.316 | 1.496 | 435 | 4.600 | 140 | 300 | 30 | 17 | **56.166** |
| 2017 | 18.500 | 8.691 | 23.476 | 3.316 | 1.496 | 435 | 4.600 | 140 | 420 | 30 | 17 | **61.121** |
| 2018 | 18.850 | 8.886 | 25.000 | 3.316 | 1.794 | 435 | 6.800 | 160 | 500 | 41 | 17 | **65.799** |
| 2019 | 18.850 | 9.203 | 26.000 | 3.316 | 1.794 | 714 | 11.100 | 170 | 540 | 41 | 17 | **71.745** |
| 2020 | 18.850 | 9.203 | 28.000 | 3.716 | 1.794 | 714 | 14.560 | 180 | 600 | 41 | 17 | **77.675** |
| 2021 | 19.500 | 9.500 | 30.000 | 4.000 | 1.794 | 1.014 | 16.000 | 250 | 600 | 41 | 17 | **82.716** |
| 2022 | 19.500 | 9.700 | 33.000 | 4.400 | 1.794 | 1.200 | 19.000 | 500 | 600 | 41 | 17 | **89.752** |
| 2023 | 21.000 | 10.500 | 35.000 | 4.400 | 1.794 | 1.500 | 20.000 | 600 | 600 | 41 | 20 | **95.455** |
| 2024 | 22.000 | 11.500 | 36.000 | 4.400 | 1.794 | 1.635 | 25.000 | 700 | 600 | 41 | 20 | **103.690** |
| 2025 | 22.000 | 14.000 | 36.929 | 4.600 | 2.000 | 1.635 | 28.000 | 900 | 600 | 41 | 20 | **110.725** |
| 2026 | 22.000 | 17.000 | 36.929 | 5.000 | 2.000 | 1.635 | 32.200 | 1.100 | 600 | 41 | 20 | **118.525** |
| 2027 | 22.000 | 17.000 | 36.929 | 6.000 | 2.500 | 1.635 | 40.000 | 1.500 | 600 | 41 | 20 | **128.225** |
| 2028 | 23.210 | 18.500 | 36.929 | 6.000 | 2.500 | 1.635 | 48.000 | 1.650 | 600 | 41 | 20 | **139.085** |
| 2029 | 31.400 | 18.500 | 36.929 | 6.000 | 2.500 | 1.635 | 48.000 | 1.650 | 600 | 41 | 20 | **147.275** |
| 2030 | 40.000 | 18.500 | 36.929 | 6.000 | 2.500 | 1.635 | 48.000 | 1.650 | 600 | 41 | 20 | **155.875** |

Table 5: Percentage distributions of the renewable energy sources in electricity generation of the scenarios, %

| | 2011 | 2012 | 2013 | 2014 | 2015 | 2016 | 2017 | 2018 | 2019 | 2020 | 2021 | 2022 | 2023 | 2024 | 2025 | 2026 | 2027 | 2028 | 2029 | 2030 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BAU | 23 | 20 | 21 | 20 | 23 | 24 | 25 | 25 | 25 | 25 | 24 | 24 | 24 | 24 | 24 | 24 | 24 | 24 | 24 | 24 |
| Mt | 25 | 23 | 22 | 20 | 24 | 28 | 31 | 33 | 36 | 39 | 40 | 42 | 42 | 43 | 44 | 43 | 45 | 46 | 43 | 39 |

Tablo 6. $CO_2$ emissions of BAU and Mt Scenarios, Mton $CO_2$

| **Year** | **BAU Scenario** | **Mt Scenario** | **Difference from BAU** | |
|---|---|---|---|---|
| | | | | **%** |
| **2006** | 86 | 86 | - | - |
| **2007** | 103 | 103 | - | - |
| **2008** | 108 | 108 | - | - |
| **2009** | 102 | 102 | - | - |
| **2010** | 101 | 101 | - | - |
| **2011** | 116 | 111 | 5 | 4.07 |
| **2012** | 127 | 121 | 6 | 4.92 |
| **2013** | 134 | 130 | 4 | 2.70 |
| **2014** | 143 | 141 | 2 | 1.54 |
| **2015** | 149 | 147 | 3 | 1.75 |
| **2016** | 156 | 147 | 9 | 5.54 |
| **2017** | 165 | 151 | 14 | 8.63 |
| **2018** | 181 | 157 | 24 | 13.37 |
| **2019** | 193 | 160 | 33 | 17.05 |
| **2020** | 207 | 163 | 44 | 21.19 |
| **2021** | 221 | 172 | 49 | 22.09 |
| **2022** | 236 | 176 | 60 | 25.38 |
| **2023** | 253 | 188 | 64 | 25.38 |
| **2024** | 273 | 201 | 72 | 26.49 |
| **2025** | 291 | 220 | 71 | 24.34 |
| **2026** | 311 | 243 | 68 | 21.91 |
| **2027** | 332 | 251 | 81 | 24.39 |
| **2028** | 359 | 267 | 93 | 25.76 |
| **2029** | 391 | 293 | 98 | 25.11 |
| **2030** | 425 | 321 | 104 | 24.46 |
| **Total** | 5.162 | 4.259 | 903 | 17.49 |
| **$CO_2$/year** | 206.5 | 170.4 | 36 | |

The results of the study can be summarized as below:

- The cumulative $CO_2$ emissions abatement of Mt Scenario for all time horizon of the study is 903 million tons where annual mean abatement is 36 million tons of $CO_2$ per year. This indicates in the Mt Scenario compared with BAU Scenario 17.5% of cumulative abatement can be achieved.
- Annual abatement ratio of the Mt Scenario compared with BAU Scenario is 21% in year 2020 and 24.5% in year 2030
- The mean share of renewable energy resources in the electricity generation through time horizon of the study in BAU Scenario is approximately 24% and 36% in the Mt Scenario. These results indicate that increased share of renewable energy sources in the electricity generation result $CO_2$ emission mitigation.
- Reducing of internal electricity consumption of power plants and distribution losses of the system cause decrease of the gross electricity demand and $CO_2$ emissions reduction.

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# AIR QUALITY MODELING IN EUROPE WITH VARIOUS EMISSION SCENARIOS FOR 2020

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## ABSTRACT

We study the effects of the revised Gothenburg target emissions in 2020 on ozone and particulate matter in Europe with a focus on Switzerland by means of the regional air quality model CAMx. We use the GAINS emissions for various snap sectors and countries to prepare gridded emission scenarios for 2020. These scenarios include the Baseline, Mid case and Maximum Technically Feasible Reductions. Simulations are performed for each emission scenario and the model results for 2020 are compared with those for the reference year 2005. In this paper, we discuss the preliminary results showing the predicted effects of various European emission scenarios on ozone and particulate matter in 2020.

**Keywords**: air quality modeling, Gothenburg Protocol, particulate matter, ozone, emission scenarios

## 1. INTRODUCTION

Ozone and PM10 levels often exceed the ambient air quality standards in Europe. In an earlier study we calculated the effects of numerous regulations enforced in Europe since 1985 and predicted the effects of Gothenburg targets for 2010 on air quality (Andreani-Aksoyoglu et al., 2008). In 2007, the Convention on Long-Range Trans boundary Air Pollution initiated the revision of its Gothenburg multi-pollutant/multi-effect protocol. In the revised protocol, PM2.5, PM10 and greenhouse gases were included. The EMEP Centre for Integrated Assessment Modeling (CIAM) and IIASA prepared various emission control scenarios for cost-effective improvements of air quality in Europe in 2020, by using the GAINS (Greenhouse gas – Air pollution Interactions and Synergies) model. Our objective is to estimate the impacts of emission mitigation measures proposed for the revision of the Gothenburg Protocol on air quality in Europe with a focus on Switzerland. This will be achieved by means of the regional air quality model CAMx that simulates gridded pollutant concentrations for different emission scenarios provided by the EMEP/CEIP and IIASA/GAINS (http://gains.iiasa.ac.at/gains/EUR/index.login).

## 2. METHOD

We use CAMx (Comprehensive Air quality Model with extension) developed by Environ [*Environ*, 2010]. Meteorological parameters are calculated by the meso scale model WRF [*WRF*, 2011]. The model domain covers Europe on a terrain-following lat-lon coordinate system with a horizontal resolution of 0.250 º x 0.125 º. We use a nested domain covering central Europe with three times higher resolution. There are 14 σ-levels, with the lowest layer thickness of about 20 m. The fine/coarse option of CAMx is used to calculate particles with different size. Initial and boundary conditions are obtained from the global model MOZART (Horowitz et al., 2003). Model validation is performed for the year 2006 using the detailed measurement data available for that year. The same meteorological data are used for all simulations with various emission scenarios. The selected emission scenarios for this project are shown in Table 1. All scenarios -except the validation case- have been defined by the

Working Group on Strategies and Review of CIAM / IIASA (CIAM4/11). Proposed emission ceilings according to the revised Gothenburg protocol that was signed recently will also be included in the future. The gridded emissions for the model domain are calculated using the annual emissions for each country (national totals) in Europe and for each SNAP code. An example of the variation of the total annual emissions for different scenarios is shown in Table 2 for Switzerland. Comparison of scenarios for 2020 with 2005 shows that the difference between Baseline and Mid scenarios is relatively small whereas emission reductions for the MTFR case are more significant (40-55 % depending on the species).

Table 1 : Description of modeled emission scenarios

| Reference year | Description |
|---|---|
| 2006 | Model validation |
| 2005 | Gains Baseline |
| 2020 | Gains Baseline |
| 2020 | Gains Mid |
| 2020 | Gains MTFR (maximum technically feasible reduction) |

Table 2: Annual emissions of Switzerland (kt $yr^{-1}$)

| species | Gains Baseline 2005 | Gains Baseline 2020 | Gains Mid 2020 | Gains MTFR 2020 |
|---|---|---|---|---|
| SO2 | 16.09 | 12.82 | 12.75 | 10.03 |
| NOx | 84.38 | 48.10 | 45.94 | 43.66 |
| NMVOC | 121.21 | 82.17 | 71.10 | 53.23 |
| PM2.5 | 10.02 | 7.08 | 6.02 | 4.45 |
| PM10 | 14.92 | 12.36 | 11.18 | 7.85 |

## 3. RESULTS AND DISCUSSION

Each scenario is calculated for one year and compared to the reference case for 2005. Results will be analyzed for ozone, PM2.5 and PM10 as well as individual aerosol species. Annual simulations for all emission scenarios have not been completed yet. In this paper some of the highlights for winter and summer periods are discussed.

### Ozone

Ozone concentrations are higher in summer due to its photochemical production. Figure 1 shows the modeled ozone concentrations (July afternoon average) for the reference case in the first domain. As seen in the figure, ozone levels are relatively higher in southern Europe. Reductions of ozone precursor ($NO_x$ and VOC) emissions lead to changes in ozone concentrations. The predicted difference in the average July afternoon ozone concentrations between 2020 baseline and 2005 is shown in Figure 2 for domain 1. The model results suggest that afternoon ozone levels would decrease by 10-20% in 2020, mainly in central Europe. A few urban sites with high emissions on the other hand, would have higher values (shown in red). In winter, emission reductions in 2020 lead to an increase (5-10 ppb) in ozone concentrations because of less ozone destruction by NO (see Figure 3 for the MTFR case).

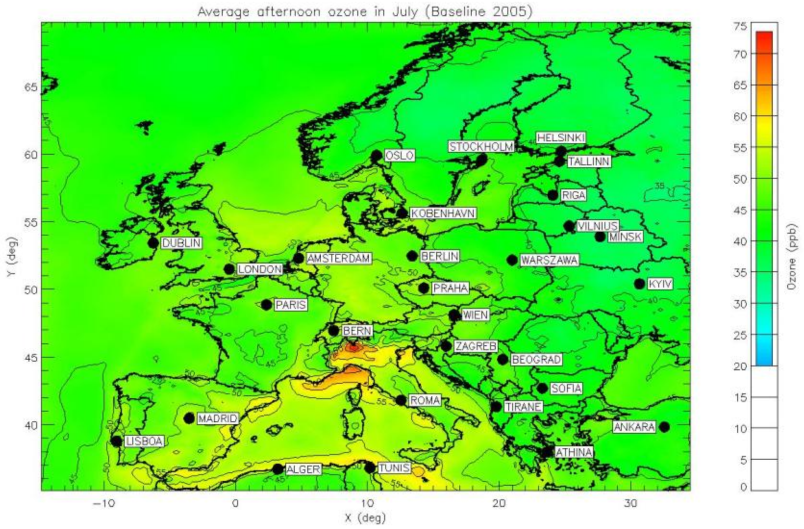


Figure 1: Average afternoon ozone concentrations (ppb) in July (Baseline 2005) in domain 1.

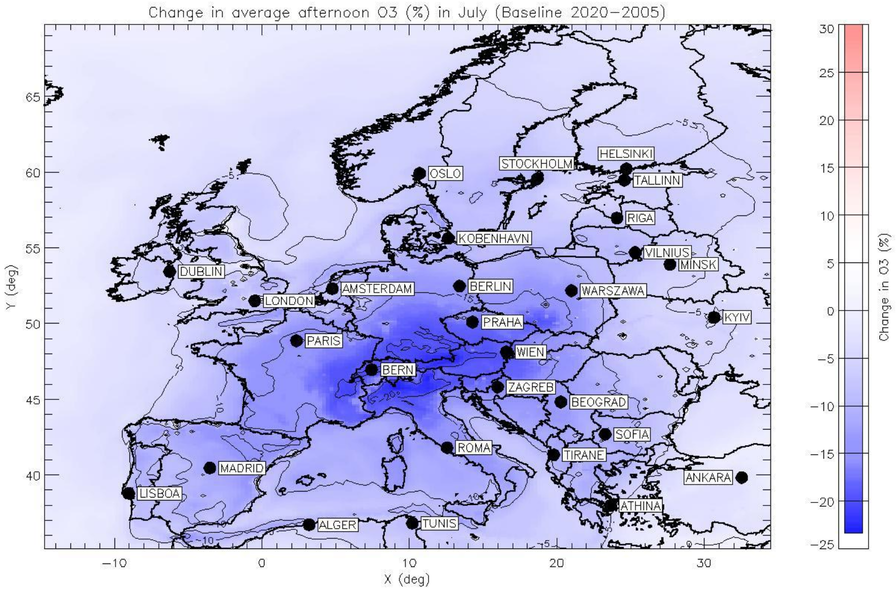


Figure 2: Change in average afternoon ozone concentrations (%) in July (Baseline 2020 – 2005) for domain 1. Blue indicates a decrease, red an increase with respect to reference case 2005.

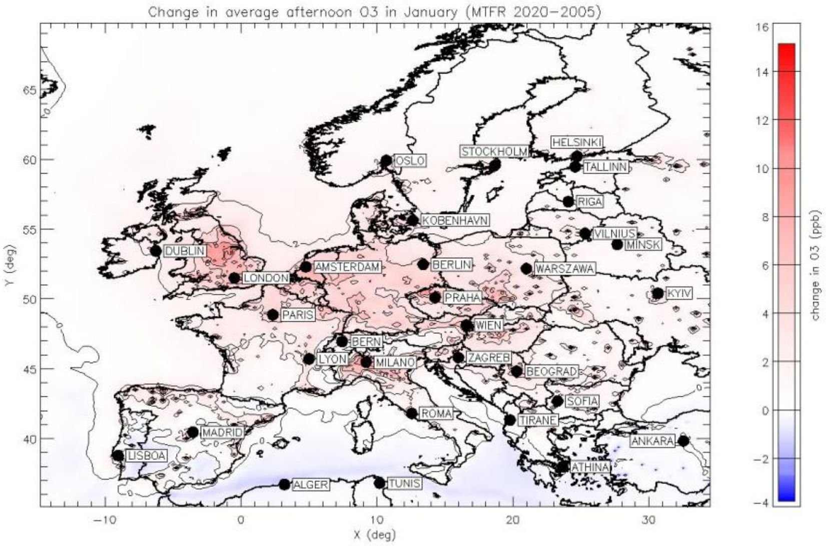
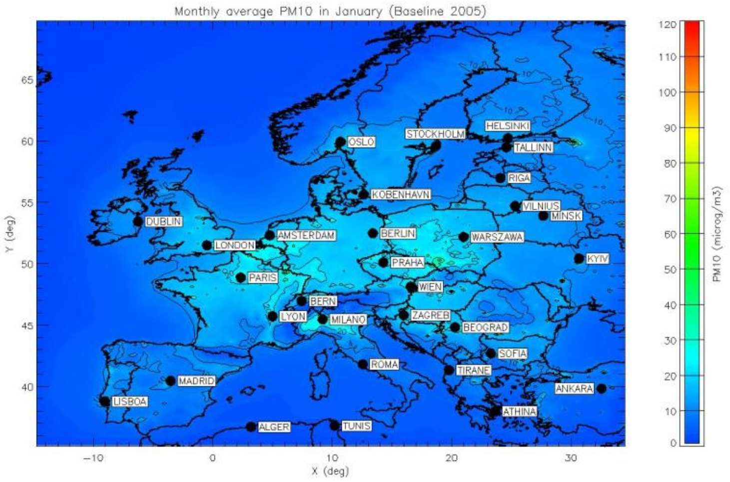


Figure 3: Change in average afternoon ozone concentrations (ppb) in January (MTFR 2020 – 2005) for domain 1. Blue indicates a decrease, red an increase with respect to reference case 2005.

## Particulate Matter

Model results suggest that PM2.5 dominates PM10 in central Europe (Figure 4). Therefore, only some of the PM10 results are shown here. The changes in monthly (January) average PM10 concentrations for the Baseline 2020 and MTFR 2020 with respect to 2005 reference case are shown in Figures 5-6 for the two domains, respectively. Model predicts that PM10 would be about 50-70% lower in the Baseline 2020 case with respect to 2005. Decrease in PM10 is predicted to be larger (up to 80%) in MTFR case.



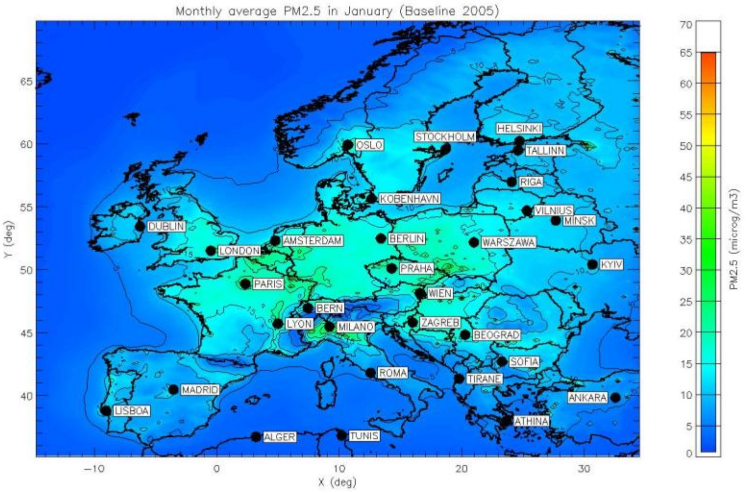


Figure 4: Monthly average PM10 (above) and PM2.5 (below) concentrations (μg $m^{-3}$) in January (Baseline 2005) for domain 1.

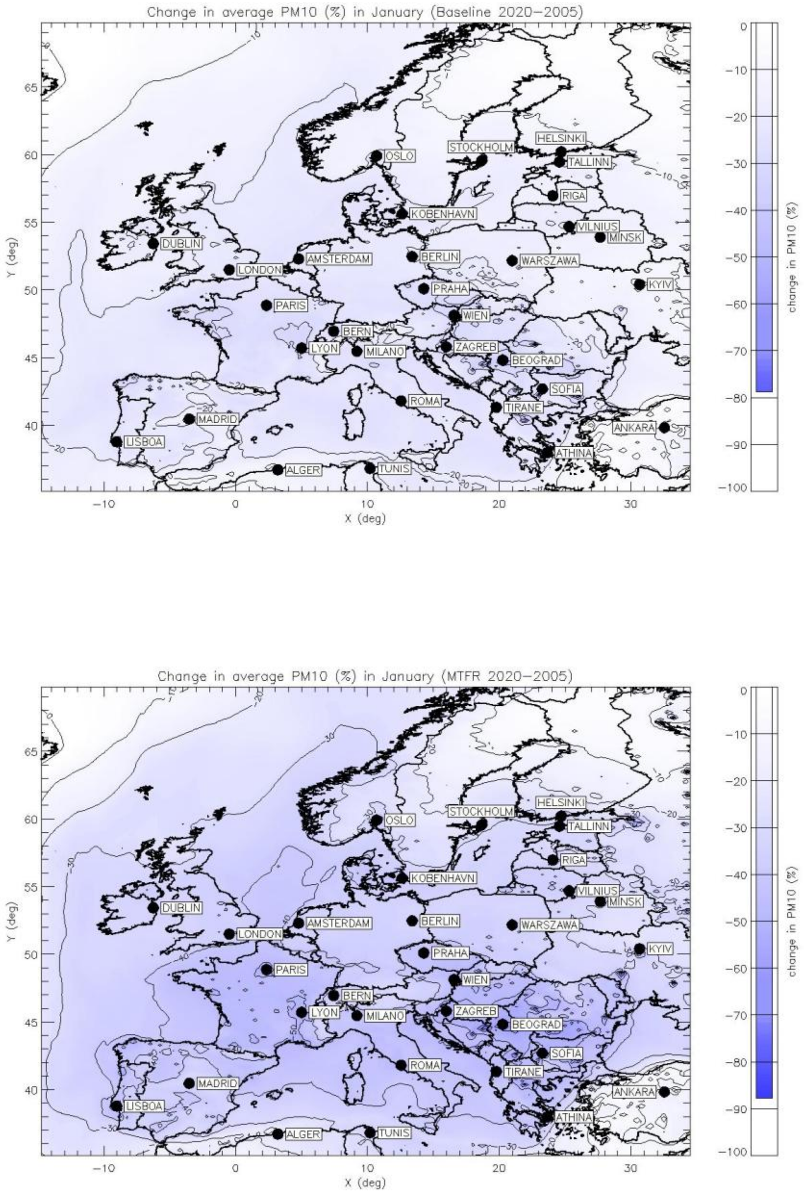


Figure 5: Changes in monthly average PM10 concentrations (%) in Baseline 2020 (above) and for MTFR 2020 (below) with respect to 2005 reference case. Domain1

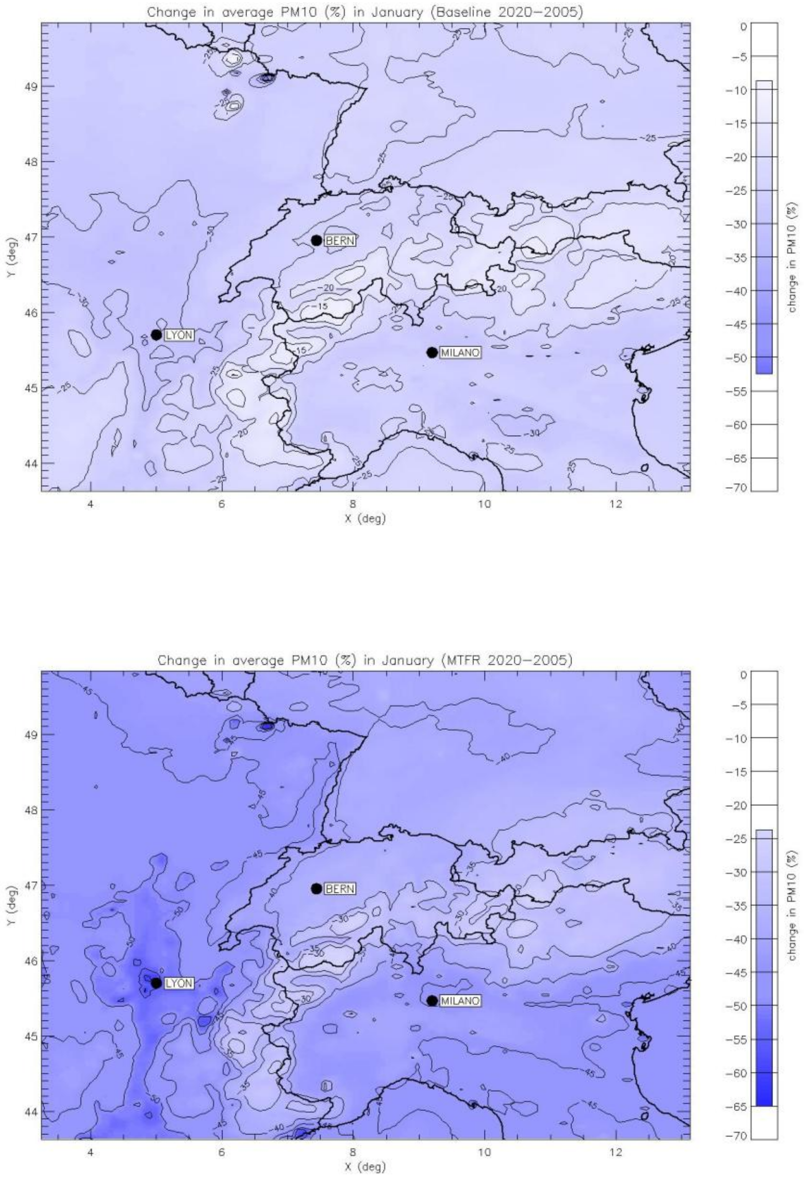


Figure 6: Changes in monthly average PM10 concentrations (%) in Baseline 2020 (above) and for MTFR 2020 with respect to 2005 reference case. Domain2

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AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES
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# A COMPARISON OF AIR POLLUTANTS CONCENTRATION BY GUUSSIAN DISPERSION MODEL WITH AMBIENT MONITORING DATA OF PHOENIX PULP & PEPER PUBLIC COMPANY LIMITED,THAILAND

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## ABSTRACT

The results of an air dispersion model with input parameters from Phoenix Pulp & Paper Company Limited, Thailand and meteorological data from Khon Kaen meteorological station created using Screening Air Dispersion Model (Screen View Version 3.5.0,) Freeware, Lakes Environmental Company, UK) were compared with ambient monitoring data. These data were collected from four stations, Ban Kumbong, Ban Nong Bua Noy, Ban Non Udom, and Ban Udomsilp stations, between 2008 and 2010, covering three air pollutants: Total Suspended Particulates (TSP), Sulfur Dioxide (SO and Nitrogen Dioxide (NO . The computed levels of these three pollutants (TSP, SO , and NO ) were lower than the ambient monitoring data by 1-250 6 and 3-8 fold, respectively. Among the several input parameters to the model, the flow rate and rate of pollutants emitted in the process were found to be the most sensitive to the estimated maximum of these three pollutant concentrations. Using this dispersion model is therefore useful for a preliminary assessment of air quality from a single source.

**KEYWORDS:** air pollution monitoring, air dispersion model, screening model, pulp and paper industry

## 1 INTRODUCTION

Phoenix Pulp & Paper Public Company Limited is a pioneer in pulp products. The company was established in 1975 and started its first line in 1982 Nampong District of Khon Kaen Province, in the northeastern part of Thailand. The location of the mill is illustrated in figure 1. In 1994, the mill underwent major expansion; by adding line-2, the mill gained the capacity to produce approximately 230,000 tons of pulp a year. The production processes consist of debarking, chipping, pulping, washing, screening, oxygen delignification, bleaching and cleaning. The pulp is further transformed into a saleable product by the process of sheet formation, drying, cutting and baling. In 2010, Phoenix Pulp & Paper Public Company Limited installed the recovery boiler for black liquor, burning 600 tons of dry solids per day. Over 90% of its products are made from eucalyptus and bamboo, which are harvested from local farmers' plantations. The company has developed partnerships with farmers by offering training, as well as seedlings, fertilizer, and guaranteed prices for trees. The mill is located within the Namphong river basin, and it frequently experiences extended periods of stagnation, especially in wintertime. With emissions from factories, power plants, and small family employee, the Namphong river basin occasionally experiences air pollution problems. In recent years, the Phoenix Pulp & Paper Company Limited has seen a rapid increase in pulp and paper production, which is anticipated to add to the effects of existing air pollution.

Figure 1 Geological map of Thailand, Phoenix Pulp & Paper Public Company Limited and original urban area receptors.

## 2. MAIN TEXT

### 2.1 Manufacturing emission inventories

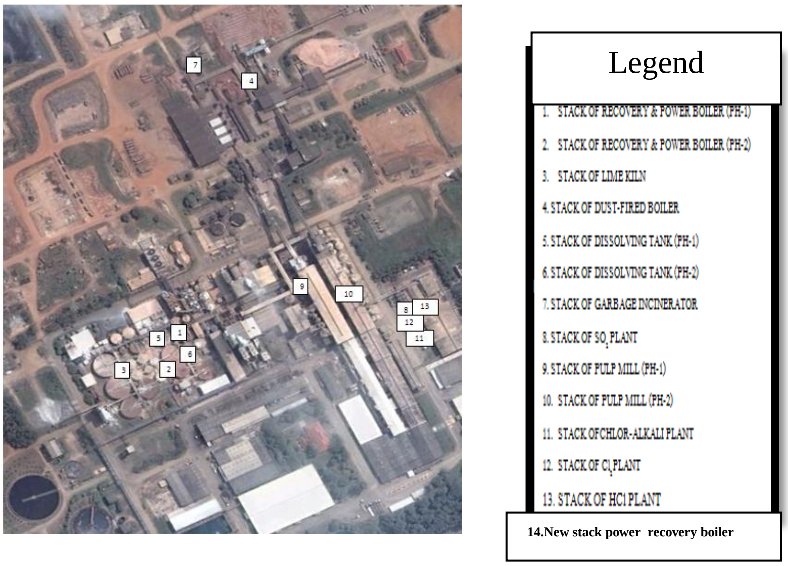


Figure 2 Locations of thirteen manufacturing emission point sources**.**

Manufacturing emission inventory data, collected twice a year for 7 days, were examined. Inventories specific for point source emissions were constructed. There were fourteen individual point sources, and three pollutants (**TSP, SO and NO** ) were modeled daily for seven emitters as area sources two times a year for 3 years between 2008 and 2010. Stacks number 4 and 8 through 13 were excluded from the model and were not included in the original inventory. The locations of the fourteen point sources for manufacturing emission and the UTM coordinates and emission characteristics for the seven point sources are shown in figure 2 and table 1, respectively. The data for the point sources were reviewed and judged to be reasonable. Uncertainty was estimated for emission rates by comparing the modeled and observed average concentrations six times for the three years (2008-2010). We were modeled using a comparison of the maximum concentration modeled and observed for each time and using the procedure, it was determined.

Table 1 Emission characteristics of seven stacks at the pulp and paper mill.

| Parameter | Unit | Recovery & Power Boiler 1 | Recovery & Power Boiler 2 | Smelt Dissolving Tank 1 | Smelt Dissolving Tank 2 | Garbage Incinerator | Lime Kiln Stack | Power Boiler 3 & 4 |
|---|---|---|---|---|---|---|---|---|
| UTM | X | 260287 | 260146 | 260267 | 260154 | 260571 | 260096 | 260245 |
| | Y | 1848278 | 1848254 | 1848257 | 1848541 | 1848390 | 1848419 | 1848537 |
| Stack Height | m | 54 | 54 | 30.2 | 56 | 11.2 | 58.5 | 80 |
| Stack Diameter Ø) | m | 2.75 | 2.75 | 1.03 | 0.9 | 0.6 | 1.18 | 3 |
| Stack characteristic | - | Circular | Circular | Circular | Circular | Circular | Circular | Circular |
| Fuel/ fuel rate | $m^3$/h | Black Liquor | Black Liquor | Black Liquor | Black Liquor | Diesel | Bunker oil/burnt lime | Fossil/ biofuel |
| Treatment | - | ESP | ESP | Scrubber | Scrubber | Scrubber | ESP | ESP |
| Treatment efficiency | % | 93.07 | 99.25 | * | * | * | 98.86 | 98.99 |

## 2.2 Monitoring Locations and SCREENING Model Setup

Between 2008 and 2010, there were 4 ambient air monitors located approximately 4 to 10 km from the factory, as shown in Figure 3. Four sites were in operation for 7 days a time twice a year. These monitors provided various types of data, but in this study, we will focus on daily ambient observations of **TSP, SO and NO** The land use and terrain elevations were edited to flat terrain, as illustrated in Figure 3. Khon Kaen meteorological station, located approximately 30 km from the mill site, provided 3 hourly surface meteorological observations,. Meteorological data were modified prior to for input into the model. Results from a wind-rose and stability index in January, February and March were inspected to ensure the reasonableness of the meteorological fields being generated. Next, maximum concentration simulations were performed with **SCREENING** to assess the reasonableness of the dispersion characterizations. For the final runs, the dispersion parameters were computed internally using similarity theory with convective eddy effects modeled.

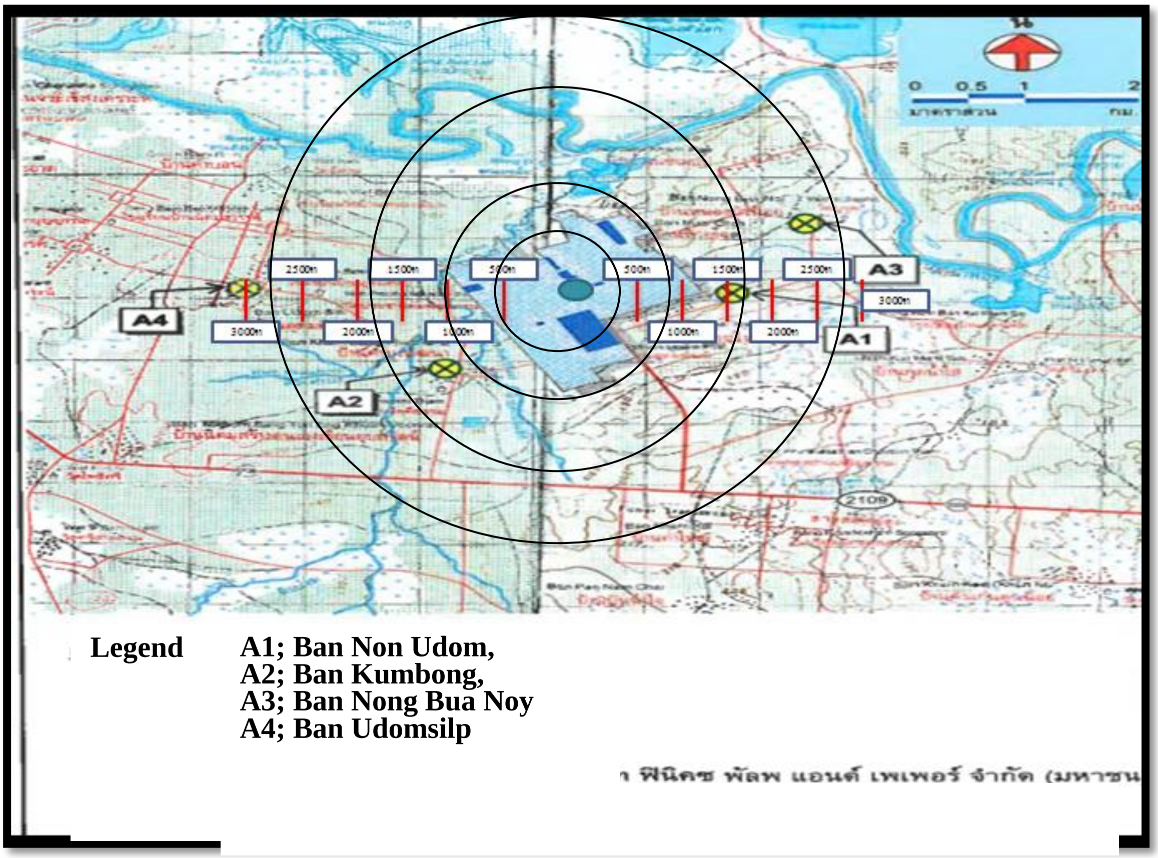


Figure 3. Four ambient air monitors associated with land use and their distance from the factory

## 2.3 Comparison of Modeling Results with Observations

The meteorological data studied during 6 periods over 3 years were wind direction, wind speed and stability class.  These data are shown in table 2.

Table 2 Meteorological observation data

| Ambient monitoring date | Wind direction | Wind speed (m/s) | Stability class |
|---|---|---|---|
| 1/2008; 27 Jan – 3 Feb | NE | 2.5 | C |
| 2/2008; 27 Aug- 3Sep | SSW | 1.7 | A |
| 1/2009; 29 Apr - 6 May | NE | 1.0 | B |
| 2/2009; 5- 12 Nov | W | 1.9 | A |
| 1/2010; 23- 30 Mar | E | 2.5 | B |
| 2/2010; 28 Nov- 5 Dec | NE | 3.1 | B |

Sensitivity analyses were undertaken for 2 scenarios, decreasing values from the base case study by 5 % in the 1$^{st}$ scenario and 10 % in the 2$^{nd}$ scenario. Various input data were analyzed. The four parameter used, emission load, wind speed, velocity, and flow rate, were sensitive to maximum concentration, as shown in table 2.

Table 2 Results of sensitivity analysis

| Parameter | Base Case study | | $1^{st}$ scenario: decreasing from base case study 5 % | | $2^{nd}$ scenario: decreasing from base case study 10 % | |
|---|---|---|---|---|---|---|
| | Data Set up | Computed maximum concentration (ppm) | Data Set up | Computed maximum concentration (ppm) | Data Set up | Computed maximum concentration (ppm) |
| Emission rate (g/s) | 9.54 | 0.004 | 10.01 | 0.004 | 10.49 | 0.005 |
| Flow ($m^3$/s) | 69.54 | 0.004 | 66.06 | 0.004 | 62.54 | 0.005 |
| Velocity (m/s) | 16.68 | 0.004 | 15.85 | 0.004 | 15.01 | 0.004 |
| Wind speed (m/s) | 3.1 | 0.004 | 2.94 | 0.004 | 2.79 | 0.004 |

**Note** Emission rates (g/s) for the $1^{st}$ and $2^{nd}$ scenarios were increased from the base case study by 5 % and 10 %

The maximum concentration measured during ambient data collection in January 2008, January 2009, and February 2010 were 0.067, 0.087, 0.124 mg/$m^3$ for TSP, and 0.01,< 0.01 and 0.023 ppm for $SO_2$ and 0.004, 0.007 and, 0.008 ppm for $NO_2$, respectively. These values are within NAAQS but are higher than the computed values by 1-250, 6 and 3-8 higher for TSP, SO and NO , respectively, as shown in figure 4. (A) A comparison of the results of the NE wind case study are shown in figure 4 (A; TSP), (B; $SO_2$), and (C; $NO_2$).

**Figure 4 (A; TSP)**

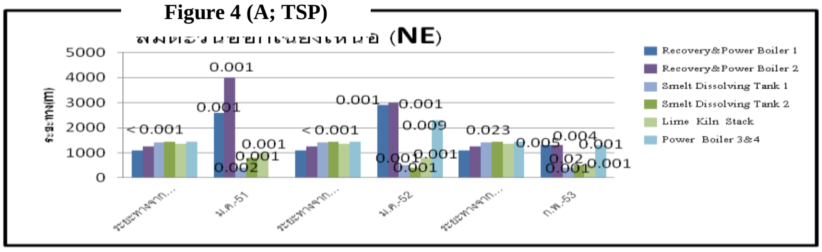
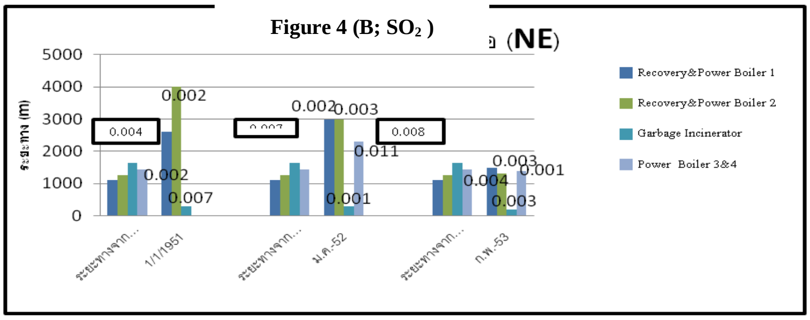


**Figure 4 (B; $SO_2$ )**



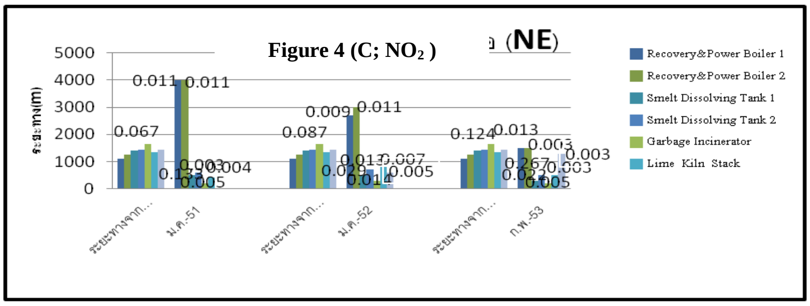


Figure 4 Comparison of results for NE wind case study

## 3 CONCLUSIONS

Screen View mathematical models successfully evaluated the concentration of air pollutants from 7 point sources at the Phoenix Pulp & Paper Public Company Limited. The maximum concentrations computed were lower than the ambient monitoring data. The concentrations of TSP, $SO_2$, and $NO_2$ were lower than the ambient monitoring data by approximately 1-250, 6, and 3-8 higher. Sensitivity analysis revealed that the emission rate and flow affect the concentration of pollutants, but wind velocity does not affect pollutant concentration. According to the microclimate and local receptors, the ambient monitoring station should be used more often in the future. Even increasing emission rate by 10% over the original data, the ambient concentration was within the Ambient Air Quality Standards. The use of Screen View simulations to estimate air pollution initiatives was not difficult, and using this dispersion model would therefore be useful for preliminary assessments of air quality from a single source. The results of the simulation can be used to predict the status of the initial management of air pollution instead of monitoring air quality, which has a relatively high cost.

## 4. ACKNOWLEDGEMENT

This work was established under cooperation education on environmental science project in the Environmental Science Department Faculty of Science, Khon Kaen University and Phoenix Pulp & Paper Public Company Limited, Khon Kaen THAILAND. Screen View Version 3.5.0, Freeware, was provided by Lakes Environmental Company, UK, and meteorological data were provided by Khon Kaen meteorological station, Meteorological Department, Thailand.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# CAQI COMMON AIR QUALITY INDEX – UPDATE WITH $PM_{2.5}$ AND SENSITIVITY ANALYSIS

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## ABSTRACT

The CAQI or Common Air Quality Index was proposed to facilitate the comparison of air quality in European cities in real-time. There are many air quality indices in use in Europe. All are different in concept and presentation and comparing air quality in cities was virtually impossible. The CAQI and the accompanying website www.airqualitynow.eu (and app) were proposed to overcome this problem. This paper describes the logic of making an index, in particular the CAQI and its update with a grid for $PM_{2.5}$. To assure a smooth transition to the new calculation scheme we studied the behaviour of the index before and after the changes. We used 2006 Airbase data from 31 urban background and 27 street stations all across Europe (that were monitoring $PM_{2.5}$ in 2006). We demonstrate the comparative behaviour of the street and urban background stations.

**Key words:** air quality index, $PM_{2.5}$, urban air quality, public awareness.

## 1. INTRODUCTION

In 2005 the Common Air Quality Index (CAQI) was proposed to facilitate the comparison of air quality in European cities in real-time (Elshout, et al. 2008). There are many air quality indices (AQI's) in use in Europe. All are different in concept and presentation and comparing air quality in cities was virtually impossible for the lay public. For examples of the difficulties of comparing air quality in cities and an overview of the available AQI-s at the time, see Elshout and Léger (2007). The CAQI and the accompanying website www.airqualitynow.eu (since a year also available as an app) were introduced as a 'lingua franca' solution to overcome this problem. This initiative currently has over 100 voluntarily participating cities. Several other air quality communication initiatives such as the obsAIRve project (www.obsairve.eu) and watch.eyeonearth.org/ (European Environment Agency), as well as a number of air quality apps, use the CAQI, making it a widely used index for informing the public on international air quality. In this paper we briefly describe the logic of making an AQI with particular reference to the CAQI. Secondly we present the update of the CAQI with a calculation grid for $PM_{2.5}$.

The CAQI and the website www.airqualitynow.eu were developed in the framework of two projects (CITEAIR and CITEAIR II). Though the projects are finished the website continues and the CAQI remains supported. Anyone interested in joining a city to the website or in using the CAQI, please contact join@airqualitynow.eu or caqi@airqualitynow.eu.

## 2 HOW TO MAKE AN AIR QUALITY INDEX – DESCRIPTION OF THE CAQI

Shooter and Brimblecombe (2009) mention two reasons for making an index: firstly linking air quality to health effects to inform the public of poor air quality and of possible remedial actions; secondly to condense complex data to provide an information overview e.g. for the development of policy or to check compliance with standards. We formulated a third reason: drawing the public's attention to air quality issues and raising awareness. Here we discuss these three reasons and their implications for the design.

## Providing real time air quality & health info - alerting people

Providing real time air quality & health information seems an obvious thing to do. However indices strongly based on health impact have several limitations. The relations between air quality and health are many, they interact in still poorly understood ways and their exact nature is hard to quantify. This implies that the index will be complex (e.g. Cairncross et al., 2007) and needs to be amended as the science evolves. Communicatively this is awkward. And more importantly, health effects occur over different exposure times (both short-term and long-term) and the reported index value usually refers to only one averaging time (usually daily). Lastly several pollutants that are currently believed to be the main causes of health effects of air pollution (e.g. elemental carbon, ultrafine particles, particle numbers) are not (yet) regulated and are not commonly monitored and included in indices.

The varying impacts of different exposure times pose a particularly awkward communication problem. A health-based index meant to warn people for short-term exposure to poor air quality is mainly in the good part of the index scale, implicitly indicating that air quality is not a problem (see for example the US-EPA index - http://airnow.gov/index.cfm?action=aqibasics.aqi) whilst at the same time annual reports often indicate that annual limit values are not met, that cities are in a situation of non-compliance etc. This dilemma is the main reason that the CAQI is not directly linked to health impacts. Indirectly there is of course a health link: it is inspired by the EU limit values that were founded on WHO recommendations. And instead of trying to capture pollutant interaction the simpler approach that the worst pollutant (at a given time) determines the index is followed. Most AQI-s use this principle.

Furthermore, current air quality rarely poses an acute short-term exposure risk to the population in general. Hence we think that today there are better, more targeted ways to inform the groups of people that really needs to adapt in case of (even moderate) pollution episodes than a general index presented on a general website. For example Sussex-air provides a messaging system that those in need of this kind of information can subscribe to (see www.airalert.info/Sussex/Default.aspx). Smartphone apps could play a similar role, even allowing individuals to set their own alert threshold (currently under consideration in the Netherlands) for example based on personal experience or recommendations of one's own physician.

## Condensing and simplifying information

This is the very essence of making an index. From a scientific point of view an AQI is a gross generalization and a serious loss of information but for communication purposes this simplification is considered essential, hence there are many indices in use. How to reduce the complex air quality information largely depends on the purpose for which the index is to be used. E.g. making a health based index leads to several other choices on the banding than an index for raising awareness. The exact index classes are a matter of subjective choices though often limit values (for example ensuing form air quality legislation such as Directive 2008/50/EC) are used for guidance. If linking the air quality information to legal limits is an important purpose the averaging times are often selected to coincide with those of the legislation (e.g. 8-hour averages for $O_3$ and CO and a 24-hour average for $PM_{10}$. For our purpose this leads to a dull presentation, so we chose hourly information.

The short-term indices are mainly used for informing the public on a daily or real-time basis. For policy development or monitoring annual information is more useful. Sometimes the number of days an index was above a certain level or the distribution of the index classes over the year is reported. However this is still quite complex information. Alternatively we propose a year average distance to target type of index (YACAQI , see Elshout 2012) that is based on the EU limit-values. Another example of a true year average index is the German LAQx (Mayer et al, 2008).

## Drawing the public's attention to air quality and raising awareness

The public is both a victim and a source of air pollution, particularly in urban areas. Traffic is often the dominant source of urban air pollution. This is particularly true for the most health relevant pollutants: the smallest particles (< $PM_1$) or the Black Carbon fraction. This pollution is mainly attributed to (diesel) vehicle exhaust (e.g. WHO, 2012). From the regulatory perspective, exceedences of the EU regulation along the streets for $PM_{10}$, $PM_{2.5}$ and $NO_2$ are of major concern for many cities in Europe[1]. Local authorities therefore have a keen interest in trying to influence the behaviour and the travel choices of the urban population and commuters. Raising awareness on the sources of pollution is one way of doing so. To draw specific attention to traffic as an important source, and roads as an awkward place to be (from the exposure point of view) the CAQI is calculated separately for roadside and city background situations.

We argue that to entice people to visit air quality websites and check the situation one would need an hourly index, hourly updated. This way people can see how pollution levels evolve throughout the day and can relate index readings to physical events: elevated afternoon ozone peaks, rush-hours, celebration fireworks, etc. This is not only informative, it also adds to confidence in the air quality measurements if concerned citizens/citizen groups can actually monitor what is occurring. Moving averages tend to obscure a lot of information.

We use a scale with considerable differentiation (1-100) to generate a more dynamic (interesting) presentation than a grid from 1 to 5 or 1 to 10. From a scientific point of view it hardly makes sense to derive index values with that kind of detail, but from a communication point of view it will help that the information is dynamic.

Lastly, the fact that citizens can compare their city to other cities (through www.airqualitynow.eu) is also considered an important feature to raise awareness and make air quality interesting. To achieve comparability across the participating cities we use the concept of core and other pollutants. Without the core pollutants ($PM_{10}$, $NO_2$ and $O_3$ - the latter not at traffic sites) the index should not be calculated. Having separate traffic and background indices helps in making the comparison between cities more fair. Otherwise the results of the comparison would be greatly influenced by a cities monitoring strategy.

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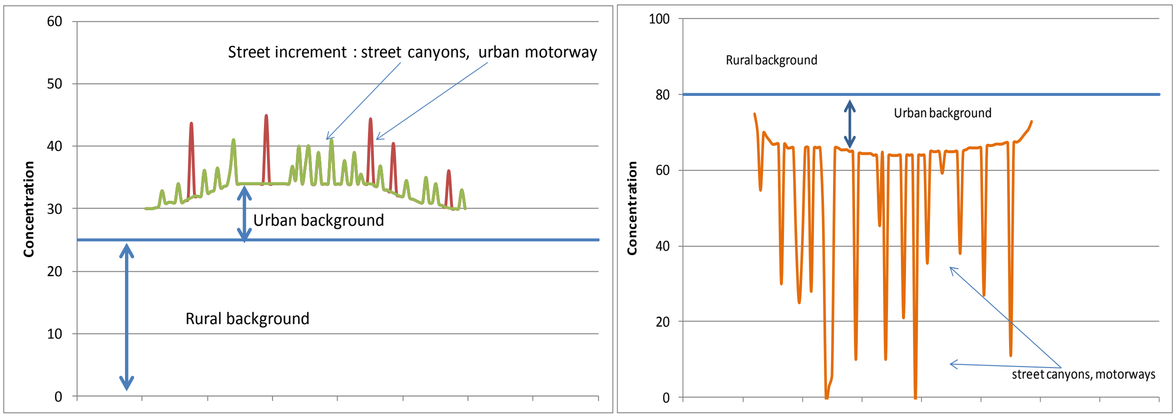
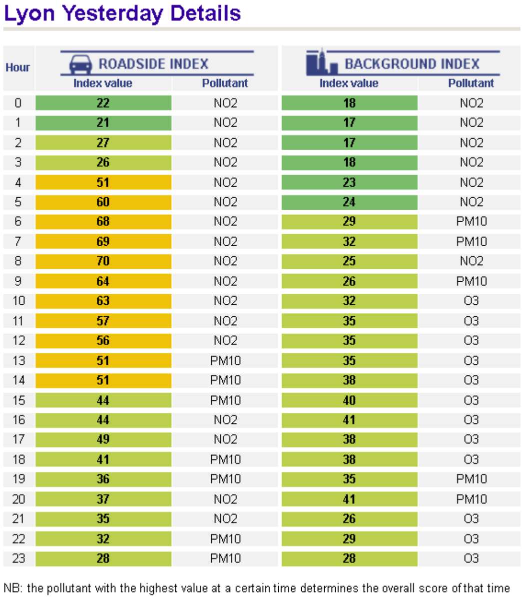
[1] Elevated background concentrations of particulate matter and particulate pollution due to wood burning in winter are also concerns for member states with difficulties meeting the EU air quality standards.

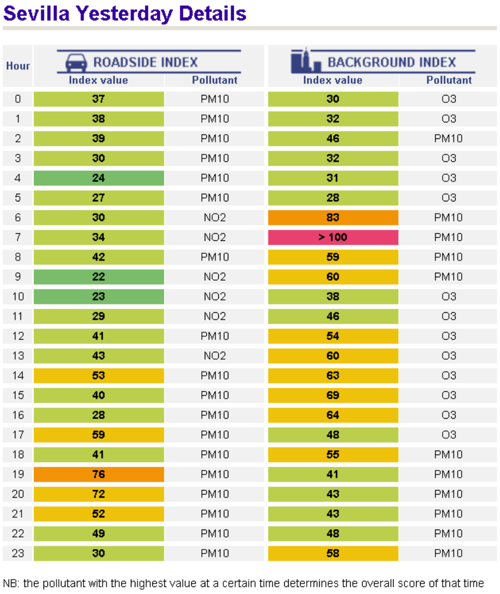




Lyon Yesterday Details

| Hour | ROADSIDE INDEX |  | BACKGROUND INDEX |  |
|---|---|---|---|---|
|  | Index value | Pollutant | Index value | Pollutant |
| 0 | 22 | NO2 | 18 | NO2 |
| 1 | 21 | NO2 | 17 | NO2 |
| 2 | 27 | NO2 | 17 | NO2 |
| 3 | 26 | NO2 | 18 | NO2 |
| 4 | 51 | NO2 | 23 | NO2 |
| 5 | 60 | NO2 | 24 | NO2 |
| 6 | 68 | NO2 | 29 | PM10 |
| 7 | 69 | NO2 | 32 | PM10 |
| 8 | 70 | NO2 | 25 | NO2 |
| 9 | 64 | NO2 | 26 | PM10 |
| 10 | 63 | NO2 | 32 | O3 |
| 11 | 57 | NO2 | 35 | O3 |
| 12 | 56 | NO2 | 35 | O3 |
| 13 | 51 | PM10 | 35 | O3 |
| 14 | 51 | PM10 | 38 | O3 |
| 15 | 44 | PM10 | 40 | O3 |
| 16 | 44 | NO2 | 41 | O3 |
| 17 | 49 | NO2 | 38 | O3 |
| 18 | 41 | PM10 | 38 | O3 |
| 19 | 36 | PM10 | 35 | PM10 |
| 20 | 37 | NO2 | 41 | PM10 |
| 21 | 35 | NO2 | 26 | O3 |
| 22 | 32 | PM10 | 29 | O3 |
| 23 | 28 | PM10 | 28 | O3 |

NB: the pollutant with the highest value at a certain time determines the overall score of that time



Sevilla Yesterday Details

| Hour | ROADSIDE INDEX |  | BACKGROUND INDEX |  |
|---|---|---|---|---|
|  | Index value | Pollutant | Index value | Pollutant |
| 0 | 37 | PM10 | 30 | O3 |
| 1 | 38 | PM10 | 32 | O3 |
| 2 | 39 | PM10 | 46 | PM10 |
| 3 | 30 | PM10 | 32 | O3 |
| 4 | 24 | PM10 | 31 | O3 |
| 5 | 27 | PM10 | 28 | O3 |
| 6 | 30 | NO2 | 83 | PM10 |
| 7 | 34 | NO2 | > 100 | PM10 |
| 8 | 42 | PM10 | 59 | PM10 |
| 9 | 22 | NO2 | 60 | PM10 |
| 10 | 23 | NO2 | 38 | O3 |
| 11 | 29 | NO2 | 46 | O3 |
| 12 | 41 | PM10 | 54 | O3 |
| 13 | 43 | NO2 | 60 | O3 |
| 14 | 53 | PM10 | 63 | O3 |
| 15 | 40 | PM10 | 69 | O3 |
| 16 | 28 | PM10 | 64 | O3 |
| 17 | 59 | PM10 | 48 | O3 |
| 18 | 41 | PM10 | 55 | PM10 |
| 19 | 76 | PM10 | 41 | PM10 |
| 20 | 72 | PM10 | 43 | PM10 |
| 21 | 52 | PM10 | 43 | PM10 |
| 22 | 49 | PM10 | 48 | PM10 |
| 23 | 30 | PM10 | 58 | PM10 |

NB: the pollutant with the highest value at a certain time determines the overall score of that time

Figure 1. Presentation of the CAQI and the website www.airqualitynow.eu

## Presentation CAQI and www.airqualitynow.eu

See figure 1. The CAQI background and traffic indices relate to a simplified theoretical air quality model of a city. For primary pollutants (often related to traffic) the figure on the top left illustrates the situation. For ozone, the top right hand picture best describes the concentrations in a city. Where and when ozone is not dominant the traffic index will likely be higher than the city background index. However if ozone is the dominant pollutant at a given time (e.g. in summer in the afternoon) the background index will be higher. This can be seen from the tables (screenshots) form www.airquality now.eu. (see figure 1, bottom part).

In the bottom left the evolution of the index on a given day in Lyon is shown. The diurnal pattern is predictable: as soon as the circulation starts to move, the roadside index becomes higher and primary pollutants determine the index. The roadside index is higher than the background throughout the day. In Seville on the same day, the roadside index (note that the peak driving hours are notably different) is lower for a large part of the day. In the afternoon: the background index is higher than the traffic index due to elevated ozone on a sunny afternoon.

## 3. CAQI UPDATE – DEVELOPMENT OF A PM$_{2.5}$ GRID

### CAQI results

Airbase data for 2006 for urban and suburban stations were obtained from the following countries (# background, #traffic): Belgium (3, 3), Czech Republic (13, 6), Germany (4, 4), Finland (1, 3), France (3, 3), Italy (3, 3) Spain (1, 2), Sweden (3, 2), and United Kingdom (0, 1). So, 31 background and 27 traffic stations were available. For 6 cities pairs of traffic and background sites were available. (For full details on sites and results per site see Elshout, 2012). If the CAQI as originally published is applied to these data we obtain the results as shown in table 1.

Table 1: Frequency (%) of the occurrence of the index and sub-index classes (hourly data)

| Dominant pollutant | Back-ground | Traffic | Index class | Background |  |  |  | Traffic |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | Overall index | Sub-indices |  |  | Overall index | Sub-indices |  |
|  |  |  |  |  | PM$_{10}$ | NO$_2$ | O$_3$ |  | PM$_{10}$ | NO$_2$ |
| PM$_{10}$ | 49 | 67 | 0-25 | 27 | 55 | 92 | 64 | 35 | 48 | 63 |
| O$_3$ | 45 |  | 25-50 | 51 | 32 | 8 | 33 | 41 | 34 | 30 |
| NO$_2$ | 6 | 33 | 50-75 | 17 | 10 | 0 | 3 | 18 | 14 | 6 |
|  |  |  | 75-100 | 4 | 2 | 0 | 0 | 5 | 4 | 0 |
|  |  |  | " >100" | 1 | 1 | 0 | 0 | 1 | 1 | 0 |

As can be seen, the majority of the sub-indices are in the first class, indicating that pollution is very low (NB: sample average). In fact medium or higher pollution occurs in less than 22% (background station) and 24% (traffic station) of the observed hours. In particular NO$_2$ seems to score very low. If we look at the overall index, based on the principal that the worst sub-index determines the overall index, the outcome is of course different. For the overall hourly index ‘low’ (26-50) is the dominant class. The index conveys the messages that air pollution by the individual pollutants is generally low (from the short-term exposure perspective).

Looking at the daily index (Table 2.) one can see that the index readings are higher. This is expected as the worst hour determines the daily index (for PM$_{10}$ a specific –more stringent -grid is used accounting for the longer averaging time). Looking at the frequency distribution of the pollutants, PM$_{10}$ is slightly more prominent in the daily index. This effect used to be much stronger as the old grid was not completely consistent between the two averaging times. This was repaired.

Table 2: Frequency (%) of the occurrence of the index and the sub-index classes; daily index as maximum of hourly index ($O_3$, $NO_2$) and daily average ($PM_{10}$); improved $PM_{10}$ daily grid

| Dominant pollutant | Back-ground | Traffic | Index class | Background |  |  |  | Traffic |  |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | Overall index | Sub-indices |  |  | Overall index | Sub-indices |  |
|  |  |  |  |  | PM10 | NO2 | O3 |  | $PM_{10}$ | $NO_2$ |
| PM10 | 56 | 71 | 0-25 | 4 | 20 | 66 | 30 | 8 | 15 | 23 |
| O3 | 40 |  | 25-50 | 56 | 44 | 32 | 59 | 41 | 39 | 54 |
| NO2 | 4 | 29 | 50-75 | 28 | 25 | 3 | 11 | 33 | 28 | 20 |
|  |  |  | 75-100 | 10 | 9 | 0 | 1 | 16 | 16 | 3 |
|  |  |  | " >100" | 2 | 2 | 0 | 0 | 2 | 2 | 0 |

## Selecting a suitable $PM_{2.5}$ grid

Inclusion of a new pollutant in the calculation should not affect the overall outcome of the CAQI in a significant way, at the same time the new pollutant should occasionally pop-up as the pollutant dominating the index. We looked at observed $PM_{2.5}/PM_{10}$ ratios in Europe to derive the $PM_{2.5}$ grid from the existing $PM_{10}$ grid. De Leeuw and Horálek (2009) report ratios in the range of 0.4 to 0.8, with a ratio between 0.6 and 0.7 typical for the urban situation. For traffic the lower of the two seemed more applicable. To obtain the $PM_{2.5}$ borders those for $PM_{10}$ are scaled with 0.6 (and rounded to nearest '5' or '0').

The updated CAQI calculation grid is shown in table 3. Note that apart from the introduction of the $PM_{2.5}$ grid some other minor repairs were done as well. They mainly relate to the $PM_{10}$ daily calculation scheme. The $SO_2$ grid was slightly changed to make it more consistent with the EU directive (EU, 2008).

Table 3. The updated CAQI calculation grid (core pollutants marked in grey); all modifications in italics.

| Index class | Grid | Traffic |  |  |  |  |  | City Background |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | core pollutants |  |  | pollutants |  |  | core pollutants |  |  |  | pollutants |  |  |  |
|  |  | $NO_2$ | $PM_{10}$ |  | $PM_{2.5}$ |  | CO | $NO_2$ | $PM_{10}$ |  | $O_3$ | $PM_{2.5}$ |  | CO | $SO_2$ |
|  |  |  | 1-h. | 24-h. | 1-h. | 24-h. |  |  | 1-h. | 24-h. |  | 1-h. | 24-h. |  |  |
| Very low | 0 | 0 | 0 | 0 | *0* | *0* | 0 | 0 | 0 | 0 | 0 | *0* | *0* | 0 | 0 |
|  | 25 | 50 | 25 | *15* | *15* | *10* | 5000 | 50 | 25 | *15* | 60 | *15* | *10* | 5000 | 50 |
| Low | 25 | 50 | 25 | *15* | *15* | *10* | 5000 | 50 | 26 | *15* | 60 | *15* | *10* | 5000 | 50 |
|  | 50 | 100 | 50 | *30* | *30* | *20* | 7500 | 100 | 50 | *30* | 120 | *30* | *20* | 7500 | 100 |
| Medium | 50 | 100 | 50 | *30* | *30* | *20* | 7500 | 100 | 50 | *30* | 120 | *30* | *20* | 7500 | 100 |
|  | 75 | 200 | 90 | 50 | *55* | *30* | 10000 | 200 | 90 | 50 | 180 | *55* | *30* | 10000 | *350* |
| High | 75 | 200 | 90 | 50 | *55* | *30* | 10000 | 200 | 90 | 50 | 180 | *55* | *30* | 10000 | *350* |
|  | 100 | 400 | 180 | 100 | *110* | *60* | 20000 | 400 | 180 | 100 | 240 | *110* | *60* | 20000 | 500 |
| Very | > 100 | > 400 | >180 | >100 | > *110* | >*60* | >20000 | > 400 | >180 | >100 | >240 | > *110* | >*60* | >20000 | >500 |

| | | |
|---|---|---|
| High* | | |

$NO_2$, $O_3$, $SO_2$: hourly value / maximum hourly value in µg/$m^3$
CO 8 hours moving average / maximum 8 hours moving average in µg/$m^3$
$PM_{10}$, $PM_{2.5}$ hourly value / daily value in µg/$m^3$

* An index value above 100 is not calculated but reported as “ > 100”

The results are shown in table 4, which is based on exactly the same data as table 1 (except for $PM_{2.5}$). The update occurred, with on average, hardly any change to the distribution of the index classes. When we look at the frequency distribution of the dominant pollutant, it shows that the role of $NO_2$ becomes even slightly smaller. The main effect is, as could be expected, with $PM_{10}$. In particular in background situations $PM_{2.5}$ overtakes $PM_{10}$ noticeably. The average results are satisfactory. The relevance of $PM_{2.5}$ as the dominant pollutant is strongly affected by the choice of the ratio between the two PM calculation grids. A sensitivity analysis was done (Elshout, 2012) using scaling factors of 0.5 and 0.7. The choice hardly affected the overall index calculation but mainly determined which PM fraction was more dominant.

Table 4: Frequency (%) of the occurrence of the index and sub-index classes of the upgraded CAQI (hourly data)

| Dominant pollutant | Background | Traffic | Index class | Background | | | | | Traffic | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Index | Sub-indices | | | | Index | Sub-indices | | |
| | | | | | $PM_{10}$ | $PM_{2.5}$ | $NO_2$ | $O_3$ | | $PM_{10}$ | $PM_{2.5}$ | $NO_2$ |
| $PM_{10}$ | 18 | 40 | 0-25 | 27 | 55 | 53 | 92 | 64 | 34 | 48 | 55 | 63 |
| $O_3$ | 39 | | 25-50 | 51 | 32 | 30 | 8 | 33 | 41 | 34 | 31 | 30 |
| $NO_2$ | 4 | 27 | 50-75 | 17 | 10 | 12 | 0 | 3 | 19 | 14 | 11 | 6 |
| $PM_{2.5}$ | 38 | 33 | 75-100 | 4 | 2 | 4 | 0 | 0 | 5 | 4 | 3 | 0 |
| | | | " >100" | 1 | 1 | 1 | 0 | 0 | 1 | 1 | 1 | 0 |

As mentioned before we use the concept of core pollutants and other pollutants to assure a minimum of comparability in the results from one city to another. $PM_{2.5}$ was not made a core pollutant. This doesn’t mean that we think it is of lesser importance than the other core pollutants. However, making it a core pollutant would imply that the number of stations for which the CAQI can be calculated will be limited, at least for the time to come. $PM_{2.5}$ is being monitored on an increasingly large scale, but is not mandatory everywhere according to EU (2008). Countries can maintain a mix of $PM_{10}$ and $PM_{2.5}$ monitoring stations to meet their measuring requirements.

## DISCUSSION

The UK AQI was recently updated and now includes a grid for $PM_{2.5}$ (COMEAP, 2011). Some points of the review are discussed here in relation to the CAQI.

The UK air quality index was and is explicitly health based. The difficulties with a health based index can be seen if the UK index is compared to the other major health based index, the US AQI (http://www.epa.gov/airnow/aqi_ tech_assistance.pdf), there are considerable differences between the two.

The review concludes that the understanding of the effects of mixtures of pollutants remains limited so the UK retains the concept of the worst sub-index determining the index (like the CAQI and most other indices).

The UK index uses the longer averaging times as found in exposure literature or in the specification of limit values. The problem with these longer averaging times are acknowledged and COMEAP proposes the use of ‘trigger’ values to allow for the prediction of episodes in real time. The CAQI uses short averaging times instead as it also has other communicative advantages.

As a basis for the review a ‘public insight study’ was conducted. The study revealed that people wanted information in terms of potential health effects, though several respondents remarked that the preset qualifications might differ for different people. The personalisation of health recommendations that is likely to become available in the near future with the arrival of smart apps will address this issue.

The relation between the $PM_{10}$ and the $PM_{2.5}$ grid was derived in a similar way (a scale factor). For the UK 0.7 was used where we use 0.6 (note that the WHO used 0.5, a worldwide average $PM_{2.5}/PM_{10}$ ratio).

The overall grids of the CAQI and the revised UK index are reasonably similar for the PM fractions. For $O_3$ the grid is virtually identical except that the CAQI is based on 1-hour readings. The CAQI is therefore a stricter index. For $NO_2$ the picture is mixed stricter at the higher end, and slightly less strict at the bottom. The new $NO_2$ grid in the UK is some 25% stricter than it used to be.

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# DOUBLE COMPRESSIONS OF ATMOSPHERIC LAYER BY GEOPONTIAL TENDENCY AND VORTICITY AND ATMOSPHERIC BOUNDARY LAYER INFLUENCED UPON ABRUPT HIGH ($PM_1$, $PM_{2.5}$ AND $PM_{10}$) CONCENTRATIONS AT A MOUNTAINOUS COASTAL CITY DURING A YELLOW DUST PERIOD IN OCTOBER

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## ABSTRACT

Double compressions of atmospheric layer of 500hPa level by geopotential tendency and vorticity and atmospheric boundary layer were investigated at a coastal city, Gangneung city and Mt. Taegulyang (alt. 896 m) located in 20 km west of the city for October 26-29, 2003, using a 3D-WRF-3.3 model. On October 26, before dust transportation from Gobi Desert to the city, hourly concentrations of $PM_{10}$, $PM_{2.5}$ and $PM_1$ were generally less than 40 ㎍/$m^3$ and continued to be until 0900LST, October 27. At 0900LST, October 27, no windstorm was detected and moderate south-westerly wind of 4 to 6 m/s prevailed in the study area, but 1700LST, windstorm was detected near the top of Mt. Taegulyang in 20 km west of a coastal city and internal gravity waves with a hydraulic jump motion was developed, resulting in a cavity of calm wind in the coastal city. From 0900LST to 2100LST, October 27, net relative vorticity of $- 2 \times 10^{-5}$/sec at 500 hPa level for 12 hours induced a downward motion of cold air from the upper level toward the ground surface with a decreasing rate of air temperature of - 4 $^0$C/day at 850 hPa level. Simultaneously, net geopotential tendency at 500hPa level of -20 m/day for 12 hours lay on the study area caused the atmospheric depth of 500 hPa level to be vertically much shrunken. Downward motion of cold air and compression of atmospheric depth resulted in merging of streamlines with higher speed more than 25 kts of isotach at 850 hPa level and produced the formation of strong surface wind speeds. As strong synoptic westerly wind blowing over the mountain toward the downwind side coast was associated with mountain-land breeze by both nocturnal cooling of the ground surface near sunset and steep mountain terrain, it could be an intensified downslope wind like katabatic wind. Furthermore, as soon as synoptic westerly wind passed over the steep mountain barrier, a strong intensified downslope westerly wind could depict a cyclonic flow pattern to cause cyclogenesis in the downwind side and wind speed was intensified into a wind storm more than 10 m/s in the mountain, but calm with a cavity in the coastal basin (city). Under the dust transportation from Gobi Desert in Mongolia to the city, high concentrations of $PM_{10}$, $PM_{2.5}$ and $PM_1$ were 60.59 ㎍/$m^3$, 26.92 ㎍/$m^3$, 19.63 ㎍/$m^3$ at 0900 LST (beginning time of office hour) and after 0900 LST, the PM concentrations continued to increase under the influence of dust transportation into the city, resulting in maxima of 154.57 ㎍/$m^3$, 93.19 ㎍/$m^3$ and 76.05 ㎍/$m^3$ at 1700 LST (ending time of office hour), underneath much shallower nocturnal surface inversion layer (NSIL) than daytime convective boundary layer (CBL) at the city. GOES-DCD satellite images and HYSPLIT model were additionally used for this study.

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**Keywords:** Geopotential tendency, vorticity, WRF-3.3 model, $PM_1$, $PM_{2.5}$, $PM_1$, streamline, cyclogenesis, katabatic wind, nocturnal surface inversion layer, convective boundary layer.

**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES 4th International Symposium and IUAPPA Regional Conference**
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# QUNTIFICATION OF THE IMPACT OF ATATURK INTERNATIONAL AIRPORT EMISSIONS ON AIR QUALITY

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## ABSTRACT

Istanbul has a potential to be an important pollution source for both local and regional pollution in Eastern Mediterranean with over 14 million population and responsible for 40% of Turkey's industrial output. Atatürk International Airport is a significant emission source as being the biggest airport in Turkey, which has around 37,5 million passengers annually. This paper investigates the impact of Atatürk International Airport related emissions on air quality considering all related sources (i.e., aircraft, ground support equipment and road traffic emissions caused due to airport). Minute by minute flight activity data were gathered by ADS-B receiver placed nearby the airport. This dataset includes flight number, location and altitude information for each aircraft. International Civil Aviation Organization database is used for the related emission factors that are based on motor type, flight mode and fuel flow rates. Emission estimation algorithm is developed to estimate minute-by-minute three dimensional (i.e., not just at the surface level) pollutant values. Ground support equipment (GSE) emission calculation is based on fuel consumption data and specific emission factors for all different types of equipment. Activity data as well as the fleet information for the GSE are obtained from General Directorate of State Airports Authority. For calculation of airport related road traffic, activity data are processed from Remote Traffic Microwave Sensors near the study area. Emission factors are gathered from CORINAIR.

**Keywords:** Airport Emissions, Modeling, CMAQ

## 1. INTRODUCTION

Air transportation has become one of the most important transportation mode in modern life and air traffic is continuously increasing over the world. Total scheduled passenger traffic increased by 6.5 per cent in 2011 compared to 2010 which represents the second consecutive growth for the air transport industry since 2009. The number of aircraft departures reached the uncompromised level of 30 million in 2011 with a 3.6 per cent increase year-on-year. According to forecasts, commercial air travel is expected to double in the next 20 years which will in turn increase the amount of contaminants emitted to the atmosphere (ICAO). The most important sources considered for air pollution inventorying and modeling are aircraft engines, airport GSEs (Ground Service Equipment) and the contribution from road traffic in the surrounding road network (Winther et al. (2005).

Airport related emissions primary species can be considered as nitrogen oxides (NOx), including nitrogen dioxide (NO2) and nitrogen oxide (NO); volatile organic compounds (VOC), including non-methane hydrocarbons (NMHC); carbon monoxide (CO); particulate matter (PM), fraction size PM2.5 and PM10; and sulphur oxides (SOx) (ICAO, Airport Air Quality Manual, 2011). Aircraft emissions are not only has effect on surrounding air quality but also on global warming (Norway Meteorological Institute, 2004). Aircraft engine emissions include carbon dioxide (CO2) and water vapor which are considered as greenhouse gases.

There are several studies shoving the adverse impact of airport related emissions on health including premature mortalities (Barrett et al. (2010), Ratliff et al. (2009), (Krzyzanowski and Cohen, 2008)). Due to the increasing amount of residential development surrounding airports and the continued growth of commercial air travel, air pollution surrounding airports has become a significant concern for local/ regional governments (ICAO).

Istanbul has a potential to be an important pollution source for both local and regional pollution in Eastern Mediterranean with over 14 million population and responsible for 40% of Turkey’s industrial output. Due to inadequate capacity of the existing airports and new urbanization plans with the increasing population, there is a debate on the need of a new airport in Istanbul. However, the debate on air quality impacts of airports has occurred without quantification of those impacts on human health on a regional scale. Atatürk International Airport is a significant emission source as being the biggest airport in Turkey, which has around 37,5 million passengers annually. According to General Directorate of State Airports Authority of Turkey statistics; aircraft operations in the Ataturk International Airport has increased 12.8% from year 2010 to 2011. The purpose of this paper is to investigate the impact of Atatürk International Airport related emissions on air quality.

## 2. METHODOLOGY

### 2.1 Aircraft Emissions

An aircraft flight trajectory database was used to calculate the aircraft emission rates for each grid of air quality model. Flight trajectory records are based on Automatic Dependent Surveillance Broadcast (ADS-B) which provides Global Positioning System (GPS) accuracy for position and time. A flight tracking station has located near İstanbul Atatürk International Airport for collecting the ADS-B messages broadcasted from aircrafts. First, ADS-B messages were collected by Airnav RadarBox which is a commercial ADS-B receiver hardware and software solution. Second, the collected data has processed to prepare the flight trajectory database. Then, International Civil Aviation Organization (ICAO) emission database was used with flight trajectory data to calculate the contribution of each flight as a pollutant source in different flight modes. Aircraft emission rates in the 3D grid structure of air quality model are summation of calculated pollutant emission of flights for specific time intervals.

### Data Preparation

ADS-B messages can contain different type of data about aircraft and flight status. For this study aircraft ID, horizontal position, barometric altitude and time information was used from messages which collected by Radarbox. Airnav RadarBox provides a communication interface over TCP sockets for software developers. ADS-B messages that have received by RadarBox can be read from local socket port number 30003 in real time. Each message comes as a row in comma-separated format. Message rows which come from RadarBox are written to corresponding text file without change. This recording process creates individual record files for each hour. Each record file consists of ADS-B message rows which received from many aircrafts in corresponding hour.

Another program reads record files for classifying messages according to source aircraft. This classification carries message rows from record files to flight files regard of to which flight they belong. Messages belonging to the same flight are kept in same flight file. Because of emission data provided from ICAO emission database is only valid for flights below 3000 feet altitude, data points which are below this limit altitude on flight trajectory has not taken account for emission calculations. Collected messages from an aircraft are not distributed equally in time due to connection issues. Data points were reconstructed for determining one position per second.

Estimation of intermediate points near runway in landing has done according to constant vertical speed up to runway. For other conditions intermediate points were estimated using linear interpolation on flight trajectory.

Emission production of an aircraft depends on its flight mode. Emission rates of aircraft engines for take-off, climb out, approach and idle modes are available in ICAO emission database. Data points were assigned a mode label after reconstruction. Mode labels are helpful for finding convenient emission rate from emission database.

This data preparation processes create flight trajectory database which consist of mode labeled data points for each second of all flights.

### Grid Data Preparation

Data points on trajectory of flights were transformed to emission rates for different pollutant types according to flight mode and engine type. Calculated emission rates of data points were added to corresponding grid box. Summation of emission rates of flights which passed through a grid box gives total emission rate of this grid box for a specific time interval.

## 2.2 Airport Related Traffic Emissions

Istanbul Metropolitan Municipality has RTMS (Remote Traffic Microwave Sensors) sensors in several locations placed near the highways and busy roads over the city. Vehicle related data gathered from RTMS sensors, include the total vehicle count, long vehicle count, average speed and road load factor. For this study, 9 RTMS data used for identifying the airport related traffic. Figure 1 shows RTMS sensors near the airport and black dots indicates the ones used in this study.

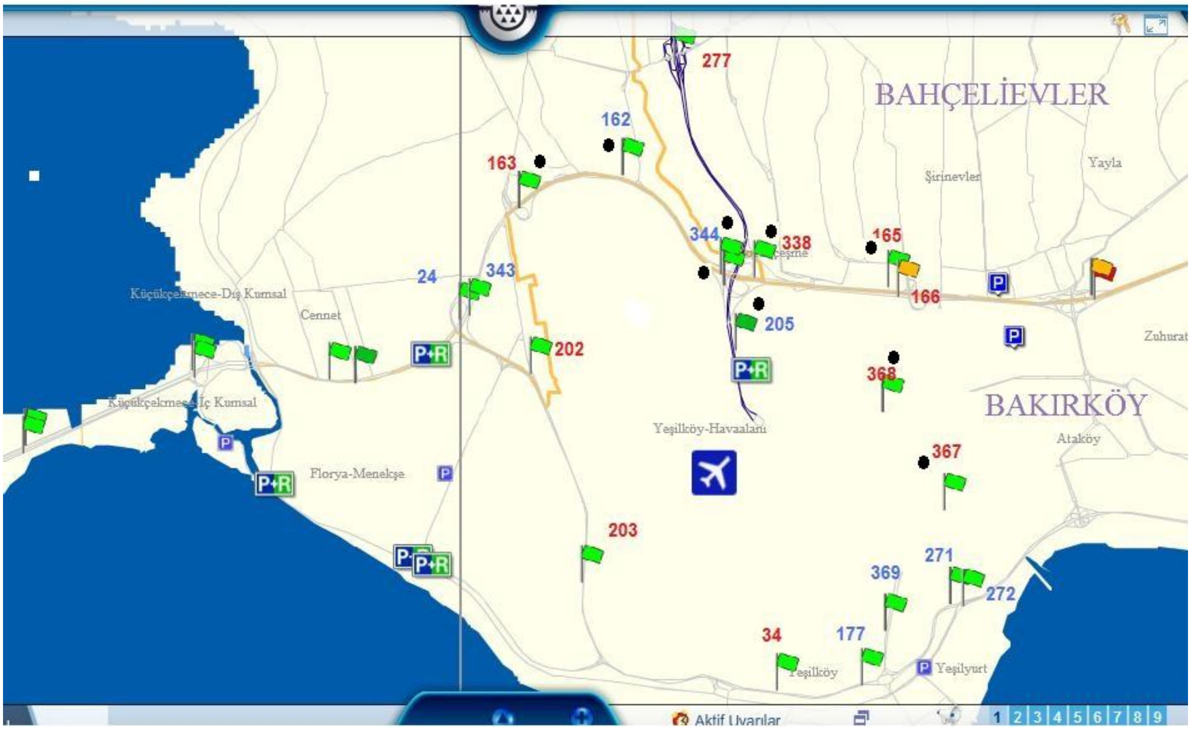


Figure1: RTMS Points Around Atatürk International Airport

Airport related traffic distributed to the districts according to population weights. Average distance between each district and Atatürk International Airport has taken into account while calculation of the distance based activity data.

Emission factors taken from the previous multiphase study that EMBARQ and Istanbul Metropolitan Municipality conducted in 2006. Study includes identification the types of vehicles in Istanbul, measurement of pollutants emitted from the vehicles in terms of type and amount and determination of specific emission factors for Istanbul.

## 2.3 Ground Support Equipment Emissions

Airport Air Quality Manual prepared by ICAO, includes the emission calculation methodologies; one of which involves the fuel use by GSE. In this approach, emissions are calculated by obtaining actual fuel-use data for GSE (or estimating such data) and then combining these data with average emission factors by (ICAO, 2011),

Emission Pollutant [g] = Σfuel types (total fuel type used [kg] × average emission factor [g/kg fuel type] (1)

Ground Support Services (GSE) currently operated by 71 different private companies in Atatürk International Airport. Information on the vehicle fleet (types of vehicles/equipments, motor type, age, motor power) and fuel consumption data gathered from the companies separately. Gathered data is 78% of the total data in terms of vehicle number. Emission factors for Europe, taken from the Airport Air Quality Manual (ICAO, 2011).

## 3. RESULTS AND CONCLUSION

Amount of the aircraft emissions depends on the motor type and operation mode. From the emission database published by ICAO, for the flights under 3000 ft, information on fuel consumption data based on motor types and operation mode and emission values. Although flight position information is available; it is still not possible to identify the points that aircrafts emit pollutants exactly because of the high speed of the aircrafts. Therefore it is more convenient to work with areas than with points. Figure 1 and Figure 2 demonstrates the emission maps prepared with this study.

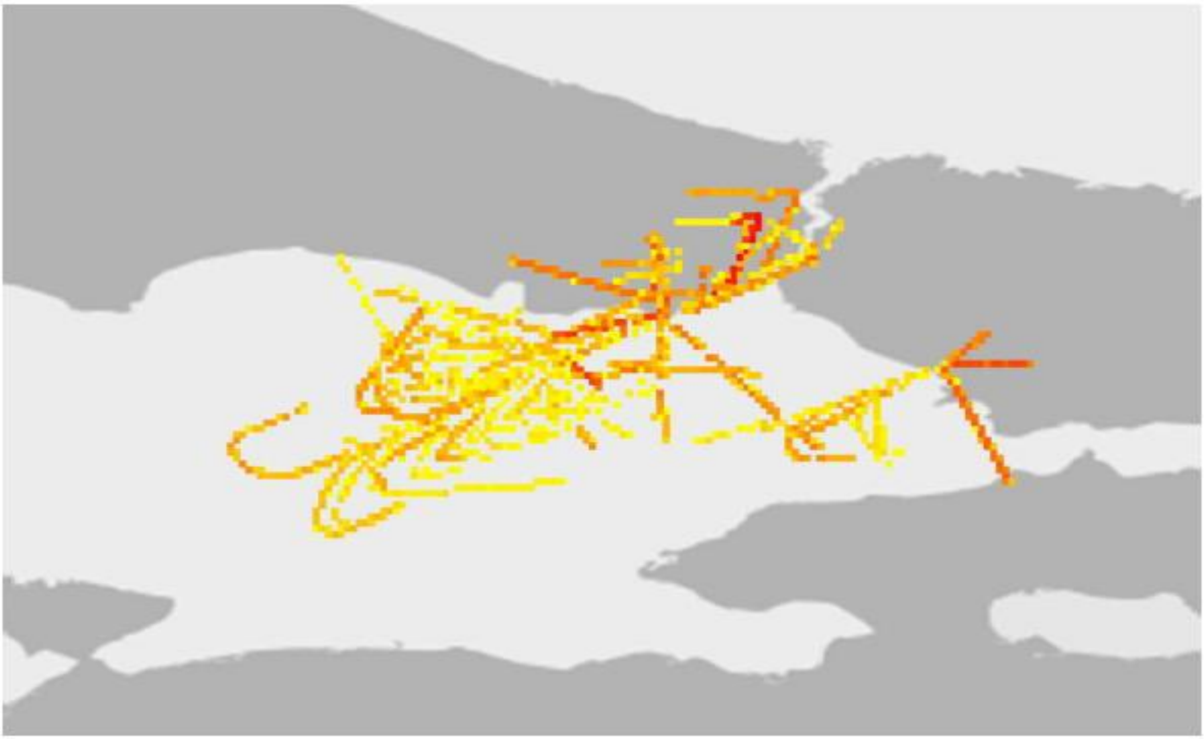
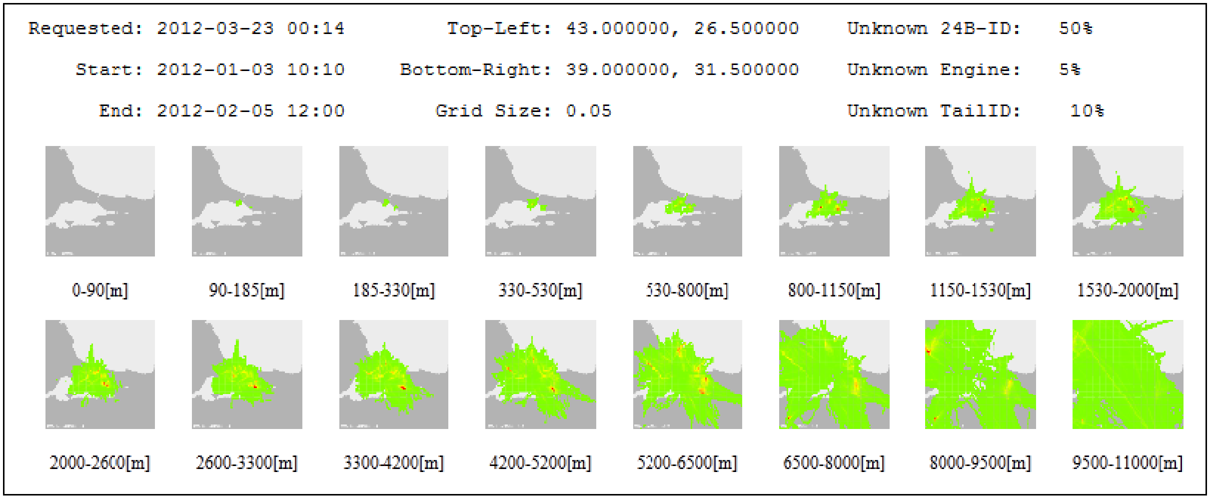


Figure 2: HC emissions of aircrafts travelling between 200ft and 3000 ft from 21.05.2011/ 00:00 to 22.05.2011/ 08:00.



```
Requested: 2012-03-23 00:14        Top-Left: 43.000000, 26.500000    Unknown 24B-ID:    50%
    Start: 2012-01-03 10:10    Bottom-Right: 39.000000, 31.500000    Unknown Engine:    5%
      End: 2012-02-05 12:00       Grid Size: 0.05                    Unknown TailID:     10%
```

Figure 3: Aircraft Emissions at Different Altitudes

Airport related traffic emissions were calculated as 728.4 t/m CO, 103 t/m VOC, 370.4 t/m NOx, 13.9 t/m PM10 and 25545.6 t/m CO2 for January 2011. Contribution of Ground Support Equipment emissions calculated as; 173.54 t/y NOx, 37.9 t/y HC, 59.51 t/y CO, 20.52 t/y PM10 and 11347 t/y CO2 for the year 2011. Our results suggest that, ground support equipments have lesser impact on air quality than airport related traffic emissions.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# BAP SIMULATIONS INCLUDING GAS/PARTICLE PARTITIONING AND DEGRADATION INTO THE WRF-CMAQ SYSTEM

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## ABSTRACT

Benzo(a)pyrene (BaP) is polycyclic aromatic hydrocarbon whose adverse effects on human health have been demonstrated. Directive 2004/107/CE of the European Union establishes a target value of 1 ng/m3 of BaP in the atmosphere. The main aim is to estimate the BaP concentrations in the atmosphere and know the main influences on BaP ground level concentrations. BaP degradation and adsorption mechanism have been integrated into the chemical-transport model CMAQ. The air quality model has been driven by the WRF meteorological model. A validation process of the BaP and other pollutant results have been conducted in the urban area of Zaragoza (Spain) during 10 weeks in 2010. The agreement is generally satisfactory.

**Key Words:** BaP, CMAQ, WRF, Partitioning

## 1. INTRODUCTION

One of the most important PAH is the Benzo(a)pyrene because of its toxicity. Bap is regulated by the Directive 2004/10/CE of the European Union, which establishes a target value of 1 ng/m$^3$. Modeling can help to assess the spatial and temporal distribution of BaP concentrations across domains and to also assess the impact of different emission reduction scenarios. It was necessary to simulate the atmospheric transport of the BaP considering dynamic atmospherics processes in addition to pollutant properties. To simulate adequately the processes that determine the transport, degradation and deposition of BaP and other PAHs, it is essential to have a chemical transport model that represents the state of the art in atmospheric modeling as well as in aerosol chemistry and dynamics.

We used the Community Multiscale Air Quality (CMAQ) model of the USE EPA (Byum and Ching, 1999). This Eulerian modelling system can be used to model the atmospheric distribution of aerosols. The CMAQ already includes a detailed representation of atmospheric aerosols and it can be expanded to other substances. It can be conveniently linked to the mesoscale meteorological model Weather & Research Forecasting system (WRF) developed by NCAR and others (Michalakes et al., 2001;Skamarock et al., 2005)., which is used here to calculate the meteorological input fields so CMAQ model is driven by WRF meteorological model with 1 hour temporal resolution. WRF model can be directly linked to CMAQ via a Meteorological Chemistry Interface Preprocessors (MCIP).

## 2. MAIN TEXT

Here we describe model development, spatial results over the different domains and compare results to measurements. The purpose of this study is to add modules to simulate BaP with the CMAQ model version 4.7.1 (June 2010) . WRF meteorological model is a 3D non-hydrostatic prognostic model that simulates mesoscale atmospheric circulations. In this work the version 3.3.1 (September 2011) is used. The link between WRF and CMAQ is developed with the MCIP version 3.6 (June 2010).

In this contribution, an extension to CMAQ (CMAQ-BaP) is presented. We use the new extended version of CMAQ (CMAQ-BaP) developed by us to investigate BaP spatial and temporal distribution over Iberian Peninsula and Zaragoza area. Two new BaP species have been added, aerosol (BAP) and gas (SV_BAP). BaP is gas phase is treated as inert gas. BaP is emitted in particle phase, 99% accumulation mode (0.1 – 2.5 um) and 1% Aitken mode (< 0.1 um). Deposition and scavenging of the aerosol BaP is the same parameterizations as for CMAQ organic aerosols. Deposition velocity of BaP gas is the same that the semi-volatile alkanes that is calculated by CMAQ.

The gas-particle partitioning has a substantial effect on transport in case of BaP. We added new developments to simulate gas phase and organic carbon(OC)-bound particulate transport and chemistry. An OC absorption model is implemented to model gas-particle partitioning of BaP bases on the absorptive partitioning model of Pankov (1994) and Odum (1996). The BaP concentration in aerosol phase is calculated according to equation:

$$C_{aer} = C_{tot} - C^{*}_{sat} \frac{C_{aer}/m}{Tot_{org}} \tag{1}$$

$C_{aer}$ : Concentration in the particle phase
$C_{tot}$ : Total concentration (gas + particle)
$C^{*}_{sat}$ : Saturation concentration
$m$ : Molecular weight
$Tot_{org}$ : Total abosorbing organic mass

The inverse of the saturation concentration of the compound is equivalent to the definition of the partitioning coefficient used in Pankov (1994). Saturation concentration is modified as a function of temperature using the equation:

$$C^{*}_{sat} = C_{sat} * T_{factor} \tag{2}$$

where $C_{sat}$ is the effective saturation concentration with a value of 5.4e-3 (μg/m$^3$) and the temperature factor $T_{factor}$ is calculated as:

(3)

$$T_{factor} = \frac{T^0}{T} e^{\left( \frac{\Delta H_{vap}}{R} \left( \frac{1}{T^o} - \frac{1}{T} \right) \right)}$$

$T^0$ : Reference temperature (298 ºK)

$T$ : Air temperature

$\Delta H_{vap}$ : BaP Enthalpy of vaporization (116.7e3 J/mol)

$R$ : Gas constant (8.314 J/mol ºK)

The total absorbing organic mass ($Tot_{org}$) used in equation 1 is defined as:

(4)

$$Tot_{org} = \sum_{j=1}^{n} \frac{C_{aer}}{m} + \frac{C_{init}}{m_{init}}$$

where n is the number of compounds in the absorbing organic particle phase, m is the molecular weight and $C_{init}$ is any additional absorbing material in the particle phase. So the total absorbing organic mass is not known a priory and the set of nonlinear equations (j=1…n) is solved by an iteration method using a globally convergent variation of Newton method.

The gas phase concentrations of the BaP have to exceed a threshold concentration before can be transferred to the particle phase. Until the threshold value defined in (5) is reached, BaP gas does not partition to the particle phase. If the pre-existing organic aerosol concentrations are zero gas/particle equilibrium is established.

(5)

$$\sum_{i=1}^{n} \left( \frac{C_{gas,i}}{C^*_{sat,i}} \right) \geq 1$$

We incorporate also BaP loss due to oxidation by Ozone ($O_3$) with a first order reaction.. Reaction with ozone can be an important degradation pathway for the particulate BaP in the atmosphere. In the Figure 1 we can see how the degradation depends of the $O_3$ degradation. Degradation of the aerosol BaP by the Ozone has been implemented into CMAQ based on Kwamena et al. (2004) following the equation:

(6)

$$K = \frac{K_{\max} K_{O_3} [O_3]}{1 + K_{O_3} [O_3]}$$

$K$ : Degradation rate constant

$K_{\max}$ : Maximum rate coefficient (0.06 $s^{-1}$)

$K_{O_3}$ : Ozone gas to surface equilibrium constant (0.028 $10^{-13} cm^3$)

$[O_3]$: Ozone conentratrion

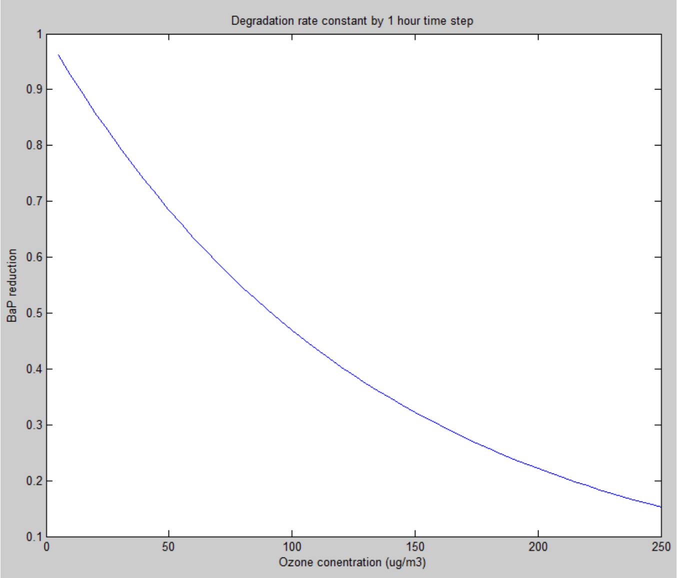

Figure 1: Degradation of BaP based on $O_3$ concentrations after 1 hour

The mother modeling domain is a Lambert Conformal Conic projection centered at 41.69N, 0.89W, with 67 x 55 grid squares of 27 Km. resolution for Iberian Peninsula. Three nesting domains have been setup centered over Zaragoza city. First nesting level is 49 x 49 grid squares of 9 Km. resolution, second 31 x 37 of 3 Km and finally 28 x 28 of 1 Km. resolution. We use 15 vertical terrain following levels up to 100hPa

Emissions of main pollutants, ammonia, nitrogen oxides, sulfur dioxide, and nonmethane volatile organic compounds as well as emissions of particulate matter with diameter of less than 10 or 2.5, including anthropogenic point and diffuse sources, were provided by the Netherlands Organization for Applied Scientific Research (TNO) with 7 Km. of resolution. In case of BaP emission we decide to use global emission from EMEP inventory with 0.5 degrees of spatial resolution. A projection process from source grids to lambert conformal conic domains was developed through an interpolation process with mass conservation. The BaP emissions are broken down into the SNAP 12 categories.

In case of high resolution domains (1Km, 3Km and 9 Km) a top- down process scheme has been used to going to the desired resolution. The downscaling process is based on surrogates to allocate the emission into the model grid. Different surrogates are used for different SNAP´s activities.

Model runs for 12 weeks (11 weeks from 2010 and 1 from 2011) corresponding to the field campaign are used to examine the model results under very different meteorological conditions. The model run was started one day before the time period of interest began to avoid the influence of the initial conditions. Now we can see in Figure 2 the BaP spatial surface results over Iberian Peninsula (27 Km. resolution) and Zaragoza (1 Km. resolution).

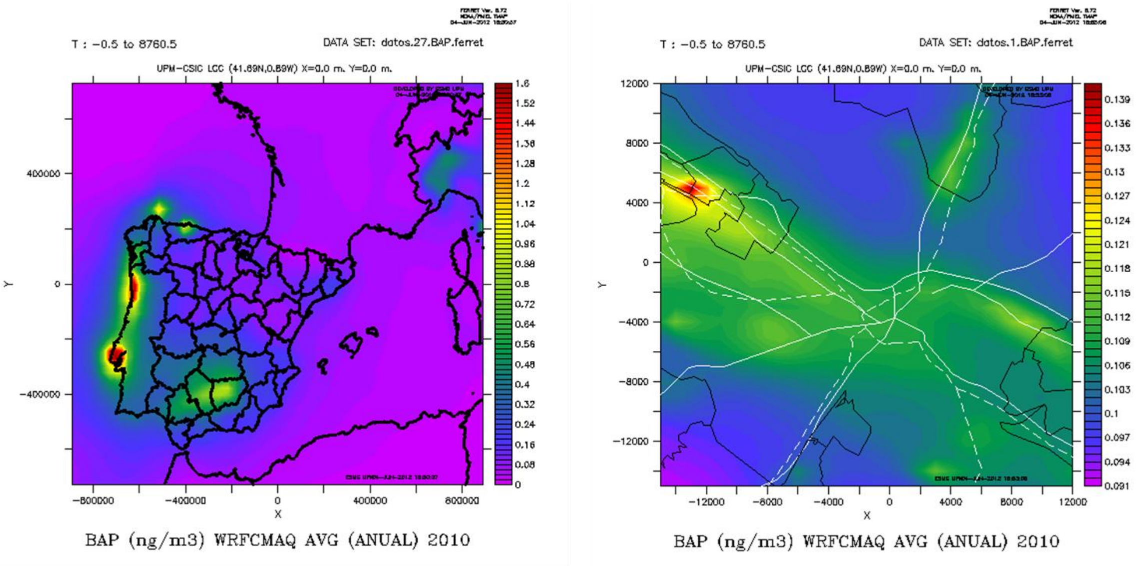

Figure 2: BaP surface results, temporal average. Left: Iberian Peninsula. Right: Zaragoza city.

The data are average of the 12 weeks simulated. The simulation shows the BaP hot spots over Iberian Peninsula and Zaragoza. In case of the 1 Km. resolution domain, higher concentrations are located close to roads (with lines) and one important emission point is located in the north-west area of the city.

One monitoring site providing daily BaP concentrations of BaP has been used to validate the new CMAQ-BaP model. The BaP monitoring data are coming from a PAH field campaign developed by ICB-CSIC (Zaragoza). BaP modeled concentrations for the monitoring location was then compared to the actual daily mean measurements. Figure 3.

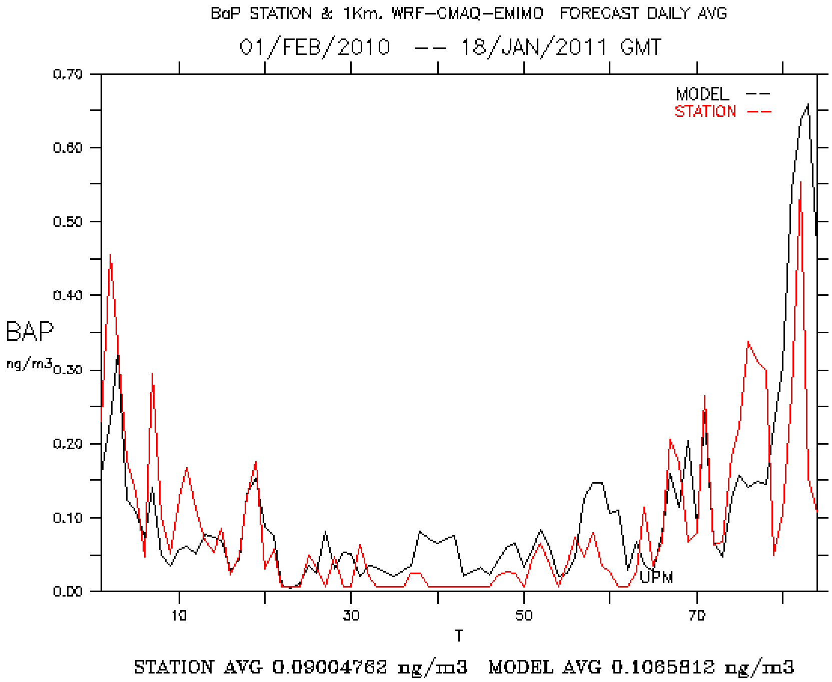

Figure 3: Comparison BaP model 1Km. resolution (black line) and BaP monitoring station (red line). Daily average during 12 weeks (1 week per month).

The CMAQ-BaP model shows mean concentration of 0.1085 (ng/m$^3$) and measurement is 0.09 (ng/m$^3$), so we obtain good results because model and measurement values are quite close. In Figure 4 we can see comparing the measured mean values with calculated from simulations in a scatterplot. It suggests that the correlation between measured and simulated values is good, as also indicated by Pearson´s correlation coefficient r of 0.86.

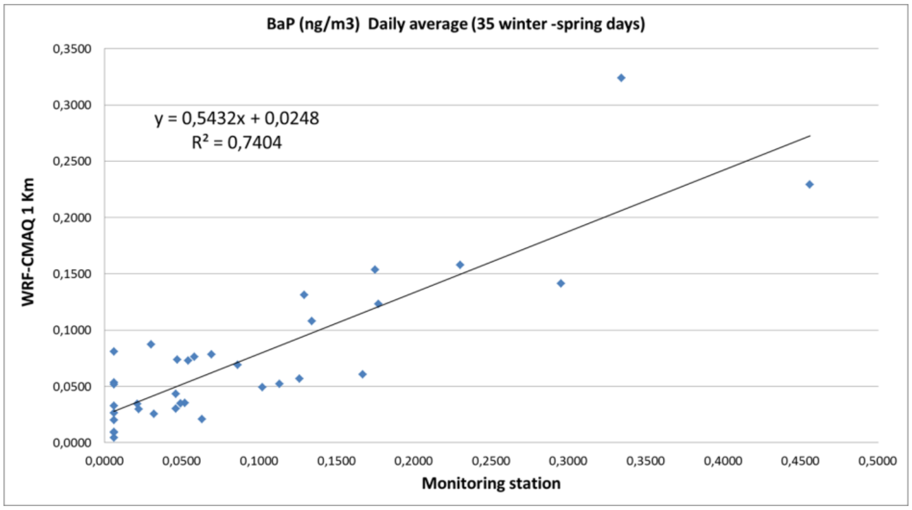

Figure 4: Linear regression of BaP model 1Km. resolution (y axes) and BaP monitoring station (x axes). Daily average during 35 winter and spring days. R=0.86

The agreement is generally satisfactory, the best results are observed in winter period, which is the most important for the BaP concentrations. The model validation shows the BaP extension performance is correct over the modeled area. The BaP concentrations agree well with the observations, particularly very high B(a)P peaks are resolved by the extended model.

The modeling system reproduces the degree of seasonality of the BaP, with higher concentrations in the winter months. This is particularly prevalent at urban locations, where domestic combustion is the major source. In the rest of areas, for example industrial zones, concentrations are affected by other meteorological parameters, temperature, boundary layer, wind speed and direction

## 3. CONCLUSIONS

We have added the ability to simulate the atmospheric behavior of BaP to CMAQ. This includes the addition of two processes: gas/particle partitioning and degradation by ozone. Other aspect such as transport and diffusion is developed using de CMAQ framework. Also the CMAQ aerosol module provides the necessary aerosol parameters to the gas/particle partitioning model

WRF-CMAQ modeling system, which has been extended to simulate BaP concentrations, can be used to get the spatial and temporal distribution of BaP concentrations across large areas domain and to also assess the impact of different emissions reduction strategies. The EU target value for BaP of ambient air (1 ng/m3) is exceeding over area close to a mineral extraction zone. Finally the results from the modeling can be used to assess the possible health impacts of BaP concentrations above the EU target value.

The evaluation results in this paper suggest that with the new CMAQ-BaP is able to simulate fairly well the ambient air concentrations of BaP. For further verification of the model performance, long-term runs will be carried out and more measurement points will be used.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# URBAN PM SOURCE APPORTIONMENT MAPPING USING MICROSCOPIC CHEMICAL IMAGING

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## ABSTRACT

To evaluate the health impacts of particulate matter and develop effective pollutant abatement strategies, one needs to know the source contributions to the observed concentrations. The most common approach involves the collection of ambient air samples on filters, laboratory analyses to quantify the chemical composition, and application of receptor modeling methods. This approach is expensive and time consuming and limits the ability to monitor the temporal and spatial impacts from different pollutant sources. An alternative method for apportioning the sources of ambient PM is the application of microscopic chemical imaging (MCI). The MCI method involves measuring individual particle's fluorescence and source attribution is based on the individual particle analysis coupled with identification from a source library. Using this approach, the apportionment of ambient PM can be performed in near real time, which allows for the generation of temporal and spatial maps of pollutant source impacts in an urban area.

**Key Words:** PM Source Apportionment, Pollutant Source Mapping, Urban Air Quality

## 1. INTRODUCTION

Over the past 20 years, an ever-increasing number of epidemiological studies have shown significant associations between the mass concentration of ambient air particulate matter (PM) and adverse respiratory and cardiovascular health effects (e.g., Dockery et al, 1993, Pope et al., 1995, Krewski et al., 2009). PM air pollution has long been linked to both acute and chronic health effects, including asthma, cardiac disease, and other conditions (e.g., Koenig et al., 2005, Shah et al., 2008). In addition, many studies indicate that fine particles (PM with aerodynamic diameter ≤2.5 μm) have a greater impact on human health than coarse particles (PM with aerodynamic diameter 2.5-10 μm) (e.g., Dockery and Pope, 2006). Based on these and other studies, a National Ambient Air Quality Standard (NAAQS) for $PM_{2.5}$ was established on 1997 and modified in 2006. The current standard is 35 $\mu g/m^3$ in a twenty-four hour period and annual average of 15 $\mu g/m^3$. At these levels, a significant number of urban areas in the US are in violation of the NAAQS and in order to develop effective abatement strategies, there is an increased need for determining the sources of $PM_{2.5}$.

One important approach used to aid in the development of cost-effective control strategies to control $PM_{2.5}$ is determining its sources through the application of various receptor modeling methods (Watson and Chow, 2004, Watson et. al., 2008). These methods are implemented by collecting PM at a receptor (a location in the community), chemically analyzing the collected material, and working backwards to determine the source contributions. Meteorological data (e.g., wind speed and direction) are not required but can provide additional information in identifying specific sources. It should be noted that receptor oriented methods are complementary to source models (i.e., dispersion models, etc.) and applying them to the same ambient case will point out deficiencies in each of the approaches (Watson and Chow, 2004).

Watson et al. (2008) presented a review of the advantages and disadvantages of a number of receptor modeling methods. There are a number of receptor models, including chemical mass balance (CMB), non-negative least squares (e.g., PMF), edge detection (e.g., UNMIX), etc. These models tend to fall into two different categories: 1) a single variable or sample type (e.g., Chemical Mass Balance - CMB), or 2) a multivariate/multi-sample type (e.g., Principal Component Analysis (PCA), Positive Matrix Factorization (PMF), and UNMIX target transformation factor analysis). Inputs to the CMB include a speciated chemical profile for the observed ambient PM along with speciated profiles for the potential sources. The CMB then performs a linear least squares regression analysis to predict the relative source contributions to the observed ambient data. Prior to performing the CMB, the chemical profiles have to be developed. This generally involves the collection of source samples followed by detailed chemical analysis. In order to reduce model uncertainty and enable the identification of additional sources, polyaromatic hydrocarbons have, in some cases, been added to the chemical profiles (Watson et. al., 1998, Fujita et al., 1998, Chow et al., 2007, Fujita et al., 2007). The multivariate approaches do not require chemically speciated source profiles but do require large, speciated ambient data sets (>100 samples). All these approaches are effective in providing estimates of source contributions to observed ambient PM; however, they are expensive (requiring multiple analytical methods) and time consuming (completion of the analysis generally takes weeks or months followed by data base development and receptor modeling).

In this paper we describe an alternative approach using microscopic imaging (MCI) to rapidly and inexpensively apportion observed ambient PM to specific source categories. Validation and limitations of the technique, along with an example of the application of the method are also presented.

## 2. DESCRIPTION OF THE MCI METHOD

Taback et al. (1999) reported on a microscopic chemical imaging approach to characterize in real time particles in air or water based on their fluorescence. The original system coupled optical microscopy with spectroscopic imaging of particle fluorescence to non-destructively monitor impurities and microorganisms. One of the tests reported was the assessment of PAHs on particles. This led Gertler and Gillies (2001) to propose the application the MCI method for PM source apportionment based on the florescence spectra of PAHs. Their hypothesis was based on the use of PAHs as source markers in previous CMB apportionment studies (Watson et al., 1998, Fujita et al, 1998, Chow et l., 2007, Fujita et al., 2007). The approach taken was to analyze previous collected ambient and source filters using an MCI instrument (FIPA-20, GreenVision Systems, Ltd., Tel Aviv, Israel) and apply the system software (similar to the linear least squares regression technique employed by the CMB) to determine the sources of the PM, and compare the results against those obtained using the CMB.

The MCI system used in this earlier study is described in Taback et al. (1999) and Gertler and Gillies (2001). Briefly, the MCI instrument (FIPA-20) employs microscopic chemical imaging coupled with adaptive learning algorithms to identify chemical species that may be present on particles. Figure 1 contains a schematic of the principle of operation. The instrument scans the collected particles and records the particle-by-particle spectra for the wavelength region of 390-900 nm using an interferometer based imaging Fourier spectrometer coupled to a fluorescence microscope with UV optics. The wavelength accuracy of the latest version FIPA-20 interferometer is 2 nm and quantification of pixels to 0.25 μm (equivalent to a particle of the same size) resolution is possible (In a sense, this is similar to scanning electron microscopy with an electron microprobe.) The image is then digitized and pixel-by-pixel spectral information is collected (Figure 2). Particle size and morphology information are also recorded. The software developed for the MCI instrument compares the spectral and morphological data collected for the sample with data in the source library and reports the presence of identified sources and their percent contribution to the mass of sample collected.

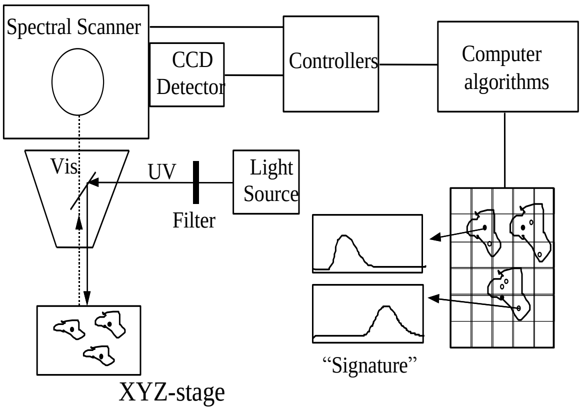

Figure 1. Schematic of the FIPA-20 instrument for MCI analysis of particle samples.

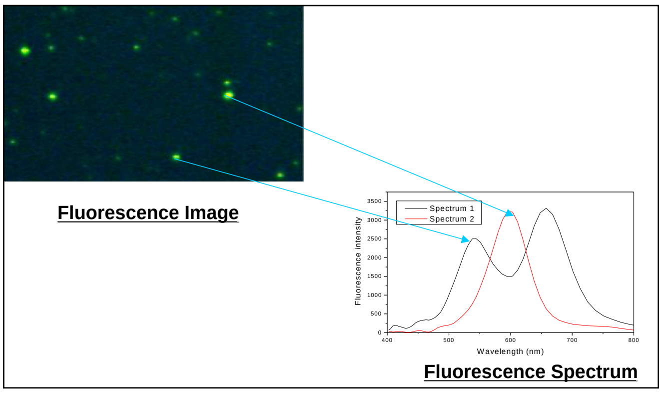

Figure 2. Example of pixel-by-pixel spectral information collected using the MCI.

The procedure employed by Gertler and Gillies (2001) consisted of two main parts, the first part was building a source profile data base using source samples collected as part of the Cairo Air Improvement Project (Abu-Allaban et al., 2002) and the second one was the routine scanning of ambient filters. Building the source profile data base enabled the system to recognize target sources (Figure 3). Different source samples were scanned into the system and analyzed. Their spectral output was then saved to a database. One important criterion they used was the samples had to have been analyzed using standard analytical methods coupled with CMB source apportionment in order to validate the MCI apportionment results. Spectral and morphological information were also obtained. The key in the identification process was a coupling of the maximum and peak shape in the observed spectrum and the comparison of these parameters with the same parameters for sources contained in the source library. As part of this preliminary work only the spectral data were used.

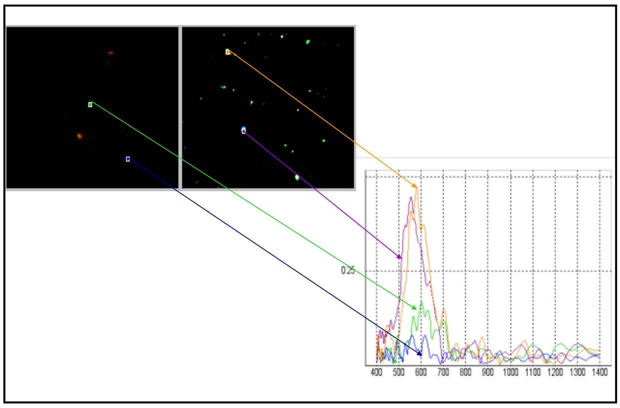

Figure 3. Example of particle spectra obtained using the MCI. Each particle has a unique florescence spectrum based on its source type. The intensity of the fluorescence signal when compared against the respective source signal allows for an estimate of concentration.

## 3. METHOD VALIDATION

Gertler and Gillies (2001) initially evaluated the apportionments predicted using the MCI method by comparison with those obtained using the CMB method. When compared against the previous CMB results, the regression analysis had a slope of 1.14 and $R^2 = 0.93$.

Recently we expanded the initial Gertler and Gillies (2001) work using additional source and ambient samples and an upgraded MCI instrument (the upgrade was a more advanced interferometer). In addition, we performed a two-step evaluation: (1) comparison against saved images to test correct identification and (2) comparison against a more complete CMB analysis performed by Abu-Allaban et al. (2002). In the first step, we observed correct classification in 83% of the cases. The results for the second comparison are presented in Figure 4 and show a good agreement, with a slope of 0.945 and $R^2$ of 0.726. Based on this assessment, we conclude the method is able to predict the sources of the observed PM. It should be noted that inherent in this comparison is the assumption that the CMB is the "gold standard" for source apportionment. Different source apportionment methods will yield variations in predicted PM apportionment. Given this variability and uncertainty (likely on the order of 20%), the conclusion of comparability seems warranted.

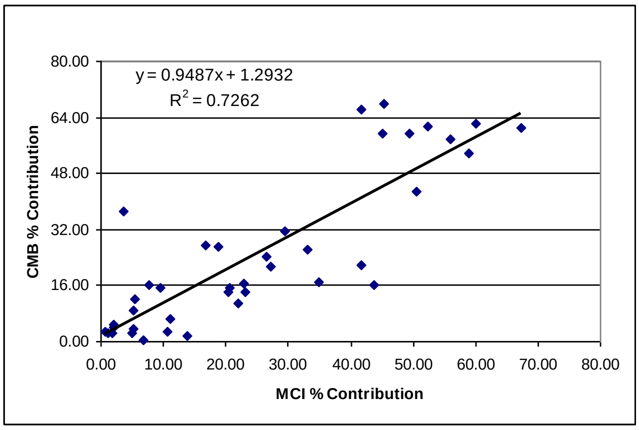

Figure 4. Comparison of MCI percent source contribution predictions developed using the intensity of the observed spectra (similar to a volume weighting) with CMB source contribution predictions.

## 4. SPATIAL MAPPING

Following validation of the method, we applied the MCI technique to develop spatial maps of PM source contributions to observed ambient PM for a number of cities including Singapore, Hyderabad (India), and Shanghai. The rationale for developing this visualization approach was to aid regulatory agencies in developing strategies to effectively mitigate source contributions. In this preliminary work, samples were collected using fixed PM monitors and the MCI analysis was performed in a central laboratory. Apportionment results from the sampling networks were interpolated and spatially mapped, as seen in Figure 5 for the mobile source contribution in Singapore. Future studies could employ distributed MCI instruments capable of both PM sampling and analysis, which would yield real time PM source apportionment information and allow for short term interventions.

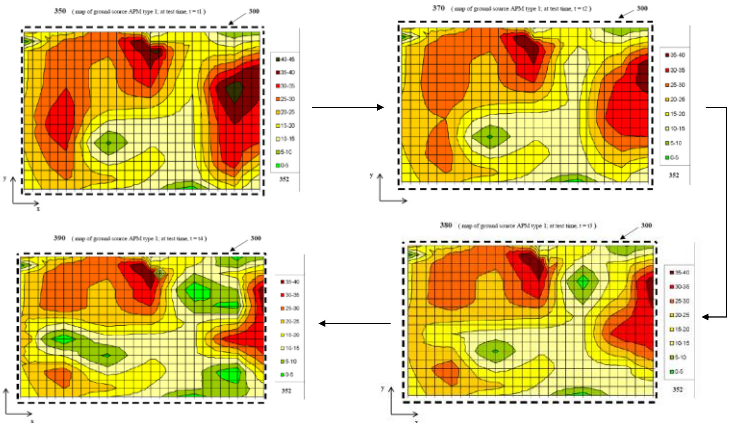

Figure 5. Modeled mobile source contributions from six sites over four days to observed $PM_{2.5}$ in Singapore.

## 5. DISCUSSION

Based on our assessment and application of the MCI method, we can identify a number of advantages and limitations of the method when used for PM source apportionment. Advantages include:

- Rapid analysis: The method is able to predict source contributions in near-real time. The primary delays are in the transport of filters to the instrument followed by the time to scan the filters. This time for scanning is approximately two hours, much less than the time involved in speciated chemical analysis. In addition, the apportionment prediction is part of the analytical procedure and no additional modeling is necessary.
- Cost: Since extensive laboratory measurements are not required, the estimated cost per filter analysis is significantly reduced. This has the potential to expand the use of receptor modeling for use in developing strategies for PM reduction.
- Increased spatial and temporal resolution: Due to the decrease in cost and number of samples required for modeling, enhanced spatial and temporal resolution of PM source contributions can be routinely obtained.
- Number of samples: While the CMB can performed on a single ambient sample, other receptor modeling methods require >100 samples to be applied. Like the CMB, the MCI method can be used on a single sample.

However, a number of limitations in the method were also identified. These include:

- Particles must fluoresce: The identification is based on fluorescence; hence non-fluorescing particles are not observed. Fluorescing particles include those from combustion sources (due to the presence of PAHs) and other fluorescing compounds (e.g., geological materials, which fluoresce due to their crystalline structure). Non-fluorescing particles include those from secondary sources (e.g., $NH_4NO_3$ and $(NH_4)_2SO_4$). Methods need to be developed to chracterize the contribution from non-flourescing particles.
- Lack of adequate uncertainty parameters: The fitting algorithm is based on peak wavelength and peak shape. While there is a “certainty” related to the fitting, it does not include adequate measures such as $chi^2$ that would aid with an assessment of the overall fitting.
- Morphology: While the principle behind the MCI allows for the use of morphological information to potentially aid in source attribution, this aspect of the analytical capability remains under-developed at this time and will need to be addressed.
- Apportionment of similar sources: Many source emissions have similar chemical profiles, leading to an inability to adequately separate these “collinear” source types. An example of this is the lack of separation between spark-ignition vs. diesel sources. We lumped all mobile source contributions into a general mobile source category. Source spectra indicate a difference; however, the earlier generation MCI instrument was unable to accurately separate the categories.
- Particle size limitations: The instrument used has a size limitation of 0.5 μm. While this is sufficient to account for much of the mass, under a number of scenarios, the PM may be dominated by particles smaller than this size. (Note, recent equipment advancements have lowered the size resolution to 0.25 μm).

## 6. SUMMARY

Current commonly applied methods to apportion the sources of ambient PM are expensive and time consuming, which limits the ability to develop and implement effective control strategies. To address these deficiencies, we evaluated the application of MCI for use in apportioning the source contributions to ambient PM. The MCI method involves measuring individual particle's fluorescence and source attribution is based on the individual particle analysis coupled with identification from a source library. Previously collected PM ambient and source samples were evaluated. The MCI apportionment results were validated by comparison against previously obtained CMB predictions and a set of sequestered particle images. Using fluorescence intensity as a surrogate for concentration we found the MCI and CMB apportionments to be in good agreement, having an $R^2$ of 0.726 and slope of 0.948. Advantages of the approach include rapid analysis, low cost/sample, increased spatial and temporal resolution, and the ability to perform assessments using a small number of samples. Limitations include the current inability to analyze non-flourescing particles, need to include particle morphology, size limitations, and ability to separate similar source types. Overall, this approach has the ability to identify and apportion the sources of ambient PM inexpensively and in near real time.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# A MODEL BASED STUDY OF IMPACT OF CLIMATE CHANGE ON GROUND-LEVEL OZONE CONCENTRATIONS IN HO CHI MINH CITY, VIET NAM

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## ABSTRACT

The potential impact of climate change on ground-level ozone concentrations in Ho Chi Minh City, Viet Nam was studied using the MM5-CMAQ modeling system under three IPCC emission scenarios A2, B1 and B2 in accordance with Vietnam's conditions. The simulations with MM5-CMAQ serve as a theoretical experiment investigating the impact of changing climate on summer surface ozone. The simulations show a strong increase in surface ozone and ozone concentrations have exceeded Vietnamese Ambient Air Quality Standard from 1.2 to 55.8 $\mu g/m^3$. Compared with current emissions scenarios, ozone concentrations can increase to 114.5 $\mu g/m^3$ for scenarios A2, 89 $\mu g/m^3$ for B1 scenario and 92.9 $\mu g/m^3$ for B2 scenario. Simulations indicate substantial potential impact of climate change on concentrations of surface ozone in Ho Chi Minh City. The increase of ozone concentrations in future can affect on health and ecosystem for Ho Chi Minh City and surrounding areas.

**Keywords:** climate change; ground-level ozone concentration; MM5 – CMAQ model system

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# DEVELOPMENT AND EVALUATION OF VOCS SPECIATION FOR AIR QUALITY MODELING IN KOREA

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## ABSTRACT

This study continues the process of updating the chemical species profiles of emitted VOC species from major sources in Korea. Previous studies that analyzed emitted VOCs from sources were used to develop our updated VOC species profiles. Data, especially those concerned with the 56 ozone precursors, including benzene, toluene, and xylene, were collected and analyzed. However, there were severe limitations in developing an updated VOC profiles because almost all of the collected previous studies were mainly data on only BTEX. Monitored VOCs data for various sources in Korea were collected and then the 22 VOC species profiles were developed using the lumping table by Carter (2011). The sources that have updated VOC species profiles from this study are household products, metal coils, graphic arts, dry cleaning and surface coating – auto refinishing. The emission proportion of these sources in solvent utilization is 48%. VOC emissions from architectural coating and marine ships are 20% and 14% of solvent utilization, respectively. However, this data has not been sufficiently investigated, so the VOC profiles for these sources could not be updated.

**Key words:** VOCs speciation, Air quality model, Korea

## 1. INTRODUCTION

Air pollutants are emitted from various sources and their characteristics are modified through dispersion, reaction, and deposition. Therefore, an air pollution analysis system which is able to analyze and estimate the complicated chemical and physical processes is necessary to develop adequate measures for improvement of air quality. One of the key factors of the air pollution analysis system is the emissions processing program. The emissions processing program converts a raw emission inventory into model-ready emission data.

An air pollutant emission inventory has been developed in Korea by CAPSS (Clean Air Policy Support System; a branch of NIER, the National Institute of Environmental Research) including criteria pollutants such as CO, NOx, $SO_2$, PM10, VOCs and $NH_3$. The air quality model, however, needs "model-ready species" or the lumping of species according to the chemical mechanism (for example CB4, SAPRC99) that is utilized to calculate the chemical reactions in the model.

This requires a chemical allocation of the individual pollutants to reactivity-based pollutant clusters participating in the photochemical reactions. Most researchers in Korea use SPECIATE (US EPA SPECIATE v.4.2, 2011) as the database for chemical composition of emissions for each source since there is not enough data specific to sources in Korea.

Therefore, the purpose of this study is to develop the chemical species profiles of emitted species from each source in Korea. This would be very beneficial in developing the proper emission reduction measures and in understanding the chemical processes that are occurring in the atmosphere above Korea.

## 2. METHODS

### 2.1 Development of VOCs species profile

Previous studies that analyzed emitted VOCs from sources were used to develop our updated VOC species profiles. Data, especially those concerned with the 56 ozone precursors, including benzene, toluene, and xylene, were collected and analyzed. However, there were severe limitations in developing an updated VOC profiles because almost all of the collected previous studies were mainly data on only BTEX.

The collected VOCs data were converted into mass percentage, and then they were mapped into the model-ready species of mechanisms such as CB04, CB05 and SAPRC99. These steps to convert from VOC emissions data to the model-ready species are needed to run the air quality photochemical model. These steps can reduce modeling calculation time by grouping the various VOC species according to similar chemical characteristics. The Carbon-Bond (CB) mechanism groups according to carbon bond structure, and SAPRC groups according to species (Gery et al., 1989, Yarwood et al., 2005, Carter, 2000, 2010, Kim, 2011).

Table 1. Example of VOCs species lumping (CB05; Carter, 2011)

| | PAR | OLE | IOLE | SUM |
|---|---|---|---|---|
| Propylene | 1.0 | 1.0 | | 2.0 |
| Cis-2-hexene | 2.0 | - | 1.0 | 3.0 |

The lumped species were converted using the mapping table in Carter (2011). Table 1 is an example of the CB05 conversion of VOC species. Monitored propylene amounts are evenly allocated to the lumped species PAR and OLE, and cis-2-hexene is allocated to PAR and IOLE at a ratio of 2 to 1.

The emissions processing model, SMOKE requires the Split Factor (SF) and Mass Faction (MF) to allocate the data into model-ready species and the equations are as follows:

$$SF_i = \sum_{j=1}^{n} \left(\frac{MF_j}{MW_j} \times A_{j,i}\right) \qquad (1)$$

$$MF_i = \sum_{j=1}^{n} \left(MF_j \times \frac{A_{j,i}}{\sum A}\right) \qquad (2)$$

i : Lumped species (PAR, OLE, …)

j : Real Organic species

MFj : Mass fraction of j

MWj : Molecular weight of j

Aj,i  Assignment of j to i

The split factor specifies the number of moles of model-ready mechanism species that is contained in 1g of Total Organic Gas (TOG) emissions.

Finally, the VOC species profile file and chemical speciation cross-reference file is developed from this information.

## 3. RESULTS AND DISCUSSION

Monitored VOCs data for various sources in Korea were collected and then the VOC species profiles, as shown in table 2, were developed using the lumping table by Carter (2011).

Table 2. Developed VOC species profiles in Korea

| Level 1 | Level 2 |
|---|---|
| Combustion from non-industry | Domestic Heating (LNG) |
| Combustion from manufacturing | Textile, Electronic/Computer/Video/Sound/Communication Manufacturing, Groceries, Chemical Product, Metallurgical, Electronic Equipment, Publication, Other Machine Manufacturing, Clothes/Fur Manufacturing |
| Petroleum and Solvent Evaporation | Transportation and Marketing of Petroleum Products,<br>Gas stations |
| Solvent Utilization | Surface Coating - Auto Refinishing, Dry Cleaning, Graphic Arts, Metal Coils, All Household Products |
| Mobile Sources | Light Duty Gasoline Vehicles, LPG Vehicles |

Figure 2 shows some VOC species profiles developed in this study along with those from EPA SPECIATE.  As shown in figure 2, the VOC species profiles of EPA and Korea showed significantly different characteristics.

For example, the emissions from the EPA dry cleaning sector mainly consist of ALK1 species. However, the Korean profile shows mostly ALK5 emissions. The solvent used in the dry cleaning industry in the U.S. is  mainly perchloroethylene while in Korea petroleum-based solvents are widely used. So this accounts for the differences in the VOC profiles of the dry cleaning sector.

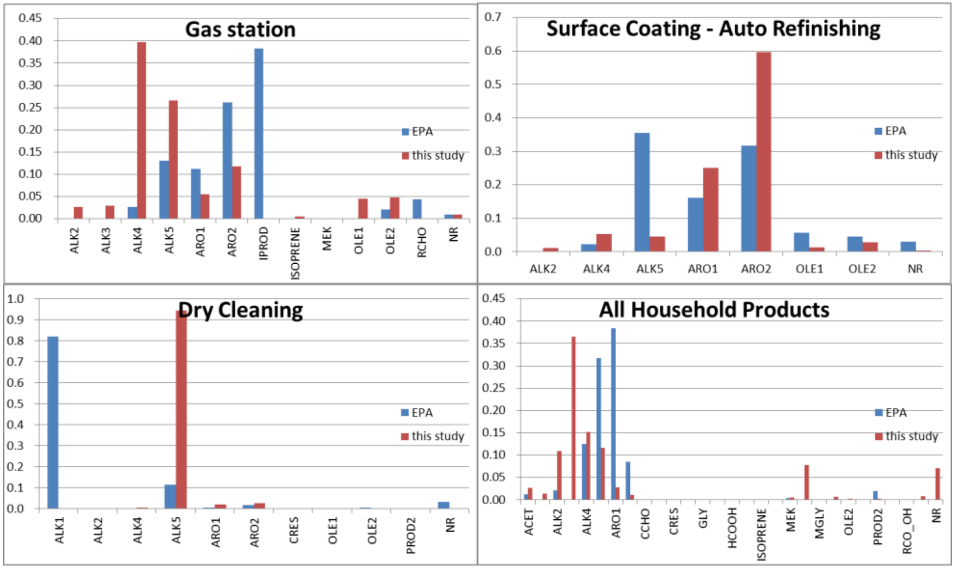

Figure 1. Comparison of VOCs profiles between this study and EPA

Figure 3 shows the source proportioning of VOC emissions in Korea (2008). The largest emission source of VOCs is solvent utilization, which accounts for 63.5%. The sources that have updated VOC species profiles from this study are household products, metal coils, graphic arts, dry cleaning and surface coating – auto refinishing. The emission proportion of these sources in solvent utilization is 48% (figure 4). VOC emissions from architectural coating and marine ships are 20% and 14%, respectively. However, this data has not been sufficiently investigated, so the VOC profiles for these sources could not be updated.

In particular, the construction sector is spread throughout the whole country and the vessel manufacturing industry in Korea has advanced to become a world top class industry, so the influences to air quality are quite high. Therefore, it is necessary to urgently develop VOC profiles for the architectural and marine ship coating sectors.

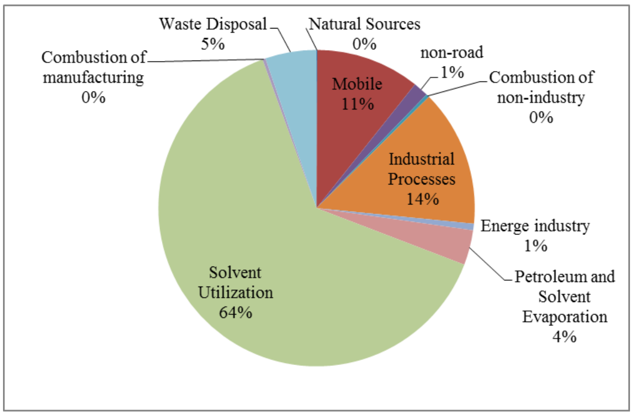

Figure 2. VOCs emissions in Korea (2008)

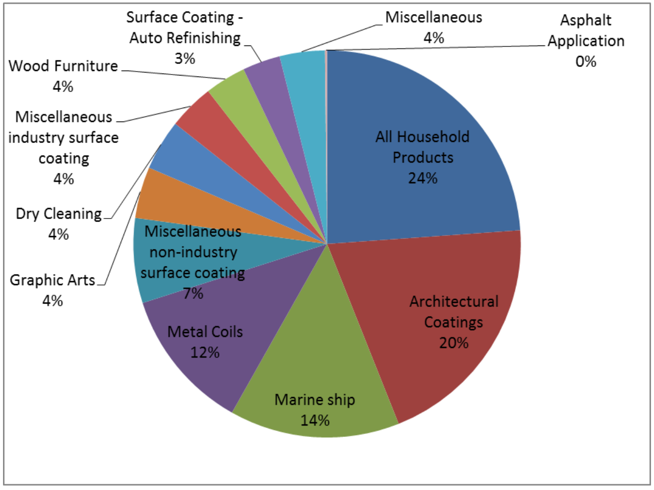

Figure 3. VOCs emissions from Solvent Utilization

## 4. SUMMARY AND CONCLUSIONS

This study continues the process of updating the chemical species profiles of emitted VOC species from major sources in Korea. Previous studies that analyzed emitted VOCs from sources were used to develop our updated VOC species profiles. Data, especially those concerned with the 56 ozone precursors, including benzene, toluene, and xylene, were collected and analyzed. However, there were severe limitations in developing an updated VOC profiles because almost all of the collected previous studies were mainly data on only BTEX. Monitored VOCs data for various sources in Korea were collected and then the 22 VOC species profiles were developed using the lumping table by Carter (2011). The sources that have updated VOC species profiles from this study are household products, metal coils, graphic arts, dry cleaning and surface coating – auto refinishing. The emission proportion of these sources in solvent utilization is 48%. VOC emissions from architectural coating and marine ships are 20% and 14% of solvent utilization, respectively. However, this data has not been sufficiently investigated, so the VOC profiles for these sources could not be updated.

## ACKNOWLEDGEMENT

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Yarwood G., Rao S., Yocke M., Whitten G. (2005) A photochemical kinetics mechanism for urban and regional scale computer modeling, J. Geophys. Res., 94(D10), 12925–12956,

# DIURNAL CYCLE OF GASEOUS (CO, $NO_X$, $O_X$) AND PARTICULATE MATTERS ($PM_1$, $PM_{2.5}$ AND $PM_{10}$) CONCENTRATIONS AT A KOREAN COASTAL CITY DURING THE DUST TRANSPORTATION FROM GOBI DESERT IN MONGOLIA

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## ABSTRACT

Diurnal cycles of gases (CO, $NO_x$, $O_x$) and particulate matters ($PM_{10}$, $PM_{2.5}$ and $PM_1$) concentrations were investigated at Gangneung city in the eastern mountainous coast of Korea from October 26 through 29, 2003. On October 26, before dust transportation from Gobi Desert to the city, hourly concentrations of $PM_{10}$, $PM_{2.5}$ and $PM_1$ were generally less than 40 ㎍/$m^3$ and showed high PM concentrations near 0900 LST (beginning time of office hour) due to the increase of gaseous and particulate matters emitted by vehicles on the road under the increase of traffic density and their maximum concentrations at 1800 LST (ending time of office hour) due to the increase of gaseous and particulate matters on the road and the operation of heating boiler from resident area. Simultaneously, much shrunken nocturnal surface inversion layer less than daytime convective boundary layer at the city could also cause the increase gaseous and PM concentrations. However, low PM concentrations were detected near noon due to the development of thermal internal boundary layer, which particles could be uplifted to the top of the boundary layer. On October 27, during the dust transportation, high concentrations of $PM_{10}$, $PM_{2.5}$ and $PM_1$ were 60.59 ㎍/$m^3$, 26.92 ㎍/$m^3$, 19.63 ㎍/$m^3$ were at 0900 LST and after 0900 LST, the PM concentrations continued to increase under the influence of dust transportation from China into the city, resulting in higher and higher PM concentrations with 154.57 ㎍/$m^3$, 93.19 ㎍/$m^3$ and 76.05 ㎍/$m^3$ at 1700 LST (ending time of office hour), respectively. After 1700 LST, dust transportation from China to the city became weak under stronger westerly surface wind to the sea and PM concentrations gradually decreased under the decrease of traffic density on the road and the cease of its operation after a couple of hours' operation of boiler in the resident area.. Especially, during the dust storm period, hourly distribution of CO and $NO_x$ concentrations showed a similar hourly variation tendency of $PM_{10}$, $PM_{2.5}$ and $PM_1$ concentrations, but $O_x$ concentration show without much sensitive variation to others. When $PM_{10}$, $PM_{2.5}$ and $PM_1$ had maximum concentrations at 1700 LST, CO and $NO_x$ had also maximum concentrations of 1700 ppb and 111 ppb, respectively one hour later, 1800 LST. It implies that the increases of emitted gaseous like $NO_x$ and CO from vehicles on the street and combustion gases from boiler operation for nighttime heating in the resident area could make a great contribution to the increase of PM concentrations. Hourly variation patterns of CO, NO, and $NO_x$ were very similar each other. However, daytime $O_3$ concentration is high due to photochemical reactions of $O_3$ from $NO_x$, but oppositely it concentration at night is generally low due to the convert of $O_3$ into $NO_x$. After sunset, even though nocturnal surface inversion is much shrunken than daytime convective boundary layer, CO and $NO_x$ concentrations rapidly decrease due to the decrease of traffic density on the road, similarly to the PM concentrations. However, after midnight to 0200 LST, $O_3$ concentration rapidly increased to 50 ppb. It might be affected by $O_3$ folding from lower troposphere to the ground surface. This work was funded by the Korea Meteorological Administration Research and Development Program under Grant CATER 2006-2308-“Generation mechanism and prediction of windstorm in the mountainous coast” and continued in 2012. WRF-3.3 model, GOES-DCD satellite images, HYSPLIT model were used for this study.

**Keywords:** CO, $NO_x$, $O_x$, $PM_1$, $PM_{2.5}$, $PM_1$, thermal internal boundary layer, nocturnal surface inversion layer, $O_3$ folding, WRF-3.3 model, GOES-DCD satellite images, HYSPLIT model

# EFFECT OF A CAVITY GENERATED BY INTERNAL GRAVITY WAVES IN THE LEE SIDE OF MOUNTAIN AND NOCTURNAL SURFACE INVERSION LAYER ON HIGH PARTICULATE MATTER CONCENTRATIONS

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## ABSTRACT

Extreme high particulate matter concentrations of $PM_{10}$, $PM_{2.5}$ and $PM_1$ measured by a GRIMM-1107 aerosol sampler in the Korean eastern mountainous coast, Gangneung city were investigated on May 6~10, 2007 using WRF-3.3 model for atmospheric circulations in coarse and fine nesting processes, HYSPLIT model for backward trajectory of air and MTSAT-IR satellite images for dust generation and transportation from the duststorm origin. Before the transportation of dust particles from Nei-Mongo in the northern China toward the Korean eastern coastal city, on May 6, ground level-$PM_{10}$, $PM_{2.5}$ and $PM_1$ concentrations were lower than 62.28μg/m$^3$, 43.07μg/m$^3$ and 30.75μg/m$^3$, respectively. However, under the transportation of dusts under westerly wind on May 7~8, $PM_{10}$, $PM_{2.5}$ and $PM_1$ concentrations reached maxima of 357.48μg/m$^3$, 83.04μg/m$^3$ and 65.76μg/m$^3$. High particulate matter concentrations occurred at 0900LST (beginning of office hour) and maximum concentrations at 1900LST (ending of office hour), due to a great amounts of gases and particulate matters emitted from both vehicles and flying dusts on the road and additionally from heating boilers in the resident area around 1900LST. During the day, most of dust particles were uplifted near the top of thermal internal boundary layer (TIBL) from the coastal basin toward the mountain top in the west and westerly wind could induce the dust particles into the sea in the east, resulting n low PM concentrations. However, under westerly wind, dust particles transported from Nei-Mongo toward the top of Mt. Taegulyang in the west of the city moved down along the eastern slope of the mountain to the coastal basin (city) and were trapped inside a cavity (calm zone) generated by internal gravity waves with a hydraulic jump motion bounding up and down in the coast and the movement of dusts were prohibited by cyclonic air flow (i.e, easterly wind) from the coast toward mountain barrier in the west, resulting in be merged into the ground surface and the highest concentrations of particulate matters at 1900LST. Simultaneously, at night, their ground level concentrations more increased again under nocturnal surface inversion layer (NSIL) much shrunken than daytime TIBL.

This work was funded by the Korea Meteorological Administration Research and Development Program under "Grant CATER 2006-2308-Generation mechanism and prediction of windstorm in the mountainous coast" and continued in 2012.

**Keywords:** $PM_1$, $PM_{2.5}$, $PM_1$, WRF-3.3 model, HYSPLIT model, MTSAT-IR satellite images, cavity, internal gravity waves, cyclonic air flow, nocturnal surface inversion layer, thermal internal boundary laye

# AMBIENT AIR QUALITY OF LAHORE CITY

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## ABSTRACT

Ambient air quality assessment of Lahore city was carried out to create a baseline data to determine and estimate the extent of pollution in the suburban area of Township and urban area of TownHall. The study involved measurement of ambient air pollutants such as CO and $NO_X$, meteorological parameters such as wind speed/direction, temperature & humidity at each site. Gussian Dispersion Model Disper 3 is used to find out the concentration of NOx and CO at Istanbul Chowk, Lower Mall around the TownHall Lahore. The reviews of 2007-2008 and 2008-2009 data have been done by comparing the data of low dispersion season with high dispersion season. The NOx simulation was done by applying Gaussian dispersion Model Disper 3 on summer and winter conditions of Istanbul Chowk and Lower Mall. It was found that during summer and winter with traffic load of 7800 vehicle/hour at Istanbul with emission rate of 87 gm/sec and 9000 vehicle/hour with emission rate of 115 gm/sec calculated by using the emission factors adapted from SIM, Air Working Paper Series, VAPIS. The maximum concentration was 136 ug/$m^3$ at maximum line distance of 78 m in summer while in winter its 229 ug/m3 at a maximum line distance of 80 m computed by Disper 3 Model at Istanbul Chowk. While the maximum concentration was 245 ug/$m^3$ at maximum line distance of 75 m in summer while in winter its 330 ug/m3 at a maximum line distance of 79 m compute by Disper 3 Model at Lower Mall. The CO simulation was carried out by applying Gaussian dispersion Model Disper 3 on summer and winter conditions of Istanbul Chowk and Lower Mall. It was found that during summer and winter with traffic load of 7800 vehicle/hour at Istanbul with emission rate of 185 gm/sec and 9000 vehicle/hour with emission rate of 249 gm/sec calculated by using the emission factors adapted from SIM, Air Working Paper Series, VAPIS. The maximum concentration was 2.917 mg/$m^3$ at maximum line distance of 49 m in summer while in winter its 6.08 mg/$m^3$ at a maximum line distance of 39 m compute by Disper 3 Model at Istanbul Chowk. While the maximum concentration was 3.36 mg/$m^3$ at maximum line distance of 69 m in summer while in winter its 5.3 mg/m3 at a maximum line distance of 79 m compute by Disper 3 Model at Lower Mall. Multi disciplinary measures should be taken for the improvement of air quality in Lahore city.

**Keywords:** Ambient Air, Dispersion of Air, Low dispersion season and high dispersion season

# MODELING THE IMPACT OF NEW EMISSION SOURCES FROM AN INDUSTRIAL-PORT COMPLEX ON THE URBAN OZONE AIR QUALITY IN CORPUS CHRISTI, TEXAS

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## ABSTRACT

Corpus Christi is small industrialized urban area in South Texas which is currently designated as ozone near non-attainment region based on the 8-hour National Ambient Air Quality Standard (NAAQS). The region is home to several large petrochemical refineries, energy complexes and industrial facilities surrounding a growing port. The expansion and development as a result of shale gas exploration in the region and the commissioning of a petroleum coke based thermal electric power generation unit has resulted in the addition of new emission sources within the urban area. The region has also been influenced by the recent global economic downturn as shown by the marine vessel traffic at the port. Therefore, it is important to study the impact of port operations and associated emissions; and assess the impact of any proposed new sources and expansion of existing units on the urban air quality within this region. The impact of air pollution from major emission sources including marine engines and new industrial installations on the ozone concentration in the Corpus Christi urban airshed was studied in detail using a photochemical model. A high ozone episode of September 8-16, 2002 was chosen as the base case for this modeling study. The emissions from each of these new sources were then added to the base case emissions in order to assess their impact on ozone concentrations using the Comprehensive Air quality Model with extension (CAMx). The modeling analysis revealed disproportionate impacts from these different emission sources on the urban air quality ranging from less than a ppb to over 3 ppb on the 8-hour averaged ozone concentration within the urban airshed. Such analyses can provide air quality planners with a decision-making framework for a comprehensive assessment of the air quality impacts of new and changing emission sources in any industrialized urban area.

**Keywords:** Port emissions, photochemical modeling, impact assessment, ozone

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# MODELLING VIEWPOINT ON OLIGOMERIZATION

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## ABSTRACT

This study aims at highlighting the strengths, weaknesses and incidences of two different modelling approaches that propose the oligomerization of atmospheric hydrophilic organic species in the aerosol aqueous phase. This topic is of interest because oligomerization is recognized as a major process in secondary organic aerosol (SOA) aging, especially that of biogenic species. The two parameterizations were implemented in the Air Quality Model CHIMERE, and a comparative study of their results was conducted. The first results show that the pH-dependent approach leads to greater SOA formation than the kinetic approach. In this last configuration, the Henry's constant value appears to be as a key parameter for SOA formation. Sensitivity tests are being conducted.

**Keywords** : Oligomerization, Air Quality Model, Organic Aerosol, Aging.

## 1. INTRODUCTION

Atmospheric aerosols are fast reactive components of the troposphere. This particulate matter is engaged into a continuous interaction with the ambient gas phase, which makes its chemical composition complex and highly variable in space and time (Zhang et al., 2007). As a consequence, aerosols contain high amounts of nitrates and sulfates, but they also comprise a large organic fraction made of condensed semi-volatile organic species covering a wide range of oxidation degrees (Jimenez et al., 2009). This organic fraction may be directly emitted into the atmosphere by combustion processes, but it mainly results from the oxidation of gas-phase organic species emissions. It is then called the secondary organic aerosol (SOA), which makes up to 70% of the OA on a mass basis (Kanakidou et al., 2005). The variability in size and composition of atmospheric aerosols has many environmental implications: it modifies their physical and chemical properties (Molnar and Meszaros, 2001 ; Kanakidou et al., 2005), which in turn affect their radiative impact (Stier et al., 2007 ; Paredes-Miranda et al., 2009) and drive their adverse health effects (Fuzzi et al., 2006). However, despite the recent scientific advances about the composition and the aging processes of the organic aerosol fraction, many aspects remain insufficiently clarified (Volkamer et al., 2006).

As a consequence, Air Quality Models (AQMs) still show an insufficient degree of understanding of the particulate matter levels and gradients, and still mainly underestimate the formation of SOA in the troposphere (Volkamer et al., 2006 ; Hodzic et al., 2009). One of the area that remains poorly characterized is the chemistry of organics in the aqueous condensed phase (Pun and Seigneur, 2007). Thanks notably to atmospheric simulation chamber data, new processes have recently been integrated into the AQMs so as to fill the gap between models and observations. These processes include the addition of new precursors (Zhang et al., 2007), the treatment of SOA hygroscopicity (Pun, 2008) and aqueous chemistry SOA formation pathways (Carlton et al., 2008). Among these last processes, the oligomerization of dissolved organic species appeared as an important evolution pathway for aqueous organic species, that may greatly contribute to a better understanding of SOA aging (Kalberer et al., 2004 ; Jang et al., 2005). Its role in SOA formation was confirmed by modelling studies (Aksoyoglu et al., 2011). Based on experimental results, two different approaches for the representation of oligomerization into AQMs have been developed. A first one, described in (Carlton et al., 2010), proposes to reproduce the formation of oligomers observed in simulation chambers using a first order rate constant for all the organic compounds present in the aerosol aqueous phase. In parallel, (Pun and Seigneur, 2007) developed a more comprehensive pH-dependent oligomer formation, to be applied to the aldehyde species dissolved the aerosol aqueous phase.

The present works aims at investigating the way oligomerization processes are represented by models. It consists in a modelling study using in parallel both approaches, so as to identify the way they constrain our understanding of SOA processing in the lower troposphere. This study was conducted with the CHIMERE model (*www.lmd.polytechnique.fr/chimere*) at the continental scale over Europe during the summer period of July 2006. We discuss the SOA yields provided by each simulation, and the spatio-temporal distribution of oligomers in each configuration, so as to learn more about the strengths and the weaknesses of each oligomer modelling approach, and their influence on simulated oligomer concentration fields.

## 2. MODELLING RESULTS

The two parameterizations proposing SOA evolution via oligomerization were implemented inside CHIMERE.

The first approach is the kinetic approach. It relies on the works of Kalberer an co-authors, who have shown that, after 20 hours of processing, 50% of the total organic aerosol mass was changed into oligomers (Kalberer et al., 2004). This results led to the definition of a first order rate constant of 9.6 x $10^{-6}$ $s^{-1}$ for the oligomerization process (Morris et al., 2006 ; Carlton et al., 2010), which corresponds to a semi lifetime of 20 hours for the concerned aqueous organic species. In this empirical parameterization, oligomerization is thus considered as an irreversible process. This approach offers several advantages from the model point of view, and notably the fact that it considers a unique behavior for all the organic precursors, one single chemical pathway, and one type of oligomer product. However, because of these simplifications, the parameterization accounts neither for the variability of the semi-volatile organic compound speciation in the gas phase (and the subsequent aqueous phase composition variability) nor for ambient parameters such as pH.

The second one combines the laboratory works of (Jang et al., 2005) who consider that the polymerization of aldehydes could happen through a variety of acid-catalyzed reactions, and the observations of (Gao et al., 2004) who indicate that for a pH value of 6, 10% of the total precursor mass is already composed of oligomers. From these results, (Pun and Seigneur, 2007) established a new equation for the gas-to-particle partitioning constant of semi-volatile aldehydes, which integrates their sink in the acid aqueous phase:

$$K_{p,eff,i} = K_{p,i} \cdot \left[1 + K_{0,eff,i,ref} \cdot \left(\frac{C_{H^+}}{C_{H^+,ref}}\right)^{1.91}\right] \qquad (2.1)$$

where $K_{p,eff,i}$ is the effective partitioning coefficient of compound i between the atmosphere and the aerosol aqueous phase; $K_{p,i}$ is the standard partitioning coefficient calculated for non-acidic conditions and $C_{H+}$ represent the aqueous concentration of hydronium ions. The reference concentration $C_{H+,ref}$ is set to $10^{-6}$ mol.$L^{-1}$ and $K_{0,eff,i,ref}$ stands for the value of 0.1, as found by (Gao et al., 2004) under the $C_{H+,ref}$ conditions. Unlike the first approach, oligomerization is thus encoded as a reversible process, and only a restricted set of species undergo the oligomerization process (Jang et al., 2005).

As oligomerization is known to happen in the aqueous phase, only the hydrophilic species can undergo such processes. Currently, in the SOA chemistry scheme implemented in CHIMERE, there exist 3 hydrophilic surrogate SOA species arising from biogenic precursors: BiA0D, BiA1D and BiA2D. The properties of these species are presented in table 1. It's important to note here that only aldehyde groups are assumed to participate in oligomerization reactions in the pH-dependent parameterization: thus, only BiA0D can under oligomerization in this approach, while all 3 species are concerned by the kinetic approach.

In both approaches, we need to provide Henry's constant values for the hydrophilic semi-volatile organic species, which dissolution in the aerosol water is governed by Henry's law. To do this, we used the predictions of GROMHE, a new structure-activity relationship based on a group contribution approach, developed by (Raventos-Duran et al., 2010). Henry's constants were determined at 298K, their values being corrected using the Van't Hoff equation in order to account for the dependence in temperature:

$$H_T = H_{298}.\exp\left[\left(\frac{\Delta H_{solv}}{R}\right).\left(\frac{1}{298}-\frac{1}{T}\right)\right] \qquad (2.2)$$

where $\Delta H_{solv}$ is the desolvation enthalpy and R is the ideal gas constant.

**Table 1.** Properties of the surrogate species accounting for semi-volatile biogenic hydrophilic compounds

| Surrogate | Molecular Structure | Molar Mass ($g.mol^{-1}$) | Henry's constant ($M.atm^{-1}$ at 298K) | $\Delta H_{solv}$ ($kJ.mol^{-1}$) |
|---|---|---|---|---|
| BiA0D | pinonaldehyde | 168 | $4,97.10^4$ | 88 |
| BiA1D | norpinic acid | 170 | $6,85.10^8$ | 88 |
| BiA2D | pinic acid | 186 | $6,03.10^8$ | 109 |

The implementation of the kinetic parameterization led to the creation of a new particulate species called BiOLG, representing the oligomers formed from the 3 hydrophilic surrogate species. For the second approach, it was necessary to take into account the acidity of the aqueous phase so as to recalculate the partitioning constant according to equation (2.1), in each cell and at each time step of the model calculation. However, as it only proposes a modification of the aldehyde partitioning constants, no species needed to be created. In this case, we calculated the difference in particulate BiA0D between a reference simulation and a modulated simulation to account for oligomerization production. The first results are presented in Figure 1 for one specific time step of July 18, 2006. When examining the maps (a) and (b) of Fig. 1, that represent the partitioning of BiA0D in the reference simulation, we can see that the distribution is largely in favor of the gas phase, as expected from the low value of the Henry's constant for this species.

In the simulation using the pH-dependent approach for oligomerization (map (c) and (d)), the concentration of BiA0D in the aerosol phase strongly increases over given areas of the European continent where biogenic emissions are high. It accounts for an important contribution of this chemical pathway to aerosol growth over the continent. We compared this result with the production of oligomers from the kinetic approach. It is summarized in Fig. 2, which sets aside the production of oligomers obtained via the pH-dependent parameterization (left map, (e)) and the production of oligomers simulated with the kinetic parameterization (directly given by the BiOLG species concentration fields).

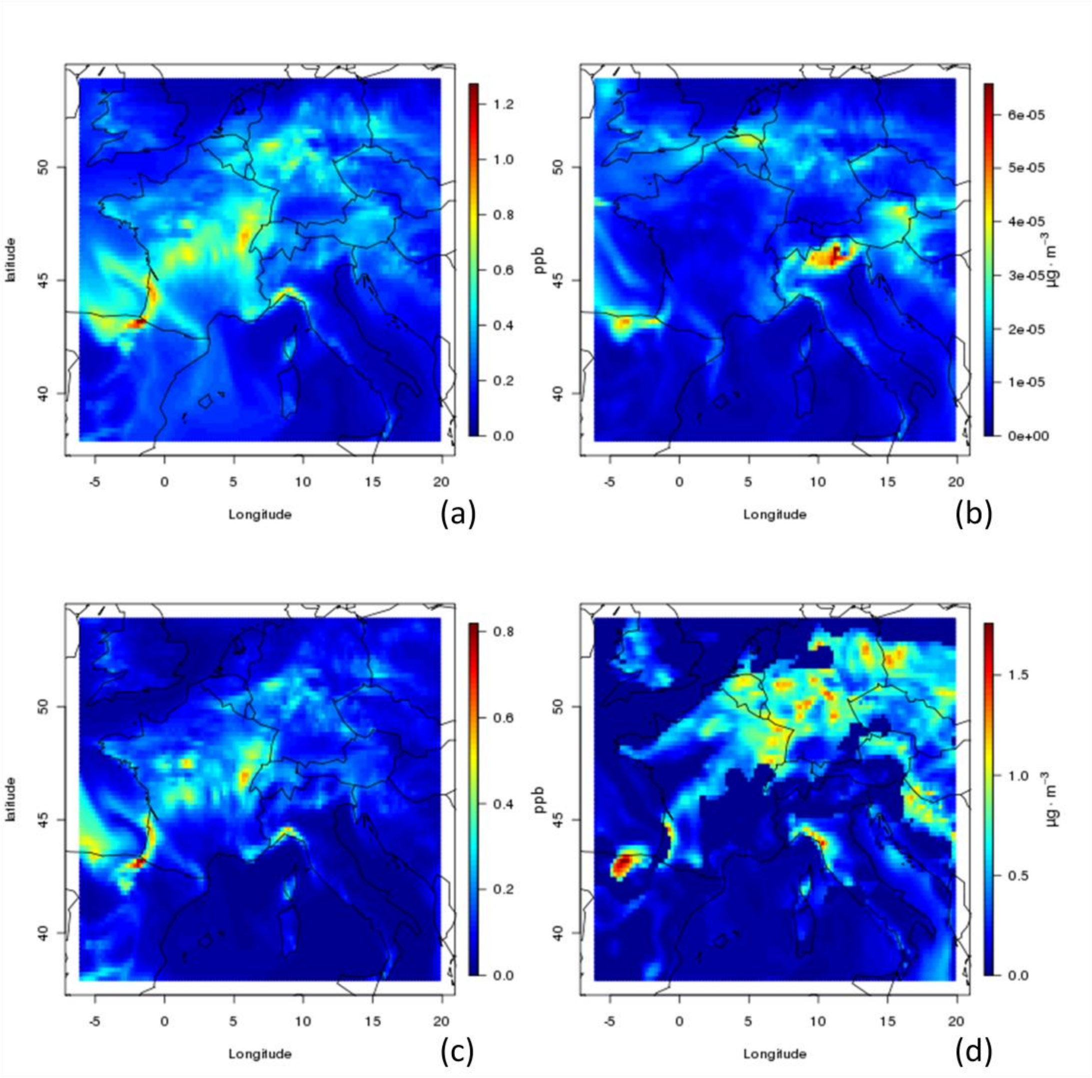

Fig. 1. CHIMERE results for July 18th 2006 at 9 p.m. On the left, BiA0D gaseous concentration fields (ppbv). On the right, BiA0D particulate concentration fields ($\mu g.m^{-3}$). The reference simulation is presented at the top (graphs (a) and (b)) and the pH-dependent configuration on the bottom (graphs (c) and (d)).

On one hand, the concentration of biogenic oligomers appears to be negligible from the kinetic approach viewpoint. The reason for this is the very low value of the Henry's constant for BiA0D, which mainly remains in the gas phase and provides little material for the concentration-dependent formation of oligomers. An underestimation of Henry's constant value was suspected to account for the gap between both approaches. Indeed, it appears that the carbon cycle present in the BiA0D surrogate species probably enhances its solubility in water well beyond the value commonly used in the models. We engaged a sensitivity study to explore the importance of biogenic species volatility in AOS evolution via oligomerization. On the other hand, when looking at the regions where the formation of oligomers takes place, we immediately see that the two approaches don't converge. This is an important element of our study. Indeed, in the kinetic approach the oligomer plume is large and it is formed far downwind the continental sources. At this time step, the marine oligomer plume is explained by the presence of a large biogenic source in Northern Europe, which emissions are transported by eastern winds towards the sea, where the low vertical diffusion limits their atmospheric dilution. On the reverse, in the pH-dependent approach, oligomers are immediately produced *in situ* from their precursors due to a fast and profound modification of the partitioning constant, which produces a multitude of high AOS concentration spots.

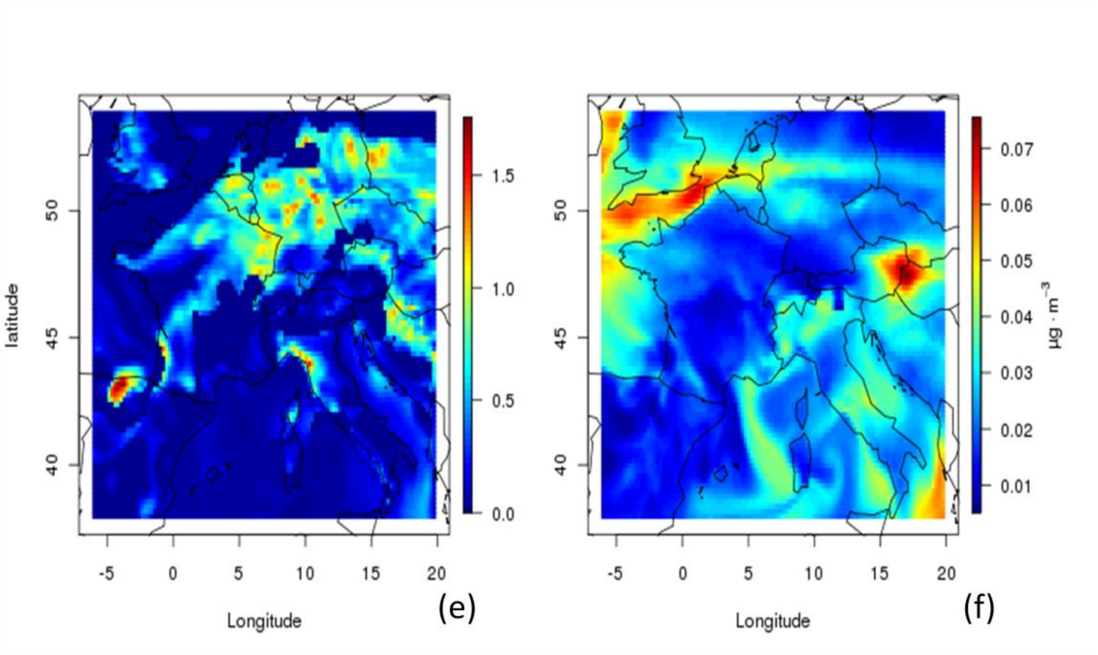

Fig. 2. CHIMERE outputs : Oligomer concentrations (µg.m$^{-3}$) for July 18th 2006 at 9 p.m simulated with (e) the pH-dependent approach; (f) the kinetic approach.

Another important point concerns the reversibility or irreversibility of the process. Still, the two approaches don't make the same hypothesis, and part of the oligomer matter is regularly sent back to the gas phase in the pH-dependent configuration. Little is known about this phenomenon, but according to some researchers, the heterogeneous reactions forming oligomers on nanoparticules could be partially or fully irreversible (Wang et al., 2010). Thus, although the pH-dependent approach produces significant AOS, the release of semi-volatile species has to be questioned and quantified. This work is also being conducted.

## 3. CONCLUSION

The contribution of oligomerization processes to secondary organic aerosol formation seems to be significant for biogenic oxidized compounds. However, depending on the parameterization of this process, Air Quality Models can propose very different views of AOS evolution in space and time. Three main aspects are tackled here:

- The spatial and temporal formation of oligomers which is highly dependent on the process encoding.
- The role of the partitioning constant: Sensitivity tests are currently conducted to evaluate the contribution of the choice of a $K_H$ value for BiA0D to the final result. The definition of a consistent value is a complex task due to the fact that BiA0D is a

surrogate species, accounting for a set of highly soluble biogenic oxidized compounds. Increasing this value in the model will enhance AOS formation via the kinetic approach but it will also provide a lower oligomer to AOS ratio in the pH-dependent approach. Thus, it may fill the quantitative (but not spatial) gap between the two approaches.

- The reversibility of the process: from this point of view, the pH-dependent approach is questioning, as oligomers can dissociate to form back monomers. Although it is infrequent due to the fact that fine particles are generally very acidic (Ludwig and Klemm, 1990 ; Keene et al., 2004), the occurrence of monomer release in the model has to be evaluated and discussed.

To fully address this question, series of oligomer measurements over continental areas are strongly required.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# ASSESSMENT OF IMPACT OF LOCAL AND REGIONAL SOURCE REGIONS USING CLUSTERING TECHNIQUE ON PARTICULATE POLLUTION IN NEW DELHI, INDIA

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## ABSTRACT

This study evaluated the impact of synoptic and localized transport on particulate matter *(*$PM_{2.5}$) at an urban site in Delhi, India with NOAA HYSPLIT model. Seventy two-hour back trajectories arriving at the site for each hour were computed to assess seasonal variability of pollutant concentrations transported in the Delhi region for a representative year 2009. GDAS meteorological data was used in the model. Cluster analysis of these trajectories data helped in understanding the potential source regions allied with high particulate pollution levels in Delhi. Non-parametric statistical procedures were employed to test if the differences in pollutant concentrations in various clusters were significant in order to get a better understanding of various distinct pollutant source regions.

**Key Words**: air mass trajectories, particulate matter, transport, non-parametric statistics

## 1. INTRODUCTION

It has been well established that elevated levels of fine particulate matter ($PM_{2.5}$) levels contribute to detrimental health effects (Dockery et al., 1993) and reduced visibility in urban centers. Particulates also influence climate change through radiative forcing (Shindell et al. 2010, 2012). Hence, initiatives have been carried out around the globe to comprehend the source and fate of aerosols (Ketzel and Berkowicz, 2005; O'Connor et al., 2008; Shindell et al. 2012) that facilitated policy decisions for curbing rising particulate matter levels. Since the last decade, similar efforts have been instigated in greatly urbanized Delhi region (Mitra and Sharma, 2002; Srivastava and Jain, 2007) to monitor and analyze the aerosol concentrations and to comprehend the dynamics of their emissions, formation, travel and removal. However the continual high concentrations of $PM_{2.5}$ in Delhi (Guttikunda, 2009, Biswas et al., 2011) despite implementation of emission control measures (Khaiwal et al., 2006) is of great concern to relevant stakeholders. Annual average particulate matter concentrations were much higher than the national standard, in Delhi during 2010 (Guttikunda, 2012).

This study aims to investigate the transboundary flux of $PM_{2.5}$ to the capital city and provide a recent perspective on sub continental, regional and local sources affecting air quality in Delhi. Flow routes of air parcels from an urban site in Delhi to local and remote continental sources were determined through back trajectory analyses and subsequent clustering of the trajectories to reduce intrinsic errors due to uncertainties in meteorological data, model assumptions and numerical analyses (Stohl et al., 2002).

## 2. DATA COLLECTION

Income Tax Office (ITO) located in the heart of Delhi is adjacent to one of the busiest traffic junctions. Two power plants, viz. I.P. Power House and Rajghat Power House are located in the vicinity of this site. For the modeling simulations 1231 hourly observations in winter and 1630 hourly observations in summer for fine particulate matter were retrieved from ITO site. The monitoring site was set up and maintained by Central Pollution Control Board (CPCB) under the National Air Quality Monitoring Program (CPCB, 2011). The meteorological data used in the model was the NCEP Global Data Assimilation System (GDAS) (3-hourly, 1 degree resolution) archived data.

## 3. METHODOLOGY

The trajectories were generated from windfield and pressure data using National Oceanic and Atmospheric Administration’s (NOAA) Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) version 4 modeling system (Drexler and Rolph, 2003). The modeling runs were conducted at an arriving height of 500 m. The trajectories were clustered according to their proximities (Moody and Samson, 1989) in homogeneous groups based on least total within-cluster spatial variance. Non-parametric statistical tests such as Kruskall-Walis (applied to three to five clusters) and Mann-Whitney test (applied to two clusters) were used to examine whether the median concentrations across independent clusters are significantly different. This decreases the number of individual clusters and hence reduces the redundancy of similar sources.

## 4. PRELIMINARY RESULTS AND DISCUSSIONS

### 4.1. Seasonal Flow Patterns

In winter season (Figure 1), most trajectories were grouped in clusters with low speed (short) transport. Slowest trajectories in clusters C3 arriving at ITO were simulated to come from west from Rajasthan and Haryana. Clusters C1 and C2 for ITO represents short trajectories arriving from north-west direction in Afghanistan and northern Pakistan respectively which travel through Punjab and Haryana which illustrate the importance of transport from north-west direction. The mean paths in C5 (ITO) and group trajectories illustrate recirculating transport around north of Delhi. C5 with 11% trajectories exhibits the importance of recirculation and local transport on this urban site. Moderate speed southwesterly trajectories (C6) were observed to arrive from the tail of Pakistan through Rajasthan. Cluster C1 (18%) demonstrates significant number of northwesterly trajectories travelling through Afghanistan, Pakistan, Punjab and Haryana to the urban site in Delhi. Short circulating trajectories in C4 cluster (10%) originates from east of Rajasthan and then travels via Uttar Pradesh to Delhi. Fast moving south-westerly maritime mass transport (C8) was noted to come from Arabian Sea through Pakistan, Rajasthan and Haryana. Fastest long trajectories, originated in Middle East countries such as Iran , Iraq and Saudi Arabia, and were simulated reaching Delhi from west in winter season of 2009. Such trajectories clusters (C10, C11, C12 and C13) though consisted of relatively small number of occurrences (2-4%). This illustrates that Delhi is more influenced by northwesterly flows from Afghanistan and

Pakistan and local recirculation wind patterns rather than long-distance flows from Iran, Iraq and Saudi Arabia.

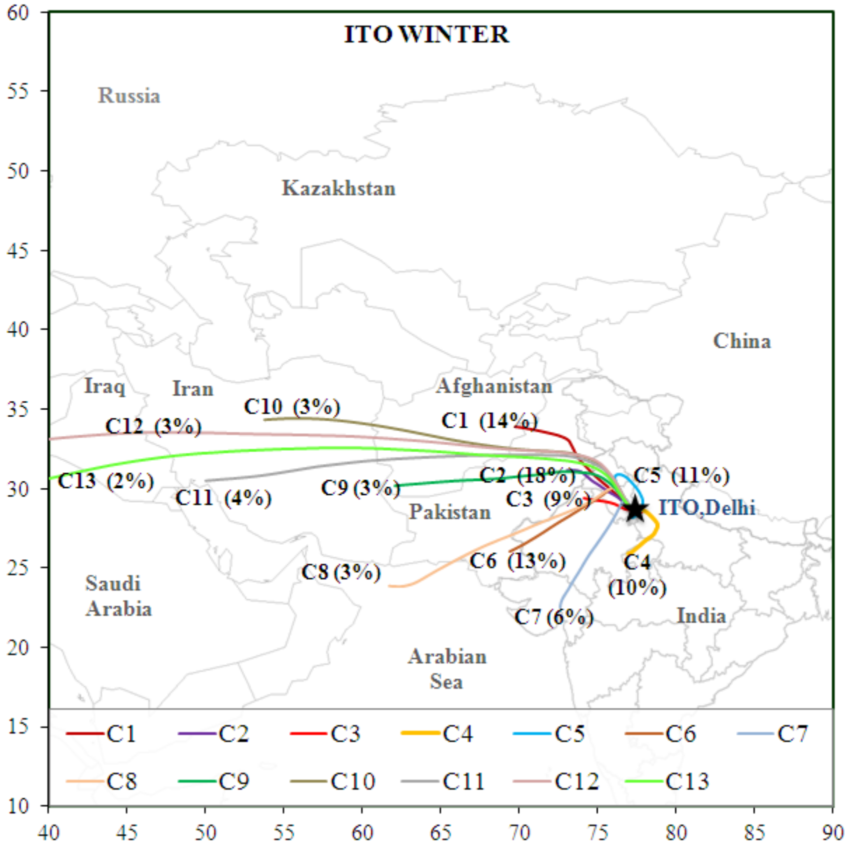

Figure 1. Cluster configuration in winter (★denotes arrival site)

Similar to winter, most of the trajectories in summer (Figure 2) were clustered to low speed short-range circulation mean routes. Also, significant fast maritime transport patterns were grouped in C9 and C10. Significant short trajectories around west of the site were simulated as depicted by C8 cluster. About 24 percent of trajectories were clustered in short northwesterly flows (C11 and C13) from Pakistan-Afghanistan region. C5 congregated moderate air flows that originated in Pakistan before bending near Punjab above north-west of Delhi. Very few trajectories were grouped together (C14) showing fastest air mass flows from Russia via Kazakhstan. Other fast trajectories were simulated to arrive from Middle East countries. In summer, as in winter, the dominant clusters based on trajectory grouping influencing the ITO site originate from Pakistan-Afghanistan and local recirculation wind patterns.

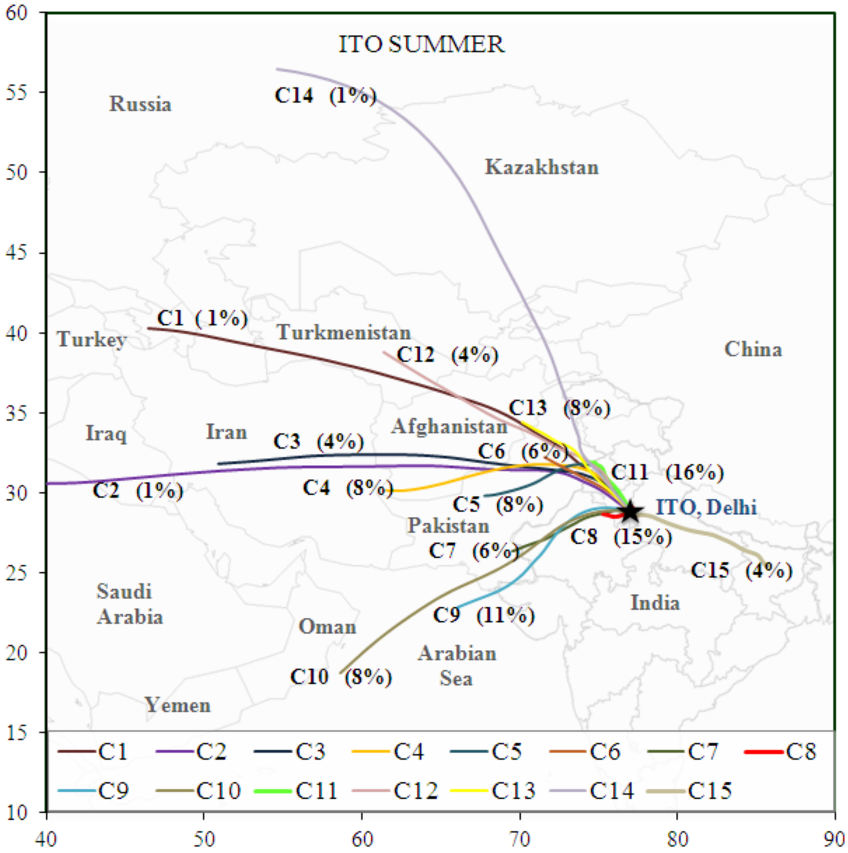

Figure 2. Cluster configuration in summer (★denotes arrival site)

### 4.2. Seasonal $PM_{2.5}$ concentrations associated with clusters

Table 1 depicts the percentile concentrations coupled with each cluster during winter and summer. In winter $PM_{2.5}$ values in northwesterly C1, C2, C3 are statistically higher than other clusters. The probable emission sources of such high $PM_{2.5}$ laden clusters could be the urban and industrial areas located across the border near Amritsar, India (Raja et al., 2008). Consistent high values are also reflected in clusters C4, C5, C6 and C7. Clusters C6 and C7 pass through Rajasthan and meet near Delhi illustrating influence of dust particles. C5 recirculates near north and probably picked up fine particles from power plants in Punjab and Uttar Pradesh. In winter long-distance clusters C11-C13 originating from middle-east do not show major loading.

The summer time cluster analysis demonstrates cluster C6 consistently observed higher values. It represents short slow moving trajectories from Pakistan and passed through Punjab and Haryana where it picked up fine particulate matter concentrations from power plants and road dust.

There is large difference in 95th and 75th percentile values in C8 cluster, but still has most values above 50 µg/m$^3$. Clusters C9 and C10 from south west depict significant dust loading as they traverse Rajasthan. C11, a local short trajectory has high $PM_{2.5}$ concentrations picked up within the Delhi region.

Table1: Summary statistics for seasonal trajectory clusters.

| Clusters | Mean | 95th percentile | 75th percentile | 25th percentile |
|---|---|---|---|---|
| **$PM_{2.5}$ (µg/m$^3$) in Winter** | | | | |
| **C1,C2,C3** | 154.0 | 261.0 | 214.0 | 96.5 |
| **C4** | 151.0 | 216.0 | 212.0 | 95.0 |
| **C5** | 143.0 | 279.0 | 214.5 | 85.0 |
| **C6** | 130.0 | 284.0 | 196.5 | 79.2 |
| **C7** | 142.0 | 252.0 | 195.0 | 86.5 |
| **C8** | 82.0 | 155.8 | 98.0 | 54.5 |
| **C9,C10,C11,C12,C13** | 68.0 | 114.0 | 84.2 | 47.8 |
| **$PM_{2.5}$ (µg/m$^3$) in Summer** | | | | |
| **C12,C13,C14** | 59.0 | 132.0 | 94.0 | 62.5 |
| **C7** | 83.0 | 97.8 | 69.2 | 45.0 |
| **C2,C3** | 69.0 | 147.0 | 83.2 | 49.0 |
| **C1,C4,C5** | 73.0 | 156.0 | 92.0 | 46.0 |
| **C6** | 93.0 | 164.0 | 134.0 | 65.2 |
| **C8** | 89.9 | 208.2 | 106.2 | 56.5 |
| **C9** | 82.9 | 144.5 | 85.0 | 63.3 |
| **C10** | 85.6 | 149.3 | 109.8 | 62.0 |
| **C11** | 85.6 | 157.7 | 109.8 | 55.0 |
| **C15** | 52.4 | 83.0 | 59.9 | 41.4 |

## 5. CONCLUSION

The simulated trajectories from north-west exhibited high $PM_{2.5}$ concentrations during both seasons. The $PM_{2.5}$ loading of these trajectories probably originated from urban regions of Pakistan and concentrations were further enhanced as the cluster traversed Punjab and Haryana. The dominant $PM_{2.5}$ sources from the north-west urban region could be industries, diesel vehicles and road dust. Recirculating short trajectories (C5) in winter picked up $PM_{2.5}$ concentrations possibly from power plants in Punjab (Ropar) and Uttar Pradesh and further picked up $PM_{2.5}$ concentrations locally within Delhi before the reaching the ITO site. This cluster showed significant high particulate loadings. A single cluster (C4) in winter illustrates high $PM_{2.5}$ loading that represented slow moving trajectories from Rajasthan. The cluster analysis also shows that there is considerable dust loading from the Rajasthan region especially in summer. The study illustrates that long-distance clusters from Iran, Iraq, Russia and Saudi Arabia do not have much impact on particulate matter concentrations at ITO site in Delhi. From this study we can also conclude that shorter length modeling simulations (24-hr - 48-hr) in urban Delhi region instead of the more prevalent 72-hr modeling simulations for remote areas (Brankov et al., 1998) would be more useful to depict the influential source regions impacting the ITO receptor site at Delhi. The clusters of the trajectories (24-hr - 48-hr) generated would be sufficient to cover the emission sources within Delhi, the influential surrounding source regions (Uttar Pradesh, Punjab, Haryana, and Rajasthan) and the northwest countries of Afghanistan and Pakistan. The clusters are dominant in westerly direction and not from the east. This study needs to be expanded further to include spatial distribution and magnitude of emission sources from the possible source regions identified in this study to get a better perspective of their relative importance. It however gives an initial understanding of impact of trans-boundary air pollution over Delhi.

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# Extreme $PM_{10}$, $PM_{2.5}$ and $PM_1$ concentrations in the mountainous coastal basin affected by lee side trapping of dust particles transported from Nei-Mongo under cyclonic motion and shrunken atmospheric boundary layer

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## ABSTRACT

Extreme high particulate matter concentrations of $PM_{10}$, $PM_{2.5}$ and $PM_1$ in the Korean eastern mountainous coast, Gangneung city were investigated by a GRIMM-1107 aerosol sampler on May 6~10, 2007. Before the transportation of dust particles from Nei-Mongo in the northern China toward the Korean eastern coastal city, on May 6, ground level-$PM_{10}$, $PM_{2.5}$ and $PM_1$ concentrations were lower than 62.28µg/m$^3$, 43.07µg/m$^3$ and 30.75µg/m$^3$, respectively. However, under the transportation of dusts under westerly wind on May 7~8, $PM_{10}$, $PM_{2.5}$ and $PM_1$ concentrations reached maxima of 357.48µg/m$^3$, 83.04µg/m$^3$ and 65.76µg/m$^3$.
High particulate matter concentrations occurred at 0900LST (beginning of office hour) and 1900LST (ending of office hour), due to a great amounts of gases and particulate matters emitted from both vehicles and flying dusts on the road and additionally from heating boilers in the resident area around 1900LST. Dust particles transported from Nei-Mongo toward the top of Mt. Taegulyang in the west of the city moved down along the eastern slope of the mountain to the coastal basin (city) and were trapped by cyclonic air flow and merged into the ground surface, resulting in highest particulate concentrations at 1900LST. After sunset, simultaneously, their concentrations more increased again under nocturnal surface inversion layer much shrunken than daytime thermal internal boundary layer. WRF-3.3 model, HYSPLIT-backward trajectory model, MTSAT-IR satellite pictures, were used for calculations of horizontal and vertical wind fields, atmospheric circulation, atmospheric boundary layer, vorticity, geopotential tendency and streamlines connected with high particulate concentrations.

This work was funded by the Korea Meteorological Administration Research and Development Program under “Grant CATER 2006-2308-Generation mechanism and prediction of windstorm in the mountainous coast” and continued in 2012.

**Keywords:** $PM_1$, $PM_{2.5}$, $PM_1$, cyclonic air flow, atmospheric boundary layer, nocturnal surface inversion layer, thermal internal boundary layer, WRF-3.3 model, HYSPLIT-backward trajectory model, MTSAT-IR satellite pictures, vorticity, geopotential tendency

# DEVELOPMENT OF A NUMERICAL MODEL TO CALCULATE RADIOLOGICAL CONSEQUENCES OF NUCLEAR ACCIDENTS

**Özge Ünver, Cemil Kocar, Gürdal Tuncel**

## ABSTRACT

A dynamic dose model is developed to estimate radiation doses and stochastic risks due to atmospheric discharges of radionuclides in the case of a nuclear reactor accident. Dose calculation software developed performs time dependent calculations. The activity in 7 animal products and, 13 vegetables and cereals as well as grass can be predicted by the model. Vegetables and cereals considered in the model are root, leafy and fruit vegetables, corn cobs, spring and winter wheat, spring and winter barley, beet, potatoes, berry and non-berry fruits; and animal products are goat milk, sheep milk, cow milk, egg, chicken, beef and lamp. In addition to individual doses from inhalation, ingestion and external irradiation pathways for 4 different age groups, collective doses and stochastic risks can be calculated by the model, as well. The model can be coupled to any long-range atmospheric dispersion model which can calculate radionuclide concentrations in air and on the ground at predetermined time intervals or measured radioactivity data. Since the Chernobyl accident, there had been an increase in real world data to assess the capabilities of softwares which are developed to calculate radionuclide concentrations in various media and resultant doses to human beings. Radioactivity data measured in grass and different food products in Helsinki, Finland after Chernobyl accident and activities calculated using different models were used for validation of the model developed in this study. Cs-137 is used in validation exercise. The Cs-137 activities calculated in pasture grass and foodstuff agreed well with measured activities and activities calculated by well documented models. Some case studies to predict the doses and risk posed by accidental release of radionuclides from proposed nuclear power plants in Akkuyu and Sinop sites will be the next phase of the study. Country specific data for food consumption, feeding regimes, yield of agricultural food products is now being generated to be used in the model calculations. Sensitivity analysis is now being performed to determine the parameters that have the strongest influence on the uncertainties of the dose and risk calculations. The sensitive parameters used in uncertainty analysis to determine the uncertainty in dose and risk will be a part of the upgraded model. Latin hypercube sampling method is used for sensitivity and uncertainty analysis.

**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
**4th International Symposium and IUAPPA Regional Conference**
**10-13 September 2012 Istanbul -Turkey**

# FORECASTING HOURLY OZONE LEVELS USING GENE EXPRESSION PROGRAMMING AND MULTI-LAYER PERCEPTRON MODELS IN BILBAO, SPAIN

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## ABSTRACT

As one of the major tropospheric photochemical oxidants, ozone ($O_3$) pollution addresses intensively concern for its adverse effects on human health and vegetation. For the sake of reducing $O_3$ related injuries and damages, the short term prediction of $O_3$ levels is needed. This paper presents the results obtained using two intelligent models such as gene expression programming (GEP) and multi-layer perceptron (MLP) to forecast ozone levels in real-time up to 3 hours ahead at Deusto stations in Bilbao, Spain. The inputs to the GEP and MLP were meteorological conditions (wind speed and direction, temperature, relative humidity, pressure, solar radiation and thermal gradient), hourly ozone levels and traffic parameters (number of vehicles, occupation percentage and velocity), which were measured in 1994. Results showed that the MLP with correlation coefficient of 0.898, 0.779, 0.685 and normalized mean squared error of 0.117, 0.235, 0.308 in forecasting $O_3$ levels 1,2 and 3 hours ahead, respectively, had slightly better performance than GEP with correlation coefficient of 0.894, 0.772, 0.672 and normalized mean squared error of 0.119, 0.238, 0.326, respectively. These small differences between GEP and MLP may be statistically significant, but for practical purposes the performance of the GEP with explicit mathematical formulations was superior to that of the MLP.

**Keywords:** Air quality modelling; Gene expression programming; multi-layer perceptron model; Ozone level forecasting.

**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# ASSESSMENT OF CLIMATOLOGICAL POTENTIAL OF TRANSBOUNDARY AIR POLLUTION TRANSPORT IN EASTERN SIBERIA AND THE RUSSIAN FAR EAST

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## ABSTRACT

Estimates of the air mass exchange in the lower troposphere (up to 3 km a.s.l.) across the Russian border in Eastern Siberia to the Russian Far East are made using climatological air sound data on layer mean wind. A simple transport box-model is employed to calculate the net air volume transport over the boundary segments of selected geographical regions in different climatic seasons and for the whole climatological year. For the regions surveyed by the stations of the Acid Deposition Monitoring Network in East Asia (EANET), a first-order evaluation of the transboundary pollution fluxes of sulfur- and nitrogen-compounds is given based on their mean air concentrations observed in 2006-2008.

**Key Words:** transboundary pollution, air mass transport, air exchange climatology

## 1. INTRODUCTION

Airborne compounds containing sulfur and nitrogen play an important role in atmospheric chemistry. Being capable of absorbing solar radiation at different wavelengths, they are recognized to have a certain potential to influence the climate evolution on Earth (Rovinsky and Yegorov, 1986). Current interest in studying these compounds arises due to their increased global input into the atmosphere. An equally important aspect, *viz.* the negative effect of these substances on human health, biota and human infrastructure, further motivates a more practical investigation of their spatial and temporal distributions.

Since sulfur dioxide and nitrogen oxides are mostly co-emitted in course of the use of fossil fuel, the increasing consumption of the latter in recent decades (assuming invariable non-anthropogenic sources) promoted a steady growth of the atmospheric load of these compounds, hence concomitant environment deterioration. Inasmuch as gases and aerosols are transported with the air flow, the observed changes in concentrations of pollutants over an area occur due to existence of short- and long-range transport of air masses susceptible to direct emission. A transboundary drift of pollutants, in turn, may have a significant impact on the ecological situation of the neighboring territories. Few earlier studies examining the environmental monitoring data (Izrael et al., 1987) firmly correlate the changes in pollutant concentrations over the territory with the direction and velocity of the air flow. The objective of this study is to evaluate a potential transboundary air transport and related pollutant fluxes by using a relatively facile technique of estimating under the circumstances of the relatively scarce available meteorological and monitoring data.

We apply our method to the detailed geographical assessment of the transboundary air pollution exchange in Eastern Siberia and the Russian Far East. A case in point here is the intensive economic development of the People's Republic of China that actively promotes its industrial throughput. The anticipated concomitant growth of industrial emissions adds further importance to the task of conducting this study. Below, we therefore focus on the brief description of the method and input data used, followed by the application to calculating the air mass and air pollutant exchange in the lower troposphere over the Asian border of Russia.

## 2. GENERAL DESCRIPTION OF METHOD AND DATA USED

The applied approach represents an indirect assessment of the pollutant transport reckoned proportional to the horizontal transport of air enclosed in the lower troposphere, and the concentration of a given pollutant in it. The horizontal transport component is evaluated as the air transition efficiency (in $m^3 s^{-1}$) in a given direction or eventually over the individual transects of the border of interest. We thereby assume that the air is transferred in particular directions scales with the corresponding mean layer winds velocities and their climatological recurrence observed at the nearest air sounding station. Figure 1 presents the domain of interest comprising the piecewise approximation of the Russian state border, locations of the aerological observational stations, and EANET air quality monitoring sites.

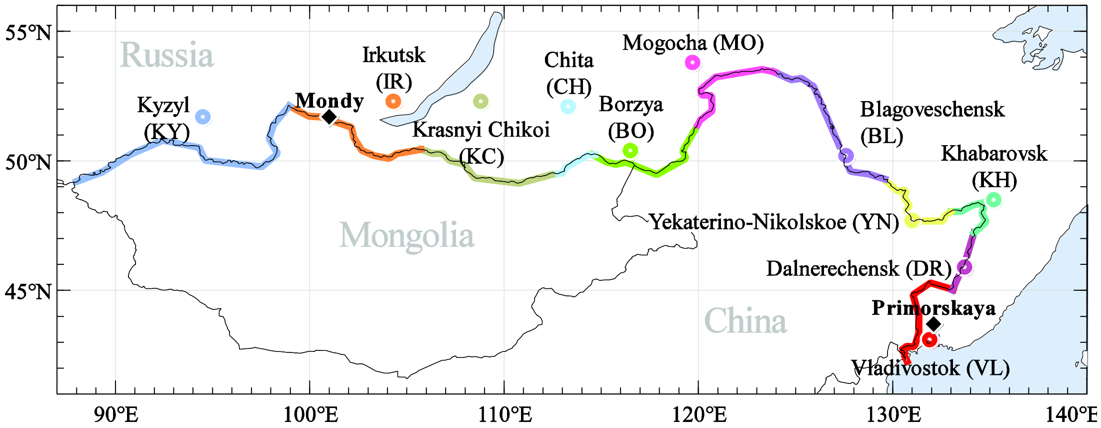

Figure 1. Location of the selected aerological (air sounding balloon) stations and EANET monitoring stations (diamonds) along the Asian border of Russia. Colors distinguish the segments pertaining to particular stations.

As wind data input we use the results of RIHMI-WDC climatological data processing (Brukhan, 1984) conducted for the atmospheric soundings at 11 aerological stations located along the continental border of East Asian territory of Russia. Data covers the 10-year period 1961−1970 selected through the highest number of operating stations and observation acquisition rate. The data provides long-term averages and statistics on the wind meteorological regime (*e.g.*, mean vector and scalar velocities, direction, standard vector deviation, steadiness) in a set of given altitude ranges; owing to the large sampling selection, the series used are expected to be representative up to date. We further employ the results of the numerical integration procedure (Brukhan, 1983) to translate the aerological statistics into the eight-rhumb wind speed and recurrence distributions (climatic wind roses) at each station for every month. Wind roses essentially provide the rhumb-integrated values of the wind speed and recurrence that would result from the normally (2D-circular) distributed probability densities of the velocities and directions matching the averages and vector deviation of the observed winds.

An example of the climatic wind roses derived for two aerological stations, Irkutsk and Vladivostok, is given in Figure 2. It highlights similar speed and opposite turn variations in winds typically observed in the south of Eastern Siberia (Baikal area) and Primorye

(Primorsky Krai), respectively. The wind regimes are commonly influenced by alternation of seasonal atmospheric action centers defining the climate characteristics of the respective regions (Khromov and Petrosyants, 2006). For instance, winter winds are dominated by the Siberian anticyclone, favoring stable and strong north-west winds with recurrence rates of nearly 40%. In contrast to that, summer conditions driven by the Asian summer depression are characterized by markedly lower wind stability and recurrence. In the case of coastal Vladivostok (and generally, at the most of Far East areas), seasonal wind shear is further enhanced by Asian Monsoon circulation, whereas winds inside continent merely show diminished variation. It is traced in Figure 3 depicting the seasonal wind patterns over the North East Asia. Nevertheless, for the majority of the considered locations, west- and north-west winds are found to prevail, selectively interrupted at summer. In some place (*e.g.*, Irkutsk) it is intensified by specific orientation of mountain ridges.

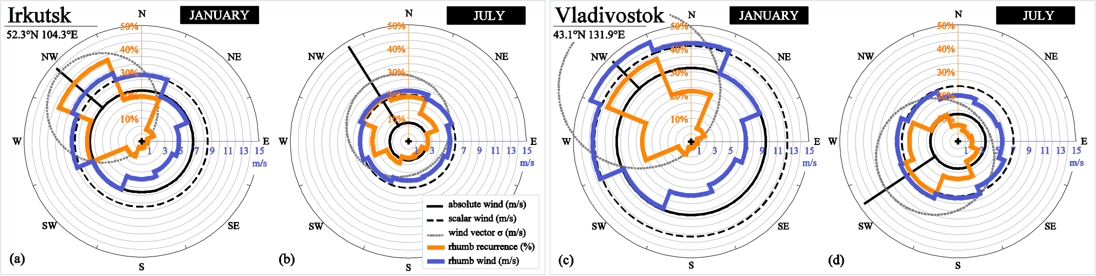

Figure 2. Eight-rhumb climatic wind roses at Irkutsk (Baikal area) and Vladivostok (Primorye) derived from the aerological climatic wind data within a 3 km layer (see text). Left (a, c) and right (b, d) panels refer to January and July, respectively. Thick contours represent the average wind speed (blue) and recurrence (orange) in respective rhumbs. The solid black circles refer to the average wind magnitude (radial lines indicate wind direction); the remaining circles denote the average wind standard vector deviation (dotted) and scalar wind magnitude (dashed). Note that the rhumb data are the result of numerical processing, as opposed to the input actual statistical data. The reader is referred to the literature (*e.g.*, Crutcher, 1956) for supplementary information on the properties of the wind rose plots.

Evidently, seasonal alterations in wind regime in combination with the complexities and irregularities of the borderline directions render the task of transboundary flux calculations somewhat intricate. To avoid ambiguous formulations, we declare the transport leading to air removal from Russian territory as *positive*, and, conversely, the influx of air masses from the neighboring territories into Russia as *negative*. This enables one to calculate the integral transport terms over each border element (BE) in both directions, as well as their sum yielding the net transport term in question. The calculation procedure (for terseness omitted here) computes the cross-boundary-relevant (*i.e.*, perpendicular to the line of the BE advance) wind components for every rhumb and appoints them an appropriate sign. The relevant wind components are subsequently multiplied by the length and specific height associated with a given BE to yield the air volumetric transfer velocity (in $m^3 s^{-1}$). The specific layer heights are assigned equal to the residue between the height of the transport upper boundary in lower troposphere (see below) and the average surface elevation of the respective BEs. Finally, the three *air transport* (AT) terms (in units of volume), *viz.* positive, negative and net, are derived integrating the respective transfer velocities over the given period, in this case of one month.

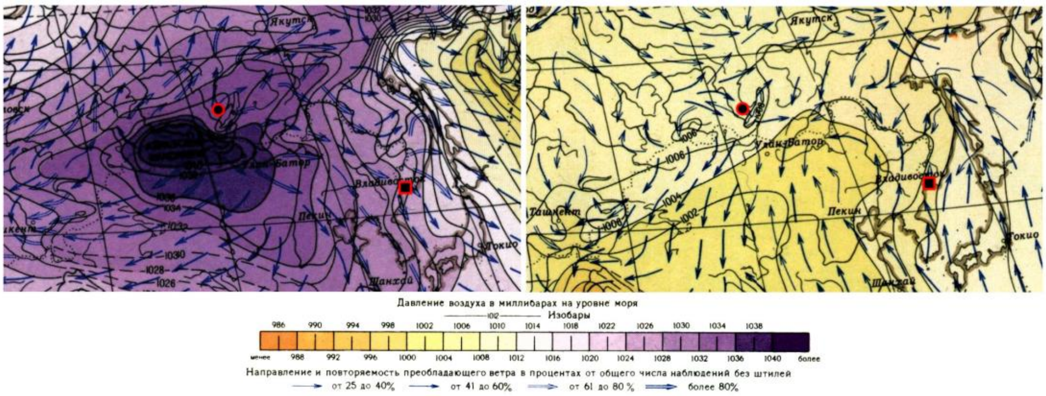

Figure 3. Mean sea level air pressure (in mbar, contours), surface prevailing winds direction and recurrence (arrows) over Eastern Siberia and the Russian Far East in January (left panel) and July (right panel) according to (Atlas, 1964). Symbols denote locations of Irkutsk (circles) and Vladivostok (squares) aerological stations for comparison.

Constraining the transport upper boundary (set to 3 km a.s.l., respectively) retains the highest possible representativeness of our results with regard to the input data used, as well as with respect to the assumptions on pollutant abundances made in current approach. For instance, lowermost climatic wind data granted by (Brukhan, 1984) typically refer to the averages reckoned for the range between the surface and matching 3 km (a.s.l.); it is unfeasible to make any inferences on the average wind properties below this altitude. On the other hand, evaluations of the vertical distributions of the compound of interest (e.g., SOx) suggest that the dominant part of their atmospheric load and, as more important, seasonal variation pertain to the domain below this altitude (Rovinsky and Yegorov, 1986). Unfortunately, the monitoring data we possess is restricted to the near-surface concentrations of species of interest. Also there are no any supplement results for these regions capable to provide near-real information on vertical profiles of these air pollutants. Although more sophisticated approaches might be available (we consider applying them in subsequent studies), in this study we adopt the zero-order approximation, taking the surface concentrations observed at the nearest monitoring station as representative for the entire segment length and up to upper height of layer. The ultimate result, the three *pollutant transport* (PT) terms (in units of mass), are thus derived as a product of the corresponding AT terms and the average concentrations observed in respective months. Noteworthy, the devised method is likely to overestimate the absolute PT terms, as concentrations are typically found to decline with height, being primarily under the influence of surface processes (*e.g.*, emission and deposition). The *net* PTs, however, result from the subtraction of the respective absolute terms, which cancels out a large part of the absolute error and emphasizes the seasonal variations in species concentrations. We remark that the uncertainty in derived net PT terms grows proportionally to its magnitude, as opposed to the absolute AT/PT terms.

## 3. RESULTS

The calculation results are aggregated in Figure 4. Panel (a) shows the detailed estimates of AT over the continental part of the Asian Russian border, apportioned between eleven segments pertaining to selected air sounding stations. Except for IR and KC (the abbreviations follow those introduced in Figure 41) whose geographical layout (in particular, mountains) renders them least sensitive to the changes in the local wind regime, all stations present marked variations in net AT. These are mainly driven by the changes in wind shear and stability, judging by the moderate variations in total AT of ±25% (median value from all stations), with the only prominent cases being the DR and VL segments (±31%). To get more insight into these figures, we note that total AT is proportional to the scalar wind speed, *i.e.* the absolute air transition at the station. The steadiness of the wind (*i.e.*, the ratio of its mean vector and scalar velocities), in turn, denotes how largely the wind is scattered about its direction. At low steadiness, more equally distributed directions contribute comparably to the absolute AT terms thus substantially attenuating the net transport. The latter is also sensitive to the average wind direction, owing to the spatial arrangement of a particular border segment: Higher sensitivities are pinpointed by larger departures of the ratio between the positive and negative AT terms from unity, respectively. All abovementioned particularities are prominent in the transport calculated at BL segment.

Overall, we estimate the entire annual transboundary net AT at −85 million $km^3$, or an order of magnitude smaller than the totals of ~1200m $km^3$ of air transported in both directions over the ~5660 km borderline. Whereas Russian territory is generally subject to influx of air in fall, total negative AT is reduced by mere $^1/_6$ owing to the outward transport in winter-spring months (see Panel (b) in Figure 4). This dynamics is further detailed in Panel (c) displaying the seasonalities segment-wise. We remark that summer conditions promote much more equilibration in air exchange, disfavoring steady winds. In other seasons, however, five of eleven segments (*viz.* BO−BL, DR−VL) are susceptible to large net AT of 30−70m $km^3$ per quarter. This result is consistent with the region-prevalent eastward transport pattern, since the aforementioned segments feature the widest longitudinal span (see Figure 1).

Interestingly, positive (outward) net AT at BO and MO parts is further reduced by the air re-entry via the BL segment; during this passage, however, air is exposed by the surface sources located in China. Similarly, all eastern segments starting from BL are generally subject to net import of the air from the neighboring territories. We reckon the net AT into Russia over this region at the considerably large annual value of −412m $km^3$, ranging within −7.4 to −61m $km^3$ per month in July−November, respectively. This contrasts with the annual net 280m $km^3$ (1.5−38m $km^3$ in July−January) exported by Russia across the CH−MO segments. These essentially large terms demonstrate the capacity of transboundary air exchange disequilibrium to promote considerable pollutant transfer.

We illustrate the application of the AT calculation results to estimating pollutant transfer at two study regions where environmental monitoring data are provided. The latter derive from unique observations performed by the Acid Deposition Monitoring Network in East Asia (EANET), long-term operating four regional and remote monitoring stations in the Asian territory of Russia (EANET, 2009). For the current inquiry we pick the observational data on $SO_2$, $SO_4$, $NO_3$ and $NH_4$ for Baikal area (at remote station Mondy corresponding to the IR segment) and in Primorye (segment VL, regional station Primorskaya) for 2006−2008, guided by the similarity in the seasonal profiles and annual averages of the observed concentrations in this period (not shown here, see Khodzher et al., 2011). From these, we compiled the averages of the multi-year monthly-binned samples into monthly “climatologies” used in the calculations (Figure 5). As expected, they show the stark difference in abundances registered in the regional (*i.e.* more susceptible to pollutant transport from distant industrial sources) and remote conditions. Notably, the net AT pattern we reckoned for VL resembles the evident seasonal variations at Primorskaya, suggesting these being driven by regional pollution transport. Indeed, a linear regression of respective concentrations *w.r.t.* the AT terms yields high correlation coefficients of 0.79−0.91 (at $R^2$=0.62−0.82) for inward and net transport, with much lower correlations of 0.41−0.67 ($R^2$=0.17−0.45) for outward one. The variations at Mondy are generally not linked to AT (average $R^2$ of 0.12 for all terms), with an exception of $SO_2$ that moderately correlates with the positive AT. That implies the likely presence of a regional $SO_2$ source to the north-northeast of site, *i.e.* contrariwise the main outflow direction at the IR segment (a plausible culprit would be the Irkutsk region industry).

Panel (d) in Figure 4 presents the seasonal evolution of the PT terms for the segments of these two regions. The dynamics at Primorye shows clear concomitance with the net AT over VL, where pollutant transfer rates reach tens of thousand tons per month over about 540 km of this border segment. Whilst winter season accounts for 50−66% of the annual PT mass, diminished net AT and concentrations render its summer share at negligible 1−2%. Unlike the case in Primorye, variations in net PT in Baikal region are much less extreme, being mainly propelled by the changes in pollutant abundances. Overall, the net PT at IR is positive (*i.e.*, outward Russia), but comprises extremely low totals for the comparable segment length of ~580 km (see Table 1). Net PT dynamics similar to VL results is marked only for $SO_2$ with winter and summer totals account for 57% and 8% of the annual transport, respectively.

Recapitulating, these cases conclude the extreme conditions of coincidentally low and high AT and observed atmospheric load of pollutants, respectively. We are not able to gain further insights on the PT in other parts of the studied domain (in particular, from VL westward up to MO) due to scarcity of monitoring data. However, if we surmise similar (*i.e.*, AT-correlated) dynamics of concentrations over the eastern segments (BL−DR), the sum net PT for this region would amount 2.5−4 times that of VL. The respective upper limit on $SO_4$ transport of ~2900 t/yr agrees well with 4000 t of intake sulfate transported into this region in 2009−2010 conferred in an alternative study (Roshydromet, 2011).

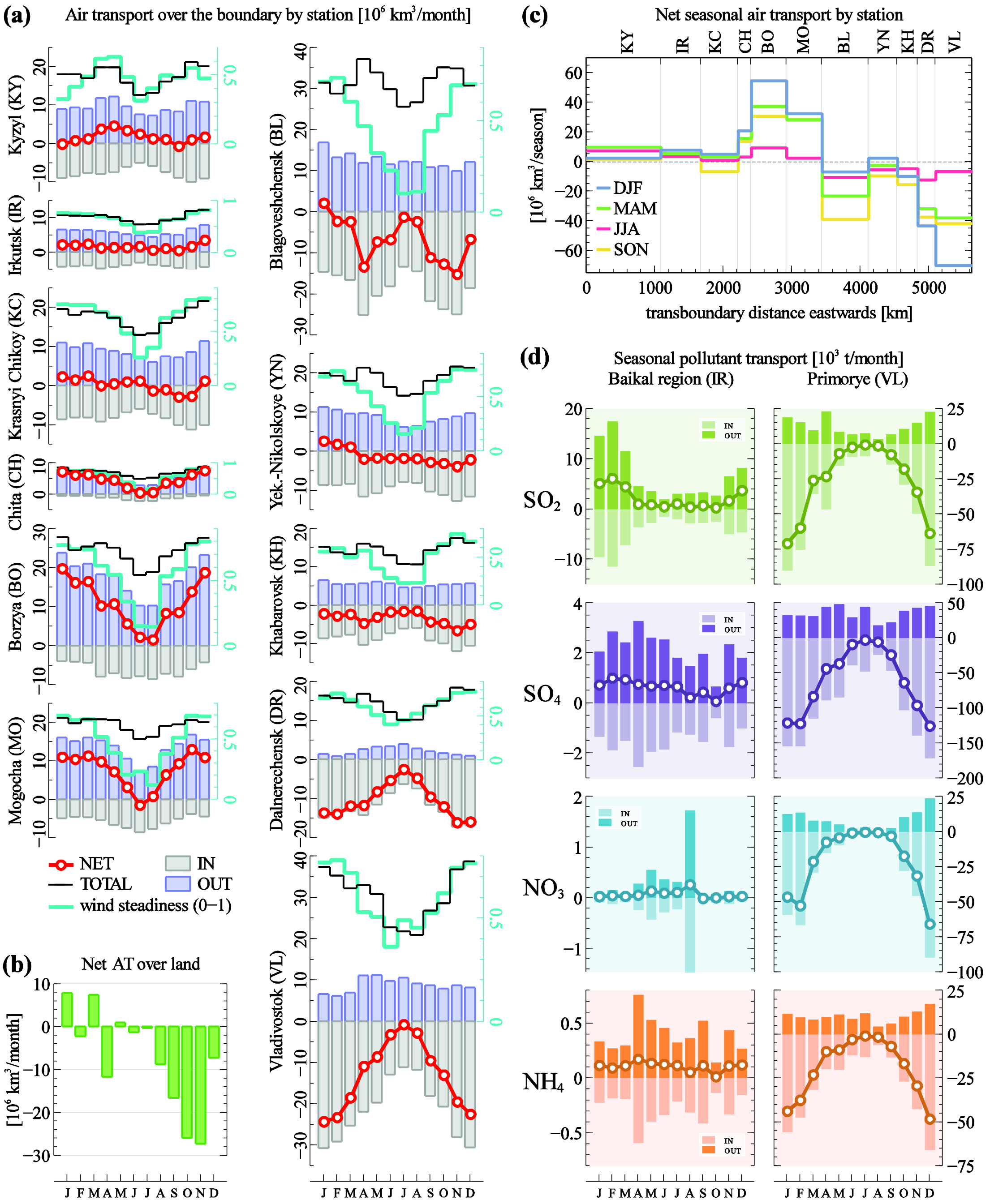

Figure 4. Transport calculation results (see text). Note the varying axis scales in panel (d).

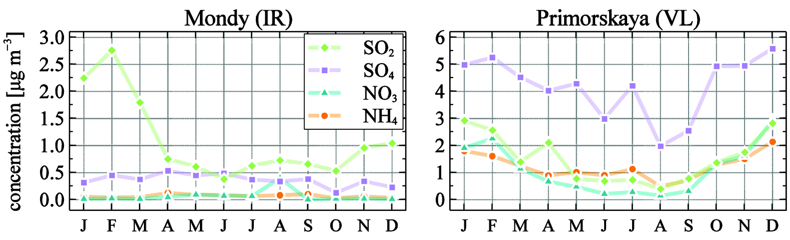

Figure 5. Seasonal average variation of pollutant concentrations observed in 2006−2008 at two EANET monitoring stations used as input data. Note the varying axis scales.

Table 1. Estimated seasonal and annual net pollutant transboundary transport across western (Baikal area) and eastern (Primorye) segments (IR/VL) for 2006−2008 [in $10^3$ tons] †

| Species | DJF | MAM | JJA | SON | Annual |
|---|---|---|---|---|---|
| $SO_2$ | 15.1 / −193.8 | 6.5 / −55.1 | 2.2 / −3.7 | 2.8 / −59.2 | 26.6 / −311.8 |
| $SO_4$ | 2.6 / −367.8 | 2.4 / −163.2 | 1.6 / −17.3 | 1.1 / −183.2 | 7.7 / −731.5 |
| $NO_3$ | 0.1 / −164.3 | 0.3 / −32.4 | 0.5 / −1.3 | 0.1 / −51.4 | 0.9 / −249.4 |
| $NH_4$ | 0.3 / −129.0 | 0.4 / −41.2 | 0.3 / −4.8 | 0.3 / −52.5 | 1.3 / −227.5 |

† Positive and negative values denote fluxes outward and inward Russia, respectively.

## 4. CONCLUSIONS

With a simple but robust approach we show that net lower tropospheric air transport over the Russian border in East Asia has a clear seasonal behavior favoring strongest air mass exchange disequilibrium in winter. The detailed analysis of the air transport and wind regime in those regions grants a slightly counterintuitive deduction: Changes in scalar wind speed magnitude contribute merely $^1/_4$–$^1/_3$ of the total variation in the net air mass transport, as opposed to the wind direction and steadiness. Furthermore, the particular geographical layout turns individual border segments into air net entry and net exit ports under seasonal transport patterns. Thus, Russia annually “exports” around 280 million $km^3$ of air to Mongolia, but “imports” roughly 1.5 times that amount from China in Far East. The situation worsens when observations suggest that the “imported” air is substantially more polluted, turning Russian eastern territories into a net pollutant sink. Estimates of the net pollutant flux in Primorye amount to several hundred thousand tons annually, with the major contribution pertaining to winter-spring months. A projection for the entire border extension between Russia and China suggests a doubling to quadrupling of these values.

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# ASSESSMENT OF THE URBAN AIR POLLUTION CAUSED BY POINT, SPATIAL AND LINEAR SOURCES IN KORFEZ, KOCAELI BY ISCST-3

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## ABSTRACT

This study is made in order to model the distribution of pollutant gases emitted into the atmosphere in the Körfez district of Kocaeli Province. In this study, sources of pollutants are grouped as three different parts: point, spatial and linear sources. While industries and locations are belonged to groups of point and spatial sources, respectively; two major highway passing through the town and connect Europe to Asia are considered as line sources. $SO_2$, $NO_X$, CO and VOCs emitted from these sources to the atmosphere are investigated. In this purpose, a Gaussian distribution modeling program developed by the USEPA, ISCST-3 (Industrial Source Complex Short Term) is used. As a result of the studies, it is determined that all the sources have become dominant for CO and $NO_X$, PM, VOC and $SO_2$emissions in this district.

**Keywords :** Körfez District, air quality, pollutant dispersion modeling.

## 1. INTRODUCTION

Air pollution could be defined as the increasing of one or more of different factors including particulate matter, smoke, gases, odor, fog, vapor and moisture in the biosphere to the levels that may cause some adverse effects on human and/or environmental health. Air pollution is generally arise from the human activities and shows different types and characteristics. The factors forming the pollution have generally different nature from the natural constituents of the atmosphere, causing adverse effects on the health and habitats of the living beings. Increasing of air pollution started in the industrialization era and tended to accelerate thereafter (Rao and Rao, 1998).

Körfez District is placed in the most industrialized area of Turkey, with a dense population and a number of transportation routes. It is on the west shore of the Izmit Bay, with a distance of 17 km to Izmit city center and covers about an area of 400 km$^2$. Due to its suitable geographical position, it has become one of the favorite locations for industrial plants, transportation routes and residences since 1960s, the time corresponding to the beginning of the rapid industrialization process in the area. Air pollution has been the most important pollution problem in the area due to the emissions of various industrial plants, residential heating and traffic. Therefore, the fate of the pollutants emitted to the atmosphere in the area should be followed carefully with regard to the dispersion in the atmosphere by the effects of meteorological conditions, atmospheric reactions and effect on the ground-level concentrations. For the estimation of these processes, a number of dispersion model have been used widely in the scientific and governmental institutions.

In the study, the emissions of the pollutants including sulfur dioxide ($SO_2$), nitrogen oxides ($NO_X$), carbon monoxide (CO), particulate matter (PM) and volatile organic compounds (VOC) emitted from point (industrial stacks), spatial (residential areas) and linear (traffic) sources were modeled by a Gaussian Dispersion Model, ISCST-3 and related pollution maps were generated. The distribution of the estimated ground-level concentrations of the pollutants over the region was displayed and the maximum concentrations were assessed. Study area was determined as a square with the dimensions of 10 km in both east-west and north-south directions, which is given in Figure 1.

## 2. AIR POLLUTION DISPERSION MODELS

Pollutants emitted to atmosphere undergo a number of complex physical and chemical transportation mechanisms, including movement by wind, dispersion, diffusion, wet and dry deposition, chemical transformation etc. Meteorological conditions and topography of the area together with the pollutant characteristics are the important factors determining the fate of the pollutant in the atmosphere. (Environment Agency of UK, 2012). A pollutant emitted from a ground-level source or stacks is subjected to atmospheric processes and tend to disperse as it undergo vertical and horizontal transportation in the atmosphere. Transportation may be defined as the transfer of gaseous or particulate pollutants by air movements. It provides a dispersion and dilution environment for the pollutants coming from different sources and affecting each other (Godish, 2004). Industrial pollutants are generally released to the atmosphere vertically by a long stack, forming a smoke called as plume in the atmosphere. This pollutant plume moves by winds to the direction of dominant winds in the area. Pollutants are then dispersed and diluted as they simultaneously undergo chemical reactions, which cause them to form another compounds called secondary pollutants, and wet and dry deposition which cause them to deposit on soil or water surfaces. In these processes, emission parameters such as emission rate, velocity and temperature of the gas, stack parameters etc. have a determinative effect on the pollutant concentrations at a distance to the emission source also, as well as the external factors mentioned above (ess.co.at, 2009). The transportation of the pollutants in the atmosphere is generally modeled by Gaussian dispersion models.

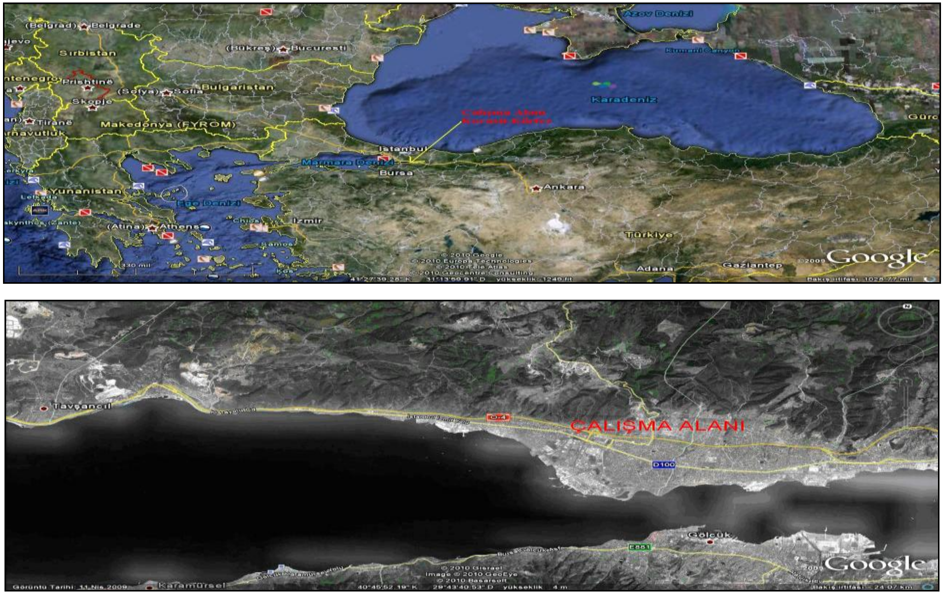

**Figure 1.** Study Area

ISCST3 (Industrial Sources Complex-Short Term3) is a air dispersion model developed by EPA to calculate the concentrations of the pollutants emitted from industrial sources based on Gaussian dispersion calculations . It can estimate the short and long term concentrations of the pollutants by using the real time meteorological data. The pollutants emitted from different sources including point, spatial and linear sources can be modeled by ISCST-3 with regard to their ground level concentrations, dry and wet depositions to get the distribution maps in the neighborhood of the sources.

The data necessary for the use of ISCST3 in modeling the pollutants includes some site-specific values and assumptions, which are given below, in addition to the data related to emissions. These are:

1. Study Area
2. Receptors
3. Meteorological Data
4. Site-specific Climate Parameters
5. Dispersion Coefficients
6. Exponential Decay
7. Terrain Elevations
8. Terrain Calculations
9. Averaging Times

For the modeling of the pollutants in the study area, the data given in Table 1 were used.

**Table1 .** Input Data for the Model

| Data | Data Properties |
|---|---|
| Map of the Study Area | in .dwg format |
| Meteorological Data | Hourly Surface Data |
| Site-Specific Parameters | Receptor Points, Terrain Elevations |
| Source Data | Point, Spatial, Linear |

The properties ISCST model can be summarized as:

- It can be used in the urban and rural areas, flat and elevated surfaces in the distances below 50 km or less.
- It can model the dispersion of primary, toxic and hazardous pollutant emissions.
- It can be used for the modeling of point, spatial and linear sources separately or together.
- Dispersion calculations can be expressed in any period of time such as yearly, monthly, daily or hourly. These results can be specialized for any source or source groups.
- It can calculate the building downwash effect close to the sources.
- It can calculate the decrease of the pollutants in the air due to exponential decay, dry and wet deposition etc.
- Receptors can be defined in different forms (Cartesian, circular etc.) and numbers in the model.

ISCST3 uses annual hourly surface meteorological data in the modeling (Balagopalan, 1984). In the study five years meteorological data (between 2005-2009) of the area provided by Lakes Environmental were used. The data includes hourly temperature, wind direction and speed, pressure, mixing height, precipitation etc. (weblakes.com, 2012). Other properties related to meteorological data and the study area used in the model are given in Table 2, while the wind rose generated by PCRAMMET by using the met data is shown in Figure 2.

**Table2.** Met Data Properties and Site-Specific Characteristics

| | |
|---|---|
| Meta Data Format | SAMSON |
| Anemometer Height | 14 m |
| Height of Data Collection | 320 m |
| Data Frequency | Hourly |
| Coordinates of the Area | 40,734564 N, 29,715517 E |
| Size of the Area | 12 km x 12 km |
| Data Period | 01/01/2005 31/12/2009 |
| Surface Roughness | 0.62 m |
| Albedo | 0.21 |
| Bowen Ratio | 1.89 |

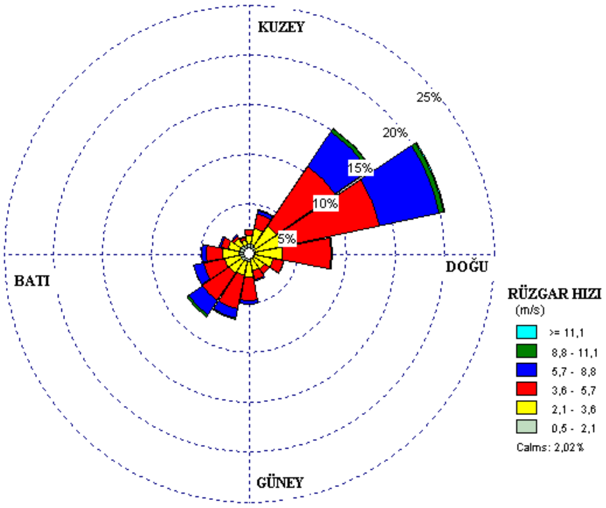

**Figure 2.** Wind Rose for the Study Area

In the modeling study, 1250 Cartesian receptor points with the grids of 740 m x 740 m were defined. Elevations of the receptors were taken from “Google Earth”.

## 4. RESULTS AND DISCUSSION

Dispersions of the pollutants of $SO_2$, $NO_X$, CO, PM and VOC emitted from point, spatial and linear sources in Körfez District of Kocaeli were modeled by ISCST3 separately. The dispersion map obtained by the modeling of the pollutants for all sources was divided into three parts, N1, N2 and N3 in west-east direction and ground-level concentrations attributed to the source groups were given under the dispersion maps. It should be noted that maps are generated by the model based on the annual maximum concentrations calculated for each receptor point.

### 4.1. CO Distribution Map

CO emissions are emitted from all three source groups in the district. Therefore, model was run for three source groups separately, and together to get the contributions of the sources to the total ground-level concentrations (Figure 3). Maximum ground-level CO concentration was estimated as 92.46 µg/m$^3$ in N2 section. As shown in the Figure 3, spatial sources are more dominant in this section, while the effect of point sources in N1 is considerable also.

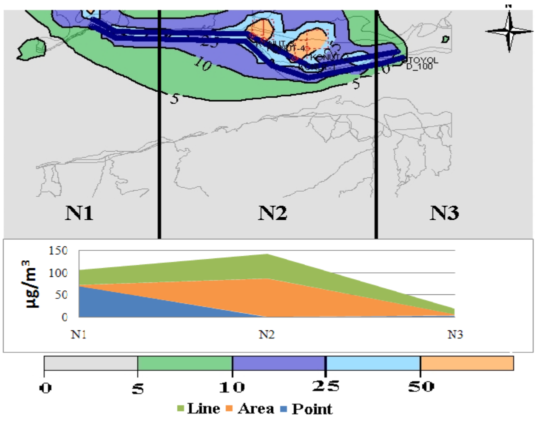

**Figure 3.** Annual CO Distribution Map

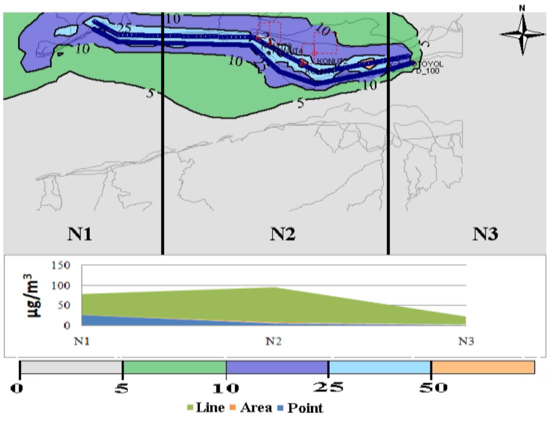

**Figure 4.** Annual NOx Distribution Map

## 4.2. NOx Distribution Map

NOx emissions were expressed as $NO_2$ equivalent in the study. As in the case of CO, all the emission sources have significant contributions to the NOx emissions in the district. Annual maximum NOx concentration was estimated as 89.98 µg/m$^3$ in N2 section (Figure 4). Figure4 shows that linear sources have the highest contribution to the ground-level NOx concentrations, while the effect of spatial sources is negligible.

## 4.3. $SO_2$ Distribution Map

Since SO2 emissions emitted from the traffic vehicles were neglected in the study, other two source groups were taken into account in the $SO_2$ modeling study. It was estimated that the maximum $SO_2$ concentration is expected to be 14.85 µg/m$^3$ in N2 section, with the dominance of point sources in forming it (Figure 5). Distribution maps shows that higher $SO_2$ levels are concentrated in the north part of the district, especially in the middle (N2) section, while there are significant levels in the south, i.e., the opposite shore of the Izmit Bay, suggesting the transportation of $SO_2$ emitted from the long industrial stacks in the district by the dominant north winds in considerable amounts.

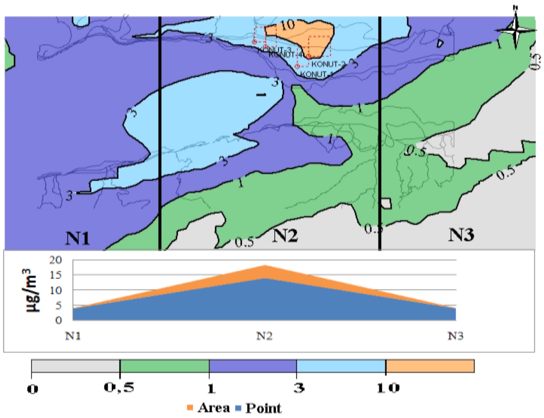

**Figure 5.** Annual $SO_2$ Distribution Map

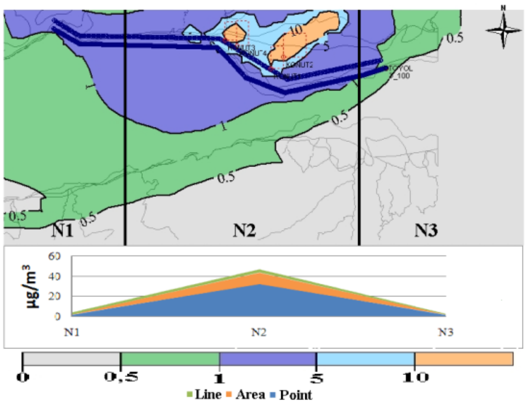

**Figure 6.** Annual PM Distribution Map

## 4.4. PM Distribution Map

All the sources were included in PM modeling study. The maximum PM concentration was calculated as 33.47 µg/m$^3$ in N2 section (Figure 6). Figure 6 indicates that higher PM concentrations are expected to be in the north of the district. As in the case of $SO_2$, point sources are dominant in the ambient air PM concentrations, while the contribution of the linear sources is very low as compared to the other source groups

## 4.5. VOC Distribution Map

Among the sources of VOC emissions, linear sources together with the point sources including industrial processes are more important as compared to the spatial sources. It was estimated that the maximum VOC concentration is expected to be 19.81 µg/m$^3$ in N2 section (Figure 7). The map indicates that VOC concentrations are concentrated in the industrial region of the district, while the effect of linear sources should also be concerned.

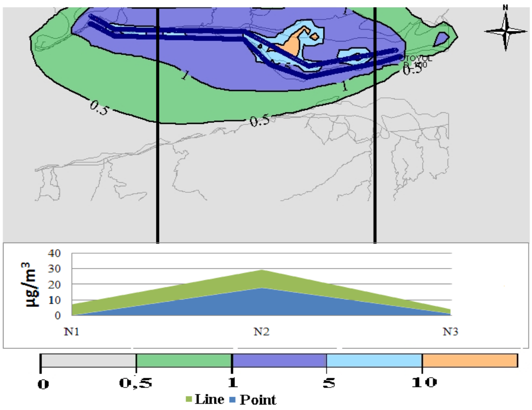

**Figure7.** Annual VOC Distribution Map

## 5. CONCLUSIONS

Results obtained in the study are summarized below.

- Maximum CO concentration was estimated as 92.46 µg/m$^3$ and the map showed that CO concentrations are concentrated on the residential areas and along two highways, D-100 and Anadolu Highway. The spatial sources are dominant in ground-level CO concentrations.
- NOx concentrations are expected to be dispersed in west-east direction, similar to CO. Annual maximum concentration was calculated as 89.98 µg/m$^3$, while the linear sources have the highest contribution to the NOx levels in the area.
- The dispersion of $SO_2$ emissions showed a distribution from the middle section of the district to the north, while the effect of them on the south of the district (opposite side of the Izmit Bay) is significant also. Maximum $SO_2$ concentration was found 14.85 µg/m$^3$, while the point sources of industries are estimated to have the highest contribution.
- The dispersion of PM emissions showed similar patterns with $SO_2$ emissions. Maximum concentration was estimated as 33.47 µg/m$^3$ and the dominant source group is industrial point sources, as in the case of $SO_2$.
- VOC concentrations concentrated on the industrial area of the district, indicating the effect of point sources of industrial processes similar to PM and $SO_2$. Annual maximum VOC concentration was 19.81 µg/m$^3$.

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# WRF-CAMx application over an urban area: parameterizations sensitivity study for air quality purposes

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## ABSTRACT

The main objective of this study is to evaluate the air quality modelling system WRF/CAMx over the Porto urban area, which was affected during the last years by PM10 and $NO_2$ concentration values higher than the European Directive (2008/50/EC) limit-values.

The performance of different combinations of physics parameterizations and a new land use (based in CLC2006) implemented in WRF was assessed comparing the obtained results with available meteorological monitoring data. CAMx results were compared with the available air quality data of the study region and the results point out that meteorology simulation has a great influence on air quality results. For Porto urban area, the selection of RRTMG scheme for radiation is the most adequate option to obtain accurate urban air quality results with the system WRF/CAMx.

**Key words:** air quality modelling systems, parameterizations sensitivy studies, atmospheric pollutants

## 1. INTRODUCTION

Urban areas, viewed as a symbol of growth and prosperity, provide a natural focus for research on air quality as they face special problems due to the high emissions from road transport and space heating, associated with high population density. Each city has their own specificities related with climate, land use, local industry, urban planning, etc. Nowadays, despite progressively stricter emission standards for pollutants from traffic and industry, as well as energy efficiency measures, in Europe, urban areas appears as the most problematic in terms of particulate matter (PM10) and nitrogen dioxide ($NO_2$) concentrations with frequent exceedances to legislated air quality standards (Directive 2008/50/EC).

In Portugal urban air pollution has become one main environmental concern, namely in Porto, the second most important national urban area. PM10 annual and daily limit values have been surpassed in Porto urban area over the last decade (Borrego et al., 2010). Also, $NO_2$ annual limit value has been surpassed in Porto urban area over the last years. These two pollutants are the most critical in this urban area in terms of air quality and, consequently, human health. For urban emergency management systems it will be important to have a reliable description and prediction of the urban-scale wind field and other meteorological parameters (Monks et al., 2009).

Air quality numerical modelling has become a fundamental tool on air quality management and meteorological models play an important role, since they provide representations of the weather processes for the air pollution simulations. The importance of meteorological inputs on regional air quality modelling has been clearly stated (e.g. Seaman, 2000) and consequently, the need to have a better insight on the sensitivity and performance of meteorological models. Parameterization of sub-grid scale phenomena persists as one of the most challenging problems in numerical modelling of the atmosphere.

The meteorological model selected to provide the meteorological fields required by the chemical-transport model CAMx (Comprehensive Air quality Model), is the Weather Research and Forecasting (WRF) modelling system. WRF model allow the application of different combination of physics parameterizations in WRF model. Several studies (Borge, R. et al. 2008, Mercader, J. et al. 2010, García-Díez, M. et al., 2011) performed a comprehensive sensitivity analysis to WRF model for different regions and for different parameterizations, such as Planetary Boundary Layer, microphysics, Landsurface model and radiation. However an analysis of the WRF over the urban area of Porto has not been accomplished before, and this is an important step for urban air quality evaluation and assessment. In terms of air quality, a special attention was given to the spatial distribution of emissions, disaggregating the national emission totals onto a spatially resolved emission inventory through the use of spatial surrogates that consider land use and population, to use also as input, with the meterological outputs, for CAMx.

A general model setup for Portugal, and particularly for Porto urban area, will be defined to be used in air quality simulations and could be an important tool for the urban air quality assessment and management.

## 2. METHODOLOGY

### a. The air quality modeling application

WRF model is a next-generation mesoscale numerical weather prediction system designed to serve both operational forecasting and atmospheric research needs. CAMx (Morris et al., 2004) is an Eulerian photochemical dispersion model that simulates the emission, dispersion, chemical reaction, and removal of pollutants in the troposphere by solving the pollutant continuity equation for each chemical species on a system of nested three-dimensional grids.

The WRF/CAMx modelling domains are shown in Fig. 1. For the meteorological simulation the two-way nesting technique has been used in the WRF model for three domains (Fig 1a): Dl with 25 km spatial resolution, centred at 41° N, 4°W. It covers the Northern part of Africa and an area of the Atlantic Ocean including the Azores and Canary Islands, and is intended to capture synoptic features and general circulation patterns. The first nested domain (D2), with a spatial resolution of 5 km,

comprises Portugal and the innermost domain (D3) is centred over the Porto urban area and consists of 61 columns and 66 rows of 1 x 1 km$^2$ grid cells.
CAMx was applied for two domains (Fig 1b): D1 with a spatial resolution of 5 km covering Portugal and the innermost domain (D2) with a spatial resolution of 1 km over the Porto urban area. These domains are smaller than the WRF domains D2 and D3, respectively.

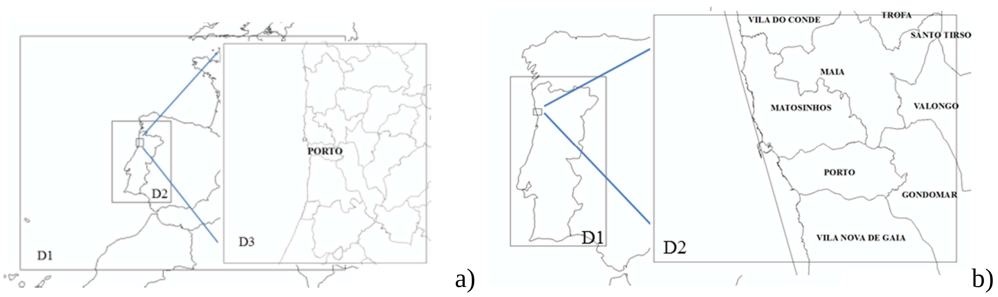

Figure 1. WRF (a) and CAMx (b) simulation domains.

The vertical structure of the WRF model includes 27 layers covering the whole troposphere. Topography, land use and land-water masks datasets were interpolated with the appropriate spatial resolution for each domain (5', 2' and 30'' for Dl, D2 and D3, respectively). The WRF simulations were driven by the ECMWF global analysis with 1° x l ° spatial resolution and temporal resolution of 6 h for surface and pressure levels.
CAMx vertical structure includes 15 layers and in terms of chemical mechanism, the gas-phase photochemistry was resolved through the Carbon Bond (CB4) (Gery et al., 1989) and the model also contains detailed algorithms for the relevant processes of aerosol chemistry (RADM-AQ; ISORROPIA; SOAP).
Anthropogenic emissions are defined on a common basis, using the national emission inventory (INERPA) of 2009 spatially disaggregated on a horizontal resolution of 5x5 km$^2$ for CAMx D1 and 1x1 km$^2$ for CAMx D2.

### b. Episode selection

The selection of the temporal domain to develop the sensitivity runs is based on the analysis of air pollution records across the area of interest (Porto, Matosinhos and Maia municipalities – D2 CAMx) in the air quality stations: urban - Antas (ANT), Ermesinde (ERM), Senhora da Hora (SHOR) and Vermoim (VER); and suburban - Vila Nova da Telha (VNT) and Custóias (CUS). Generalized high concentration values of particulate matter (PM10) and nitrogen dioxide ($NO_2$) were observed in Porto urban area during the winter period (Figure 2).

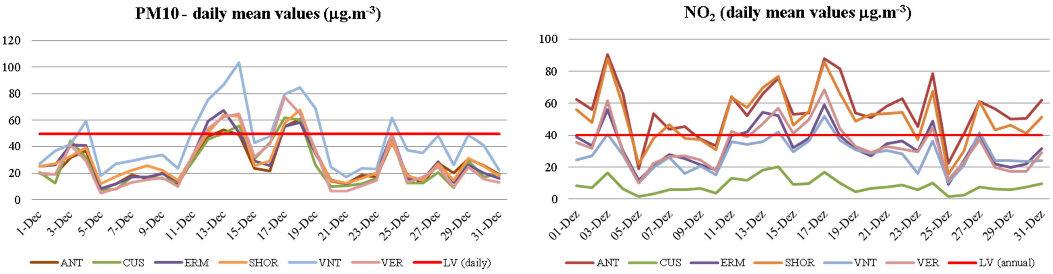

Figure 2. PM10 and $NO_2$ concentrations over the Porto urban area (December 2010).

Simulations were conducted for the month of December of the year 2010 since is a period with air quality problems for PM10 and $NO_2$.

### c. Scope of the sensitivity analysis

WRF model has the possibility to choose the physics parameterizations for each simulation and in this work is intend to performed a sensitive analyses of the different options for land-surface models (LSMs) and solar radiation for the study area and its impacts on air quality simulations.

LSMs combine atmospheric information from the surface layer scheme with land surface properties (dependent on land uses). The three options currently available in WRF are: 5-layer thermal diffusion LSM (Dudhia, 1996), Noah LSM (Chen and Dudhia, 2001) and Rapid Update Cycle (RUC) Model (Smirnova et al., 2000), and only the first two were tested.

The radiation schemes in WRF provide atmospheric heating due to radiative flux divergence and surface downward longwave (LW) and shortwave (SW) radiation for the ground heat budget. The LW schemes available in WRF V3.3.1 are the Rapid Radiative Transfer Model (RRTM) (Mlawer et al., 1997), the Eta Geophysical Fluid Dynamics Laboratory (GFDL) scheme (Fels and Schwarzkopf, 1981), the NCAR Community Atmospheric Model (CAM) scheme (Collins et al., 2004), the Rapid Radiative Transfer Model (RRTMG) scheme (Iacono et al., 2008), the new Goddard scheme (Chou and Suarez, 2001).The schemes included to represent SW processes are the Dudhia (Dudhia) scheme (Dudhia, 1989), the Goddard scheme (Chou and Suarez, 1994), the NCAR Community Atmospheric Model (CAM) scheme (Collins et al., 2004), the Rapid Radiative Transfer Model (RRTMG) scheme (Iacono et al., 2008), the new Goddard scheme (Chou and Suarez, 2001) and the Eta Geophysical Fluid Dynamics Laboratory (GFDL) scheme (Fels and Schwarzkopf, 1981).

Additionally, WRF has the possibility to choose different land use/land cover classification: USGS 24-category and IGBP-Modified 20-category or also introduce new input data set. So, a Corine Land Cover 2006 (CLC06) dataset for Portugal and, more specifically for the Porto urban area was introduced as input data set.

A combination of the model simulations was performed has described in Table 1. Besides changing land surface model, land use data set and LW and SW radiation, in all the tests some options were keeped constant, such as Microphysics - WSM5 (WRF Double-Moment 5-class scheme) (Hong et al., 2004), Planetary Boundary Layer – YSU (Hong et al., 2006) and Cumulus schemes - Kain-Fritsch (Kain, 2004).

Table 1. WRF options considered in each WRF simulation.

| Test | Microphysics | LW radiation | SW radiation | PBL scheme | Cumulus scheme | Land surface model | Land use input data set |
|---|---|---|---|---|---|---|---|
| 1 | WSM5 | CAM | CAM | YSU | Kain-Fritsch | NOAH | USGS-24 |
| 2 | WSM5 | RRTMG | RRTMG | YSU | Kain-Fritsch | NOAH | USGS-24 |
| 3 | WSM5 | RRTMG | RRTMG | YSU | Kain-Fritsch | 5-layer | CLC06 |

## 3. RESULTS

To evaluate the WRF/CAMx results, a comparison with measured data in the selected meteorological and air quality stations was performed, using quality indicators (Table 2): BIAS and r. BIAS indicates how the model follows the variations of the observed values: if positive, the model overestimates the results, and if negative, the model underestimates the results. A good correlation between model results and measurements is considered when the Pearson Correlation Coefficient (r) value is nearly 1.

Table 2. Quality indicators applied in the WRF/CAMx validation.

| Indicator | BIAS | Pearson Correlation Coefficient (r) |
|---|---|---|
| Equation | $BIAS = \frac{\sum_{i=1}^{N}(Oi - Pi)}{N}$ | $r = \frac{N\left(\sum_{i=1}^{N} O_i P_i\right) - \left(\sum_{i=1}^{N} O_i\right)\left(\sum_{i=1}^{N} P_i\right)}{\sqrt{\left[N\left(\sum_{i=1}^{N} O_i^2\right) - \left(\sum_{i=1}^{N} O_i\right)^2\right]\left[N\left(\sum_{i=1}^{N} P_i^2\right) - \left(\sum_{i=1}^{N} P_i\right)^2\right]}}$ |
| Ideal value | 0 | 1 |

$O_i$ – observed values, $P_i$ – predicted values; N – Number of values

### a. WRF validation and analysis

Statistical results from the evaluation of WRF outputs for each test are presented in this section (Table 3). The meteorological stations selected are Aveiro (AVR), Porto (POR), Lisboa (LIS), all situated in Atlantic coastal zone of Portugal and Viseu (VIS) that is approximately 50 km east of the Atlantic ocean, located in Portugal northern-centre.

WRF application with both LW and SW radiation scheme (CAM and RRTMG) shows similar model performance for temperature, wind speed and wind direction. The use of CLC06 as input land use data set improve the model performance, however not significantly, therefore the UGS24 data set represent well Portugal land use, at least for WRF applications at this resolution (> 1 km).

Table 3. WRF Statistical analysis for T (ºC), WSPEED (m.s$^{-1}$) and WDIR (º).

| Variable | Statistic | Test | Monitoring Network | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | AVR | | POR | | | LIS | | VIS | |
| | | | D1 | D2 | D1 | D2 | D3 | D1 | D2 | D1 | D2 |
| T | BIAS | 1 | 0.68 | 0.69 | -2.04 | 0.03 | 0.01 | 0.46 | -0.03 | -0.58 | 0.20 |
| | | 2 | 0.23 | 0.26 | -2.33 | -0.45 | -0.45 | 0.28 | -0.62 | -0.92 | -0.07 |
| | | 3 | 0.07 | -0.05 | -2.13 | -0.85 | -0.95 | 0.27 | 0.10 | -1.43 | -0.49 |
| | r | 1 | 0.85 | 0.84 | 0.91 | 0.88 | 0.87 | 0.84 | 0.91 | 0.83 | 0.85 |
| | | 2 | 0.85 | 0.84 | 0.91 | 0.88 | 0.88 | 0.82 | 0.89 | 0.83 | 0.84 |
| | | 3 | 0.92 | 0.89 | 0.93 | 0.91 | 0.91 | 0.82 | 0.86 | 0.85 | 0.87 |
| WSPEED | BIAS | 1 | -3.03 | -2.93 | -5.52 | -4.22 | -4.24 | -3.10 | -0.92 | 0.15 | -0.09 |
| | | 2 | -2.87 | -2.83 | -5.48 | -4.22 | -4.28 | -3.05 | -1.05 | 0.15 | -0.09 |
| | | 3 | -2.53 | -2.12 | -5.11 | -2.59 | -2.58 | -2.28 | -0.18 | -0.21 | -0.23 |
| | r | 1 | 0.56 | 0.57 | 0.45 | 0.68 | 0.65 | 0.61 | 0.67 | 0.65 | 0.72 |
| | | 2 | 0.57 | 0.58 | 0.40 | 0.62 | 0.60 | 0.60 | 0.65 | 0.65 | 0.72 |
| | | 3 | 0.59 | 0.54 | 0.42 | 0.65 | 0.61 | 0.63 | 0.70 | 0.67 | 0.75 |
| WDIR | BIAS | 1 | -14.55 | -20.99 | -94.89 | -92.89 | -92.71 | -25.69 | -21.21 | -15.84 | -16.90 |
| | | 2 | -17.78 | -23.31 | -94.32 | -94.16 | -94.67 | -27.77 | -24.38 | -15.84 | -16.90 |
| | | 3 | -9.99 | -11.13 | -92.18 | -89.96 | -88.68 | -27.73 | -25.68 | -12.96 | -12.27 |
| | r | 1 | 0.12 | 0.28 | 0.24 | 0.16 | 0.17 | 0.57 | 0.61 | 0.50 | 0.54 |
| | | 2 | 0.19 | 0.25 | 0.16 | 0.16 | 0.16 | 0.54 | 0.60 | 0.50 | 0.54 |
| | | 3 | 0.15 | 0.23 | 0.17 | 0.17 | 0.15 | 0.62 | 0.69 | 0.53 | 0.52 |

### b. CAMx validation and analysis

CAMx results of the three tests were compared with air quality monitoring data for PM10 and $NO_2$ at the Porto urban area (Table 4).

Table 4. CAMx statistical analysis for PM10 and $NO_2$ concentration levels (μg.m$^{-3}$).

| Variable | Statistic | Test | Monitoring Network | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | ANT | | CUS | | ERM | | SHOR | | VNT | | VER | |
| | | | D1 | D2 | D1 | D2 | D1 | D2 | D1 | D2 | D1 | D2 | D1 | D2 |
| PM10 | BIAS | 1 | 8.13 | 11.83 | 4.43 | 9.94 | 11.13 | 18.76 | 9.00 | 12.56 | 24.55 | 33.12 | 6.79 | 15.49 |
| | | 2 | 12.89 | 10.73 | 11.33 | 9.04 | 19.16 | 18.50 | 14.71 | 12.27 | 34.11 | 33.72 | 16.58 | 15.44 |
| | | 3 | 7.88 | 6.74 | 5.51 | 5.70 | 15.43 | 15.78 | 9.76 | 9.30 | 28.70 | 29.50 | 11.33 | 11.89 |
| | r | 1 | 0.21 | 0.30 | 0.09 | 0.27 | 0.07 | 0.22 | 0.12 | 0.23 | 0.00 | 0.11 | -0.01 | 0.17 |
| | | 2 | 0.38 | 0.16 | 0.36 | 0.26 | 0.27 | 0.17 | 0.36 | 0.20 | 0.25 | 0.21 | 0.28 | 0.23 |
| | | 3 | 0.43 | 0.37 | 0.56 | 0.48 | 0.42 | 0.41 | 0.44 | 0.40 | 0.27 | 0.26 | 0.48 | 0.43 |
| $NO_2$ | BIAS | 1 | 28.42 | 28.93 | -25.45 | -29.52 | 12.58 | 16.69 | 20.56 | 17.90 | -1.53 | 3.28 | 3.35 | 8.43 |
| | | 2 | 28.33 | 24.54 | -25.76 | -31.31 | 15.38 | 14.84 | 20.15 | 14.88 | 2.16 | 3.44 | 8.54 | 8.20 |
| | | 3 | -5.50 | -7.87 | -16.17 | -19.21 | 6.23 | 7.30 | -8.75 | -12.09 | 14.06 | 15.27 | -3.58 | -3.22 |
| | r | 1 | 0.60 | 0.60 | 0.42 | 0.50 | 0.55 | 0.48 | 0.58 | 0.60 | 0.45 | 0.43 | 0.43 | 0.44 |
| | | 2 | 0.60 | 0.47 | 0.57 | 0.44 | 0.50 | 0.42 | 0.66 | 0.48 | 0.48 | 0.45 | 0.43 | 0.47 |
| | | 3 | 0.27 | 0.23 | 0.45 | 0.39 | 0.18 | 0.14 | 0.28 | 0.24 | 0.12 | 0.09 | 0.28 | 0.21 |

On the contrary of WRF, CAMx statistical analysis shows different model performances for each test and for each pollutant. For PM10 test 3 shows better correlations for all the air quality stations, however, in terms of $NO_2$, this test shows weak correlations. Test 1 and test 2 demonstrate similar behavior for $NO_2$, having correlations ranging between 0.4 and 0.7. On the other hand for PM10 test 2 shows significantly better results than test 1.

## 4. CONCLUSIONS

The results from this study show the importance of performing a sensitivity analysis of the air quality system over a study area, to achieve accurate urban atmospheric numerical modelling outputs. WRF/CAMx was applied for three different tests at Porto urban area and all the three tests results were distincted from each other in terms of air quality. The statistical analysis of WRF shows that choosing CAM scheme or RRTMG scheme do not change the model performance in the study area. Also, replacing the original WRF land use data set by the CLC06 land use data set, only slightly improve the model performance. In terms of air quality the differences are significant: PM10 statistical analysis shows that test 3 had better performance than the other two and for $NO_2$ test 1 and 2 had better results than test 1.

The main conclusion of this study is that for each pollutant the meteorology simulation has a significantly contribution for the simulated air quality concentrations. From this sensitive analysis for this study area, the options selected in test 2 are the most adequated for evaluate both PM10 and $NO_2$ with the air quality modelling system WRF/CAMx.

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# INTER COMPARISON OF AIR QUALITY DATA USING GENE EXPRESSION PROGRAMMING AND MULTIPLE LINEAR REGRESSION AND FORECASTING AIR POLLUTANT CONCENTRATIONS IN TEHRAN, IRAN

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## ABSTRACT

The forecasting of air pollutant trends has received much attention in recent years. It is an important and popular topic in environmental science, as concerns have been raised about the health impacts caused by unacceptable ambient air pollutant levels. Of greatest concern are metropolitan cities like Tehran, Iran. The aim of the present work is to evaluate the potential of gene expression programming (GEP) in comparison with multiple linear regression (MLR) to provide reliable predictions of $PM_{10}$ and $O_3$ hourly concentrations, a task that is known to present certain difficulties. The modeling study involves five measurement locations within the Greater Tehran Area named Azadi, Golhak, Hesar, Pardisan and Vila stations which experience significant air pollution problems. The $PM_{10}$ and $O_3$ data used cover the year of 2005. The results of GEP were rather satisfactory, with values of the coefficient of determination ($R^2$) for independent test sets ranged between 0.7263 and 0.852 for $PM_{10}$ and between 0.598 and 0.915 for $O_3$ for the five stations and values of the relative absolute error between 0.363 and 0.419 for $PM_{10}$ and between 0.318 and 0.661 for $O_3$. The performance of examined GEP was superior in comparison with MLR models that were developed in parallel ($R^2$ for MLR models ranged between 0.714 and 0.859 for $PM_{10}$ and between 0.572 and 0.909 for $O_3$). The results of the study clearly demonstrate the proficiency of the gene expression programming method in comparison with multiple linear regression in estimation of air pollutants.

**Keywords:** Air pollution modeling, Gene expression programming, Ozone level, Particulate matter, Prediction.

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# MEGACITIES AND POLLUTION PLUMES

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## ABSTRACT

Worldwide, cities are in constant growth. During this process, regional air quality and climate change issues don't influence the city planning choices. However, in the lower atmosphere, the production of oxidants depends on the density of primary plumes, which in turn are shaped by urban structures. This work proposes a model study about the impact of megacities on their environment. It investigates the relationship between city location, density and size on one side, and air quality and continental export of pollutants on the other side. The results show that both the city environment and its structure play a role in its environmental impact, and that its structure also affects the nature of the pollution that is exported towards the rest of the continent.

**Keywords :** Megacities, Plumes, City shape, Air Quality Modeling.

## 1. INTRODUCTION

The release of anthropogenic primary pollutants in the atmosphere is shaped by the size and density of the highly emitting urban structures. In the lower troposphere, these features may also influence the rate of secondary pollutant production, as well as the characteristics of pollutant transport to the larger scale. Thus, in the frame of emission control policies, one needs to take into account the organization of large city emissions, so as to estimate the impact of urban management on tropospheric pollution, from the regional to the continental scale. This is of primary importance, as many cities worldwide continue growing, undergoing either heart densification or urban sprawl without considering the atmospheric incidence of urban development choices (Gurjar et al., 2008;Lawrence et al., 2007;Molina et al., 2004;Molina and Molina, 2004).

Air Quality Models (AQMs) have reached a degree of understanding of atmospheric processes that allow their use for mediating between city planning options. This can be done through sensitivity studies, or via emission scenarios proposing the test of several prospective situations for a given city. Although a realistic representation of city evolution (in terms of energy consuming, habitation and services) is sorely missing, models can provide clues about the relative impact of emission sprawl and emission densification on air quality and climate. To bring elements of answer to these questions, we first run the CHIMERE AQM over Europe using a tagging approach, in order to observe the "atmospheric footprint" of the largest European cities, which is a complex parameter (Greg and Grant, 2000). Then, in the second part of the study, we focused on the simulation of the pollution plumes of 2 critical urban areas: Paris and the Belgium-Netherlands-Luxemburg (BeNeLux) area. The objective of this part is to analyze the relationships between city structure, regional air quality and continental pollutant export. The simulation of 2 different existing urban structures intends to provide a realistic sensitivity study. Besides, their similar positioning in latitude allows to free ourselves from differences in the intensity of photochemistry. This work is part of the European programs MEGAPOLI (megapoli.info/) and CityZen (cityzen-project.eu/), which both aimed at characterizing the impact of European megacities on their multi-scale environment.

## 2. STUDY OF CITY EMISSION EXPORT

CHIMERE (www.lmd.polytechnique.fr/chimere) is a chemistry-transport model that is intended for daily pollution forecasts (see www.prevair.org), as well as for *a posteriori* analyses of pollution event. It focuses both on gaseous regulatory pollutants and particles. Its performances are daily evaluated by 9 French air quality networks through a systematic comparison of CHIMERE forecasts with field measurements (Honoré et al., 2008). Finally, CHIMERE is also used for research purposes by more than 15 European institutes, and it is regularly confronted with other European models during international research programs (ESQUIF, CAFE, CITY-DELTA, ESCOMPTE, GEMS, MACC, CityZen, MEGAPOLI…). Our version of CHIMERE uses (www.lmd.polytechnique.fr/chimere; Siour, 2012):

- The second-order Van Leer Scheme for air mass transport (Van Leer, 1979)
- A deposition module parameterized from (Wesely, 1989)
- The SAPRC07 chemical scheme (Carter, 2010)
- An aerosol module describing the physical and chemical evolution of atmospheric particles ranging from 40nm to 10µm. The processes include coagulation, nucleation for sulfuric acid, and the absorption of both inorganic and organic gaseous species into particulate matter (Bessagnet et al., 2005).

Our simulation domain is presented in Figure 1 through the spatial representation of hourly carbon monoxide anthropogenic emissions. It has a horizontal resolution of 0.15° and includes 8 levels from 0 to 500hPa. The model is forced at its boundaries by climatological chemical fields calculated with the models MOZART2 / LMDz-INCA2 for gaseous species, and with GOCART / LMDz-INCA for aerosols. Meteorological fields are obtained from WRF runs (http://www.wrf-model.org/) conducted on a similar grid as CHIMERE. Anthropogenic emissions at the European scale were produced at a resolution of 7km by TNO for the MEGAPOLI project. Finally, biogenic emissions are obtained from the MEGAN model (Guenther, 2006).

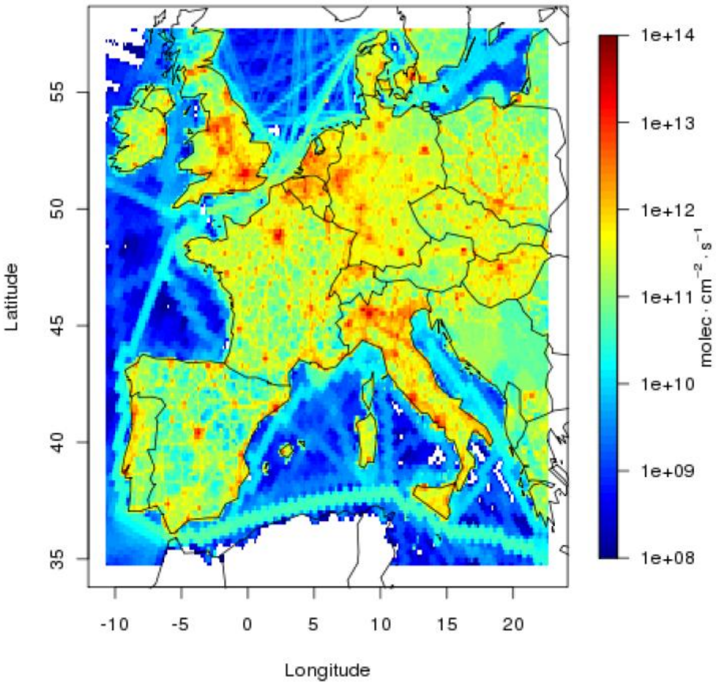

Fig. 1. CO anthropogenic emissions over the simulation domain for a given timestep, in molec/cm²/s.

The whole summer 2005 was simulated. In a first step, we estimated the average area of the continent that is impacted by each megacity. We used reactive tracers reproducing CO emissions of each large city (see Figure 1) and imitating its loss in the atmosphere. The reason for using a CO-like tracer is the low reactivity of CO, which gives us a superior limit for the calculation of the city footprint on the atmosphere, in terms of primary species. We then mapped the surface where CO from a given city exceeds x % of the CO atmospheric content at the ground level: Figure 2 reproduces the mean COtracer-to-CO ratio for 4 of the largest urban areas of the European continent. A value of 10% can be considered as the limit for a detectable impact of the city on the atmosphere composition. In most cases, we can see that the ratio is greater than 0.1 over several hundreds of kilometers. Further than 500km from a city, the COtracer concentrations rarely exceed 1ppbv. We can see that the shape of the city footprint strongly varies from one type of urban structure to another:

- The Pô Valley mainly exports pollutants towards East and South, due to the presence of mountains at the North, but also to local atmospheric recirculations along the Mediterranean coast (Dosio et al., 2002; Maurizi et al., 2011), which favor the transport of pollutants above the sea. These phenomena participate in reinforcing the impact of coastal anthropogenic activities over the basin. The weakly dispersive meteorological conditions that are usually observed there maximize the persistence of pollutants over the emitting area.

- As for Paris, the pollutants emitted by the BeNeLux area impact a large latitudinal band that is orientated towards the South-West due to the orientation of the dominant winds. In both cases, the distance of impact is larger towards the West, which corresponds to low-dispersive anticyclonic conditions. However, the impacted surface is always larger in the case of BeNeLux because the emission area is also larger.

- In the case of London, the pollutants are mainly transported over the Northern seas and countries. The maximal distance of impact of the tracer is close to that calculated for Paris. Thus, when there is no natural barrier, the city size appears to be a determinant factor for its primary atmospheric footprint.

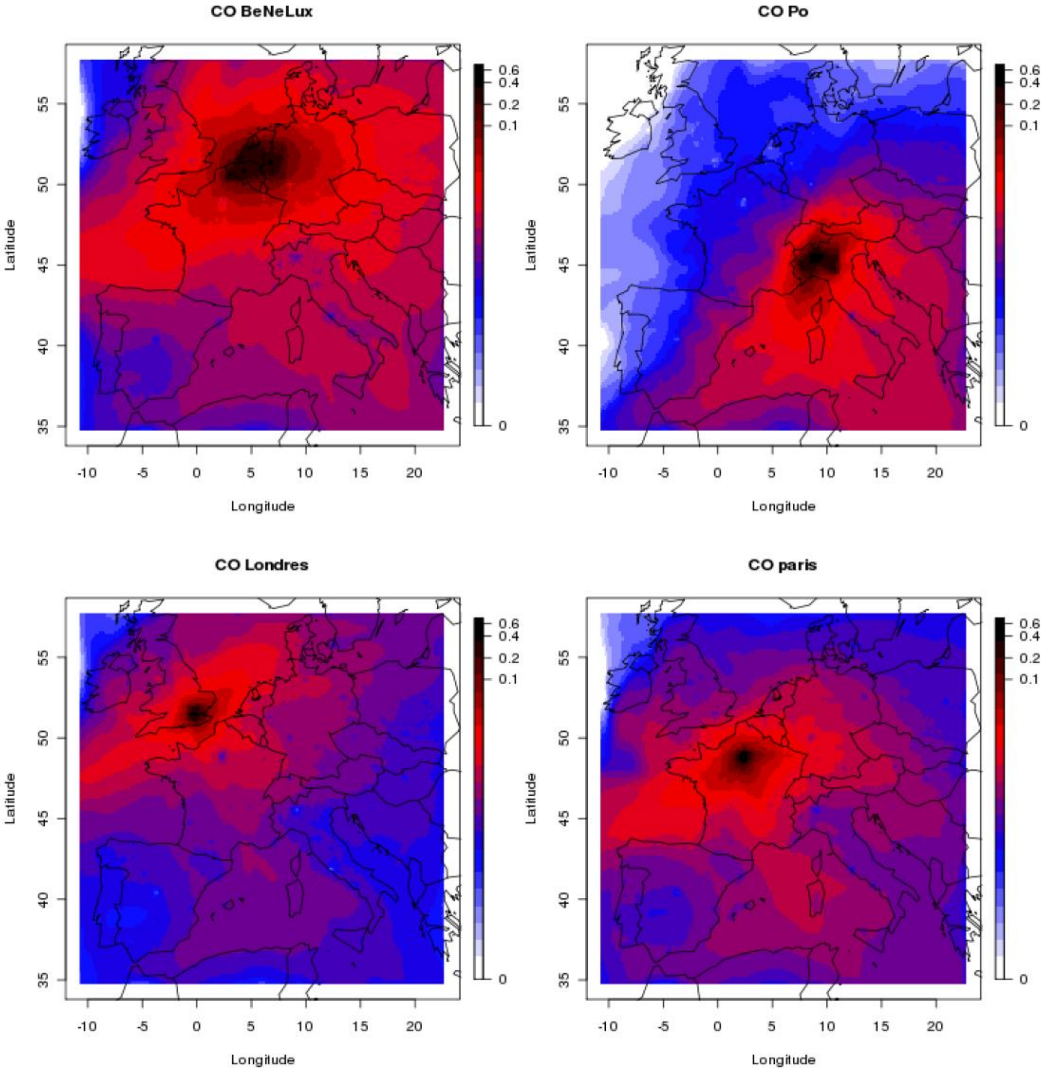

Fig. 2. Average COtracer-to-CO ratios as calculated by CHIMERE over summer 2005.

In a second time, we focused on the pollution events of the 20th of June. We present in Figure 3 a longitudinal section of 3 plumes simulated by CHIMERE at ground level: one from the Paris area, and two from BeNeLux. The graphs represent NOy at 18:00 UT (coloured surfaces, left axis), as well as ozone instantaneous production rates (pink lines, left axis) and ozone concentrations (blue lines, right axis) for 3 different hours of the day. The wind direction is from left to right. The urban area is shown in red under the x axis: we can see that BeNeLux is made of wider urban areas, although emissions are much less concentrated than at Paris. In all plumes, the model predicts a significant production of PANs and of organic nitrates ($RNO_3$), which are susceptible to transfer part of the plume reactivity towards the continental scale. Through late NOx release, the impact of megacities on air quality may thus exceed the 100-200km regional area, and may participate in the local oxidant production of remote cities. Other important information brought by this figure is the fundamental difference in the plume structure, with steeper concentration gradients over Paris and progressive pollutant accumulation over BeNeLux. From the point of view of NOy final concentrations, the model calculates comparable values around 20-30ppbv downwind the cities. However, ozone production is less intense by a factor of 2 – 2.5 in the second case. Thus, considering a similar ozone background level (approximately 80ppbv), the increment of ozone produced by the model reaches 50ppbv under the influence of Paris against only

10ppbv in case B. Logically, in case B, the plume exports much more nitrogen oxides, and probably much more other primary species. It means that a larger part of the city impact on the atmosphere is postponed to the larger scale.

## 3. CONCLUSION

Our works propose a characterization of the impact of megacities on their environment, as a function of their location, size and structure. We use 2 main indicators: the average impact distance of the emissions of each city over the continent, and the chemical nature of this impact, through a one-day case study.

As expected, air mass circulations at the continental scale make most of what we called here the city atmospheric footprint. However, the model confirms that locally constrained circulations (and in particular Mediterranean coastal breezes) strongly participate in redirecting the pollutants towards specific areas or in limiting their continental impact. We also showed that the emitting surface is a key element of the city influence on its environment, in terms of primary pollution extent. In this second part, we highlighted the role of organic nitrates in the composition and reactivity of the plume. As their chemistry in the atmosphere is badly known, further efforts should be put on the determination of organic nitrate reactivity so as to quantify and to map the nitrogen capture and release by city emissions over Europe. Finally, it appears that urban management choices (sprawl or densification) may have a huge impact on regional air quality and a significant one on the composition of the troposphere, which is important for climate change issues. To help city planning, more realistic scenarios proposing a refined representation of future urban tissues and of the associated energy consumption should be produced. Then, simulations should be conducted with AQMs that have been optimized to reproduce the long-distance reactivity of city plumes in the continental troposphere. This work needs to be extended to atmospheric particulate matter.

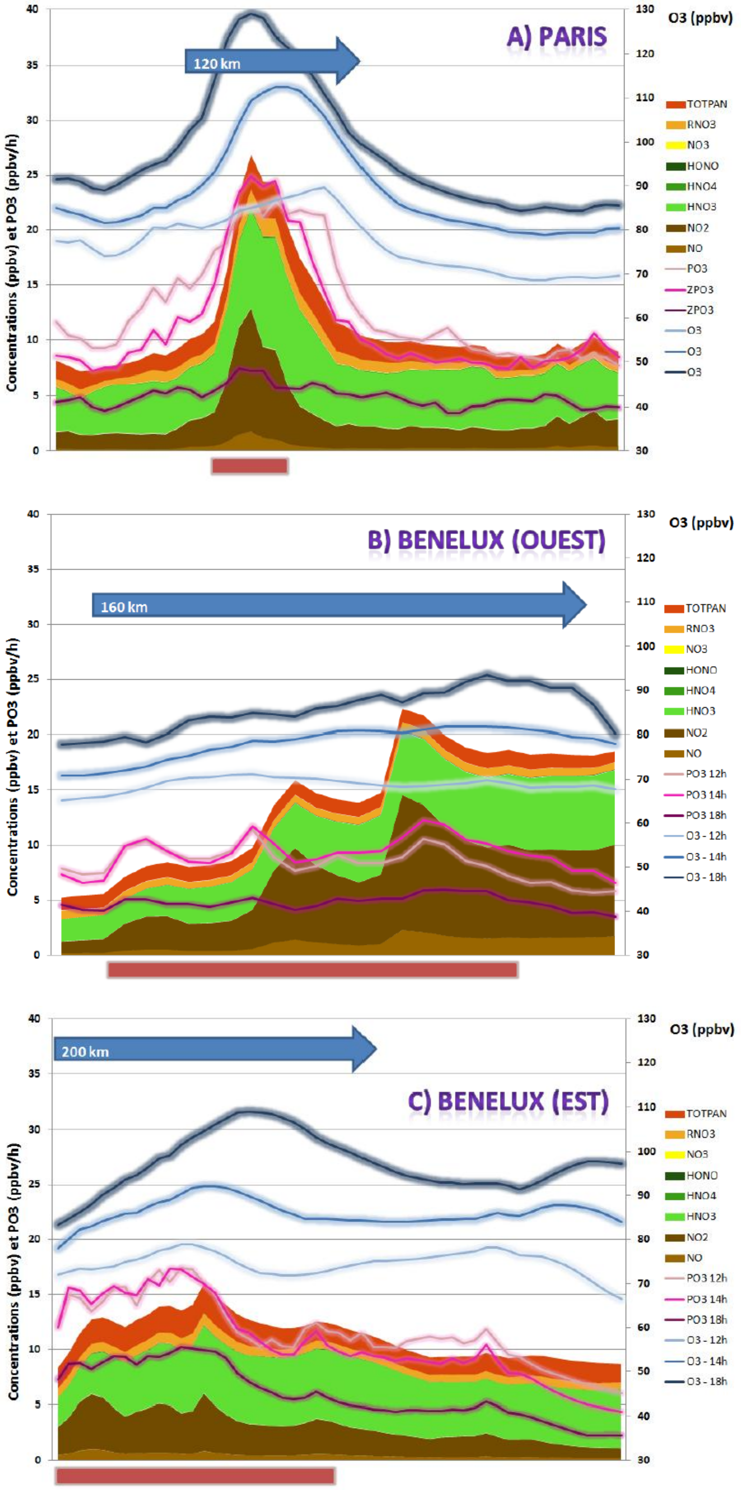

Fig. 3. Concentrations and production rates along the plume (from left to right) as simulated by CHIMERE for 3 different locations in Europe at 18:00 UT on June 20. The length of the plume is illustrated by the blue arrows. The city extent is represented by the red rectangle below the x axis.

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# ANALYSIS OF EUROPEAN OZONE DISTRIBUTION USING A JOINT ASSIMILATION SYSTEM USING GROUND AND SATELLITE MEASUREMENTS WITH A REGIONAL CTM

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## ABSTRACT

In the last decade, there has been an increased need in developing air quality standards, guidelines and strategies for air quality management. In Europe, it results in the implementation of EU legislation concerning air quality thresholds and in the development of operational services for monitoring and forecasting AQ. In particular, special attention has been attached to ozone. European projects such as GEMS (Global and regional Earth System (Atmosphere) Monitoring using Satellite and in situ data) and MACC (Monitoring Atmospheric Composition and Climate) have attempted to integrate enhanced observing systems and modeling tools to develop a comprehensive atmospheric composition monitoring and forecasting system. Although local contributions to European ozone budget are well sampled by surface networks (gathered by Airbase, the European Air quality database), there was a lack of height-resolved continental scale of ozone in the lowermost troposphere. Moreover, only continental areas are covered by these networks. Recently, the infrared IASI instrument (operational since 2006) observes the vertical ozone distribution with several degrees of freedom, a twice daily revisiting frequency and a good horizontal resolution (about 12km×12km at nadir). In order to combine the high accuracy of in situ observations with the high spatial coverage of satellite platforms and model information, we use data assimilation. In particular, we have set up an Ensemble Kalman Filter coupled with the CHIMERE RCTM. This system has already been tested, independently, for the assimilation of ground measurements and 0-6 km ozone partial columns provided by the IASI instrument (Coman et al., 2012). First, we evaluated the relative gain for analysis and forecast when assimilating each data source separately and second, results of the joint assimilation (of surface and satellite data) are presented and discussed. This evaluation is made using independent data sources like vertical ozone soundings from balloons and commercial aircraft (MOZAIC).

**Keywords:** ozone, data assimilation, ground measurements, IASI instrument, air quality

**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# THE EFFECTS OF SYNOPTIC CIRCULATION TYPES ON $PM_{10}$ CONCENTRATIONS IN THE NORTHWESTERN OF TURKEY

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## ABSTRACT

In this study, the analysis of synoptic weather types and its influence on $PM_{10}$ concentration are investigated. Lamb Weather Types (LWTs) classification method is utilized to NCEP/NCAR daily sea level pressure data. An increase in average $PM_{10}$ concentrations are observed when anticyclonic patterns dominate the region. Southerly (S and SW) patterns also cause elevated levels of $PM_{10}$. On the other hand, Cyclonic and Northerly patterns (N and NE) result in lower $PM_{10}$ concentrations. It is suggested in the monthly analysis that November has the worst air pollution . $PM_{10}$ concentration exceeds threshold values in this month, due to an increase in the frequency of Anticyclonic (~20%) and SW(~25%) patterns. This paper will present the LWT methodology as well as the correlation between prevailing synoptic weather types and $PM_{10}$ concentrations over the Marmara region.

**Key words:** $PM_{10}$, Marmara region, Synoptic conditions, Lamb Weather type

## INTRODUCTION

Particulate matter are known as one of the most important air pollution parameters in Europe (Jol and Kielland, 1997; Brunekreef and Holgate, 2002). Since it was defined, $PM_{10}$ values are known to cause adverse health effects. Accordingly, some precautions fort the reduction of this polluter and certain threshold values were identified European Institutions (European Community, 1999; WHO, 2000, 2005). Despite the taken measures, $PM_{10}$ concentrations and health problems continue to increase (van der Wal and Janssens, 2000; Medina et al.,2004; Schlink et al., 2006). The reasearchers investigated the causes of high $PM_{10}$ values for the last decade and it was understood that industrial, social and meteorological factors play an important role in this increase. Meteorological factors influence the air pollution such as transport, emission, chemical transformations, wet and dry processes (Seinfeld and Pandis, 1998). The distribution and transport of pollutants depend on atmospheric circulation at synoptic scale and various weather/climatic drivers (Giorgi and Meleux, 2007). In the last decade, interest on the relation between air quality and climate change started to grow (Andersson and Langner, 2007a; Jacobson, 2008). However, present time atmospheric process impacts must be recognized well to understand the full evolution of air quality at local and regional scale.

The main aim of this paper is to study synoptic climatology – air quality relation at both regional and local scales. For this purpose, a proper synoptic method (high accuracy, feasibility, low computional cost) is needed to use outputs to the climate models (Semazzi, 2003). Mainly two types of techniques are used fort the classification of patterns (Yarnal,1984, 1993): Subjective and objective. Knowledge and experience of meteorologists appear as the main advantage of subjective classification, however, with this kind of technique, the results cannot be reproduced and the methods can only be applied for certain geographical regions. To date, many subjective classification studies have been conducted: the Grosswetterlagen for Central Europe (Baur et al., 1944; Hess and Brezowsky, 1969), Lamb weather types (1972) for the British Isles, Dzerdzeevskii (1968) for the extratropical latitudes of the Northern Hemisphere, and Krick (1943) and Elliott (1949) for the United States. Objective techniques provide fast classification based on algorithms and are applicable to any geographical region. Objective classification methods include the k-means clustering (Wilson et al., 1992); methods based on physical quantities (Jenkinson and Collison, 1977) developed as an objective scheme for the Lamb classification and used also for the Iberian Peninsula (Goodess and Jones, 2002) and Southern Sweden (Linderson, 2001); fuzzy classification based on subjectively defined rules (Ba´rdossy et al., 1995); principal component clustering (Goodess and Palutikof, 1998); principal component analysis coupled with k-means (Boga´rdi et al., 1994); and neural networks methods (Cawley and Dorling, 1996).

There is as yet no research concerning the relation between circulation weather types and air pollution in Turkey. Main focus of our study is the use of Lamb Weather Types (LWTs), one of the circulation classification schemes being widely used (Goodess and Palutikof, 1998; Wilby, 1998; Chen, 2000; Linderson, 2000; Trigo and Dacamara, 2000; Lorenzo et al., 2008; Demuzere et al., 2009; Tang et al., 2009; Brisson et al., 2011; Lorenzo et al., 2011), to investigate the relation between synoptic circulation and $PM_{10}$ concentrations. We used the same technique to analyze the mentioned relationship of circulation and PM10 in the northwest part of Turkey (Fig. 1) for the period 2008-2010. This region was chosen considering the fact that it is the most populated and industrialized area of Turkey.

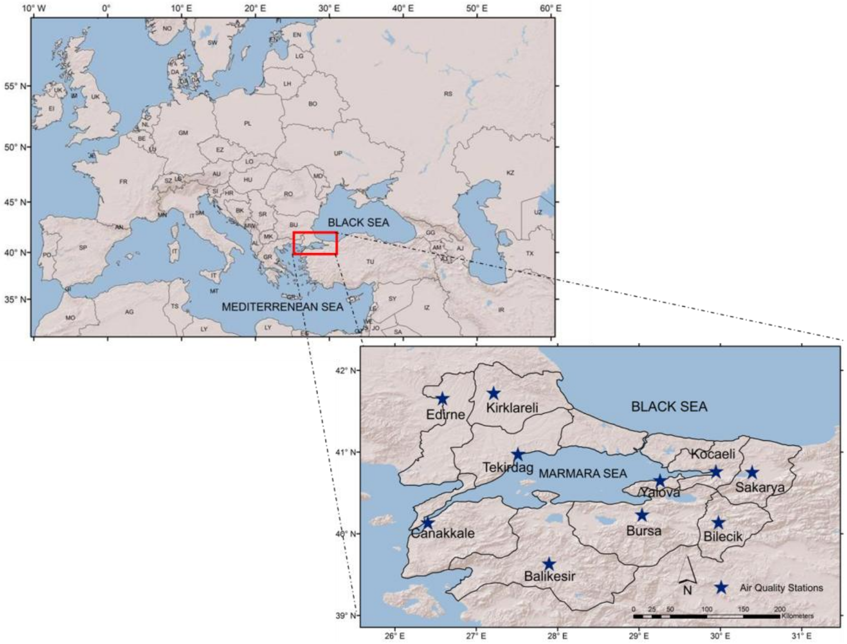

**Figure 1.** Location of air quality stations in Marmara Region

## 2 Data and Methods

In this study, daily $PM_{10}$ data of 10 air quality stations in Marmara Region were used between the period 2008 and 2010. $PM_{10}$ data were obtained from National Air Quality Monitoring System (http://www.havaizleme.gov.tr/Default.ltr.aspx). Monthly and annual $PM_{10}$ values for each station were defined from daily concentrations. It can be shown from Fig.2 that, maximum daily $PM_{10}$ concentrations are observed in March, November and winter months.

Also, the lowest daily medians are found in September and summer months. Minimum monthly mean concentrations are observed in summer months whereas maximum monthly means coincide with winter months and November. The number of days exceeding $PM_{10}$ threshold (identified as 50 $\mu g/m^3$ by EU Parliment for Europe) for 10 urban air quality stations range between 30-76% $yr^{-1}$ . This values indicate that, high $PM_{10}$ concentrations arise in certain times in the region and possible causes of this increase are needed to be investigated.

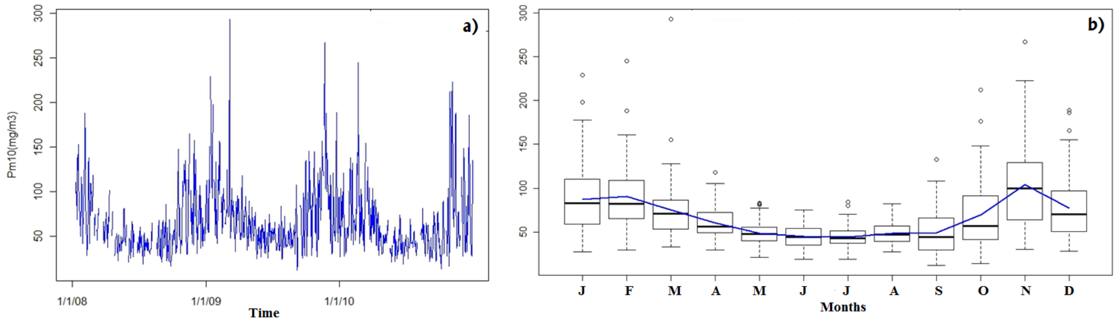

**Figure 2.** Daily(a) and monthly(b) $PM_{10}$ concentrations measured at Edirne, one of the air quality stations in Marmara Region, between the period 2008-2010. The boxes, mark the median, the first and third quartiles, while the whiskers and dots indicate, the minimum and maximum value, blue line is monthly mean concentration.

The synoptic conditions in the region are analysed using Lamb Weather Types (LWT hereafter) method to subsequently relate them with PM10 concentrations. We have used large-scale daily mean sea level pressure data from NCEP/NCAR Reanalysis on a 2.5° X 2.5° grid resolution between 5° W-55° E longtitude and 30° N-60° N latitude. It was identified from the previous studies that, 5° X 5° grid resolution and 16 grid configuration represents synoptic circulations best (Demuzere et al., 2009). This method consists of 27 synoptic types, including directional (N, NE, E, SE, S, SW, W, NW), Hybrid (CN, CNE, CE, CSE, CS, CSW, CW, CNW, AN, ANE, AE, ASE, AS, ASW, AW, ANW), Cyclonic, Anticyclonic and Unclassified types. The data period was selected identical to that of the air qualiy observations. The grid points were chosen in order to place Marmara Region in the centre of the area (Fig. 3). The numbers in Fig. 3 explains the equations for the circulation indices. The indices used are the following: westerly (zonal) flow (WF), southerly (meridional) flow (SW), resultant flow(FF), westerly shear vorticity (ZW), southerly shear vorticity (ZS) and total shear vorticity(Z-to describe the rotation of the atmosphere). These indices were calculated using daily mean sea level pressure values obtained for the retained number of grid points in hPa. In the weather type classification, circulation is grouped into directional types with coherent wind direction ($|Z|<FF$) or cyclonic and anticyclonic types ($|Z|>2*FF$), where Z is pozitive for cyclonic types and negative for anticyclonic types. When ($FF<|Z|<2*FF$) the circulation is classified as a hybrid between the directional and the cyclonic/anticyclonic type. If $|Z|<6$ and $FF<6$, the circulation is unclassified. The direction of flow (D) is in accordance with the 45° sector is calculated as

$$D=\arctan(SW/WF) \text{ if } WF<0 \qquad D=\arctan(SW/WF)+180 \text{ if } WF>0 \qquad (1)$$

Daily mean sea level pressure data for Marmara Region are used between 2008 and 2010. Grid point values of each day are normalized to avoid intensive low or high pressures in the mean values due to the geographical position.

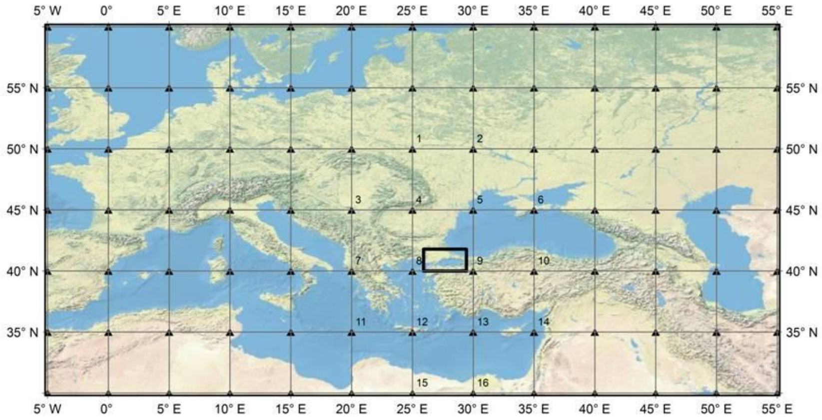

**Figure 3.** Locations of grid points in this study. Numbers indicate the pressure data ($P_1$-$P_{16}$) which was used in the equations. Solid rectengule shows the study area.

## 3. RESULTS AND DISCUSSION

### 3.1 Analysis of Synoptic Weather Types

We produced composite pressure maps to understand the relation between LWTs conditions and air quality. It was shown from Fig. 4 that, low pressure centers (LPC), located in Italy, Black Sea, Marmara Sea, Basrah and high pressure centers (HPC), located in Caspian Sea and Azore dominate the region in definite times.

During Northwesterly flows, low pressure center positioned over the northern Black Sea brings strong NW pressure gradients from Balkans, and results in positive correlation with wind speed and negative correlation with $PM_{10}$ concentrations. In Westerly Flows (W), the region is located between low pressure system centered on Italy and high pressure center located on northern Caspian Sea, extending over to the central Anatolian Peninsula. This condition transports moist and dusty particles from the Eastern Mediterranean and Africa to the region and correlates positively with $PM_{10}$ values, and negatively, with wind speeds due to the fewer frequency of pressure gradients. The SW composite MSLP map resemble with that of westerly flows, but this pattern has a positive correlation with wind speeds due to the location of deep low and high pressure centers. As a result of SW patterns, high $PM_{10}$ values are observed. The S flows exhibit weak pressure gradients as a result of the weaking of low pressure center in southern Italy and the high pressure centered over the Caspian Sea. This results with positive correlation with wind speed. In SE flows, Locations of pressure centers are alomost identical to those in S patterns, but the main difference is the occurence of deeper LPC and HPC. Three isobars pass over the region of interest, therefore high wind speeds can occur. In Anticyclonic patterns, HPC in Caspian Sea are more active and divided into two parts, one of them is located in Marmara, this condition results in high subsidence. During Cyclonic flows, LPC is located over Marmara Region, preventing the HPC in the Azores and Caspian Sea from extending into the region, which creates a large convergence zone. N composite MSLP maps shows that, Azore HPC covers the whole Europe and directs the northerly flows to study area with weak pressure gradients.

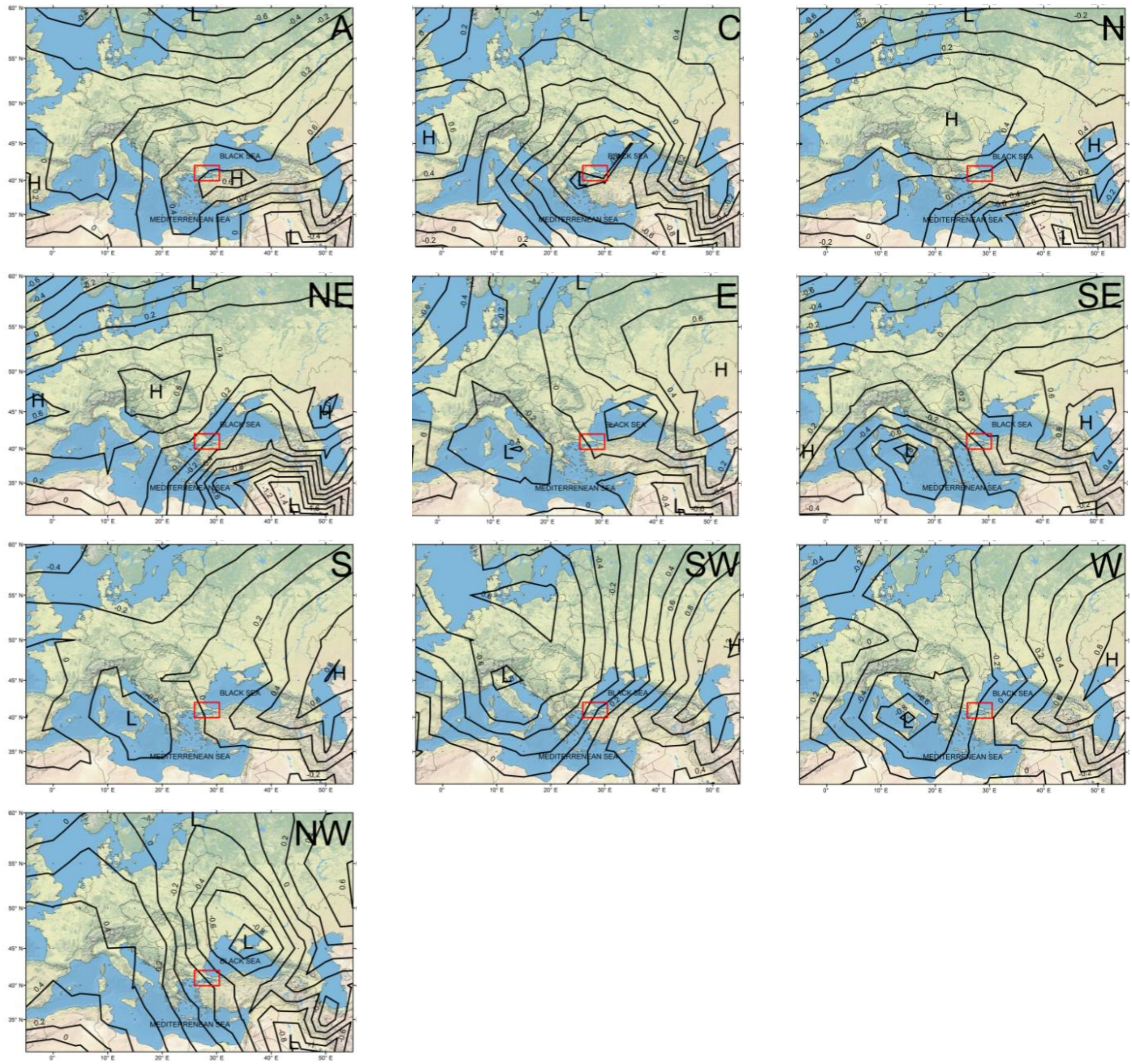

**Figure 4.** Composite of mean surface pressure fiels for each synoptic types

### 3.2 Frequencies of Synoptic Weather Types in annual, seasonal and monthly cycles

Mainly ten types of synoptic conditions (directional, cyclonic and anticyclonic) represent 90% of all flows when LWTs method was applied to the region between the period 2008 and 2010 (Fig. 5). Nearly one of every 2 patterns is northerly flows whereas one fourth is southerly. In winter months, southerly patterns, which lead to flows from Sahara, are observed 60% more frequent than the annual average and dominate the region. During summer, northerly flows, which brings moist and cool air from the Black Sea, are more effective in region. Anticyclonic flow frequency are much higher in Autumn and Spring months 11% and 10%, respectively. Cyclonic flows are observed more often in summer months due to spreading of the low pressure center located Middle East, while they have minimum occurence in autumn (3%). Westerly and Easterly patterns have uniform distribution in all seasons.

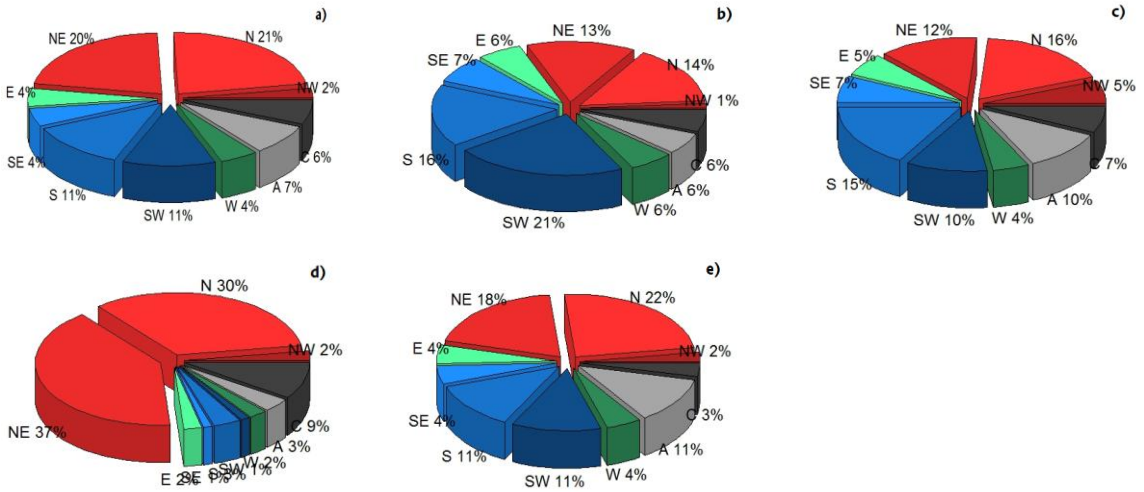

**Figure 5.** Frequencies of weather types on annual(a), winter(b), spring(c), summer(d), fall (e) for the period between 2008 and 2010.

In monthly cycles (Fig. 6), anticyclonic synoptic conditions are observed mostly in November(20%), May(15%) and March(%13). Northerly patterns have maxima in summer, especially in June(50%) and August(45%) and minimum in November(4%) and March(5%). Southerly flows are more dominant in November (25%) and winter months.

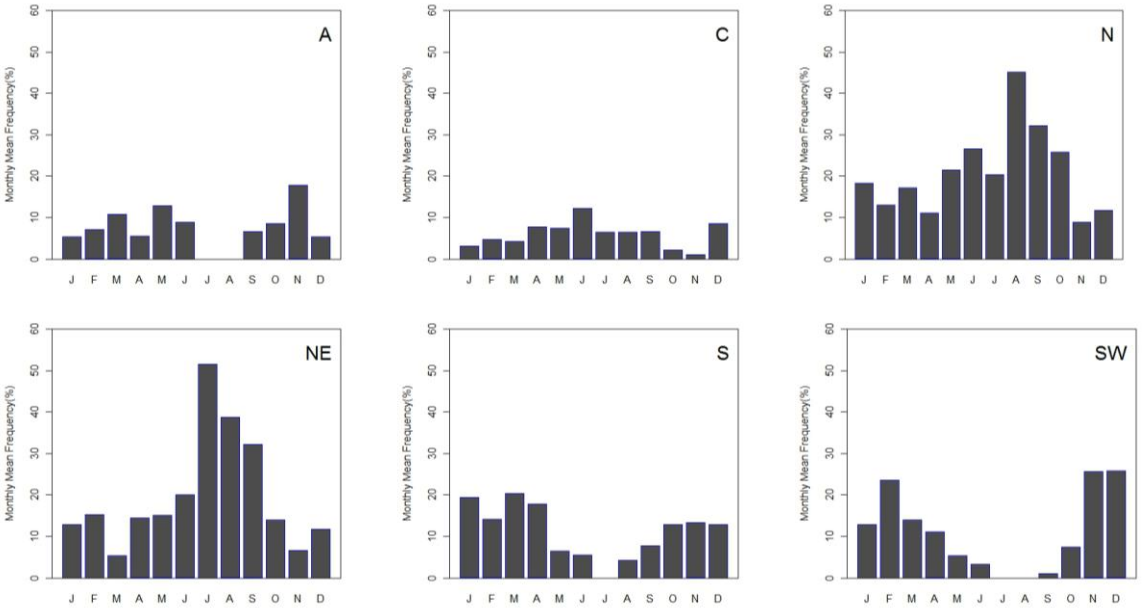

Figure 6. Monthly frequencies of each weather types.

### 3.3 Impacts of Circulations to air quality stations

In order to analyse the relation of synoptic conditions on air quality stations 'circulation-to-environment' approach was used. For this reason, $PM_{10}$ values of 10 air qulity stations related to ten synoptic conditions are plotted yearly (Fig. 7). Firstly, in all urban stations, $PM_{10}$ concentrations exceed EU threshold standards in annual cycles. When anticyclonic conditions dominate the region high mean $PM_{10}$ values (nearly 100 $\mu g/m^3$ ) are observed (except Canakkale and Bilecik) and daily maximum concentration range between 200-400 $\mu g/m^3$ in all stations. When low pressure centers are located over the northern Black Sea, northerly flows (i.e. N, NE, NW) bring moist and cool air to the region, during which time, the lowest daily and mean $PM_{10}$ concentrations are also observed. SW patterns bring dust particles from Sahara, resulting in maximum daily and mean particulate matter concentrations in all stations (especially south of region).

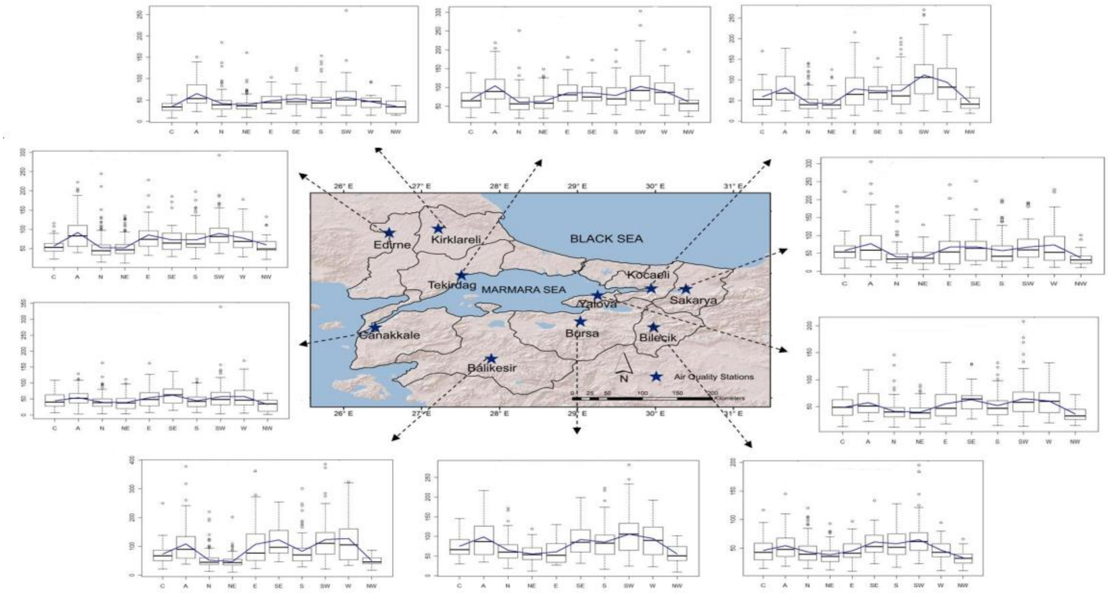

**Figure 7.** Annual $PM_{10}$ concentrations according to LWTs for 10 air quality stations in Marmara for the period 2008-2010.

## 4 SUMMARY AND CONCLUSION

Large-scale circulations play direct or indirect roles in phenemona such as flash floods, dust outbreaks, and ozone spells (Ulrickson and Mass, 1990; Kalthoff *et al*., 2003). In this study , a circulation-to-environmant approach was applied to find out the effects of synoptic circulation on air pollution. For this purpose, we investigated the influence of the synoptic climatology on $PM_{10}$ concentrations in 10 air quality stations in the nortwest part of Turkey, using Lamb Weather Types (LWT) approach. The main results are summarized as follows:

- As a result of LWTs, Anticyclonic (A),and Southerly (i.e. S and SW) flows increases the $PM_{10}$ concentrations,while Cyclonic and Northerly(i.e. N,NE and NW) are associated with low $PM_{10}$ values in the region.
- In winter and spring, southerly flows fare more frequent than they are in other seasons, resulting in higher particulate matter values in these seasons.
- November is the critical month for air quality. Anticyclonic and SW pattern, which increases the PM10 values, frequency higher than other months, while northerly and cyclonic pattern, which decreases the PM10 values, have minimum.
- Highest PM10 concentrations are observed in the south of Marmara such as Bursa, Balikesir than other parts as a result of Southerly pattern

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# AIR QUALITY STATE AND MANAGEMENT PRACTICE IN HO CHI MINH CITY, VIETNAM

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## ABSTRACT

Ho Chi Minh is a big city of Vietnam with a population of nearly 10 million people. It is the most important economic center of the country with many fast growing activities such as industry, construction, services and transportation. Besides creating positive economic achievements, these activities have also been generating negative environment problems, especially air pollution. The United Nations Environment Programme's Global Environment Outlook in October 2007 listed Hanoi capital and Ho Chi Minh City as two of six cities suffering the most serious air pollution in the world. Similarly in 2010, Ho Chi Minh City was kept ranking in the top ten most air- polluted cities worldwide by World Bank. Therefore, this paper aims to reveal and analyse the state of air quality in Ho Chi Minh in recent fifteen years. Besides, air quality management practices are also discussed in order to find the way forward to better air environment for the city.

**Keywords:** air pollution, air quality management, Ho Chi Minh City

## 1. INTRODUCTION

In Ho Chi Minh City (HCMC), there are more than 30,000 industrial units and 5,000,000 automobiles and motorcycles operating. Hence, air pollution issue is currently one of the most significant problems of the city. According to Clean Air Initiative – Asia (CAI – Asia) assessment of Air Quality Management (AQM) capacity of selected Asian cities, Ho Chi Minh City is ranked in Moderate I, two levels higher than Hanoi (capital of Vietnam). This achievement was quite modest and generally shows how the status of air quality in the city was. In 2010, in annual report, World Bank ranked Ho Chi Minh City as one in 10 highest dust pollution cities around the world.

Based on assessment of international organizations, we can assume that the city's authorities are facing a lot of difficulties and challenges when dealing with air pollution problem. However, we cannot deny they had already gained some achievements in their AQM practice. This paper aims to analyse the air quality status in Ho Chi Minh City. From this point, AQM practice of the city's authorities will be discussed in two sides, strength and weakness.

## 2. OVERVIEW OF MONITORING NETWORK IN HCMC

HCMC has been operating its air quality monitoring networks since 1994, started with several air quality measuring points located at traffic hotspots and in residential areas. After 20 years of development, the network has been developed to a comprehensive system as listed below.

***1) Six (6) road side manual air monitoring stations:*** are located at traffic hot spots of the city where the traffic flow are very crowded such as big roundabouts, intersections and arterials.

At these positions, $NO_2$, CO, total dust, lead and noise are measured in 10 days a month and 3 times a day at 7 am, 10 am and 3pm. Each time samples are taken in 1 hour.

***2) Nine (9) automatic air monitoring stations:*** including 4 stations located in residential areas and 5 located at roadsides. Parameters such as $PM_{10}$, $SO_2$, NOx, CO, $O_3$ are measured per 5 minutes in 24 hours. Data collected from these stations are used for calculating Air Quality Index (AQI).

***3) One (1) radioactive monitoring stations:*** this station is monitoring $^{238}U$, $^{232}Th$, $^{40}K$, $^{7}Be$, $^{137}Cs$ with a frequency of once per month.

***4) Eight (8) Benzene – Toluene – Xylene (BTX) monitoring stations:*** The establishment of these stations was rooted from the real situation of fuel bad quality especially quality of gasoline. Hence, all of them are located at roadsides with the measurement frequency of once per month.

Figure 1. Map of air monitoring stations in Ho Chi Minh City

## 3. STATE OF AIR QUALITY IN HO CHI MINH CITY

Monitoring data used in this paper are cited from Environmental Status Report in period 2005 - 2009 of HCMC Department of Natural Resources and Environment – DONRE [2]. Each key pollutant will be assessed based on data collected from all monitoring stations such as manual, automatic, BTX.

### a. Air quality at roadsides

#### i. Dust and PM10

As mentioned above, in 2010, in annual report, World Bank ranked HCMC as one in 10 highest dust polluted cities around the world. The monitoring data obviously showed that fact. According to the measuring results, dust is manly generated from traffic activity due to bad quality of road, vehicles and fuel.

The concentrations of total dust measured by manual stations during 2005 – 2009 were in a range of 0.38 – 0.76 mg/m$^3$ which exceeded the national technical regulation for ambient air quality QCVN 05: 2009 (permitted standard 1 hour concentration: 0.3 mg/m$^3$) from 1.26 to 2.55 times. In some months, dust concentrations were 5 times beyond QCVN 05: 2008. Making a statistical estimation, there were 98% of the whole data and 100% of data collected from 3 stations in 5 years did not meet the permitted standard.

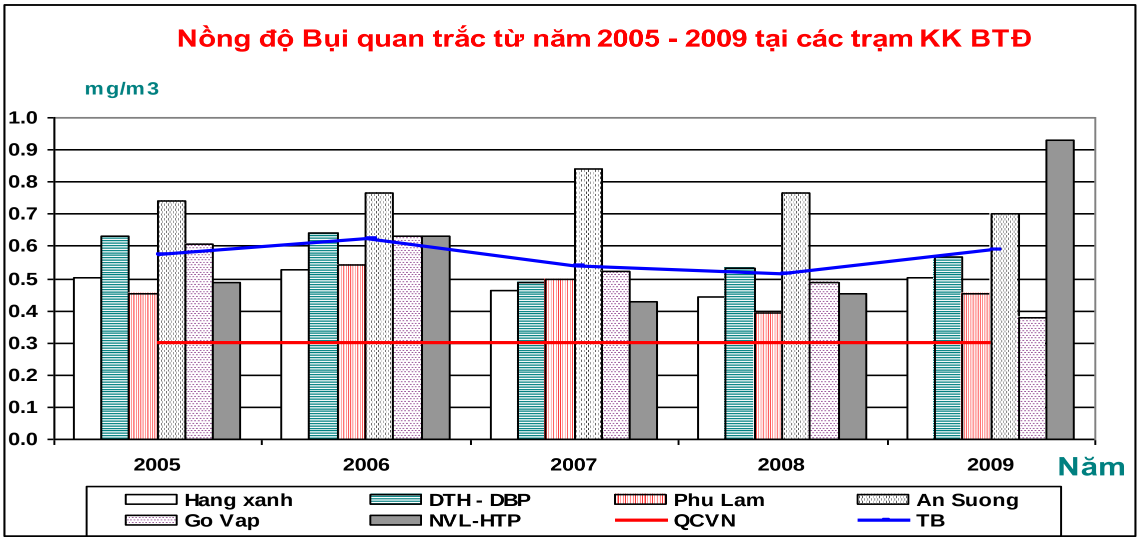

Figure 2: Average 1- hour dust concentrations monitored in 2005- 2009 (manual stations)
(Source: [2])

The same situation can be seen at PM10. Data from roadside automatic stations showed that average 1 year concentrations of PM10 from 2005 -2008 always exceeded QCVN 05: 2009 (1 year level: 50 ug/m$^3$) from 1.2 to twice. Figure 3 shows that average 1 hour concentrations have changed in the same way during 1 day. They all increased from 6 am to 11 am and peaked at around 8 am when there are biggest traffic volume circulating on roads.

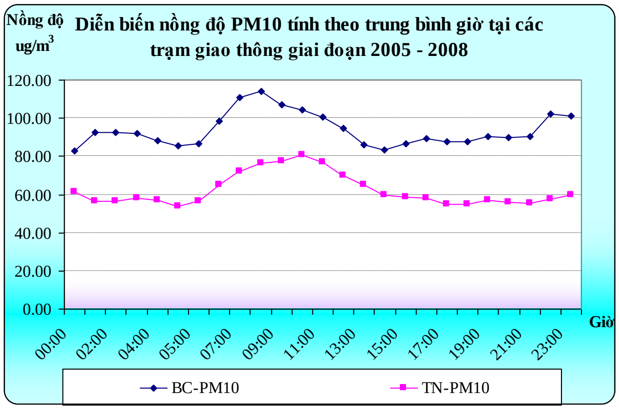

Figure 3. Change of average 1 hour $PM_{10}$ concentrations in 1 day at roadsides in 2005 – 2008 (automatic stations)

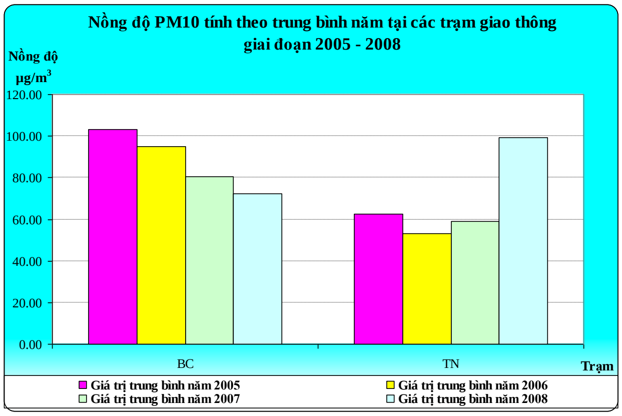

Figure 4. Average yearly $PM_{10}$ concentrations monitored in 2005- 2008 (automatic stations)

*(Source: [2])*

ii. Carbon monoxide (CO)

Carbon monoxide 1 hour concentrations monitored at manual stations fluctuated from 7.66 to 18.72 mg/m$^3$ and monitored at roadside automatic stations ranged from 1.2 to 10.7 mg/m$^3$. All values were much lower than QCVN 05: 2009 (1 hour concentration: 30 mg/m$^3$). . Figure 5 shows that average 1 hour concentrations in have changed in the same way during 1 day. They all peaked at rush hours such as around 8 am and 6 pm. Monitoring data also showed the trend of slight decrease of CO concentration from 2006 to 2009.

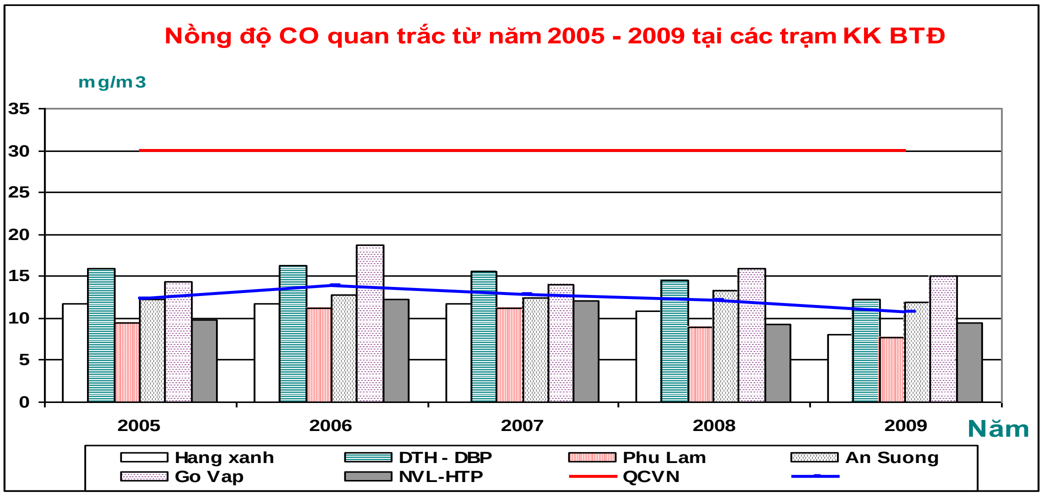

Figure 5. Average 1- hour CO concentrations monitored in 2005- 2009 (manual stations)

*(Source: [2])*

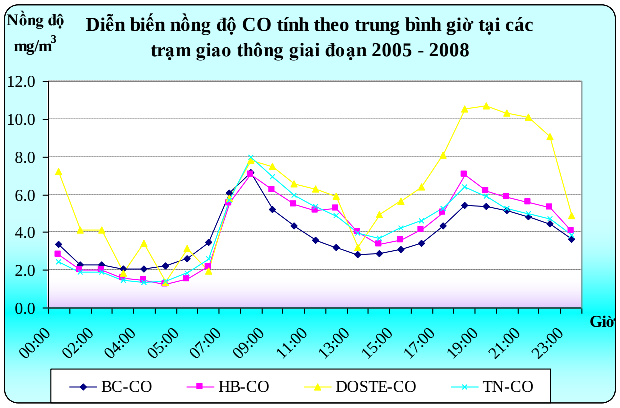

Figure 6. Change of average 1 hour CO concentrations in 1 day at roadsides in 2005 – 2008 (automatic stations)

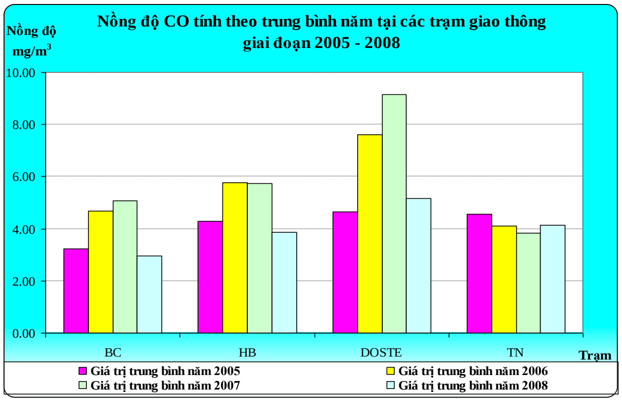

Figure 7. Average yearly CO concentrations monitored in 2005- 2008 (automatic stations)

(Source: [2])

iii. Nitrogen oxide ($NO_x$)

In manual stations, only nitrogen dioxide ($NO_2$) is measured (not $NO_x$). The average 1 hour values in 5 years ranged from 0.11 to 0.26 mg/m$^3$. In QCVN 05: 2009, only permitted standard for $NO_x$ is specified. If comparing with this standard in this case, there were 45% of values did not meet QCVN 05: 2009 (1hour value: 0.2 mg/m$^3$).

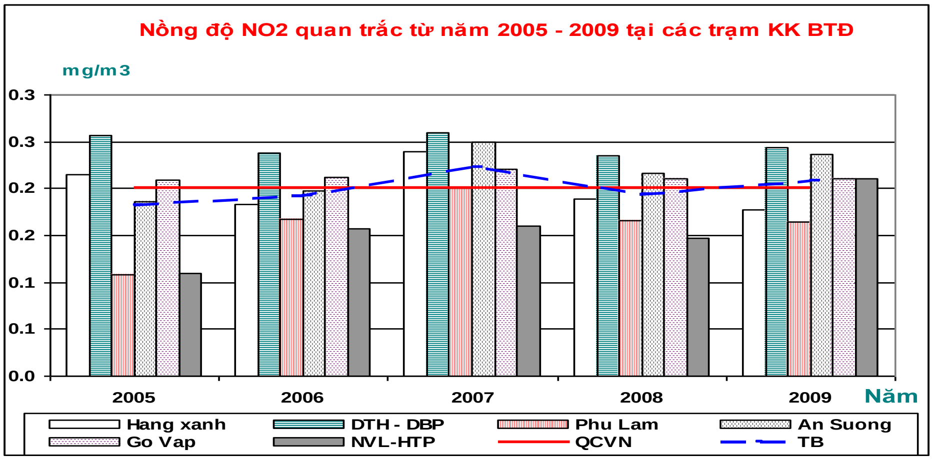

Figure 8. Average 1- hour $NO_2$ concentrations monitored in 2005- 2009 (manual stations)

*(Source: [2])*

Average 1 hour NOx concentrations monitored at roadside automatic stations fluctuated from 21.54 to 127 ug/ m$^3$ exceeding QCVN 05: 2009 (1hour value: 20 ug/m$^3$) from 1.07 to 6.35 times. The change average 1 hour values of NOx during 1 day shows the right rule. They all peaked at around 8 am and at night when ozone concentrations decreased to lowest. NOx bottomed at around 2 pm when the strongest sunlight intensity and photochemical reaction (converting NOx to Ozone) are available.

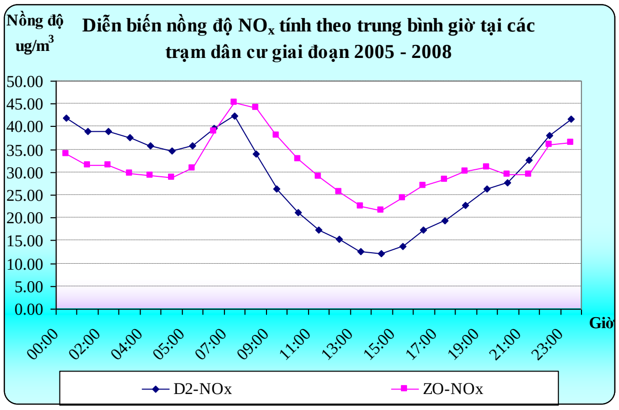

Figure 9: Change of average 1 hour NOx concentrations in 1 day at roadsides in 2005 – 2008 (automatic stations)

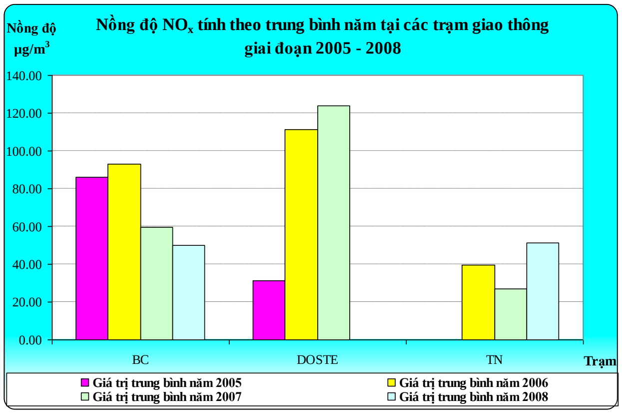

Figure 10: Average yearly NOx concentrations monitored in 2005- 2008 (automatic stations)

(Source: [2])

### *iv. Ozone ($O_3$)*

Average Ozone concentrations collectec from roadside automatic stations during 2005 -2009 were very much lower that QCVN 05: 2009 (1 hour statndard: 180 ug/ m$^3$) with values from 6.97 to 54.80 ug/m$^3$. The change of average 1 hour values during 1 day of this parameter were contrary to the change of NOx. It peaked at 2 pm when NOx concentrations were lowest in a day.

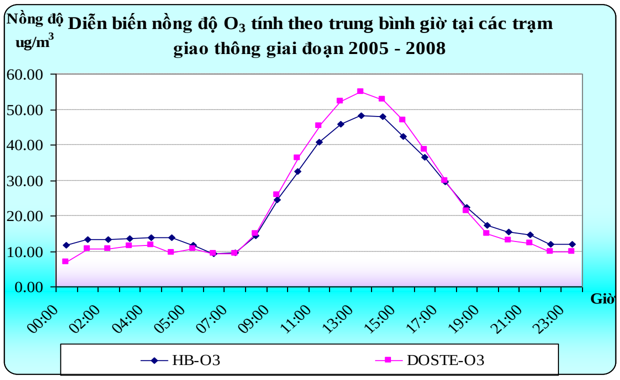

Figure 11: Change of average 1 hour Ozone concentrations in 1 day at roadsides in 2005 – 2008 (automatic stations)

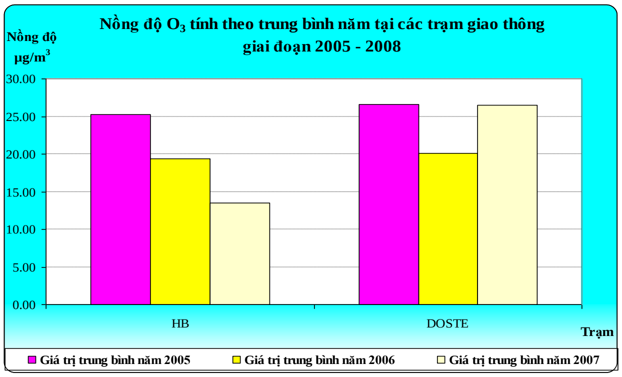

Figure 12: Average yearly Ozone concentrations monitored in 2005- 2008 (automatic stations)

*(Source: [2])*

### v. Lead (Pb)

During 2005 -2009 period, average concentrations of lead fluctuated from 0.24 to 1.31 ug/m$^3$. Among those years, levels of lead peaked in 2006 and 2007 and decreased dramatically in 2008. This fact resulted from the ban of lead in fuel (gasoline) at the end of 2007.

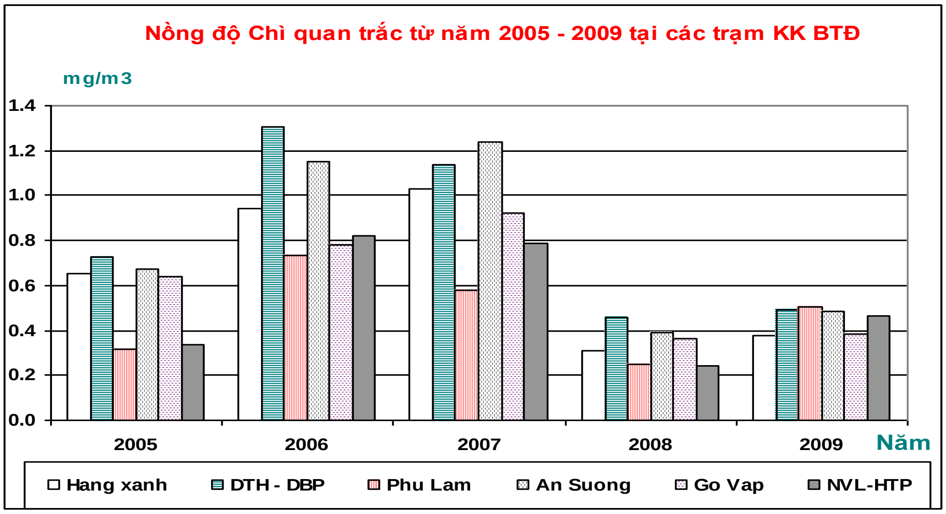

Figure 13. Average 1- hour Pb concentrations monitored in 2005- 2009 (manual stations)

*(Source: [2])*

vi. Benzene – Toluene - Xylene

While Toluene and Xylene vaules monitored during 5 years were always lower than permitted standard specified in QCVN 06: 2009, benzene with the average concentrations form 18.02 to 57.91 ug/m$^3$ usually exceeded QCVN 06 : 2009/BTNMT (average annual standard: benzene 10ug/m$^3$). 67% monitored values did not meet the standard, especially sometimes they are 10 times higher than the standard.

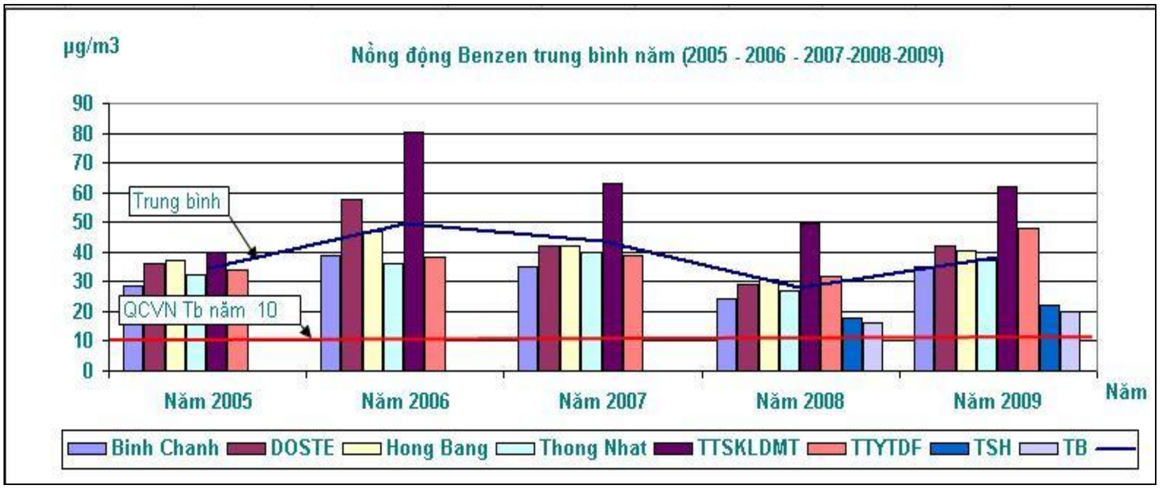

*Figure 14.* Average yearly benzene concentrations monitored in 2005- 2009

*(Source: [2])*

## b. Air quality in residential area

According to the table below, $NO_x$ and $SO_2$ were not problems of air pollution in residential area. With Ozone, there is no Vietnamese standard for average annual concentration so we look at average hourly values. In this period, the average hourly concentrations of ozone ranged from 11.51 to 102.72 ug/m$^3$ meeting QCVN 05:2009/BTNMT (average hourly standard: 180 ug/m3). The situation of PM10 was not too different from that at roadsides. Dust was still the key pollutant in residential area with majority of average annual concentrations exceeding the standard.

*Table 1.* Air quality in residential area from 2005 to 2008

| Parameter | Station | Average Annual Concentration | | | | QCVN 05:2009/BTNMT ug/m$^3$ |
|---|---|---|---|---|---|---|
| | | *2005* | *2006* | *2007* | *2008* | |
| $NO_x$ ug/m$^3$ | D2 | 28.39 | 28.39 | 26.92 | 33.54 | 40 |
| | Zoo | - | 28.39 | 26.92 | 33.54 | |
| $SO_2$ ug/m$^3$ | Zoo | 31.63 | 19.06 | 17.39 | 22.09 | 50 |
| | TSH | - | 28.91 | 28.45 | - | |

| | | | | | | |
|---|---|---|---|---|---|---|
| $O_3$ ug/$m^3$ | D2 | 40.01 | 41.13 | 39.90 | 32.53 | - |
| | QT | 60.22 | 28.26 | - | - | |
| | TSH | - | 32.77 | 33.01 | 26.74 | |
| | Zoo | 35.22 | 33.15 | 35.41 | 27.37 | |
| $PM_{10}$ ug/$m^3$ | D2 | 73.21 | 63.21 | 61.82 | - | 50 |
| | QT | **92.56** | **70.87** | - | - | |
| | Zoo | **79.06** | **94.44** | 45.61 | **62.59** | |

*(Source: [2])*

## 4. AIR QUALITY MANAGEMENT PRACTICE IN HO CHI MINH CITY

### 4.1. Achievements [6]

*4.1.1. Air quality management strategy and action plan*

On 21 August 2002, HCMC People’s Committee issued Decision No. 94/2002/QĐ-UB on approving HCMC Environmental Management Strategy up to 2010 and Environmental Programs towards 2025 [4]. Among those, Air quality management program set the targets on:

- Air pollution reduction at roadsides.
- Maintaining air quality in other areas inside permitted standards.

The targets were quantified by air quality index and air quality management measures concentrated in:

+ Controlling of air pollution from traffic vehicles, included:

- Master planning for transportation system in HCMC and surrounding areas
- Reducing traffic congestion
- Strictly complying with traffic regulation
- Developing public transport
- Improving fuel quality
- Street water spraying and cleaning

+ Controlling of air pollution from stationary sources:

- Complying with industrial pollution control regulation
- Applying air pollution reduction measures in industry.

So far, many measures discussed above have been carried out, contributing to improvement of air environment in Ho Chi Minh City

### *4.1.2. Air quality monitoring*

Since 1994, HCMC has been operating its air quality monitoring program. After years of development, HCMC became the city which has the best air monitoring system in the whole country with 9 automatic stations, 06 manual stations, 08 BTX stations and 1 radioactive station.

Monitoring results were not only regularly reported to the city relevant authorities but also posted on TV screen at public place and on daily newspaper.

### *4.1.3. Program "Relocation of polluted industrial units to industrial parks and adjacent areas"*

This program was initiated by Decision No. 80/2002/ QĐ-UB in 2002. Target industrial units to be located in period 2002 -2004 were 260 highly polluted units placed inside residential areas. Among those, there were 130 unit generating air pollution and 89 units discharging both heavy polluted waste water and air emission [3]. During implementation the number of units needed to be relocated increased up to 1.402 so the deadline for the project was extended to 2006. At the end of 2006, there were nearly 90% of total target units (1261) relocated. Although the target was not accomplished on time, the project did contribute to the improvement of environmental quality and air quality in particular in residential areas of HCMC.

### *4.1.4. Scientific Research on air quality*

HCMC is one of cities which have a lot of scientific studies on air environmental protection. Most of studies focused on the following topics:

- Conducting surveys and assessment of air pollution situation in the city.
- Studying the new technologies and equipments for emission treatment, especially in industrial sector.
- Modeling of air pollutant dispersion such as applying some popular models (i.e. Gaussian, Berllian) in Vietnamese conditions.
- Impact of air pollution on public health (i.e. "Air pollution, poverty and health" study projects carried out by HCMC Department of Public Health, HCMC Environmental Protection Agency and Health Effect Institute (USA)) [7].

### *4.1.5. Community awareness raising*

In order to enhance air environmental protection, many public awareness raising activities have been organized. Hundreds of training courses were organized in order to provide basic knowledge on environment and air quality for hundred thousands of people from different organizations such as politic, economic and social in HCMC. Thousands of brochures and posters on air environment protection were delivered to city folks.

These efforts did contribute to the improvement of air quality, even limited, in Ho Chi Minh City. The best result could be seen in residential areas where most of pollutant levels stayed below permitted standard. In these areas, although PM10 concentrations exceeded permitted standard, they tended to decrease year by year. Air quality at roadsides has still been facing with NOx, dust and benzene problems, but most of their concentrations kept stable year by year. The levels monitored at some stations even tended to decrease.

## 4.2. Weakness

Besides achievements, there are still weaknesses remaining in HCMC air quality management. Among those, the following problems could be considered as key weaknesses:

### *4.2.1. Community awareness*

Inappropriate and inadequate awareness of community on air environment protection is the biggest shortcomings of HCMC air quality management. It is shown not only in the improper attention of relevant authorities but also in the irresponsible attitude of enterprises as well as inadequate understanding of city folks on negative effects of air pollution.

### *4.2.2. Lack of air pollution sources control*

Traffic and industry are identified as two main sources of air pollution in Ho Chi Minh City. However, they have not been controlled strictly leading to unstoppable and unplanned increase of traffic vehicles and factories (both outside and inside industrial parks). Almost sources have not been controlled properly to satisfy emission standards. For instance, 100% motorcycles have not been controlled, only 20% of industrial factories installed emission treatment systems.

### *4.2.3. No consistent program to fight against air pollution available*

Even though the city air quality management strategy was approved in 2002 and there were a director board with members coming from relevant sectors, almost of targets and measures specified in the strategy were not concretized into action plan of each relevant sector. Therefore, after 5 years of implementation, majority of targets were not achieved. Besides, the budget for investment in air environment protection measures has been also a big problem.

## 5. RECOMMENDATION

Basically, the following recommendations are not new solutions but they are still not implemented adequately because they are not simple and needs great effort of many different parties. This paper proposes two groups of solutions for two key air pollution sources, industry and transportation.

### a. For industrial source

Firstly, command and control measures should be strengthened and implemented more strictly such as environmental impact assessment (EIA) and follow up supervision both regular and irregular on compliance with air quality permitted standards. Emission quota licensing should be considered to apply for enterprises.

Secondly, planned industrial park model should be continued to develop. Investments outside industrial parks shall be restricted. Authorities should determinedly continue relocating pollution factories to outside the inner city and into planned industrial parks.

Thirdly, enterprises shall reduce pollution by applying cleaner production or emission treatment

### For traffic sources

There should be an authority who is strong enough to be in charge with air pollution control from transportation. With current management structure, this responsibility is shared by too many parties resulting in ineffective management.

Besides the increase of traffic vehicles, bad road quality is main cause of high dust concentration. Road systems also cannot afford the increasing transportation leading to serious traffic congestion and air pollution. Thus, planning and investment of road network is an important solution to improve air quality.

Currently, city authority is unable to control the unstoppable increase of personal vehicles while public transportation such as bus is serving with low quality. According to experiences in many countries, development of public transport plays a vital in fighting back air pollution. Hence, HCMC should try to improve the public bus in short term and call for investment for other modern public means of transport such as metro or sky train in long term.

Clean fuel is also a good solution. This fact was proved in 2007 when lead was banned to be available in gasoline. Immediately, lead level monitored in air environment decreased dramatically from the year later. In the future, cleaner fuel such as electricity, natural gas, hydrogen or even solar power should be considered to be used for transportation.

In 2010, the Prime Minister signed Decision No. 909/ QĐ-TTg on approval of motorcycle emission inspection program. According to this decision the inspection will be applied at pilot scale in Hanoi and HCMC from 2010 to 2013 and applied for cities in the whole country after that. However, until now, this initiative has been failed to be implemented. This is because no control mechanism was available to force people having their vehicles inspected such as fines. In order to make this program effective, regulations on people's liability shall be specified in details and the supervision of implementation should be strengthened.

Generally, in order to implement measures proposed above uniformly and effectively, an Action Plan for Urban Air Quality Improvement should be developed as soon as possible following direction of Decision 256/2003/QĐ-TTg of the Prime Minister on approval of National Environmental Protection Strategy towards 2010 and with a vision to 2020 (Program 23) and Planning Framework for Program 23 issued by Ministry of Transportation.

## 6. CONCLUSION

Air quality management in HCMC has gained certain achievements, contributing to reduction of pollution in one of big cities in the region. This is a highlight of the city which national and international experts working in air environmental protection sector have highly evaluated. However, besides achievements, there are still weaknesses remaining in HCMC air quality management. As a result, there is a fact that HCMC is currently staying in the group of cities which have most polluted atmosphere in Asia and in the world. The fight against air pollution in HCMC requires great effort of different sectors and parties and different measures such as command and control, economic, scientific and awareness raising should be implemented uniformly in long term. If following this way, we can expect a significant improvement of air quality in HCMC. Generally, in order to implement measures proposed effectively, an Action Plan for Urban Air Quality Improvement should be developed to make a foundation for air environmental protection in HCMC.

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# ANALYSIS OF NITROGEN DIOXIDE MEASUREMENTS DURING NOVEMBER 2011 CAMPAIGN USING MAX-DOAS.

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## ABSTRACT

The air pollution in the metropolitan area is determined mainly by vehicular traffic and industrial emissions. Investigations of tropospheric chemistry In Central America have reported than metropolitan area of San Salvador (AMSS) has the highest levels of nitrogen dioxide compared with other capitals like Panama and Nicaragua blamed on quality and quantity of the vehicle fleet (Jang and Majano 1999). But these previous works only report monthly average values obtained using measurements punctual techniques and don’t explain daily behavior of nitrogen dioxide. In this work we present time series for tropospheric nitrogen dioxide differential slant column density (dSCD) by ground-based MAX-DOAS performed with compact spectrographs (OceanOptics USB4000). The MAX- DOAS measurements were taken on November 2011 in AMSS (13.041$^{o}$ N 89.07$^{o}$ W, 635 m a.s.l.), allowed simultaneous measurements of aerosols and gases, including ozone (O 3), sulfur dioxide (SO2), nitrogen dioxide (NO2), Glyoxal (CHOCHO) bromide oxide (BrO), chlorine dioxide (OClO), oxygen diner (O4), formaldehyde (HCHO) and nitrous acid (HONO) by integrated optical path. It is a no-invasive technique and the maintenance and operational costs are low (Kramer *et al.* 2008, U. Platt, Differential optical absorption spectroscopy (DOAS), 1994). The time series for tropospheric nitrogen dioxide showed a typical behavior (U-Shape) caused by an increase in atmospheric light path with solar zenith angle on sunrise and sunset (Sinreich *et al.* 2005). For a working day is expected for time series for NO 2 be affected traffic and industrial emissions, showing local maximums that match with maximum of vehicular traffic and industrial emissions that are carried by the wind. However when a cold front has arrived to the area the maximums of the time series of NO2 dSCD had been decreased.

**Keywords:** Nitrogen dioxide, Cold front, troposphere, pollution, MAX-DOAS.

# URBANISATION AND AIR POLLUTION: A CASE STUDY OF HYDERABAD, INDIA

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## ABSTRACT

Hyderabad is the capital of Andhra Pradesh state located in southern India. Hyderabad is the fifth largest city in the country and has recorded a rapid growth rate in the last decade. The annual average concentrations of Respirable Suspended particulate matter (RSPM/PM10) from the 21 monitoring stations placed in a circular grid pattern reveal that, the concentrations are exceeding the National Ambient Air Quality Standards (NAAQS) by 50%. At traffic junctions the concentrations are exceeding by 100%. Thus Hyderabad is one of the top ten cities in air pollution in the country. A study to assess the contribution of different sources to the particulate matter was undertaken by State Pollution Control Board along with USEPA and other agencies. The study reveals that 50% of the Particulate matter of size 10 microns and 2.5 microns is directly contributed by fossil fuel combustion from the vehicles. The last five years growth in fossil fuel consumption, vehicles and air pollution was studied along with the other demographic data. It reveals that, though there is an annual increase of 9-10% of vehicular growth and 14% increase in consumption of the fossil fuels there is no corresponding increase in the particulate matter pollution. An action plan is being implemented in Hyderabad since 2003 under the supervision of the Supreme Court appointed committee to reduce the air pollution in the top ten air polluted cities. The action plan being implemented in the city has a direct relation in checking the air pollution. The paper elucidates the action plan being implemented, the direct and the indirect affects on the air pollution. The policies that lead to centralization and migration of the population hampering the goal of clean air were critically reviewed. The contribution of particulate matter from other sources that are not addressed in the action plan and suggestions for reducing the air pollution levels are presented.

**Keywords:** Particulate matter, Action Plan, NAAQS,

AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES
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# ENVIRONMENTAL ASSESSMENT OF A STEEL MILL BY CHEMICAL CHARACTERIZATION OF PM10 AND DEPOSITIONS IN THE URBAN AREA OF AOSTA (ITALY)

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## ABSTRACT

Aosta is a small town where there is a single industrial plant: a steel mill. A monitoring program, lasting from 2008 to 2011, was established to compare the environmental impacts of the steel mill with respect to the other sources of urban pollution. Sampling and analysis of the ambient air and depositions have been performed according to national and European standard methods.
Chemical characterization of particle emitted by steel mill led to obtain a metal profile ("fingerprint") of both diffuse and stack emissions. A correlation has been found in the composition of PM10 and the depositions of some urban measuring sites.

**Keywords:** PM10, deposition, steel mill, nickel, chromium.

## 1. INTRODUCTION

The Valle d'Aosta region is situated in the North-West side of the Italian Alps, where the mountain chain is changing its orientation from south-to-north to west-to-east, and where its peaks reach the highest elevations. Most of the urban sites, including Aosta, are in the middle of the valley known as "Central Valley".
Aosta is a small city with a population of around 35.000 people. Only one industrial plant, producing stainless steel by melting scrap, is operating not far from the city centre.
The Regional Emission Inventory of Valle d'Aosta reports that the relative contribution to PM10 emissions of the different emission sources in the city of Aosta are respectively: traffic 50%, industry (steel mill) 40%, heating 10%.
It is known that dust emissions of the steel mill have a high content of metals that are typical from stainless steel production: Fe, Zn, Mn, Cr e Ni.
Traffic and stationary combustion (heavy fuel) are considered important sources of heavy metals in national inventories, but they have a much smaller impact than steel mill in the Valle d'Aosta region. According to the Regional Emission Inventory, steel emissions contribute for more than 70% to the total emission of Ni and for more of 90% for the total emissions of Cr and Zn.
The steel mill produces mainly austenitic stainless steel with a content of Cr 18-20% and Ni 8-10% by weight. Therefore, Cr and Ni can be considered as markers of pollution due to steel mill emissions.

Zn can be considered a marker, too. Increased use of galvanized steel in automotive industry has increased the Zn content in the scrap metal over the years. When steel scrap is melted in the Electric Arc Furnace (EAF), most of the Zn vaporizes and ends up in the dust (Rizescu et al., 2010).

The purpose of this study is to distinguish the still mill emission contribute with respect to other urban sources in atmospheric PM.

Although metals represent a small fraction of the PM10 mass, the exceeding concentration and/or long-term exposure to metals could cause severe toxic effects on human health.

## 2. MATERIALS AND METHODS

The environmental monitorings were conducted by ARPA Valle d’Aosta (Regional Agency of Environmental Protection) and are referred to the years from 2008 until 2011. Stack and diffuse emissions data were carried out within the integrated pollution prevention and control (IPPC) permit in the same years.

PM10 and metals determinations in ambient air quality monitoring have been performed according to the EU Directive 2004/107/EC and UNI EN 14902-2005. The temporal coverage of the series extended to 100% of the considered years.

Monitoring of total depositions has been conducted following the Italian laws and regulations (National Institute of Health, 2006) according to EU Directive 2004/107/EC. Total depositions are determined as sum of dry and wet fractions collected by passive exposure of a HDPE bottle/cylindrical funnel system with standardised dimensions, for one month exposure time. The deposited samples are filtrated, then both the particulate matter collected on filter and the filtrate are processed and carried out according to UNI EN 14902-2005 method.

Measurements of metals in stack emissions have been carried out according to the UNI EN 13284-1 method.

## 3. MONITORING SITES

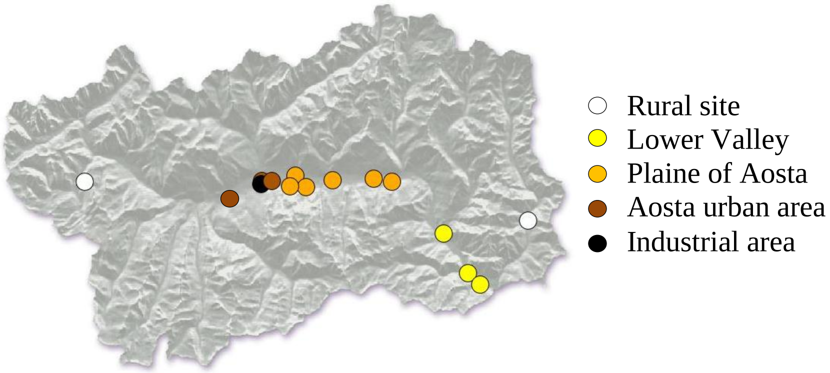

Figure 1 – Monitoring sites in Valle d’Aosta region

The domain of the study includes (Figure 1):

1. Area inside the industrial plant;
2. Urban residential area of Aosta;

3. Extended urban residential area of Aosta included in the first section of the central valley with W-E orientation, called “Plaine of Aosta”;
4. The urban area included in the section of the central valley in the direction of NNW-SSE called “Lower Valley”;
5. Rural areas in adjacent valleys.

*Industrial area*

The monitoring sites in this area include:

- One monitoring site located approximately 50 meters from the steel mill, at the border with the urban area;
- One monitoring site on the roof of the steel mill building (depositions of diffuse emissions);
- Stack emissions of off-gas extraction systems of the steelmaking process.

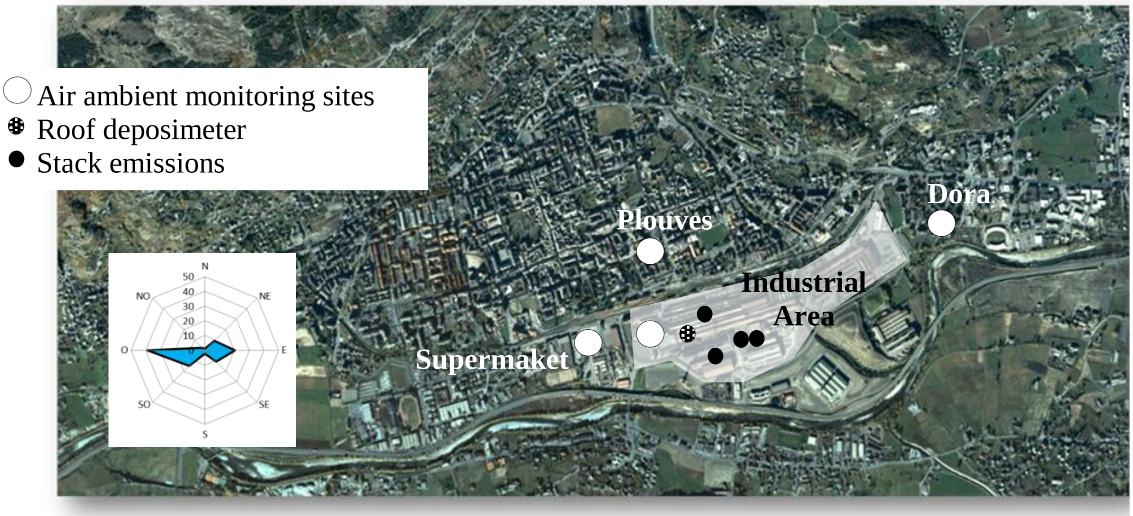

Figure 2 – Monitoring sites in Aosta and main direction of the dominant winds

*Urban Residential Area of Aosta*

- “Plouves” and “Dora” sites, north and east of the industrial area respectively, which represent the urban area of Aosta.
- Supermarket site, situated west of the industrial area, at distance 200 m and downwind relative to the steel mill building.

*“Plaine of Aosta”*

- Six monitoring sites, located in villages in the central valley, west of Aosta.

*“Lower Valley”*

- Three monitoring sites located in the villages situated at the end of the “Central Valley” close to the neighboring region of Piemonte. In this portion of the central valley, the valley direction abruptly changes from E-W to the NNW-SSE direction. The geography of the central valley prevents the dispersion of pollutants from the Plaine of Aosta to the Lower Valley. The model of dispersion of pollutants confirm that ambient air quality of Lower Valley is not affected by pollutants originating in Aosta.

*Rural Area*

- Two monitoring sites, located in lateral valleys in south-east and in the west of the region respectively.

## 4. RESULTS

The metallurgical process carried out in the Aosta steel mill consists of the following main steps:

- furnace charging with scrap and additives (lime, coal, alloys);
- electric-arc furnace (EAF) scrap melting;
- de-slagging;
- secondary metallurgy refining, carried out in the argon oxygen decarburization (AOD) converter and in the ladle furnace (LF) treatment;
- casting.

Electric steelmaking emissions can be distinguished in primary and secondary emissions. Primary emissions are derived from melting and refining operations, secondary emissions are derived from other production steps, such as furnace charging, de-slagging, liquid steel transfers, handling of additives.

The dust collection systems equipped with the steel mill are not able to ensure the complete collection of secondary dust emissions, giving rise to diffuse emissions from the roof of the steel mill building.

EAF dust is formed under steelmaking operations due to the high processing temperature (around 1600°C and above). Certain metals such ad Zn, Pb, Cd, Na, Mn and Fe are volatilized and oxidized when passing into the vapour phase and cooled in the extractive air flow. EAF dust contains mainly zinc ferrite ($ZnFe_2O_4$), zincite ($ZnO$) and Fe oxydes ($Fe_3O_4$, $FeO$) (Rizescu, 2010).

EAF dust particles can be distinguished in two categories: fine particles with diameter < 20 µm and large particles from 20 µm to a few thousand micrometers (Guézennec et al., 2005).

Fine particles account the major part of EAF dust, with a range that can vary from 0,2 to 20 µm, and consist of homogeneous or heterogeneous spheres whose composition corresponds either to the slag or to the steel bath with an enrichment in zinc, or submicronic spheres of pure zincite (ZnO). The finest particles are frequently agglomerated to each other or around a bigger particle.

Large particles are of three morphological types:

- particles of coal and lime with irregular shape and size 20-500 µm, produced by the direct fly-off of solid particles during the introduction of powder materials into the EAF (scrap, coal, additions, recycled dust, etc);
- sphere-like particles whose size ranges from 20 to 200 µm, with a chemical composition that corresponds to that of the slag (Ca, Al, Fe, Si).
- Agglomerates of fine particles whose size range from 20 to 1000 µm.

Only about 15% of the particles are coarser than 10 µm and the median particle size is around 0,5 µm (Chirila et al., 2011).

Off gases coming from EAF, AOD and LF plants are treated in fabric filters before the emission into the atmosphere. Therefore, dust from stack emissions can be assimilate to PM10.

Direct measurements of stack emissions allows to define a characteristic fingerprint of the metals content in primary emissions dust formed during the whole production process, calculated as a weighted average based on annual mass flow (tonnes/year) of stack emissions deriving from dust collection and abatement systems.

Ambient air monitoring carried out inside the industrial area in the same period, reveal a marked correlation between stack emissions fingerprint and the metals content in PM10 (Figure 3)

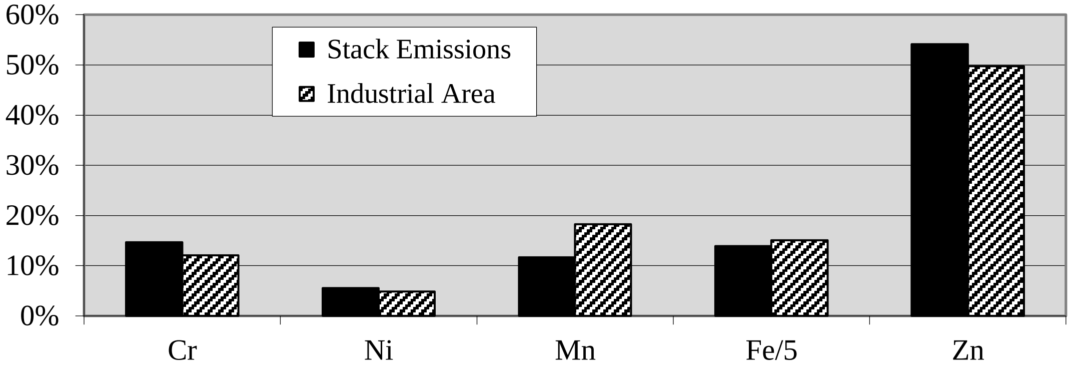

Figure 3 – Distribution of metals content (% on weight) in PM10 with respect to the sum of Cr, Ni, Mn, Zn and Fe (divided by 5 for a better reading)

Bulk depositions in the same industrial site have a significantly different composition than PM10, with a much higher content of Cr and a much lower content of Zn.

A characterization of diffuse emissions has been carried out by installing a bulk deposimeter on the roof of the steel mill building, just above the hoods of the secondary emissions collecting system.

The analysis of the bulk deposition sampled on the roof of steel mill building allows to define a metal fingerprint of diffuse emissions, which consists of secondary dust emissions described below.

A strong correlation is observed between the diffuse emissions fingerprint and the metal composition of depositions in the industrial site and in urban area in the supermarket site (Figure 4).

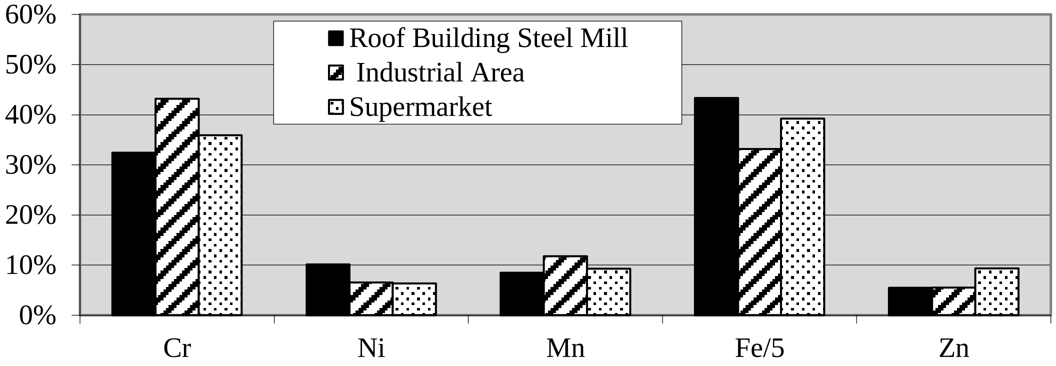

Figure 4 –Distribution of metals content (% on weight) in depositions with respect to the sum of Cr, Ni, Mn, Zn and Fe (divided by 5 for a better reading)

The chemical composition of depositions could be determined by the presence of coarse particles coming from steel mill emissions which have a greater mass, even though they are much fewer than fine particles.

Coarse particles are derived from diffuse emissions, that are not captured by emission collecting systems and therefore are not treated by a dust remove treatment.

Large particles emitted by EAF process have the same composition of the slag (Guézennec et al., 2005).

This is confirmed by the comparison of metal content of slag obtained from waste controls analysis and the metal content of bulk depositions sampled on the roof of the steel mill building (Figure 5).We note that Zn is almost absent in the slag and the content of Cr is higher in the slag than in primary emissions dusts. This can be explained by considering that Zn is volatilized and oxidized passing into the vapour phase and cooled in the extractive air flow and is not restrained by the slag layer surface (Rizescu et al., 2010). Cr has a greater affinity to oxygen than Fe, Mn, Ni and during the melting process is partially converted in $Cr_2O_3$ that is incorporated in the slag (Nicodemi et al., 2011).

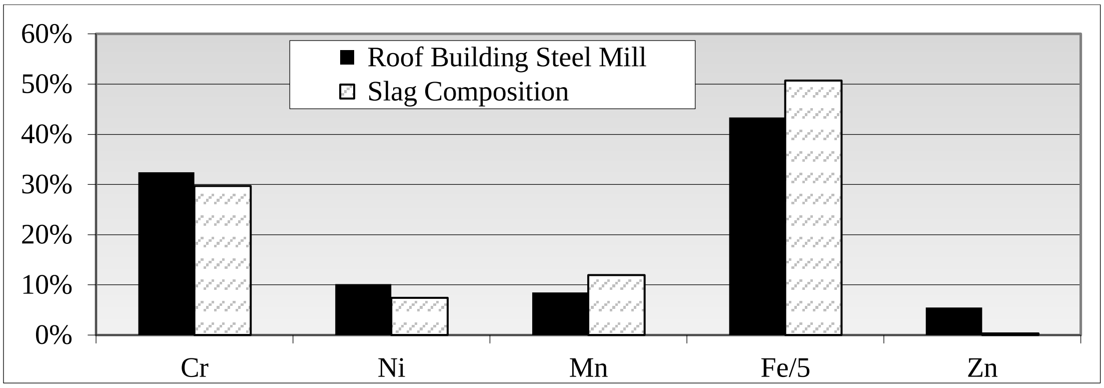

Figure 5 – Comparison between metal slag composition and the fingerprint of depositions of the roof of the steel mill building

The presence of Zn in depositions is due to fine particles with high content of Zn coming from collected and diffuse primary emissions.

In three urban residential areas of the considered domain, the PM10 levels are very similar (~ 27 µg/m$^3$) but metals levels greatly differ from one to another (Figure 6A).

Levels of Ni and Cr in PM10 measured in Aosta and in the Plaine of Aosta are similar and higher with respect to Lower Valley (Figure 6B).

Therefore, fine particles dispersion occurs uniformly along the urban area of Aosta and the Plaine of Aosta, and Cr and Ni content in PM10 in these areas are determined by steel mill primary emissions. Conversely, metals levels in PM10 in the Lower Valley, are comparable with rural areas.

Levels of Pb, of which the steel mill is not a dominant source with respect to traffic and heating, are comparable in the different areas considered.

The winds that blow from west to east are steady and less turbulent than winds that blow in the opposite direction, and facilitate the transport of pollutants in areas downstream to Aosta.

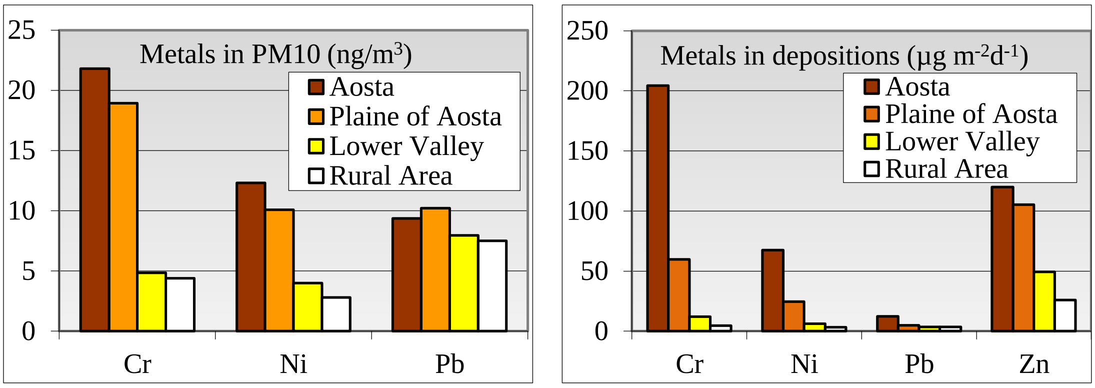

Figure 6 – Metals levels in PM10 (A) and in depositions (B) in different areas

Cr and Ni levels are higher in Aosta and Plaine of Aosta with respect to Lower Valley and rural areas in depositions, too. However, the levels of Cr and Ni in Aosta are much higher than in the Plaine of Aosta.

This finding is further evidence that the metal content in deposition is determined by coarse particles coming from diffuse emissions, which are emitted in atmosphere with low velocity and deposit quickly on the ground nearby the emission source.

Likewise Zn in PM10, Aosta deposition levels of Zn are comparable with Plaine of Aosta, since it is present prevalently in fine fraction of the steel mill dust emissions.

PM10 levels and Ni in PM10 levels in Aosta are lower with respect to limit values of directive 2008/50/EC. However Ni in PM10 levels (~12 $\mu g/m^3$) are significantly higher compared to other Italian cities (~2-7 $\mu g/m^3$).

Much more critical are Ni and Cr deposition levels, that are in general 10-100 times respectively higher with respect to other Italian and European urban sites and comparable with levels measured near metal processing plants (European Commission, 2001).

Average level of Ni deposition in Aosta is around 70 $\mu g\ m^{-2}d^{-1}$, much higher with respect to standard level of 15 $\mu g\ m^{-2}d^{-1}$ reported in Germany TA Luft.

Cr depositions are determined mainly by coarse slag particles, in which Cr is present as $Cr_2O_3$ in trivalent oxidation state (CrIII). Experimental test work with powdered slag materials exposed to an ambient atmosphere indicates that very gradual oxidation to the hexavalent form (CrVI) does occur in a deposit scenario, resulting in 0,1-1% of the chromium being transformed within 6-9 months of free contact to oxygen (Pillay, 2003).

In the long term, accumulation of toxic metal compounds (Ni, Cr, CrVI) in soil can cause problems by increased uptake and contamination of plants. In the short term, dust deposits also cause contamination of above-ground plant parts. This can enhance transfer to humans via contact - children having contact with plants, bare soil or objects and take up heavy metals via contaminated hands - or by the consumption of vegetables (EC, 2001).

## 5. CONCLUSIONS

Chemical characterization of metal content of stack and diffuse emissions of the steel mill allowed to determine two different fingerprints referable to primary and secondary emissions of steelmaking processes respectively.

A marked correlation of fingerprint emissions has been found in ambient air particulate matter samples collected nearby the industrial area.

Fine particles (PM10) disperse uniformly along the urban area and the Plaine of Aosta, and Cr and Ni content in PM10 in these areas are determined by steel mill primary emissions, and result significantly higher respect to other Italian cities. Conversely, in the Lower Valley, metals levels in PM10 are comparable with rural areas.

Coarse particles from diffuse emissions determine critical levels of deposition of Cr and Ni in urban area, comparable with levels measured near metal processing plants and higher with respect to TALuft – Germany standard values.

Taking into account these results, appropriate management and technical measures should be applied to prevent diffuse emissions and to reduce stack emissions from steelmaking process.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# ADAPTIVE TRAFFIC MANAGEMENT IN CITIES – COMPARING DECISION-MAKING METHODS

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## ABSTRACT

Traffic is the dominant source of air pollution in cities. We simulated 'Adaptive traffic management' aimed at reducing traffic related air pollution. The potential impact of the traffic measures was assessed using Black Carbon and $NO_x$-concentration observations in a busy urban street in Rotterdam, the Netherlands. Results show that generic traffic information (counts, speed, composition) in combination with general knowledge about the atmospheric conditions during the day will do as a basis for operational decision making. There is no need for an extensive air quality monitoring/sensing network. However, the results show that the *net* benefits of adaptive traffic management are small and that the impact of permanent measures such as lowering the traffic density during the rush hours - park & ride, road pricing - and avoiding stop & go traffic, is higher than measures taken for short time periods when air pollution is high or expected to be high.

**Key words:** Adaptive traffic management, real-time decision making, urban air quality, black carbon.

## 1. INTRODUCTION

Traffic is the dominant source of air pollution in cities. Restricting the amount of traffic in a city is of course the best way to reduce traffic emissions. This, however, is not easy and often politically sensitive. The question arises if the impact of traffic on air quality can be minimized by clever interventions, *given* a certain amount of traffic. This can be done on two time scales. First, 'temporary adaptive traffic management' strategies, manipulating traffic for relatively short (day, a few hours) periods with the aim to reduce the traffic emissions during unfavorable conditions. Second, by long-term optimization ('permanent adaptive traffic management') assuring the optimum flow of traffic through the city or along potential hotspots.

Temporary traffic measures are needed when: air pollution is high *and* traffic is the (main) cause. Episodes of for example high $PM_{10}$ concentrations also occur when secondary aerosol is formed or when polluted air masses are transported to a city from surrounding areas. Taking traffic measures on such occasions is obviously not helpful in reducing air pollution levels. An example is given by Vanderstraeten et al (2011), showing a car-free Sunday (an extreme "traffic measure") with nevertheless very high $PM_{10}$ concentrations, obviously caused by something else than traffic.

When adaptive traffic management is considered we ask ourselves: firstly, does air pollution has to be measured for operational decision making on traffic management. If yes, a dense network of monitoring or sensor equipment is needed to make informed decisions (e.g. as in the MESSAGE project, Norton et al 2009). The second question is if other information can be used to base operational traffic management decisions upon, e.g. traffic numbers and speed, meteorological data. In that case, using existing proxy information could be an efficient and cheap alternative. After all the combined effects of traffic emissions *and* dispersion conditions (atmospheric stability, wind speed, mixing height) determine the degree of air pollution. Lastly we assess what the positive impacts of a set of traffic measures are, if there are negative impacts (elsewhere, at other moments) and, if so what the net impact is.

## 2. CASE DESCRIPTION

In this study we use measured concentrations of Black Carbon (BC) and $NO_x$, in a busy urban street in Rotterdam, the Netherlands. In the morning the dominant traffic flow is towards the city centre and in the afternoon in the opposite direction. The city employs an intelligent traffic management system (ITS) that manipulates the traffic lights in such a way that a minimum speed of 25 $km.h^{-1}$ is maintained along a 1.2 km corridor. Seven weeks of traffic observations, evenly spread over the year 2011, resulting in a dataset of 1001 hours were analyzed. The data on fleet composition (private cars & vans, medium duty and heavy duty trucks), traffic density and traffic velocity were obtained from the Rotterdam Traffic Department. The average hourly traffic density was 1056, 62 and 8 vehicles for respectively private cars, medium duty and heavy duty vehicles. The street has 4 lanes (two in either direction). The distance between the buildings is approximately 45m. The street is tree-lined. Hourly concentrations of BC and NOx were obtained from a monitoring station alongside the same street and from a nearby (< 500m) background station. BC is a very health relevant pollutant and a good indicator for traffic related air pollution (Janssen et al 2011, Keuken et al 2011, Lefebvre et al 2011) and is therefore the main air quality indicator used in this study. The meteorological information was obtained from Rotterdam Airport just north of the city.

### Assumptions

- The increment between the concentrations measured at the traffic station and the background station ($\Delta BC$ or $\Delta NO_x$) is due to traffic emissions. If the observed increment was <0 it was set to 0.
- According to their BC emission factors (Velders et al 2012) medium and heavy duty trucks have the impact of 4.7 and 6.8 private vehicles respectively. For $NO_x$ these ratios are 19 and 29.4. Using these weighting factors a weighted traffic density *Dw*, (expressed as private vehicle equivalent/hour - $pve.h^{-1}$) is calculated.
- Since the Traffic Department succeeds in maintaining average speeds above $25 km.h^{-1}$ at all times no major in- or decreases of the emission/vehicle occur as a function of *Dw*. Hence we assume that the street increment normalized by traffic density at a given hour is mainly the result of the atmospheric dispersion conditions and to a small extent of the ease of the traffic flow.
- Poor dispersion conditions lead to higher concentrations given the same amount of emissions. Poor dispersion often occurs in the morning under stable atmospheric conditions, when wind speed is low or the mixing height is small. These indicators of poor air quality can be used for operational decision making.

### Traffic scenarios

Assuming that $\Delta BC/Dw$ and $\Delta NO_x/Dw$ remain constant when small changes are made to traffic density we can assess the impact of measures that change traffic density at a given hour, using observed air quality, meteo and traffic data. The traffic scenarios remove up to 700 $pve.h^{-1}$ (on average 500 real vehicles). Figure 1 (right) shows that removing 500 vehicles hardly affects the speed so it is a fair assumption that $\Delta BC/Dw$ and $\Delta NO_x/Dw$ remain constant upon changes in *Dw*. This is further supported by looking at figure 1. (left) and figure 2.

(right): despite considerable variation in traffic density $\Delta BC/1000\ pve$ is very stable between 06.00 and 18.00h.

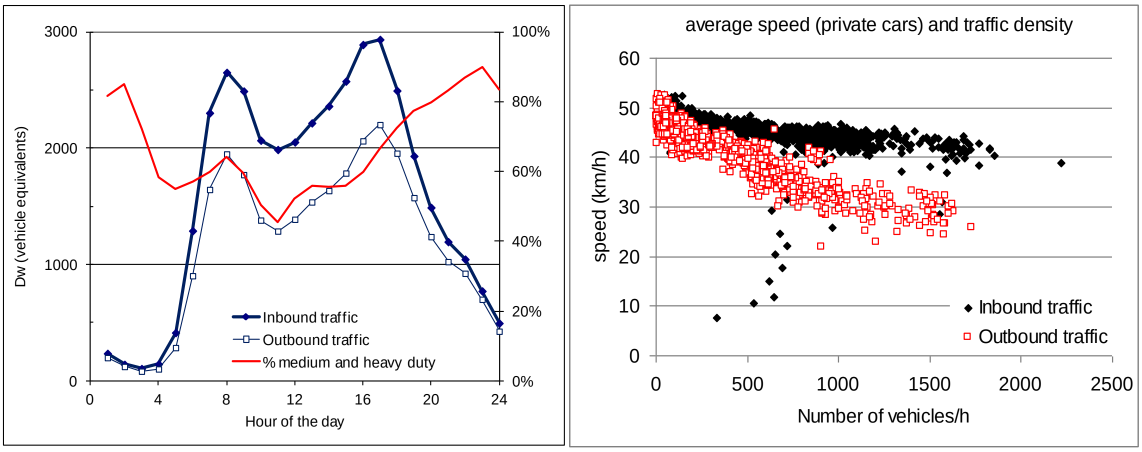

Figure 1: $Dw$ (in $pve.h^{-1}$) in two directions on the road section studied and the percentage medium and heavy duty traffic (left); traffic speed and density of private cars (right).

Temporary adaptive traffic management measures are invoked if:

1. Poor dispersion indicated by a mixing height <= 200m. **AND** $Dw$ >=2000 $pve.h^{-1}$
2. Poor dispersion indicated by a wind speed <= $2m.s^{-1}$. **AND** $Dw$ >=2000 $pve.h^{-1}$
3. Air quality observations are used to decide on a measure. The top 10 % of the hourly observed road increment for $NO_x$ and BC can be used to invoke a measure. By studying historic data a threshold value can be set. **AND** $Dw$ >=2000 $pve.h^{-1}$
4. $NO_2$ has a distinct diurnal and yearly concentration pattern with hourly concentrations below and above the year average limit value. A concentration reference pattern was established that takes into account the typical concentration variation. If an hour has a concentration of >= 20 ($\mu g.m^{-3}$) above the reference concentration for that hour, it is considered as too high and a measure is needed (the use of a reference pattern was described in Elshout et al. 2009).

The traffic measures aim to temporarily reduce the weighted traffic density $Dw$ under circumstances when $\Delta BC/Dw$ and $\Delta NO_x/Dw$ are high. A temporary ban of all medium and heavy duty trucks is the applied measure. The traffic ban is lifted as soon as the criteria for the case are no longer met.

Permanent adaptive traffic measures occur, irrespective of environmental criteria. They are either truly permanent (number 6 and 7) or active at a fixed hour of the day/day of the week (number 5). Note that 6 and 7 have actually been implemented.

5. On working days between 6.00 and 8.00h: 500 $pve.h^{-1}$ are removed during this rush-hour by an imaginary road pricing scheme. The vehicles are allowed back-in between 09.00 and 11.00h when average dispersion conditions are better.
6. Using an ITS the Traffic Department manages the traffic lights in such a way that a minimum velocity of 25km/h is maintained. The likely impact of this measure is estimates assuming that stagnating traffic would otherwise occur on working days for at least 30 minutes during both the morning and evening rush-

hour. Emission factors for stagnating traffic are 1.5 and 1.4 times higher respectively for $NO_x$ and BC (Velders et al. 2012).

7 A park-and-ride facility near a subway station next to this route. On working days this theoretically removes 350 cars during the morning and evening peak hours (7.00-8.00h and 17.00-18.00h). This reduces the average *pve*.$h^{-1}$ from 2681 to 2331 during the hours considered. Using the average ΔBC/Dw and $\Delta NO_x$/Dw ratios during these hours the impact can be calculated.

## 3. RESULTS AND DISCUSSION

Figure 1 shows some transport characteristics. It appears that more vehicles enter than leave the town using this road; people use this route to go to the northern ring road. Fig. 2. (left) shows the close relation between ΔBC and $\Delta NO_x$. The diurnal pattern (during neutral atmospheric stability) strongly resembles the traffic pattern so both are good indicators for traffic related air pollution.

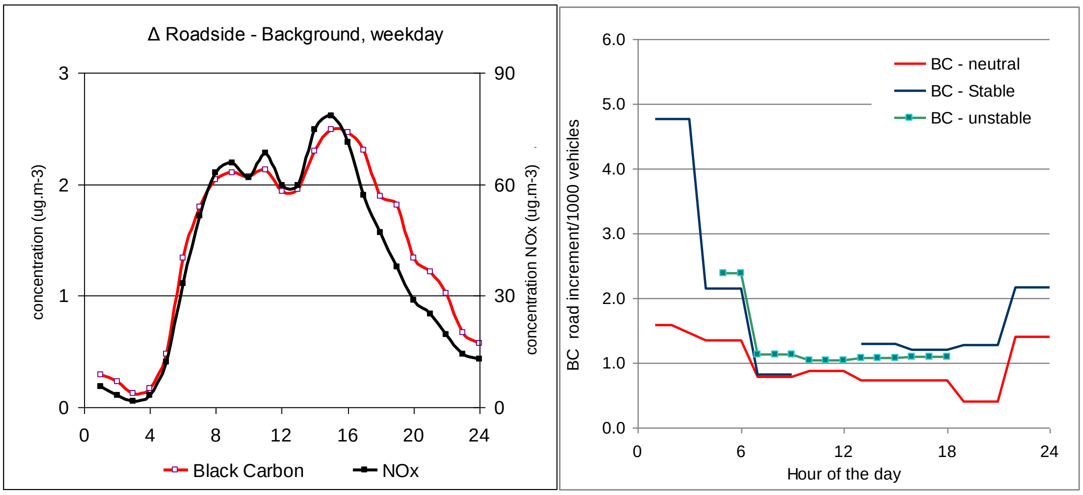

Figure 2: Diurnal pattern of ΔBC and $\Delta NO_x$ (neutral conditions) (left) and *ΔBC*/1000 *pve* (3 hour averages) for 3 atmospheric stability classes (right) both on weekdays.

Neutral stability is the only stability class that occurs throughout the day. Stable and unstable conditions lead to higher concentrations with the same amount of emissions. See the right-hand side of figure 2. Stable conditions often occur in the morning and evening. The Monin-Obukov length (calculated by the KEMA Stacks model, Erbrink et al, 2012) was used to determine the stability classes. By showing the average concentrations during the same stability class a more direct relation between *Dw* and concentrations is obtained (Elshout et al, 2011).

Stability determines to a large extend the concentrations resulting from an emission and explains a considerable amount of the variation in the road increment. If stable atmospheric conditions can be avoided (often occurring in the morning) in theory this can reduce the concentrations and be the basis of a temporary traffic measure.

### Impact and net-impact

If a measure is taken during an hour with high concentrations or unfavorable conditions there obviously is a positive impact. However, if traffic is banned at a given hour, it will have to enter at another time. One can’t cue cars indefinitely at the edge of town. So either the same amount of traffic has to enter at a later hour, or via different roads. This causes additional pollution partly offsetting the gains during the measure. We therefore calculate the impact during the measure and the net impact, taking into account the emissions shifted to another place or time.

The net impact is particularly important for BC. As mentioned before this is a health relevant pollutant with no safe threshold (like $PM_{10}$ /$PM_{2.5}$). Hence it doesn't matter when or where the emissions take place. Only if traffic could be channeled through a less populated area an exposure benefit could be achieved. For $NO_2$ the situation is slightly different. If the traffic measure is devised for the purpose of meeting the limit value (and not to reduce exposure) spreading traffic over the network in such a way that in all streets the limit values are met, could be an option. Spreading traffic over different roads, however, has practical limitations. In most cities the network works at near full capacity and the practical possibility to reroute traffic in the face of adverse air quality conditions is severely limited.

## Results

The results of the 7 traffic scenarios are summarized in table 2. Looking at the impact during a traffic measure it shows that those based on the actual occurrence of high concentrations (3 and 4) do pick the hours where the impact is highest. However, if the measure was based on meteorological parameters like mixing height and wind speed (like in 1 and 2) the results are similar. Looking at the net benefits it shows that these temporary measures are not very successful. The hours where the measure is invoked apparently occur on unfavorable days where the dispersion remains quite poor for prolonged periods. Allowing the banned vehicles back into town still creates substantial concentration rises, nullifying the previous gains. Sometimes it was even impossible to allow all the cars banned during the day back into town on the same day. Sometimes even the net impact is negative. The maximum impact for the temporary measures is calculated assuming that all cars banned during a measure can be held back until average conditions occur. This is highly theoretical as it might involve banning cars for days at an end. So the temporary measures shifting traffic to hours with more favorable conditions, though theoretically attractive, yield very small net benefits under practical circumstances in Rotterdam.

Table 1. Results of the different traffic measures

| case | Average *pve*.h$^{-1}$ involved in measure a) | Number of hours when measure is invoked | % of time | Average impact of the measure during the measure (µg.m$^{-3}$) |  | Average net impact per hour of measure (µg.m$^{-3}$) |  | Maximum net impact per hour of measure (µg.m$^{-3}$) |  | Observed average road increment per 1000 *pve* when measure is invoked (µg.m$^{-3}$) |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | BC | NOx | BC | NOx | BC | NOx | BC | NOx |
| 1 | 641 | 104 | 10% | 0.85 |  | <0 |  | 0.10 c) |  | 1.33 |  |
| 2 | 645 | 73 | 7% | 0.89 |  | 0.03 |  | 0.14 c) |  | 1.38 |  |
| 3 | 718 | 71 b) | 7% | 1.37 | 88 | 0.04 | <0 | 0.53 c) | 33 c) | 1.91 | 30 |
| 4 | 585 | 184 | 18% | 0.90 | 61 | <0 | <0 | 0.22 c) | 16 c) | 1.54 | 26 |
| 5 | 500 | 70 | 7% | 0.59 | 9 | 0.06 | 1.7 | 0.06 | 1.7 | 1.18 | 18 |
| 6 | 2331 | 35 | 3% | 1.04 d) | 37 d) | 0.94 e) | 33 e) | 1.04 | 37 | 1.12 | 18 |
| 7 | 350 | 70 f) | 7% | 0.39 | 6 | 0.39 | 6 | 0.39 | 6 | 1.12 | 18 |

a) Weighting shown based on BC emisison factors (NB: for measures 3-7, the $NO_x$ results are calculated with the $NO_x$ weighting factors).

b) The 90 percentile of $\Delta$BC/*pve*.$h^{-1}$ would suggest 100 out of 1001 hours in the sample. However 29 hours were lost as the criterion of having suffient traffic was not met.

c) Theoretical maximum: cars wait until average circumstances return. In reality it is impossible to achieve this; cars would sometimes have to wait for a day or more.

d) The impact is calculated (example BC, see measure 6) as 0.4 * # *pve*.$h^{-1}$ * $\Delta$BC/*pve*.$h^{-1}$

e) If improving the flow on the main road causes extra stagnation on the side roads the net benefit is smaller than the benefit during the measure. According to the Traffic Department, the cycle times on the branches are hardly affected and no negative impact of measure is expected. A maximum trade-off of 10% was included.

f) We assume that the park and ride facility fills in one hour during the morning peak hours and empties in the evening rush-hour so the benefit occurs twice a day.

Table 2. Summary statistics, whole sample studied (1001 hours)

| | Average *pve*.$h^{-1}$ | | Average road increment ($\mu$g.$m^{-3}$) | | Observed average road increment per 1000 *pve* ($\mu$g.$m^{-3}$) | |
|---|---|---|---|---|---|---|
| | BC | NOx | BC | NOx | BC | NOx |
| Whole Sample | 1400 | 2445 | 1.63 | 46 | 1.17 | 19 |
| Private cars | 75% | 43% | 1.23 | 20 | | |

The “road pricing” scheme (5) shifting cars from the rush hours to a more quiet time a few hours later gives a lower impact during the measure than the temporary measures based on environmental criteria, but the net impact is slightly higher. If the road increment/1000 *pve* during this measure is compared to the sample average (table 2.) it is clear that the selected hours are only marginally worse than the average. However, the “pay back hours” apparently are not exceptional as well, so a small net benefit remains (contrary to the first measures directed at adverse conditions).

The ITS scheme (6) that keeps cars moving at a reasonable speed gives the highest net impact. Without this scheme the concentrations would have been substantially higher during the hours affected. Similarly the park and ride scheme that removes 350 cars (in the morning as well as the afternoon rush-hour), is quite effective in reducing concentrations during these hours. This is the only measure not shifting but actually reducing traffic.

## Discussion

From the results it seems that the permanent measures (not based on environmental conditions) are more effective than the temporary measures. One could argue that the period of time when the temporary measures are invoked is small. E.g. instead of selecting the hours with the top 10% of $\Delta BC/Dw$ or $\Delta NO_x/Dw$ one could select more hours thus increasing the impact of the measure. This is not likely to improve the net impact. If the sample is enlarged, the average impact during the measure becomes smaller and furthermore, it becomes even more difficult to allow the cars banned during the peak hours back into town.

Looking at absolute improvements (net effect for the time of the measure * fraction of time) of the year average concentrations only the permanent measures have a small impact. In 6 and 7 (ITS and park &ride) the BC road increment is reduced by 0.03 µg.m$^{-3}$. For $NO_x$ the road increment is reduced by a maximum of 1.2 µg.m$^{-3}$ (by the ITS measure). Serious reductions are only possible if the total amount of traffic is reduced. E.g. if we assume that on average 10 % of the traffic is removed (140*24 = 3360 *pve* are removed from the fleet this is about 5 times the number of vehicles in the the park and ride scheme) the impacts for BC and $NO_x$ go up to 0.16 and 4.6 µg.m$^{-3}$ respectively. If we assume that all medium and heavy duty traffic could be electrified (e.g. switch to other vehicles before entering town) net impacts of 0.40 resp. 26 µg.m$^{-3}$ could be achieved for BC and $NO_x$.

## 4. CONCLUSIONS

1. Given a certain atmospheric stability there is a strong link between the traffic density and the observed road increment of air pollution. The traffic counts, speeds and composition (usually already available for traffic management) and general knowledge about atmospheric conditions are sufficient for decision making on adaptive traffic management. There is no need (to wait) for a dense network of monitoring or sensor equipment to manage the air quality impact of traffic.

2. Hours with adverse dispersion conditions ‘produce’ more air pollution per unit of emission. Proportionally, the benefit of a measure will be high in these periods. Poor dispersion conditions often occur in the morning and evening in periods that traffic is dense. Identifying dispersion conditions, or simply selecting the rush-hours are a good basis for decision-making on adaptive traffic management.

3. The adaptive traffic measures studied produce improvements when the measure is taken, though the net benefits are often very small or absent.

4. If a certain amount of traffic is accepted in town, avoiding ‘stop and go’ traffic, is the most effective traffic measure. ITS solutions to optimize the efficiency of the road network seem to be the most efficient environmental measures as well. Traffic data are key input in assuring this.

5. If one is dissatisfied with the traffic contribution to air pollution, reducing the total amount traffic (or electrification) is the only viable way (once ITS solutions are in place) to achieve meaningful pollution reductions.

## ACKNOWLEDGEMENTS

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
**4th International Symposium and IUAPPA Regional Conference**
**10-13 September 2012 Istanbul – Turkey**

# URBAN AIR POLLUTION & ITS ASSESMENT OF LUCKNOW CITY- THE SECOND LARGEST CITY OF NORTH INDIA

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## ABSTRACT

In the present study, investigation were carried out during the summer season (March-June2012) to observe the status of indoor air quality by monitoring and assessing some selected air pollutants viz. Particulate Matter (PM2.5 and PM10), Sulphur dioxide (SO2), Nitrogen dioxide (NO2), Carbon monoxide (CO), Carbon dioxide (CO2) at 15 different locations, categorized as densely populated colony, well planned colony and Roadside colony, covering the whole area of Lucknow city. In collaboration with doctors of top Medical Colleges, a survey was carried out by means of questionnaire to find out different diseases/symptoms being faced due to indoor pollution. Full day monitoring was also done to find out the fluctuation of concentration of pollutants. We are still in the process of gathering data for our study.The data collected for summer season showed that the PM10 & PM2.5 levels were above the permissible limits mostly at roadside houses.

**Keywords:** Indoor air quality, survey, urban city, I/O ratio.

## INTRODUCTION

In India, over the past two decades there has been a rapid increase in urbanization and industrialization in many cities. The urbanization process has both positive and negative effects on Indoor Air Quality in many cities of the world (Kim 1992). Hence there is an urgent need to know Indoor Air Quality issues, to share the latest information, to make people aware of the risks of Indoor Air pollution and let them know how to avoid it. Various regulations and guidelines have been published attempting to limit human exposure to potentially harmful particulate in environment (WHO and NAAQS). But these standards are based upon exposure to pollutants measured outdoors. The problem is that in urban environments, people spend most of their time indoors- at home or at work (US-EPA, 1995). Outdoor pollutant concentrations may not be reliable indicators of indoor and personal pollutant sources (Wallace 1997). Thus, for many people, the risk to health may be high due to exposure to air pollution indoors than outdoors. In addition, people who may be exposed to indoor air pollutants for the longest periods of the time are most susceptible to the effects of indoor air pollution. Such groups include the young, the elderly and physically ill, especially those suffering from respiratory or cardiovascular disease (Morawska, et al., 2001).

Research indicates that more than 900 contaminants are present in indoor environment (David 1992). Burning of fuel in any form largely releases various kinds of unburned or waste product in the environments as Particulate Matter, (Khan 2010). Some sources of indoor air pollution in homes are solvents used in cleaning, building materials, paint, radon, allergens, cooking, smoking, plastics, carpets, and biomass burning for fuel or cooking (Ballester 2009, Brown 2010, Kaplan 2010, Roberts 1995, Zhang 2003). Indoor air pollutant levels are affected by trends in building design and construction practices, such as reduced ventilation rates, more tightly sealed buildings, and synthetic building materials and furnishings. Solvents involved in renovations and painting in homes have been associated with increased risk of general respiratory symptoms for children under 5 years (Ballester 2009). Many can be respiratory and sensory irritants, carcinogens, developmental toxins, neurotoxins, hepatotoxins, and immunosuppressants, and may cause symptoms that manifest as sick building syndrome.(Prazad 2008).

According to the WHO report, particulate matter (PM) affects more people than any other air pollutant. Even low concentrations of PM have been related to a range of adverse health effects (Agrawal, 2012). Very limited work has been carried out in relation to Air pollution from growing urbanization and its effect on human health in Lucknow city. Population and Pollution are strongly correlated to each other, if population increases so does the pollution (Bark, 2005). Population explosion, industrial growth and increase in vehicles are the main reason for air pollution nowadays (Bell, 2006). Lucknow is the capital of the most populated state i.e. Uttar Pradesh, it is the second largest city in northern and central India. It is placed among the fastest growing cities and now it is a metropolitan city in India and is rapidly emerging as a manufacturing, commercial and retailing hub. According to the World's Bank's survey in 2004, Lucknow ranks 7th in the world regarding air pollution. Report of Census report 2011 reveals that the total population of Lucknow is more than 4.5 million and by 2021 it will cross 7 million i.e. a growth of approximately 90%. Total vehicle population is more than 13 lacs with a growth of 8.68% during 2011-2012 (IITR Report 2012). Thus all these data indicate an urgent need of assessment and research on indoor air quality in urban houses to ameliorate the incoherent risks from these pollutants on health and well-being of the concerned population.

## EXPERIMENTAL METHODS

Lucknow city, the capital of Uttar Pradesh (the most populated state of India) is located at 26º51□N and 80º55□E. It is the second largest city in north India. The present study was being conducted from January to March 2012 (as a part of ongoing measurement from January 2012 to January 2014). The Sampling sites were distributed according to the population distribution as 'unplanned and densely populated colonies', 'well planned colonies', and 'roadside colonies'. For each type of sampling area, five different houses were selected so as to cover most of the area of Lucknow city.

Concentration of indoor CO (Non-dispersive Infrared (NDIR)), CO2 (NDIR), SO2 (Improved West and Gaeke method), NO2 (Arsenite method), PM2.5 and PM10 (Gravimetric method) were measured in the living room of the houses, where people spent most of their time. Indoor and outdoor concentrations of the above pollutants were simultaneously measured for a period of 8 hours. For outdoor measurement of pollutant concentration, the sampler was placed 1 m away from any potential source and at a height of 2m above the ground level. The data collected was then used to determine the Air Quality of Lucknow city.

The occupants of each house were also asked to complete activity diary/questionnaire providing information related to house characteristics, number of occupants, different activities of cooking, cleaning, storing wastes etc.

**Table 1:Questionnaire prepared for the Occupants of the sampling sites.**

1. Name: **Dheeraj Agarwal**
2. Location/site (address): **538k/112 triveni nagar -1, sitapur road, Lucknow.**
3. Characteristics
    3.1. Area( High(√)/Low population)
    3.2. Building material**: Cement and wood**
    3.3. Age of house: **27 yrs old**
    3.4. Height of house:**12ft.**
    3.5. Number of rooms: **4**
    3.6. Living room area: **8 square ft.**
    3.7. Ventilation
        3.7.1. Acceptable
        3.7.2. Somewhat acceptable (√)
        3.7.3. Somewhat unacceptable
        3.7.4. Unacceptable
    3.8 Any plants located near or inside your house? Specify. **Yes, at the gate**
4 Details of occupants
    4.1. Number of family members (**4**adults, **2**children &**1** sick)
    4.2. Average time you stay indoor. **12Hrs.**
5 Activity schedule
    5.1. Number of persons who smoke/ duration of smoking.**2 persons/appr.4 hrs a day.**
    5.2. Quality of oil used for cooking/ cooking hours. **Refined/6hrs**
    5.3. Material used during prayer time/ prayer time. **Incense/Morning**
    5.4. Material used for sweeping/ sweeping time. **phenly/Morning**
    5.5. Type of fuel used/purpose. **LPG/Cooking**
    5.6. Heating material used. **Heater and blower during winters**
    5.7. Any other remark: **A shop of small bakery inside house.**
7 Do you have any other related exposures such as an additional job, hobbies, farming, welding, auto repair, etc.? Yes / No
If yes, please list or describe: **Not related to job, but have a welding shop near my house.**
8 Can you offer any other comments or observations that may be helpful in determining the environmental condition of your home? **Actually, there are dirty drainage system and traffic which added up the pollution.**

Nishat

**Nishat Fatima**
**Research Assistant**

**Date: 3rd Feb.2012**

6. Health status
6.1 What health complaints you have experienced?
Select any symptoms you have experienced in your Home. (This is a random list - not all symptoms listed have been noted in Houses).

| Symptom | Occasionally | Frequently | Not related to House. | No |
|---|---|---|---|---|
| Difficulty in concentrating | √ | | | |
| Dry or sore throat | √ | | | |
| Dizziness | | | | |
| Itching | | | √ | |
| Heartburn | | | | √ |
| Nausea | √ | | | |
| Noticeable odors | | √ | | |
| Sinus congestion | | | | √ |
| Sneezing | √ | | | |
| High stress levels | | | | √ |
| Chest tightness | | | √ | |
| Eye irritation | | | | √ |
| Hyperventilation, | | | | √ |
| shortness of breath | | | | √ |
| Headache | √ | | | |
| Fatigue/drowsiness | | | √ | |
| Temperature too hot | √ | | | |
| Temperature too cold | √ | | | |

Other (specify): **Yes. Coughing sometime in the morning.**
6.2 Are the symptoms more likely to appear at particular times of the day/year? **yes, during seasonal changes.**
6.3 Do these symptoms clear up within 1-2 hours after leaving house? Yes / No **No**
If no, do they clear up over night or over the weekend? Yes / No **Yes on Sundays.**
6.4 Have you sought medical attention for your symptoms? Yes / No **Yes**
If yes, please specify the medicines taken routinely. **Sometimes take medicine such as painkillers for Headache.**
6.5 Do you have any allergies or other health problems that may account for any of the listed symptoms? Yes / No. If yes, please describe: **No, I don't have any allergies.**

Alfred Lawrence

**Dr. Alfred Lawrence**
**Principal Investigator.**

D. Agarwal (Signature of the occupant)

This Questionnaire was aimed to obtain a real picture of patient's home internal environment in general. It also gives us an idea about their daily activity and lifestyle. An indication whether adequate procedure/ method are there or not can be determined from the survey. The Questionnaire was prepared under the guidance of Doctors from the Medical Colleges of Lucknow (Chattpati Sahuji Maharaj Medical University and Sanjay Gandhi Post Graduate Institute of Medical Sciences). In order to insure the validity of the data generated from the study and to meet the data quality objectives set forth by the study, regular quality assurance checks were made. Every instrument was calibrated before and at the end of every monitoring period or 30 days whichever is less. While doing calibration, calibration forms and control charts were filled.

## RESULT

The data collected so far indicates that the indoor concentrations of pollutants increase from well planned colonies to densely populated areas and were highest at the roadside houses.

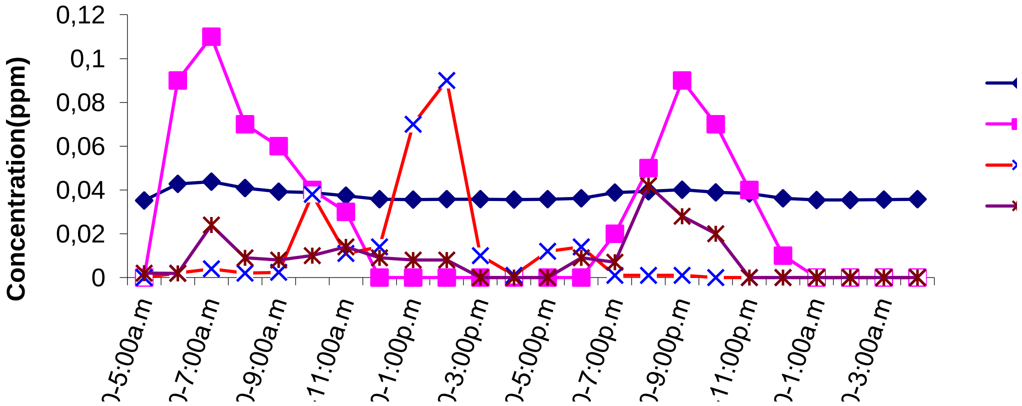


Fig 1: Full Day Indoor variation for CO2,CO,NO2 and SO2 pollutants at Roadside houses

In all the three different colonies i.e. well planned colony, densely populated colony and roadside colony full day and night monitoring was done once a month. Full day variations mean round the clock (24 hours) monitoring of pollutants, which covers all the indoor and outdoors activities taking place in a day.

Table 2a. **Results in ppm (otherwise mentioned) of all the pollutants (TWA$^{\#}$) for summer season at *well planned* microenvironment with their I/O ratio.**

| **Pollutant** | **March** | | | **April** | | | **May** | | | **June** | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Indoor** | **Outdoor** | **I/O** | **Indoor** | **Outdoor** | **I/O** | **Indoor** | **Outdoor** | **I/O** | **Indoor** | **Outdoor** | **I/O** |
| **$CO_2$** | 362±5 | 375±14 | 0.96 | 356±2 | 384±3 | 0.92 | 358±3 | 368±9 | 0.94 | 360±7 | 372±28 | 0.96 |
| **CO** | 0.2±0.1 | BDL | ---- | BDL | BDL | --- | 0.1±0.09 | BDL | --- | BDL | BDL | --- |
| **$NO_2$** | 0.004±0.001 | 0.001±0.0008 | 4.0 | 0.003±0.002 | 0.007±0.001 | 0.42 | 0.001±0.0008 | 0.003±0.001 | 0.33 | 0.01±0.007 | 0.016±0.007 | 0.625 |
| **$SO_2$** | 0.017±0.005 | 0.031±0.005 | 0.54 | 0.027±0.003 | 0.035±0.006 | 0.77 | 0.023±0.002 | 0.042±0.004 | 0.54 | 0.0009±0.0004 | 0.001±0.0009 | 0.9 |
| **PM2.5*** | 42±1.6 | 29±1.1 | 1.36 | 14±0.04 | 19±0.2 | 0.74 | 33±1.7 | 29±0.03 | 1.14 | 15±0.8 | 26±0.6 | 0.58 |
| **PM10*** | 62±4 | 98±5 | 0.63 | 67±9 | 107±21 | 0.63 | 77±13 | 115±14 | 0.66 | 78±18 | 93±12 | 0.84 |

Table 2b. **Results in ppm (otherwise mentioned) of all the pollutants (TWA$^{\#}$) for summer season at *densely populated* microenvironment with their I/O ratio.**

| **Pollutants** | **MARCH** | | | **APRIL** | | | **MAY** | | | **JUNE** | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Indoor** | **Outdoor** | **I/O** | **Indoor** | **Outdoor** | **I/O** | **Indoor** | **Outdoor** | **I/O** | **Indoor** | **Outdoor** | **I/O** |
| **$CO_2$** | 382±4 | 490±14 | 0.77 | 386±8 | 492±12 | 0.78 | 359±13 | 403±24 | 0.86 | 362±10 | 408±7 | 0.88 |
| **CO** | 0.1±0.1 | 0.6±0.3 | 0.16 | BDL | 0.1±0.1 | ---- | BDL | 0.2±0.1 | | 0.3±0.2 | 0.9±0.3 | 0.33 |
| **$NO_2$** | 0.021±0.009 | 0.047±0.02 | 0.44 | 0.032±0.02 | 0.074±0.11 | 0.43 | 0.051±0.006 | 0.084±0.01 | 0.60 | 0.054±0.005 | 0.091±0.003 | 0.59 |
| **$SO_2$** | 0.012±0.006 | 0.019±0.005 | 0.63 | 0.009±0.002 | 0.029±0.01 | 0.31 | 0.0008±0.001 | 0.0012±0.0003 | 0.66 | 0.019±0.003 | 0.053±0.02 | 0.25 |
| **PM2.5*** | 82±3.2 | 60±7.8 | 1.44 | 44±0.06 | 84±7.1 | 0.52 | 47±6.8 | 91±7.1 | 0.516 | 54±4.9 | 78±5.8 | 0.69 |

Table 2c. **Results in ppm(otherwise mentioned) of all the pollutants (TWA$^{\#}$) for summer season at *roadside* microenvironment with their I/O ratio**

| **Pollutants** | **MARCH** | | | **APRIL** | | | **MAY** | | | **JUNE** | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Indoor** | **Outdoor** | **I/O** | **Indoor** | **Outdoor** | **I/O** | **Indoor** | **Outdoor** | **I/O** | **Indoor** | **Outdoor** | **I/O** |
| **$CO_2$** | 382±4 | 490±14 | 0.77 | 386±8 | 492±12 | 0.78 | 359±13 | 403±24 | 0.86 | 362±10 | 408±7 | 0.88 |
| **CO** | 0.1±0.1 | 0.6±0.3 | 0.16 | BDL | 0.1±0.1 | ---- | BDL | 0.2±0.1 | | 0.3±0.2 | 0.9±0.3 | 0.33 |
| **$NO_2$** | 0.021±0.009 | 0.047±0.02 | 0.44 | 0.032±0.02 | 0.074±0.11 | 0.43 | 0.051±0.006 | 0.084±0.01 | 0.60 | 0.054±0.005 | 0.091±0.003 | 0.59 |
| **$SO_2$** | 0.012±0.006 | 0.019±0.005 | 0.63 | 0.009±0.002 | 0.029±0.01 | 0.31 | 0.0008±0.001 | 0.0012±0.0003 | 0.66 | 0.019±0.003 | 0.053±0.02 | 0.25 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **PM2.5*** | 82±3.2 | 60±7.8 | 0.51 | 44±0.06 | 84±7.1 | 0.78 | 47±6.8 | 91±7.1 | 0.76 | 54±4.9 | 78±5.8 | 0.86 |
| **PM10*** | 122±9 | 167±26 | 0.73 | 124±30 | 156±14 | 0.79 | 137±23 | 189±35 | 0.72 | 161±8 | 132±34 | 1.21 |

*µg/$m^3$

# TWA: Time weight Average concentration for a normal 8-hour workday.

I/O= Ratio between Indoor and Outdoor

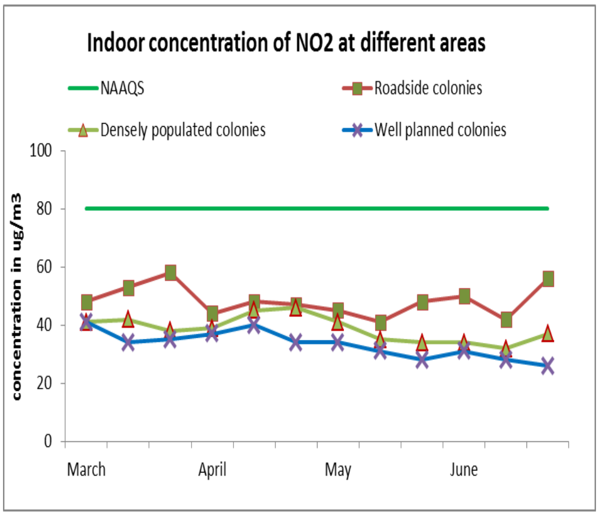


Fig 2

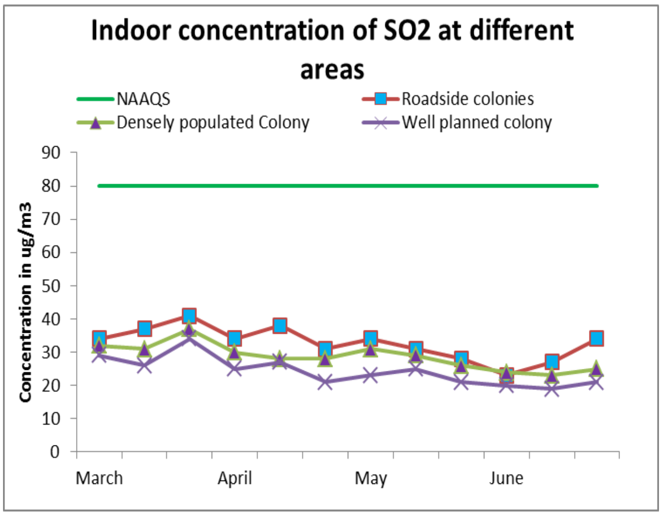


Fig 3

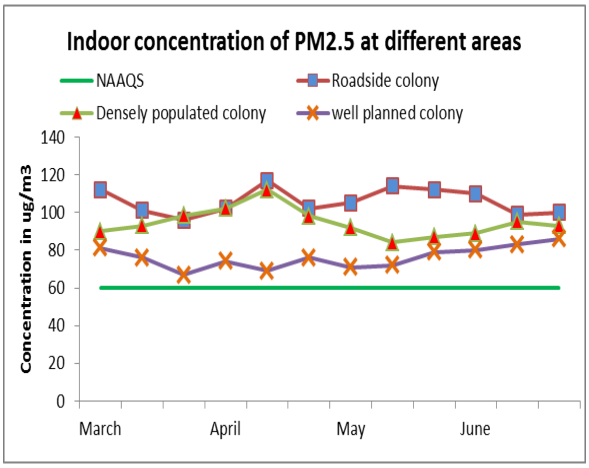


Fig 4

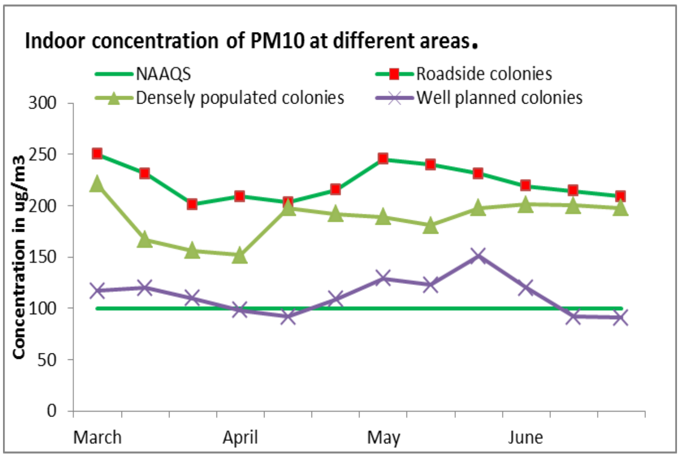


Fig 5

The figure2-5 shows a comparision of the Different microenvironment in the month of summer.

Fig. 1 shows full day indoor variation for roadside houses during the month of March 2012 and it reveals one major difference as compared to other sites. This site had lots of vehicular emission especially after 9:00 p.m. and till 6:00 a.m. in the morning when heavy diesel vehicles were allowed inside the city, which results in the peaks of CO and $CO_2$ rises that settles down after some time.

*AIR QUALITY INDEX:*

The average values of all the pollutants have been used to calculate "Air Quality Index" (AQI). The AQI focuses on health effects experienced within a few hours or days after breathing polluted air.

The formula used for calculating the AQI for each pollutant is

$$\boxed{Ip = \frac{IHi - ILo}{BPHi - BPLo}(Cp - BPLo) + ILo}$$

Table 2: The significance of each colour code and its health effects.

| Descriptor | AQI | Risk Message |
|---|---|---|
| Good | 0 - 50 | No message |
| Moderate | 51 - 100 | Unusually sensitive individuals (ozone) |
| Unhealthy for Sensitive Groups | 101 - 150 | Identifiable groups at risk – different groups for different pollutants |
| Unhealthy | 151 - 200 | General public at risk; groups at greater risk |
| Very Unhealthy | 201 - 300 | General public at greater risk; groups at greatest risk |

Where

Ip = the index for pollutant p

Cp = the rounded concentration of pollutant p

BPHi = the breakpoint that is greater than or equal to Cp

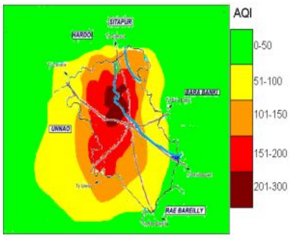
BPLo = the breakpoint that is less than or equal to Cp

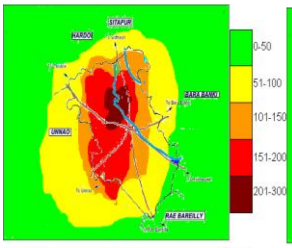
BPHi = the breakpoint that is greater than or equal to Cp

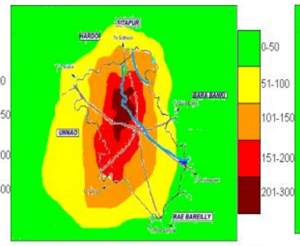
IHi = the AQI value corresponding to BPHi

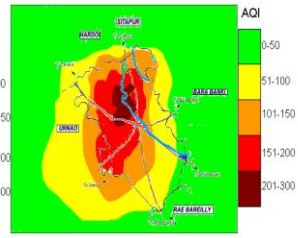
ILo = the AQI value corresponding to BPLo

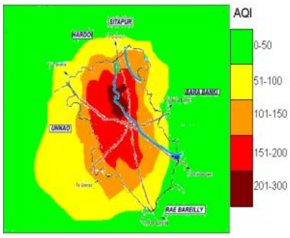
The pictures showed below indicate the weekly AQI variation in summer season in Lucknow city.

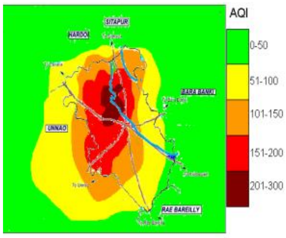


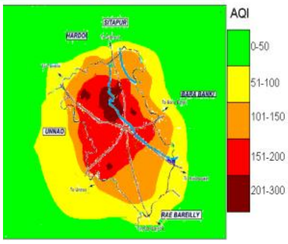


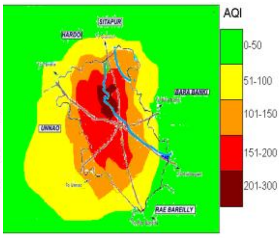


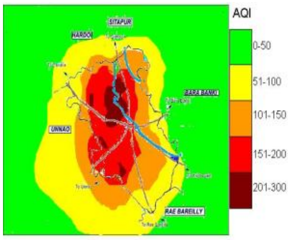


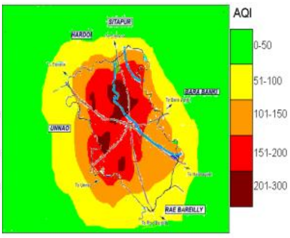


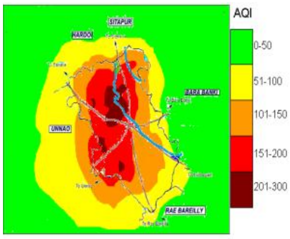


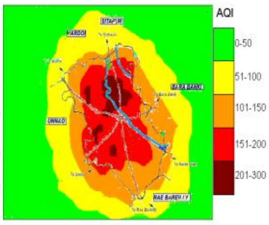












So far survey results shows that due to indoor air pollution some urban people are suffering from acute respiratory infections like pneumonia, allergic rhinitis, bronchial asthma, chronic obstructive airway disease (COAD), headache, depression and dizziness. On this basis, some interventions and precautions were also suggested.

## CONCLUSION

This study provides an example of systematic assessment and choice of indicator pollutants in Lucknow where a diverse set of energy use, housing, and exposure patterns exists. In absence of data of all seasons we cannot make any definitive conclusions but the summer season observations suggest that in well planned houses during summer season, the low value of regression coefficient indicates that indoor pollution occurs mainly from indoor activities while at roadside houses the indoor air largely depends on outdoor pollution. All the gaseous pollutants were found to be within permissible limits. Only short-term exposure seemed to exceed the limits for a few minutes. Moreover PM10 concentrations exceeded the permissible limits suggested by WHO, making it an important pollutant for assessing potential impacts of interventions. Thus, their physical and chemical characterization should be focused on, as they may offer higher reliability for predicting health impacts.

High level of $PM_{10}$ & $PM_{2.5}$ is mainly responsible for unhealthy Indoor Air Quality which can affect the urban peoples with severe respiratory diseases. Long term database of pollutants and air quality levels indoors and outdoors in these 15 houses in different microenvironments of urban Lucknow will be useful to state and federal regulatory agencies, the, researchers, consultants, and the general public, and help decision makers formulate and implement policies to manage and control environmental pollution. Awareness through education, advertising, and other avenues directed at influencing the behavior of occupants will play an important role in the near future.

## ACKNOWLEDGEMENT

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# MERGING AIR POLLUTION DATASETS: PITFALLS AND OPPORTUNITIES

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## ABSTRACT

Science assessments typically rely on archived data in national air pollution databases, data published in peer review journals, and data available in the grey literature such as agency reports published by different levels of government. Such data is sometimes supplemented by short term sampling campaigns intended to improve spatial representativeness and investigate the effects of local sources. Merging such datasets within and across regional and national borders has great potential for increasing the power of a study, and for linkage to large, spatially dispersed and diverse human health databases to evaluate health effects of air pollution. However, indiscriminate inclusion of all available data without regard to data quality, data comparability, and the availability of metadata may lead to unexpected results. The objective of this study was to identify essential criteria to be used in the selection of datasets that can be legitimately merged. Questions arise, for example, about what to do with datasets where the target species have been measured with different types of instruments, reported under different conditions, or where essential metadata is absent. An attempt is made to evaluate the error introduced when datasets are merged that do not meet essential criteria for inclusion.

**Keywords**: air pollution, database, merging data, data validation

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# COMPARISON OF EQUIVALENCE TESTS FOR PM SAMPLERS

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## ABSTRACT

Daily PM10, PM2.5 and PM1 samples were collected simultaneously by referent and home made samplers during 2010 on different types of quartz filters. Study compares different samplers and different quartz filters according to the procedure defined by European standard EN 12341, as well as by the equivalence test utility software developed in Dutch Institute for Public Health and Environment (RIVM). Investigation showed that results are not dependent on filter brand and type and the way of their preparation before sampling. Non-referent home made samplers passed comparability test according to EN 12341 for all investigated particle fractions as well as equivalence test performed by utility software. The main contribution of this investigation is applicability of equivalence test utility software on particle fraction samplers in spite of the fact that it was basically developed for equivalence testing of automatic samplers. In addition, calibration procedure defined in utility software is fully applicable for the correction of the results obtained by non-referent samplers.

**Key Words:** EN 12341, equivalence test utility software, gravimetric method

## 1. INDRODUCTION

European standard EN 12341 defines field test equivalence procedure between candidate and reference samplers for PM10 particle fraction sampling. Field test equivalence procedure between candidate and reference samplers for PM2.5 and PM1 particle fraction sampling has not heretofore defined in any standard.

In other hand, Dutch Institute for Public Health and Environment (RIVM) developed equivalence test utility software for PM automated methods versus referent gravimetric method regardless on particle fraction in question.

Requirements defined by EN 12341 are:

- Calculated reference equivalence function shall be bounded within the acceptance envelope defined as $y = (x \pm 10)$ for concentrations values $x \leq 100\ \mu g/m^3$ or $y = 0{,}9 \cdot x$ respectively $y = 1{,}1 \cdot x$ for concentrations values $x > 100\ \mu g/m^3$.
- Variance coefficient $R^2$ of the calculated reference equivalence function shall be $\geq 0{,}95$.

Equivalence test utility software calculates reference equivalence function by orthogonal regression, calculates confidential level and relative expanded combined measuring uncertainty. Very useful tool of utility software is automatic calibration data given by candidate sampler or method according to calculated reference equivalence function.

Relative expanded combined measuring uncertainty is calculated relative on daily PM10 and PM2.5 limit values. According to EU CAFÉ Directive 2008/50/EC, daily PM10 and PM2.5 limit values are 50 $\mu g/m^3$ and 35 $\mu g/m^3$ respectively. Limit values for PM1 particle fraction has not been defined yet, so we calculated relative expanded combined measuring uncertainty for PM1 relative to daily PM2.5 limit value of 35 $\mu g/m^3$.

Aims of this article were comparability investigation of different kind of quartz filters, as well as equivalence investigation of candidate samplers according to the procedure defined by European standard EN12341. Furthermore we investigated the applicability of equivalence test utility software and calibration procedure on particle fraction samplers in spite to the fact that it was basically developed for equivalence testing of automatic samplers.

## 2. MATERIALS AND METHODS

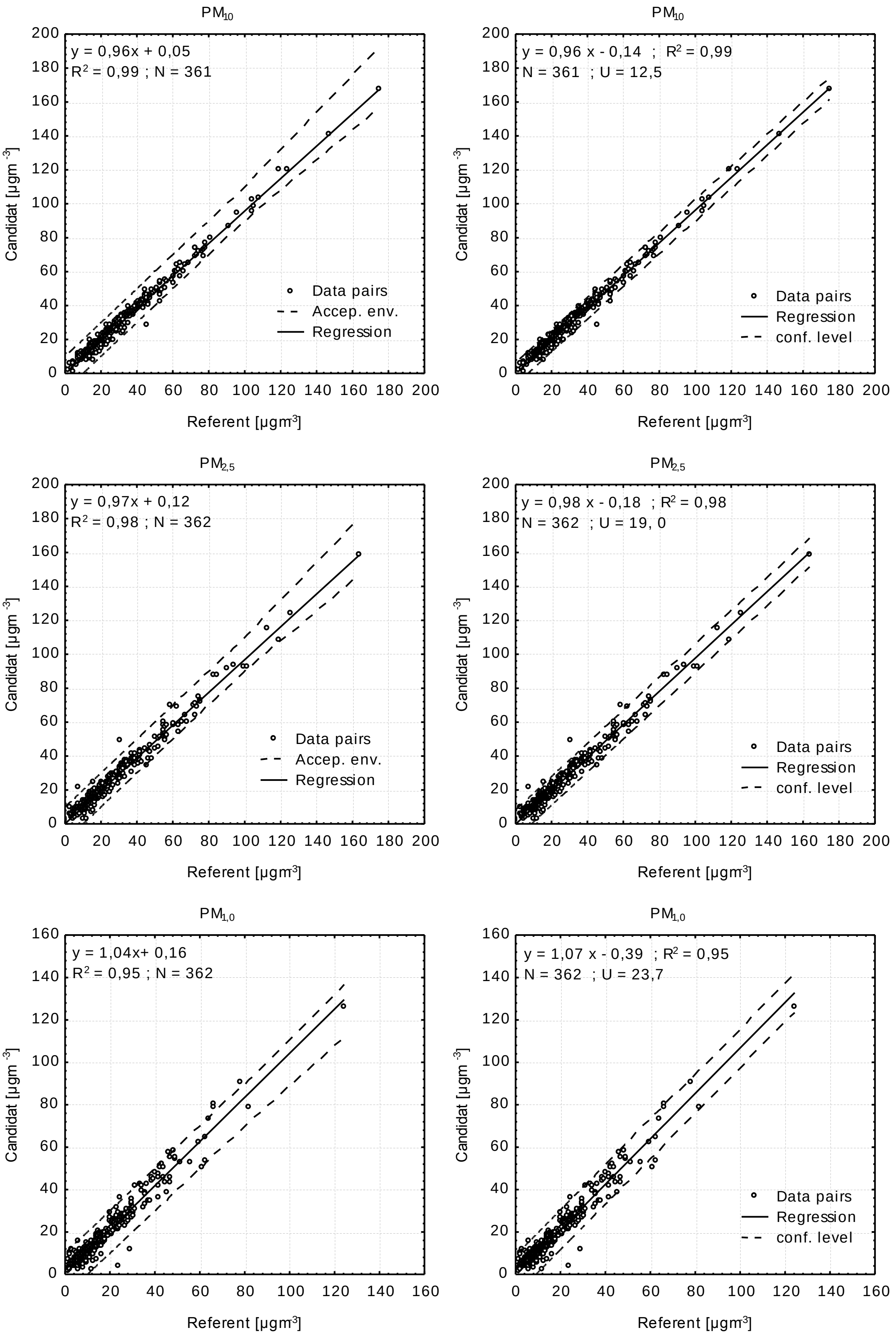
During 2010, daily PM10, PM2,5 and PM1,0 samples were collected simultaneously by referent Swen Leckel LVS samplers and non-referent home made samplers with reference inlets but pumping system and flow control constructed at Institute of Medical Research and Occupational Health. Referent samplers collected particulate matter on Whatman QMA quartz fibre filters, whence candidate samplers collected on Pall Tissuequartz 2500QAT-UP quartz fibre filters pre-fired for 3h at 900 ºC. All filters were weighed twice before and twice after sampling. Weighing was preformed after 48 hours conditioning at (20±1) °C and relative humidity of (50±5) %, and again after 24 hours conditioning on microbalance Mettler Toledo MX5. Sampling was performed at urban background measuring site in Zagreb, Croatia.

No outlier test was performed during the statistical analysis.

## 3. RESULTS AND DISCUSION

Figure 1a shows field test equivalence results according to EN12341 for all particle fractions. Calculated reference equivalence functions are bounded within the acceptance envelope and $R^2 \geq 0{,}95$ for all particle fractions. It can be concluded that candidate samplers satisfy requirements of equivalence regardless to filter brand.

Calculated orthogonal equivalence functions by utility software are shown in Figure 1b. Expanded combined measuring uncertainties (U) are lower compared to the limit value of 25% according to EU Data Quality Objectives (DQO) for PM2.5 given in chapter 9.4 of European standard EN 14907.



a b

Figure 1. Results of equivalence test according to EN12341 (a) and by equivalence test utility software (b).

Effects of calibration procedure on statistical parameters for air quality assessment are shown in Table 1. Average annual value and number of the daily limit exceedances obtained by the results of candidate sampler coincide better to the statistical parameters obtained by the results of referent samplers after the calibration was performed.

Table 1. Effects of calibration procedure on statistical parameters for air quality assessment

| **PM10** | | | |
|---|---|---|---|
| **Parameter** | **Referent** | **Non-referent before calibration** | **Non-referent after calibration** |
| **N** | 363 | 363 | 363 |
| **$C_{avg}$ [$\mu gm^{-3}$]** | 30,85 | 29,57 | 30,85 |
| **> 50** | 48 | 42 | 46 |
| **U [%]** | | 12,5 | 10,1 |
| **Regression line** | | y = 0,96·x – 0,14 | y = 1,00·x – 0,00 |
| **PM2,5** | | | |
| **Parameter** | **Referent** | **Non-referent before calibration** | **Non-referent after calibration** |
| **N** | 362 | 362 | 362 |
| **$C_{avg}$ [$\mu gm^{-3}$]** | 25,17 | 24,46 | 25,20 |
| **> 35** | 70 | 70 | 70 |
| **U [%]** | | 19,0 | 18,9 |
| **Regression line** | | y = 0,97·x – 0,18 | y = 1,00·x – 0,0 |
| **PM1,0** | | | |
| **Parameter** | **Referent** | **Non-referent before calibration** | **Non-referent after calibration** |
| **N** | 362 | 362 | 362 |
| **$C_{avg}$ [$\mu gm^{-3}$]** | 18,03 | 18,93 | 18,03 |
| **> 35** | 40 | 44 | 40 |
| **U [%]** | | 23,7 | 19,2 |
| **Regression line** | | y = 1,07·x – 0,39 | y = 1,00·x – 0,01 |

N – number of data pairs

Cavg – average annual mass concentration value

> 50 ( > 35 ) – number of the daily limit exceedances

U – relative expanded combined measuring uncertainty

## 4. CONCLUSIONS

Non-referent home made samplers satisfy all requirements according to European standard EN 12341. Different brands of quartz fibre filters have no influence on particle fraction concentration in spite of different preparation of filters (pre-fired for 3h at 900 ºC).

Equivalence test utility software (RIVM) is applicable to particle fraction samplers in spite of the fact that it was basically developed for equivalence testing of automatic analyzers. Expanded combined measuring uncertainties for all particle fractions are less than limit values of 25%.

Calibration procedure defined by utility software is very applicable to the results obtained by non-referent samplers. Statistical parameters obtained by the results of candidate samplers coincide better to the statistical parameters obtained by the results of referent samplers after the calibration was performed.

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European standard EN 12341

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# AN EMISSIONS INVENTORY AND AIR QUALITY MANAGEMENT FOR TWO MEGACITIES (DELHI AND CHENNAI) OF INDIA

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## ABSTRACT

The National Capital Region of Delhi and the Greater Chennai areas are equally industrialized, with a large operational vehicle fleet, and a population of more than 10 million. The deteriorating air quality is a concern for both the cities, in spite of regular interventions to control pollution sources. A multi-pollutant and multi-sectoral emissions inventory was established and validated for the two regions, covering a geographical area of 80km x 80km for Delhi and 50km x 50km for Chennai. The inventory includes all the conventional sources such as transport, road dust, residential, power plants, and industrial hot spots and the unconventional sources such as diesel generator sets, and biomass burning for winter heating. The contrasting feature includes a large sea port in Chennai, supporting the freight movement along the Southeastern coast. In brief, the estimated emission totals in tons/year for the base year 2010 are ~69,050 and ~26,000 for $PM_{2.5}$, ~133,900 and ~56,500 for $PM_{10}$, ~37,000 and ~15,100 for $SO_2$, ~1,520,000 and ~857,500 for CO, and ~492,250 and ~268,200 for $NO_x$, for Delhi and Chennai, respectively. The inventory is geo-referenced with a spatial resolution of one kilometer, including diurnal and seasonal cycles, for incorporation into the chemical transport models, validation, and further analysis.

In this paper we present an overview of the emissions inventory estimates, contributions of source sectors, validation of the inventory with dispersion modeling, estimated health impacts based on epidemiological studies, and a summary of pollution control strategies which the authorizes are contemplating to implement for better air quality and public health in the cities of Delhi and Chennai.

**Keywords:** Delhi; Chennai; India; Emissions Inventory; Dispersion Modeling; Particulate Pollution; Air Quality Management

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# ENERGY EFFICIENCY IN RAIL SYSTEMS AND COMPARISON BETWEEN RAIL SYSTEM IN ISTANBUL AND BUS TRANSPORTATION IN TERMS OF CARBONDIOXIDE ($CO_2$) EMISSION

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## ABSTRACT

In this study, energy efficiency in rail systems and urban rail system in Istanbul and bus transportation have been researched in terms of Carbondioxide ($CO_2$) emission. As a result of energy efficiency, which has been implemented, how the use of rail system could be more efficient has been shown by both simulation studies and inspections implemented on site. There is a saving opportunity up to 33% with saving ways which could be named in three main topics as rail system substructure, vehicles and operation. It has been seen that there has been a decrease as 248,36 gr $CO_2$ per passenger and 253.844,94 tons $CO_2$ through preferring rail system in Istanbul. This decreased amount and the results which are shown upon the energy efficiency have been indicating that it would be useful environmentally to plan transportation systems as rail system predominantly.

**Keywords:** Railway Systems, Energy Efficiency, Carbondioxide (CO2) emission, transportation.

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# STUDY OF EFFECT OF DUST ON THE NEXT PHENOMENON QESHM ISLAND TOURISM

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## ABSTRACT

Qeshm is the largest island in the Persian Gulf, South of Iran. Considering the geographical position, Qeshm can attract international tourists, especially in cold seasons is. But in recent year’s phenomena of dust and a major obstacle to the increase in tourism has become involved. A dust with high temperatures and humidity, including the most important obstacles in attracting tourists is the island.

The results of this study indicate that in recent years the number of dust days in Qeshm has increased and the dust, especially in the spring as the biggest problem in attracting tourists has become the Qeshm.

**KEYWORDS**: International Tourism, Qeshm Island, Dust

## 1. INTRODUCTION

One of the most important information needed for tourists is the destination climatic conditions and most of the tourists take the climatic considerations the most important item. Among all of the climatic elements, temperature has the most effect on human's body and the calmness feeling. But, there are many other climatic elements which affect on temperature and as a result on human's body. Air humidity, sunshine, air flaw and windflaw are the most significant of these elements. Comfort indices are tables and diagrams which indicate the simultaneous cumulative effect of all the effective factors on comfort feeling at the same time. Thermal indices could be used for assessment of tourism conditions and notify tourists from the destination climatic conditions; also, the tourism climatic potential of various regions could be specified. Tourism comfort climate index is an index which indicates the climatic elements effect on tourism systematically. This index utilizes the climatic elements such as temperature, rainfall, humidity, sunshine and the wind.

In 2001, Perry et al studied and surveyed the climate effects on international tourism through a research. They came to this conclusion that different and specific climatic conditions of urban, coastal, mountainous, etc. regions have various influences on tourism attraction which they should be considered seriously. (Perry, 2001)

In 2001, Daniel Scott & Geoff McBoyle in a research found out that until 2050 and 2080 (anno domini years) according to the climatic variations procedure in the world, the tourism comfort climate index condition of the most regions of Canada will be better than nowadays conditions. (Scott and McBoyle, 2001)

In 2007, Jacqueline et al came to this conclusion that in the future years in Britain and Ireland, tourism attraction will have a gentle movement toward the North; and in Germany cause of warming up the weather and development of more favorable conditions in interior regions in comparison with coastal areas, tourist attraction flow will be toward the south. (Jacqueline et al, 2007)

In a study, Farajzade (2009) categorized the tourism climate in Gillan province by the usage of TCI index. They concluded that May and July months in Gillan contain the best climatic conditions, while January and December have the worst one for tourist's presence. (Farajzade, 2009)

In a research, Ziaei and Bakhtiari (2009) by surveying the tourism comfort climate index in Kish Island came to this conclusion that the island has a winter like situation for tourism comfort; and March, December, January and February are the months which consist of the best conditions for tourist attraction. (Ziaei and Bakhtiari, 2009)

Shayan et al (2009) studied and surveyed the tourism comfort climate index in Kish Island and came to this conclusion that January, February, March, October, November and December have the best conditions for tourist attraction; while June, July, August and September are not suitable months for tourist arrival. (Shayan et al, 2009)

In 2009, Matzarakis and Farajzadeh in a research in northwest of Iran, by the usage of TCI index concluded that Makoo, Ahar, Ardebil, Takab, Khoy, Oroomieh and Sarab cities have a summer like situation and each of them, at least in one month of the summer contains a score above 80 according to the great climatic condition; Makoo, Ardebil and Takab cities contain a score above 90 and an ideal situation; in addition, Ardebil has the best conditions for tourist attraction in summer. (Matzarakis and Farajzadeh, 2009)

## 2. METHODOLOGY

In this research with statistical survey of the tourism comfort climate condition in Qeshm Island and according to the synaptic station data of this Island, during 1996 and 2005, the monthly procedure of TCI index of the Island was provided; then, by reforming of irradiance coefficient and entrance of dust phenomenon influence, condition of the index was monitored and reformed; in addition according to the number of dusty days procedure in this Island, the future condition will be surveyed and analyzed.

In this case, TCI model and then the reformed models have been used; then, Results have been analyzed according to table 1.

Table 1: Status of Tourism Climate Index

| TCI Range | Rank | Status |
|---|---|---|
| 90-100 | 9 | Ideal |
| 80-90 | 8 | Excellent |
| 70-80 | 7 | Very Good |
| 60-70 | 6 | Good |
| 50-60 | 5 | Acceptable |
| 40-50 | 4 | Marginal |
| 30-40 | 3 | Unfavorable |
| 20-30 | 2 | Very Unfavorable |
| 10-20 | 1 | Extreme Unfavorable |
| 0-10 | 0 | Impossible |

## 3. DISCUSSION

According to TCI index and by the usage of seven climatic parameters including monthly average of temperature, monthly maximum average of temperature, monthly average of relative humidity, monthly minimum average of relative humidity, monthly precipitation average, average of sunny hours, and monthly average of wind speed, in January to May and October to December months, Qeshm Island consists of appropriate and acceptable to great conditions for the tourist presence. On the other hand, in June to September months, there are no appropriate climatic conditions for the presence of the tourist (figure 1).

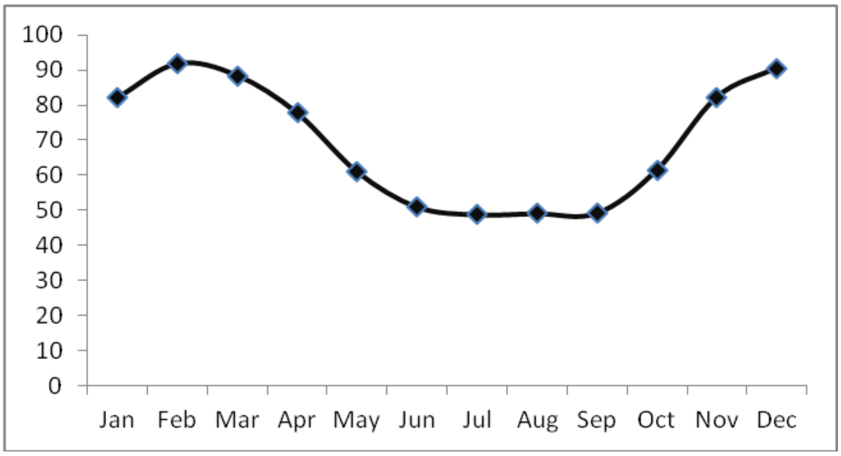

Figure 1: Qeshm monthly TCI

After the above mentioned surveys, by reforming of irradiance coefficient and sunshine degree reduction in warm months of the year, the reformed comfort climate diagram was traced (figure 2).

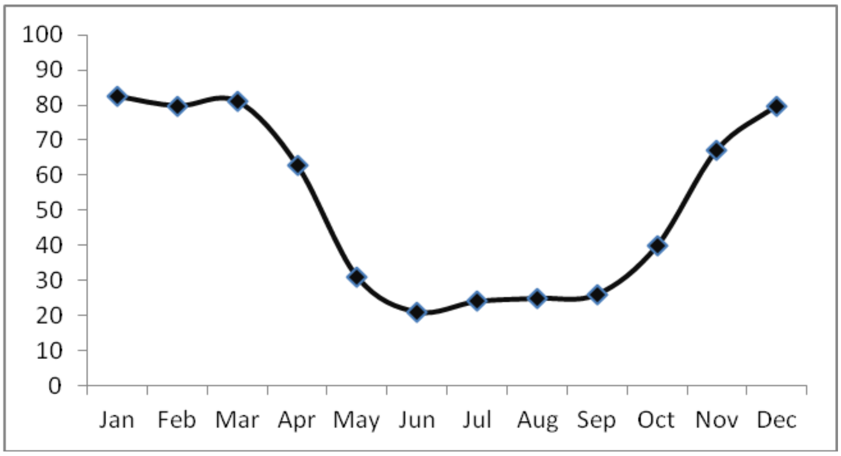

Figure 2: Qeshm monthly TCI with Score improved radiation

Therefore, it is observable that January to April and November to December months have suitable climatic conditions for tourist presence, but other months of the year do not. On the other hand, overbearing heat besides the high humidity, acute sunshine, and warm wind flow lead to the climatic comfort degree reduction of Qeshm Island; so, the tourist presence in this Island from May to October months will be difficult.

In recent years, dust phenomenon has led to the TCI index degree reduction in Qeshm Island. According to figure 3, the average number of dusty days in this Island has varied from about 3 days in January to about 16 days in May and averagely in March to September months, each month has contained more than 10 dusty days.

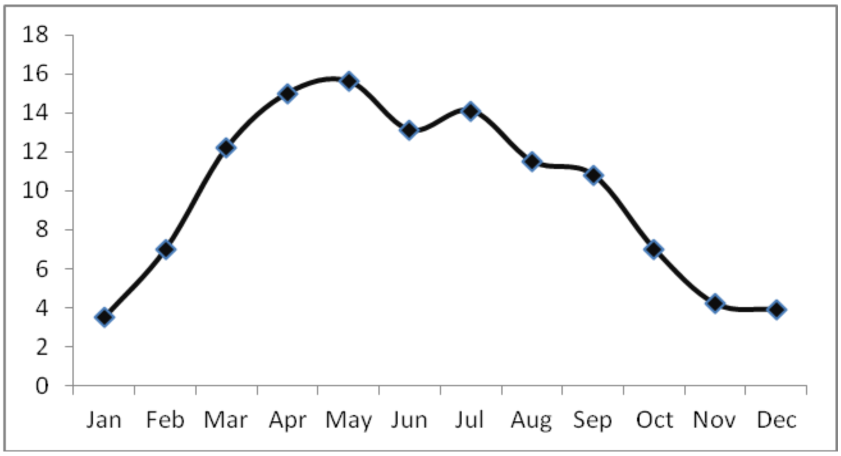

Figure 3: Monthly dust day in Qeshm Island

Therefore, by entering of dust negative influence in TCI model of Qeshm Island and according to figure 4, only 3 months of the year which are January, February, and December contain the appropriate conditions for tourist arrival and two months of March and November have rather desirable conditions; but, the other seven months of the year are not suitable for tourist presence.

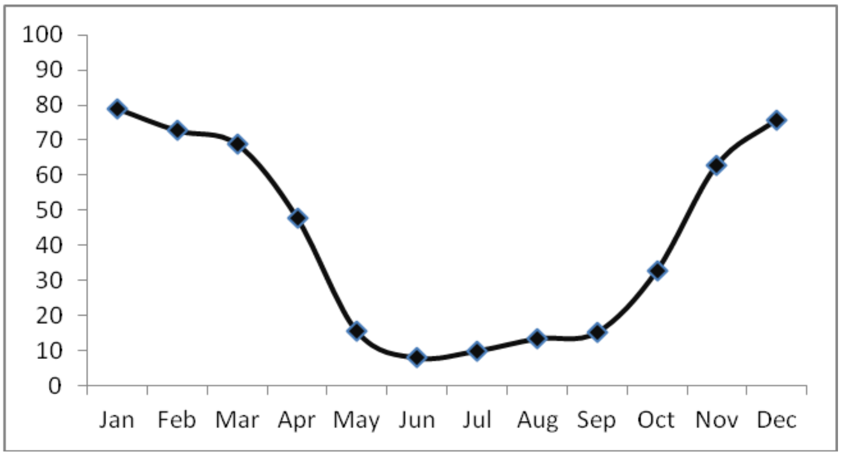

Figure 4: Qeshm monthly TCI with Score improved dust

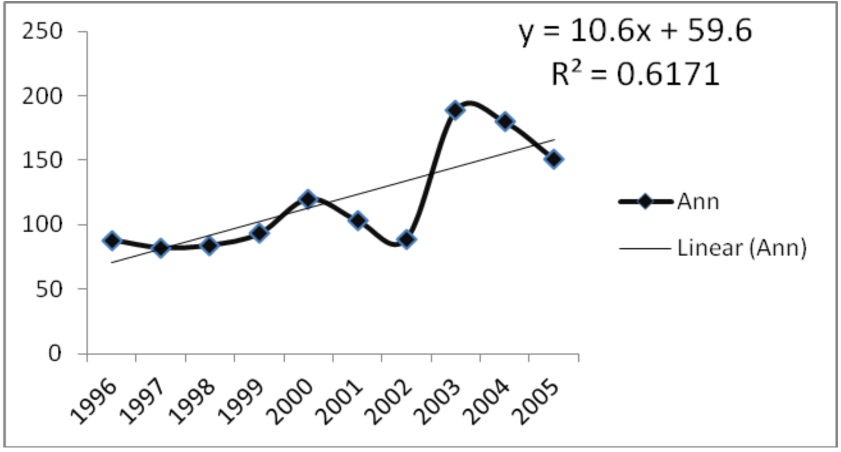

Figure 5: Annual dust trend in Qeshm Island

By surveying the variation procedure of dusty days number in Qeshm Island (figure 5), it seems that in recent years, the number of dusty days in the Island have been increasing and during these years, this procedure has been continuing; so, the number of dusty days in the island have reached above 150 days. Continuation of this process can lead to more problems for the Island; therefore, this fact should be studied and surveyed.

## 4. CONCLUSION

Qeshm Island is among the tourism and strategic regions of Iran. According to its specific location and also the existence of trading open region, this Island has been considered and been the focus of local and international tourists in recent years; in addition, in winter and Norouz days (New Year days) specifically it has encountered a lot of enthusiasm.

By surveying the tourist comfort climate of Qeshm Island and the effect of irradiance coefficient in warm months of the year, and also entrance of dusty days influence into this model, it is obvious that there are desirable climate conditions for the tourist presence in the Island just in 3 months of the year; in addition, there are acceptable conditions in the other two months of the year. But, during the seven months- from April to October- the weather condition is not appropriate for the tourist's presence. In recent years, an increase in the number of dusty days of the Island has led to the decrease of the above mentioned index.

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# NATURAL AND ANTHROPOGENIC AEROSOLS IN THE MEDITERRANEAN REGION AND MIDDLE EAST: PATTERNS AND IMPACTS

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## ABSTRACT

Physical and chemical properties of airborne particles have significant implications on the microphysical cloud processes. Maritime clouds have different properties than polluted ones and also the final amounts and types of precipitation are different. Mixed phase aerosols that contain soluble matter are efficient CCN and enhance the liquid condensates spectrum in warm and mixed phase clouds. Insoluble particles such as mineral dust and black carbon are also important because of their ability to act as efficient ice nuclei (IN) through heterogeneous ice nucleation mechanisms. Also, entrainment of particles at various cloud heights may either enhance cloud formation or invigorate cloud burn off due to radiation absorption. In this work, several model simulations have been designed to analyse such properties and some recent results are presented.

## 1. INTRODUCTION

The Mediterranean region and Middle East are well known places of high aerosol and ozone concentrations. The characteristic paths and scales of transport and the changes in the physical and chemical properties of the aerosols along the followed paths has been the subject of several past studies. Aerosol levels have several impacts on various gaseous pollutants but the most important effects are associated with radiation, clouds and precipitation (direct and indirect effects). Airborne particles of natural or anthropogenic origin, may act as efficient Cloud Condensation Nuclei (CCN), depending on their concentrations, their size distributions and their chemical composition. Some particles – such as mineral dust and soot- may also act as Ice Nuclei (IN) and contribute in the formation of ice particles in high clouds. For example, sea salt, sulfates, nitrates (soluble aerosols), are responsible for the formation of cloud drops as the air rises and the relative humidity increases to slightly above saturation near cloud base (Levin and Cotton, 2009). Moreover, the role of natural or anthropogenic particles, such as mineral dust and black carbon, as IN has been demonstrated by several studies (e.g. Pruppacher and Klett 1997; Liu et al., 2009). There is increased evidence that the suspension of sulfate and soot particles produced during fossil fuel use, biomass burning, and aircraft emissions, increase the ice number concentrations through ice nucleation mechanisms (Penner et al., 2009). On the other hand, formation of secondary particles and atmospheric ageing of aerosol lead to particles with substantially different properties than those at source regions. For example, desert dust particles being initially not very soluble and ineffective CCN can become coated with soluble material turning them into effective GCCN. These types of processes can be addressed within the framework of integrated atmospheric and air pollution models. In this study, several experimental runs were performed with RAMS/ICLAMS model, (Solomos et al., 2011) focusing mostly on the amount of available airborne particles that could be activated as CCN or IN for each particular case and examining both the effects on precipitation and the effects on the microphysical structure inside the clouds.

## 2. EFFECTS OF AIR QUALITY ON CLOUD DEVELOPMENT

The model includes an advanced microphysical scheme with eight categories of water (vapor, cloud droplets, rain droplets, pristine ice, snow, aggregates, graupel and hail) and also interactive mineral dust and sea salt cycle, biogenic and anthropogenic pollutants emission/transport/depletion processes, gas and aerosol chemical reactions. The radiative transfer scheme in the model includes aerosol feedbacks on radiation fluxes and the activation of cloud droplets is explicitly calculated based on the properties of airborne particles. The formation of ice condensates is also calculated based on air quality properties. The model was set up in a 2D configuration so that the effects of microphysics in cloud processes can be isolated from the possible topographic forcing. Initial conditions were taken from a single sounding that is representative of unstable atmospheric conditions and a warm and moist bulb was applied in the centre of the domain in order to trigger convection.

Model runs for twelve different mixtures of aerosol particles were implemented, as seen in Table1. Each run lasted for six hours. The distribution of the particles in the model was represented by a three-modal lognormal distribution (fine-accumulated-coarse) with constant geometric dispersion ($\sigma=2$) and modal diameters varying according to the needs of each experiment. The chemical composition and the aerosol concentrations also varied for each model run (see Table1). Activation of the different aerosol types as CCN resulted in significant variation in the total accumulated precipitation as indicated in Figure 1. The aerosols that consisted of dust particles externally coated with soluble material produced similar precipitation amounts - within the range of 300-350 mm. These results seemed not to be affected by the chemical composition of the soluble fraction as seen for Cases 1-3, where the soluble fraction was sodium chloride (NaCl) and Cases 9-11, where the soluble material was ammonium sulphate $(NH_4)_2SO_4$. However, by increasing the hygroscopicity of the particles (the percentage of soluble material), the accumulated precipitation was reduced (i.e. Case3, Case11). This is due to the increased number of cloud droplets resulting in slower auto-conversion rates of cloud to rain sizes. In Cases 6-8, the particles were assumed to be completely soluble (NaCl) with different size distribution characteristics (see Table1). The results indicate a slight reduction in total precipitation for the aerosols with the greater particle diameters per size mode that is possibly related to the formation of bigger cloud and rain droplets and suppression of the precipitation from the ice phase of the cloud.

Table 1. Aerosol characteristics for the twelve modelling scenarios.

| Case | Chemical Composition | Soluble Fraction | Concentration ($cm^{-3}$) | Mean diameter (fine-accumulated-coarse) (μm) |
|---|---|---|---|---|
| 1 | Dust+NaCl | 0.2 | 1000 | 0.02-0.2-2 |
| 2 | Dust+NaCl | 0.5 | 1000 | 0.02-0.2-2 |
| 3 | Dust+NaCl | 0.7 | 1000 | 0.02-0.2-2 |
| 4 | NaCl | 1.0 | 1000 | 0.02-0.2-2 |
| 5 | NaCl | 1.0 | 2000 | 0.02-0.2-2 |
| 6 | NaCl | 1.0 | 1000 | 0.05-0.2-2 |
| 7 | NaCl | 1.0 | 1000 | 0.02-0.5-2 |
| 8 | NaCl | 1.0 | 1000 | 0.02-0.2-5 |

| | | | | |
|---|---|---|---|---|
| 9 | Dust+$(NH_4)_2SO_4$ | 0.2 | 1000 | 0.02-0.2-2 |
| 10 | Dust+$(NH_4)_2SO_4$ | 0.5 | 1000 | 0.02-0.2-2 |
| 11 | Dust+$(NH_4)_2SO_4$ | 0.7 | 1000 | 0.02-0.2-2 |
| 12 | $(NH_4)_2SO_4$ | 1.0 | 1000 | 0.02-0.2-2 |

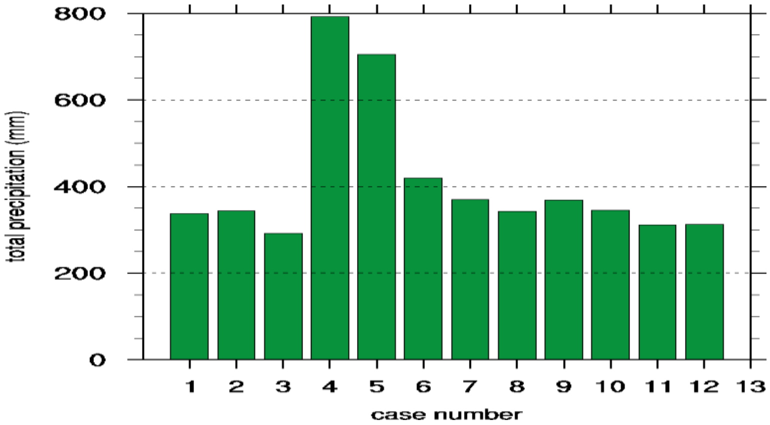

Figure1. Domain total accumulated (6h) precipitation (mm) for the twelve aerosol scenarios.

An interesting result is the almost 100% increase in total precipitation that was found for Cases 4-5 (completely soluble particles) compared to Cases 1-3 (partially soluble particles). In both Case 4 and Case 5 runs, the precipitation rates remained relatively high even during the latest stages of cloud development. This is an indication of significant contribution of ice processes to the overall precipitable water. In order to illustrate the differences attributed to chemical composition we selected to compare the cloud properties between Case 4 and Case12 as depicted in Figure 2. These cases are representative of totally soluble aerosol particles with the same size and concentration properties but with different chemical characteristics, namely NaCl (Case 4) and $(NH_4)_2SO_4$ (Case12). As seen in Figure 2a, after the first modelling hour the precipitation rate for Case 12 falls below 4 mm/h while after three hours the rainfall has been ended. In contrary, the rate remains very high for Case 4 (blue line in Figure 2a). These results illustrate the crucial role of the chemical properties (Table 2) in the temporal evolution of the microphysical processes. For example, the activation of ammonium sulphate particles as CCN resulted in increased cloud droplet concentrations throughout the modelling period, thus suppressing the formation of precipitable rain droplets (Figure 2b).

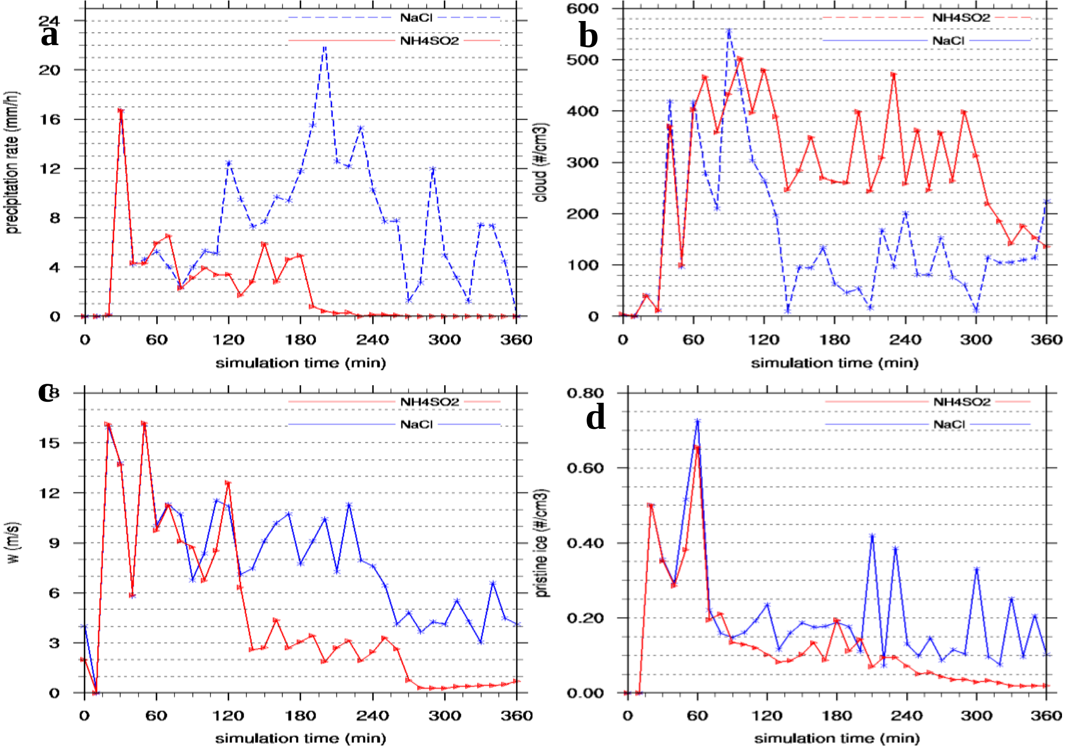

Figure2. a) Maximum precipitation rate (mm/h) b) Maximum cloud droplet concentration (cm$^{-3}$) c) Maximum updrafts (m/s) d) Maximum ice concentration (cm$^{-3}$) for Case 4 (blue lines) and Case 12 (red lines).

However, the most significant difference between the two runs comes from the ice stage of the cloud. As seen in Figure 2c the cloud updrafts in Case 4 where significantly higher than in Case 12. This cloud contained more ice near the cloud top (Figure 2d). Melting and rimming of the frozen elements invigorated the production of graupel and hail at the middle and higher cloud layers and the major part of precipitation during 4-6 hours simulation was generated from this stage of the cloud. Additionally, one more run was performed for the same air quality properties as in Case 4. In this run the initial conditions were slightly changed and the dew point temperature was reduced by 1°C in the initial sounding. The total accumulated precipitation for this case was 234.41 mm - which is more than two times lower than the 792.92 mm of Case 4. Such results imply the importance of the synergetic effects between air quality and meteorology since a minor change in any of the two can lead in significant precipitation variability.

Table2. Chemical properties of the aerosol soluble fraction

| | Density (kg m$^{-3}$) | Molar mass (kg mol$^{-1}$) | Van't Hoff factor (ions molec$^{-1}$) |
|---|---|---|---|
| NaCl | 2165 | 0.058 | 2 |
| $(NH_4)_2SO_4$ | 1760 | 0.132 | 3 |

The interplay between air quality and high clouds has also been tested within the framework of the model, assuming initial conditions that are representative of a cold cloud structure. The amount of ice particles that will activate during cloud formation depends on the IN concentration, atmospheric conditions and also on the competition between homogeneous and heterogeneous ice processes, as seen in Figure 3a. For example, by considering twelve different concentrations of dust or soot particles that can be activated as IN, the respective accumulated precipitation performed great variance as seen in Figure 3b. In general, the precipitation remained similar for both species until an aerosol concentration of 50 μg $m^{-3}$. After this threshold, the results varied considerably. Maximum precipitation values were found for the 500 μg $m^{-3}$ and for the 1000 μg $m^{-3}$ of soot and dust particles respectively. A significant amount of precipitation for the 1000 μg $m^{-3}$ of soot scenario was hail. Further increase of the aerosol concentrations resulted in less precipitation as these clouds contained great amounts of small ice elements and finally burned off before these condensates managed to grow up to precipitable sizes.

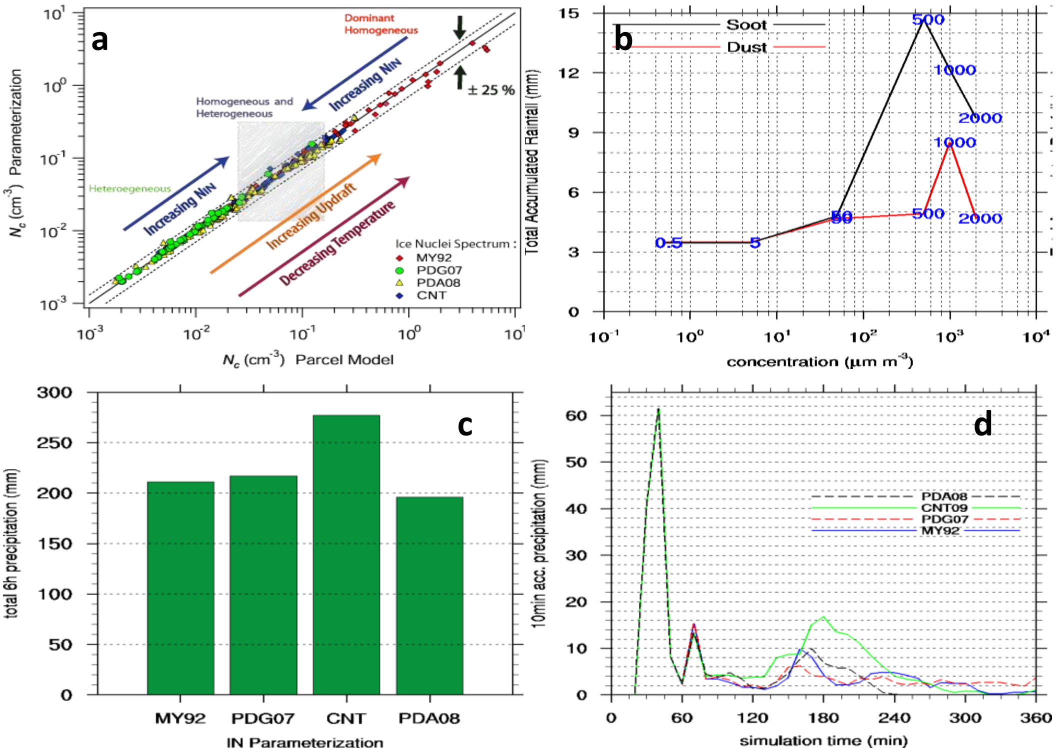

Figure3. a) Parameterization of the competition between homogeneous and heterogeneous ice formation processes (Barahona and Nenes, 2009). b) Total accumulated precipitation (mm) for various concentrations of soot (black line in μg $m^{-3}$) and dust (red line in μg $m^{-3}$). c) Total domain precipitation (mm) d) Ten minutes accumulated precipitation (mm).

The sensitivity of precipitation towards IN properties was also tested for four different IN spectrums namely : MY92 (Meyers et al.,1992), PDG07 (Philips et al., 2007), PDA08 (Philips et al., 2008), CNT (Pruppacher and Klett, 1997; Barahona and Nenes 2008). These distributions have been derived from in-situ measurements and field campaigns. As seen in Figure 3c, explicitly resolving of the competition between homogeneous-heterogeneous freezing resulted in about 25% more precipitation. The precipitation rate was similar for all IN spectrums during the first modeling hour (Figure 3d). During this stage all of the precipitation came from the warm phase of the cloud. Significant variability was evident after two hours run when production of rain from ice processes was dominant.

## 3. CLOUD-AEROSOL INTERACTIONS OVER MEDITERRANEAN

On 29 January 2003, an event of heavy precipitation took place over Eastern Mediterranean. Previous studies on this event (Solomos et al., 2011; Levin et al., 2005) indicated that mineral dust and sea salt particles penetrated the base of the clouds and provided significant amounts of hygroscopic particles. A considerable percentage of these particles were activated as cloud condensation nuclei. In the present study, this event was examined taking also into consideration the anthropogenic aerosols over the region (sulfate particles) and their role on cloud and precipitation. Measurements of fine aerosol particles (diameter < 1μm) during this event showed that, below 1000m, anthropogenic sulfate represented 11.6 % of the total sample (Levin et al., 2005). For measurements above 1000m the respective ratio reached 35%. Corresponding model results were in good agreement with these observations. The average ratio of the modeled number concentration of sulfate aerosols to the total particles was 11.9% below 1000m and 39.6% for above 1000m (Kushta et al., 2012).

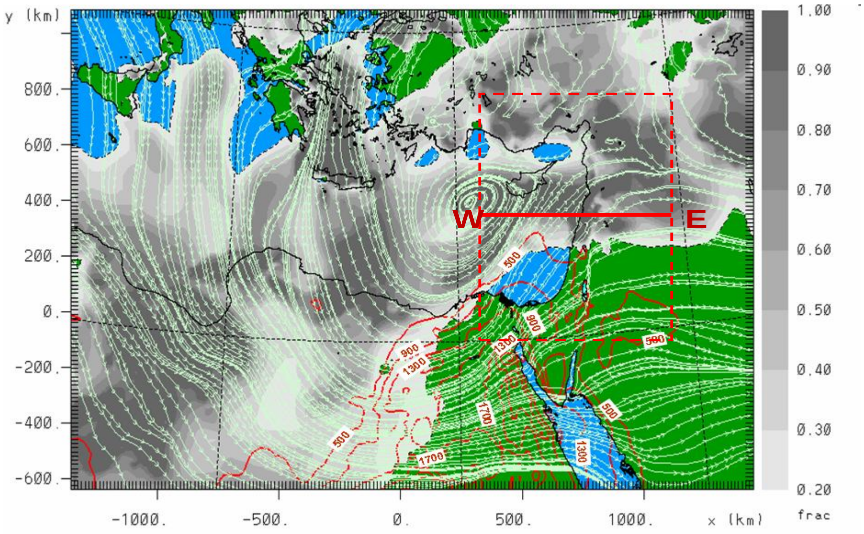

Figure 4. Model cloud cover (grey colour scale), wind flow (green lines) at the first model layer and total column dust load (red lines) in mg m$^{-2}$ on 28 January 2003, at 11:00UTC. The bold red line indicates the location of the vertical cross sections from the second model grid (dashed red line).

The averaged values of hourly precipitation for January 29th, 2003, for the two cases (without sulfates and with sulfate aerosols) showed similar variation. However, including the sulfate aerosols in the cloud condensation scheme modified the cloud structure and the spatial distribution of precipitation over the region. The area of maximum precipitation during the anthropogenic run was transposed towards SW compared to the natural particles run. As depicted in Figure 5, including the sulfate aerosols in the computation of cloud droplet activation resulted in suppression of cloud development over the sea. The clouds in this case exhibited more vigorous development inland towards the eastern part of the domain. Despite the differences in the horizontal and vertical structure the two cloud systems reached the same top height (10km) at 10:00UTC.

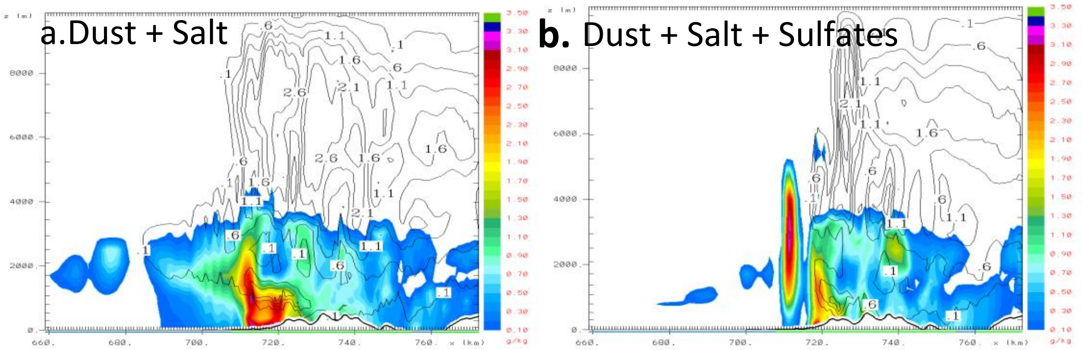

Figure 5. Mixing ratio (g kg$^{-1}$) of liquid condensates (color scale) and ice condensates (black contours). Vertical cross-section along 32.8°N at 10:00 UTC on 29 January 2003.

## 4. CONCLUSION

Model results indicate that cloud and precipitation properties are very sensitive to variations in both concentrations and chemical composition of the airborne particles. Small changes in the aerosol/CCN field can result in significant modification of precipitation. Also, several aerosols such as anthropogenic soot particles or mineral dust can be efficient IN. Certain combinations of air quality and atmospheric conditions are likely to trigger flood events or, in contrary, to supress rainfall. When the ice processes were favoured, the accumulated precipitation was found to increase significantly (up to 2 times). These differences are attributed to the complex role of the aerosols in cloud microphysics for both the warm and cold stages of the clouds. Similar concentrations and size distributions of dust and soot can modify the cloud structure in different ways, thus adding to the complexity of the system. Interaction between natural and anthropogenic aerosols and meteorology resulted in significant modification of the cloud properties and different spatial distributions of precipitation for a case study over Mediterranean. Additional model runs utilizing also in situ and laboratory experimental measurements are currently underway in order to improve our understanding on the role of air quality in cloud microphysics.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
**4th International Symposium and IUAPPA Regional Conference**
**10-13 September 2012 Istanbul -Turkey**

# SHIPBORNE OBSERVATIONS OF AIR POLLUTANTS OVER THE WESTERN MEDITERRANEAN

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## ABSTRACT

Measurements of air pollutants in the Mediterranean Basin on monitoring stations and during short term campaigns have shown high levels of ozone as well as particulate matter. The sources appear to be local as well as long range transport. However large parts of the area is not covered by monitoring stations and there is in particular a lack of observations over the sea. In order to fill this gap and provide data that allow learning about sources of air pollutants and transformation processes, the JRC has initiated a long-term monitoring program in collaboration with the Italian cruise line Costa Crociere. Measurements have been performed regularly during spring-summer-autumn since 2006 from a monitoring station placed on Costa Crociere cruise ships following a fixed weekly route in the Western Mediterranean. Ozone and Black Carbon (using an Aethalometer) are measured, along with $SO_2$, NOx and particle size distributions. Also week-long campaigns with filter-sampling and subsequent chemical and OC/EC analysis have been carried out, as well as time-resolved analysis of the elementary composition of submicron aerosols by streaker-sampling followed by PIXE analysis. The data have been analyzed with the aim of gaining knowledge about the contributions of different sources to air pollution in the area. This analysis has been carried out by a combination of back-trajectory calculations, observations of correlations among trace gases as well as chemical and elemental components of aerosol and the use of a receptor model (Positive Matrix Factorization, PMF) to perform source apportionment. The largest contributions to particle mass were found to come from sulphate and organic matter. Using nickel and vanadium as tracers of ship emissions, strong evidence of a large contribution of ships to $SO_2$ and sulphate concentrations in the area was found. Occasionally also dust and sea salt gave important contributions to particle mass. Elevated concentrations of ozone over the sea was found to be frequently associated with subsidence of ozone rich air masses.

**Keywords:** Western Mediterranean, air pollution, measurements, shipborne

**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# QUANTIFICATION OF SAHARAN DUST ON ANATOLIAN PENINSULA VIA RAQMS MODELING

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## ABSTRACT

Sahara dust is correlated with high levels of aerosols in the Anatolian Peninsula. Ambient measurements conducted in 2008 show significant levels of PM10. These results are also consistent with MODIS Aqua (MYD04) and MODIS Terra (MOD04) aerosol product with aerosol optical depth (AOD) values between 0.6 and 0.8. Spatial and vertical distribution of aerosols, as obtained from CALIPSO data, suggest that dust cloud reach up to 6 km for the episode of April 11 to 18, 2008. In this study, we have utilized RAQMS (The Real-Time Air Quality Modeling System) model to explain the possible effect of Saharan dust on high levels of PM10 measured in the Anatolian Peninsula. Comparison of RAQMS model results with ground observations suggest a significant contribution of Sahara dust to high levels of PM10 in the Anatolian Peninsula.

**Keywords:** Sahara dust, RAQMS model, air quality, remote sensing

## 1. INTRODUCTION

Dust, typically mineral dust, which is injected into the atmosphere by surface winds from dry soils, contributes major part of aerosol mass loading (Tagen and Fung, 1994). Sahara originated dust is the most significant natural source of particulate matter (PM), which get transported towards the Atlantic Ocean, to the Mediterranean Sea and as well Southern Europe (Mitsakou et al., 2008; Kallos et al., 2007: Querol et al., 2004). It has been shown that high levels of PM10 is correlated with the African dust intrusion into the Mediterranean (Querol et al., 2009). The epidemiologic studies show that there is a clear link between the particulate matter and adverse health problems such as respiratory (i.e., asthma) disease, cardiovascular diseases (i.e., accelerated atherosclerosis, altered cardiac), pulmonary and systemic inflammation, lung cancer and even cause-of-death mortality (Pope, 2004; Atkinson, 2001; Peters, A., 2000). Aside from its effects on human health, particulate matter

also influences climate system due to either direct effects through scattering and absorbing the shortwave solar radiation or indirect effects by acting as a cloud condensation nuclei (CCN). Studies show that Saharan dust particles commonly act as CCN, modifying the cloud development and precipitation formation. (Twohy et al., 2009; Levin et al., 2005). Also change in the amount of dust load affects surface radiative heat flux and sea surface temperature (SST) (Foltz, 2008). Due to the high variability of dust loading over the Eastern Mediterranean, it is difficult to quantify the basin wide impact (Kubilay et al., 2000). There are several studies conducted for the Mediterrenean to quantify the relationship between Saharan dust outbreaks and PM10 concentration using satellite data, ground measurements and modeling systems. Mediterranean Sea is one of the areas in the world having optically thick aerosol layer. It is shown that all Saharan dust outbreaks over the Eastern Mediterranean follow a pathway starting from the source areas to the Eastern Mediterranean Sea (Papayannis et al., 2005). In their work, Gerasapoulous et al. (2006) identified the factors that control PM levels in Eastern Mediterranean region and they stated that the significant PM10 levels should be contributed to the dust outbreaks that is transported via southerly air mass from the Sahara desert. Bouchlaghem et al. (2009) presented Saharan dust outbreaks affecting Tunisian coast and its impact on PM10. The relationship between high levels of PM10 and intrusions of Saharan dust over the Iberian Peninsula is studied by Rodriguez et al. (2001). In both studies it is found that the average daily PM10 concentration values are higher on the days with Saharan dust contribution than the days with no dust event. Kallos et al. (2006) and Mitsakou et al. (2008) both used SKIRON modeling system to compare dust event forecasts with PM10 concentrations obtained from monitoring stations.

In this study, we have utilized RAQMS (The Real-Time Air Quality Modeling System) model to explain the possible effect of Saharan dust on high levels of PM10 measured in the Anatolian Peninsula. The focus of this study is to compare in-situ PM10 levels and the Sahara originated dust over the Anatolian Peninsula. The climatic impact of dust is also investigated via radiation budget analysis.

## 2. DATA

### 2.1. Ground-based Data

We used the ground observations conducted in Turkey by Turkish Ministry of Environment and Urbanization. Daily averages of PM10 data are obtained from 118-air quality stations distributed throughout Turkey for 2008. Figure 1 presents the monthly averages of PM10 throughout the year. As seen in the figure, monthly PM10 averages have a decreasing trend in the warm seasons. Annual average of PM10 concentrations in 2008 is 81.7 µg/m$^3$. Seasonal averages reach 109 µg/m$^3$ in winter, 80 µg/m$^3$ in spring, 62.5 µg/m$^3$ in summer and 72.5 µg/m$^3$ in fall months. High levels of PM10 for winter is expected as during this period pollution sources (both local and regional) are significant and atmospheric conditions do not favor dispersion. It is important to note that month of April had significantly high values with an average of 86.7 µg/m$^3$. Maximum PM10 values were recorded on April 14, 2008 with a daily average of 170 µg/m$^3$ (which is also the maximum PM10 observation measured in the year 2008). It is known that peak PM10 values caused by Saharan dust outbreaks occur in the transition seasons (Rodriguez et al., 2001; Gerasapoulous et al., 2006; Kallos et al., 2007; Mitsakou et al., 2008; Querol et al., 2009). A preliminary analysis of PM10 data for April 2008, as seen in Figure 2, suggested that Saharan dust might be an important contributor for high PM10 levels over the Anatolian Peninsula. Therefore, we have selected the period between April 11 and April 18 2008 as our episode in this analysis.

### 2.2 Model Description

NASA Langley Research Center/University of Wisconsin (LaRC/UW) Real-time Air Quality Modeling System (RAQMS) is a unified, meteorological and chemical modeling system for assimilating satellite observations of atmospheric chemical composition. The model also gives real time prediction information of trace gas and aerosol distribution (Pierce et al., 2003, 2007, Verma et al., 2009). It is a portable, multi-scale chemical transport model that can run either globally or regionally to predict stratospheric and tropospheric chemistry. RAQMS combines two meteorological forecast models developed at UW with a chemical prediction scheme, which was developed at LaRC (Pierce et al., 2003). It extends from surface to around 60 km via 35 vertical levels. The UW hybrid isentropic coordinate model, which is a global atmospheric model, is the dynamical core for the global component of RAQMS (Schaack et al., 2004; Pierce, 2007). The RAQMS aerosol model incorporates the Goddard Ozone Chemistry Aerosol Radiation and Transport (GOCART) model (Chin et al., 2002, 2003). It simulates sulfate, dust, black carbon (BC), organic carbon (OC), and sea-salt aerosols that are know as the major tropospheric aerosol components (Chin et al., 2002; Verma et al., 2009; Natarajan et al., 2012). The setup used in this paper to analysis dust emission has 2°x2° horizontal resolution.

### 2.3 Satellite Data Overview

High-resolution vertical profiles of clouds and aerosols are provided from CALIOP, which is the primary instrument carried by the Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observations (CALIPSO) satellite. CALIPSO includes a two-channel (532 and 1064 nm) polarization lidar that provide qualitative information on particle size. It helps not only in discrimination of cloud and aerosol, but also the identification of aerosol type (Winker et al., 2007). Aerosol subtype features and vertical structure of the atmosphere on April 14, 2008, when the highest PM10 concentration observed by the ground monitors, show that the dust aerosols reach up to 6 km over Anatolian peninsula (figure not shown). MODIS (The Moderate Resolution Imaging Spectroradiometer) Aerosol Product (MOD04 for Terra, MYD04 for Aqua), Collection 5 is used to get information about AOD, which represents columnar aerosol loading of the atmosphere at 550 nm. Figure 3 (a) and (b) shows the aerosol optical depth obtained from Terra and Aqua MODIS, respectively. AOD values vary between minimum of 0 and a maximum of 1. AOD seem to be between 0.5 and 0.7 for the western part of the peninsula whereas it is between 0.7 and 1.0 for the eastern part (Suggesting higher dust concentration) for Terra MODIS. For Aqua MODIS, similar conclusions can be made with a slight change in the AOD values.

## 3. RESULTS

Surface level output from the RAQMS model is used for the comparison of in-situ PM10 observations. For this purpose we have utilized the sum of the dust mass mixing ratios (kg/kg), which is the ratio of condensed particles to the total number density of the atmosphere, normalized by the air density at standard pressure and temperature. Figure 4 shows time series of April 2008 dust mass mixing ratio obtained from RAQMS modeling. There are two values seem to be over the 2 standard deviations from the mean value, April 14 and April 29 with values of 3.39 kg/kg and 3.61 kg/kg respectively. Figure 5 shows surface level dust aerosol RAQMS outputs for Eastern Mediterranean for 11-18 April 2008. In Figure 5a (11 April) high levels of PM10 can be seen over Italy and Greece and southeastern part of Turkey. It is likely that high levels of PM10 over the Southeastern Turkey is due to previous dust intrusions from Sahara or another source. Dust cloud moves towards northwestern part of Turkey on April 12 (figure 5b) and on April 13 (figure 5c), the cloud dominates the whole region. Sahara originated dust clouds cover the entire Anatolian peninsula on April 14, coinciding with the maximum PM10 concentration measured at ground stations. The Saharan transport also continues on April 15 and it gets weaker by the end of the episode. The model also shows the maximum dust loading on April 14, 2008 with mixing ratio value of 3.39 kg/kg, which is also 2 standard deviations (1.92 kg/kg) from the mean value (1.33 kg/kg). Overall, the model prediction is consistent with the ground observations as the model captures the increasing and decreasing trends. The only exception is for the period between 28 and 30 April, where the model shows an increasing trend while the observations have a decreasing trend. Even though RAQMS shows significantly high levels of dust in the eastern and southeastern part of Turkey, limited number of air quality stations located in those regions might be the reason minimizing the overall dust concentration effect. The correlation between the model and in situ observation is found to be 0.76. Further analyses will be conducted to compare model results and observations at a regional level.

## 4. CONCLUSIONS

In this study, we have utilized RAQMS (The Real-Time Air Quality Modeling System) model to explain the possible effect of Saharan dust on high levels of PM10 measured in the Anatolian Peninsula. Analyses show that PM10 levels change according to the time of the year. During the cold season, high PM10 levels are usually related to low boundary layer height and local pollution. In warm seasons, however, PM10 concentrations are reasonably lower than the cold season (see part 2.1). Since Saharan dust outbreaks occur in the transition seasons, high level of measured PM10 in April 2008 might be related to Saharan dust outbreak. Daily averages of dust mass mixing ratio are obtained from RAQMS to compare with in situ observations. The results suggest a significant contribution of Sahara dust to high levels of PM10 in the Anatolian Peninsula. The two datasets are found to be in agreement with a correlation of 0.76.

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## LIST of FIGURES

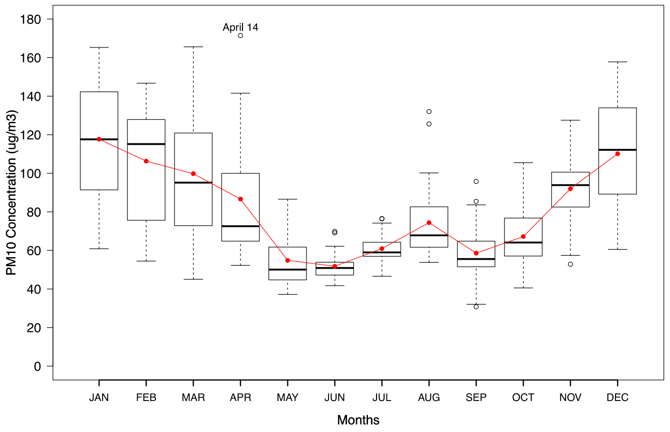

Figure 1: Monthly PM10 concentration of 2008 for Anatolian Peninsula. Maximum PM10 values were recorded on April 14, 2008 with a daily average of 170 µg/m$^3$ (which is also the maximum PM10 observation measured in the year 2008).

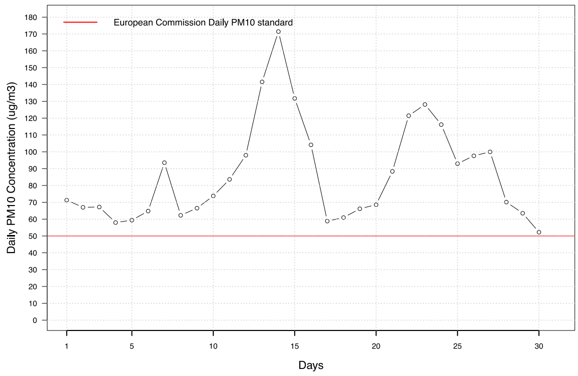

Figure 2: Time series of daily PM10 concentration for April 2008. All values seem to be over the European commission daily PM10 standard (50 ug/m$^3$). Monthly average of April is 86.7 µg/m$^3$.

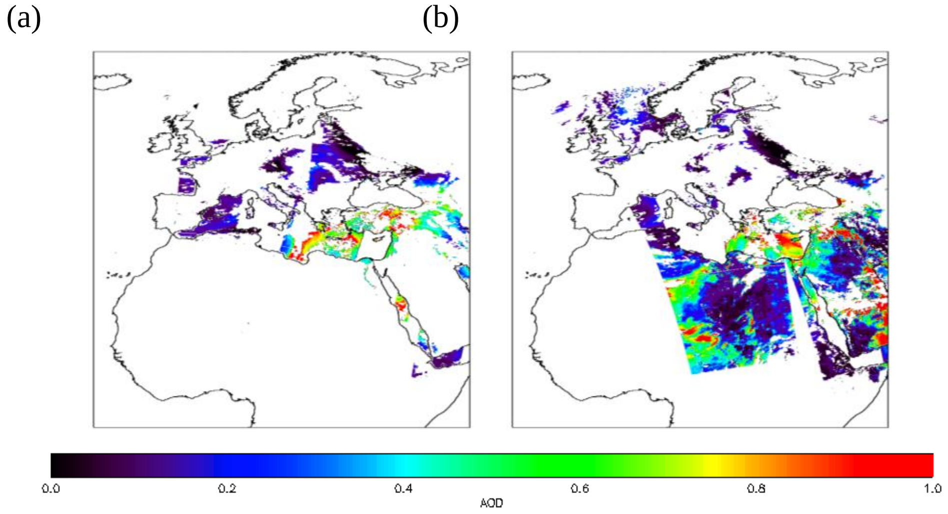

Figure 3: AOD obtained from (a) MOD04 (Terra) and (b) MYD04 (Aqua) aerosol product for Eastern Mediterranean Basin analyzed for April 14, 2008 when the maximum PM10 level was recorded.

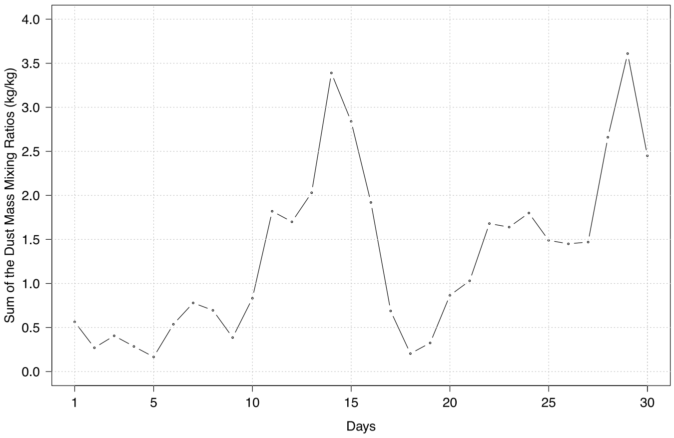

Figure 4: Time series of April 2008 dust mass mixing ratio obtained from RAQMS modeling.

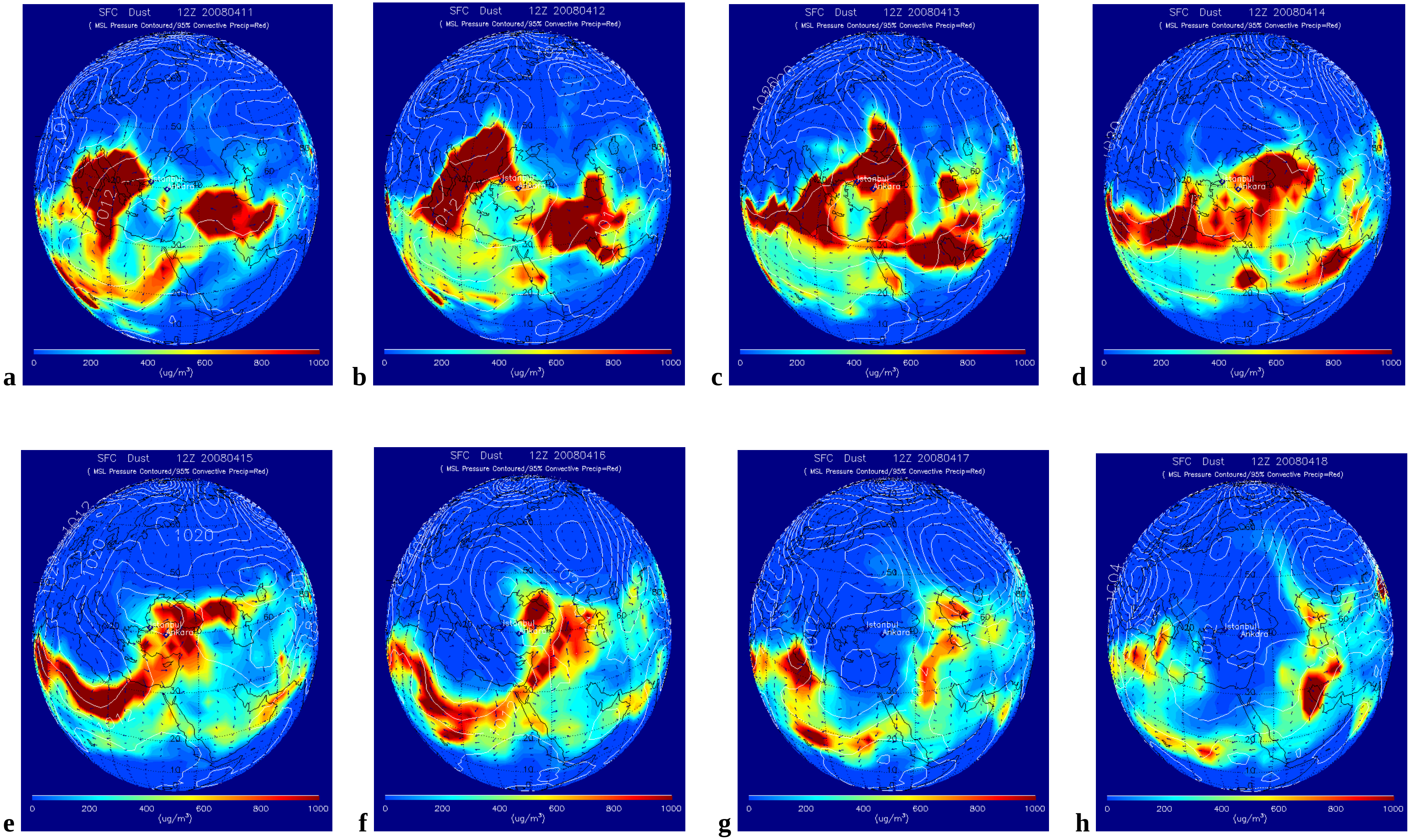

Figure 5: RAQMS outputs for Eastern Mediterranean for the selected episode (a-h refers to 11-18 April 2008, respectively).

**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
**4th International Symposium and IUAPPA Regional Conference**
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# AIR POLLUTION IN THE NORTHERN ADRIATIC COASTAL AREA - EVIDENCE OF LONG-RANGE TRANSPORT

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## ABSTRACT

Second indistrialization in mid-seventies caused high air pollution during the mid-eighties in the city of Rijeka. The extention of air pollution monitoring network to the further islands within the Kvarner bay area, gave evidence of the long range transport of pollutants, with primarely western origin (except Saharan sand episodes). Results of precipitation chemistry, PWA concentrations and wet deposition of sulphur and nitrogen, and high $NH_4^+$ contribution in total N deposition are in favour of regional transport of pollutants. The regional transport of ozone from the northern Adriatic was found to somewhat enhance the afternoon ozone concentrations in Rijeka.

**Key-words:** regional transport, precipitation chemistry, S and N deposition, Saharan sand episode, ozone

## 1. INTRODUCTION

Air quality monitoring in the city of Rijeka started in the early seventies, prior to building up new industrial plants in the eastern suburban area (new petroleum refinery facilities, coke-plant, oil fired power plant). Such intensive industrialization resulted in high air pollution within the city in mid eighties, that was one of the most polluted with $SO_2$ and other combustion products in Croatia. The outbreak of war and subsequent reduced industrial production and consequently emissions (Matkovic and Alebic-Juretic, 1998) led to considerable improvment of air quality within the wider city area since mid-nineties, following similar European trends.

Due to existing air quality problem in the area, the air pollution monitoring network was extended to remote island in the Kvarner bay (Cres, Losinj) in mid-eighties, and to the the background highlands area (Lividraga, Delnice) in mid-nineties ( Figure 1). The results of air quality monitoring on these remote stations indicated the impact of regional transport of air pollution, primarely affecting precipitation chemistry, wet and dry deposition of sulphur and nitrogen, and ozone.

## 2. RESULTS

Northern Adriatic Area (Figure 1) is affected by seasonal transport paths typical for south east Europe. The main trajectory directions are classified into:

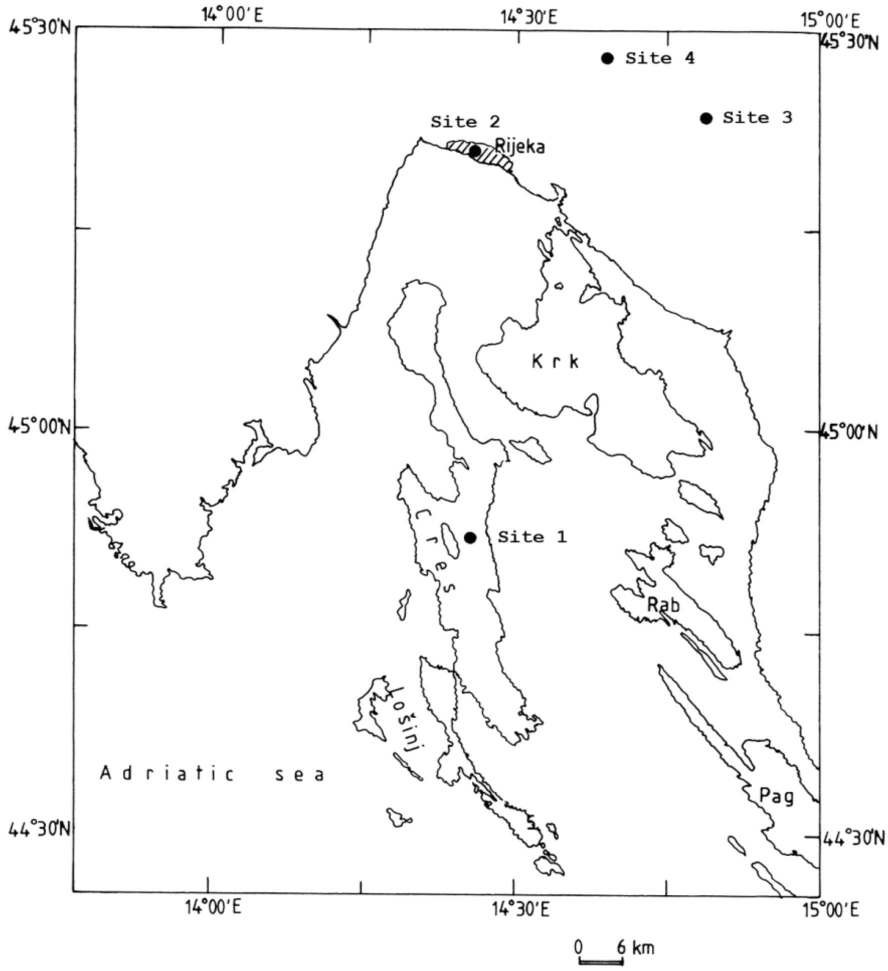

Figure 1: Location of remote monitoring sites in the Northern Adriatic area relative to the Site 2 (city of Rijeka, population cca. 130.000, 20 m a.s.l.,):

Site 1: Vrana, Island of Cres, an uninhabited remote site, about 60 km south of Rijeka, 250 m a.s.l.

Site 3: town of Delnice (population 6,200) in the mountainous inland area, 700 m a.s.l., about 50 km east of Rijeka

Site 4: Lividraga; an uninhabited mountainous resort, 930 m a.s.l., about 25 km NE of Rijeka.

a. The long track of maritime air masses from north-western Europe, predominantly in winter, that resulted in long-range transport of pollutants
b. Northeasterly continental flow originating from Eastern Europe that is dominant in summer
c. Westerly maritime flow from the Mediterranean, most frequent in autumn and winter with highest precipitation and deposition
d. South-southwesterly flow from North Africa, mostly during winter and spring, bringing Saharan sand (Katsoulis and Whelpdale 1990)

### 2.1. **Precipitation and deposition**

The first analyses of precipitation within Kvarner Bay area (1984-1991) indicated, besides the city, Site 1 to be affected by acidic rain ( pH medians=5.2-5.6). Having in mind the dominant air masses flows, the acidity was likely to be the result of regional transport. Thus, in the early nineties (1990/91), the wet deposition of nss-S-[$SO_4^{2-}$] was three times (0.44 vs 1.35 g $m^{-2}y^{-1}$) and total-N [$NO_3^-$+$NH_4^+$] two times (0.91 vs 2.06 g $m^{-2}y^{-1}$) lower than the corresponding values obtained in the city center of Rijeka, due to the local washout of the atmosphere. In spite of higher elevation at Site 1, 50% of sulphates were of marine origin (Alebic-Juretic, 1994). Total deposition of sulphur S-($SO_2$+$SO_4$) in the multiyear period 1988-1993 was also two times (1.64 vs 3.06 g $m^{-2}$ $y^{-1}$) and dry deposition of S-$SO_2$ even five times lower (0.2 vs. 0.97 g $m^{-2}$ $y^{-1}$) at the remote Site 1, comparative to the city of Rijeka in the same period (Alebic-Juretic, 1995).

If there were some doubts about the origin of the air pollution and long range transport, they were clarified through extension of precipitation analyses to the highlands district north from the city since 1996. Precipitation weighted average (PWA) concentrations of sulphates, nitrates and ammonium obtained at the remote Site 1 (island Cres) and highlands Site 3 (Delnice, approx 50 km east from Rijeka), were practically the same, thus indicating that the wet deposition of sulphur and nitrogen in the highlands area is mainly due to the long range transport (Figure 2).

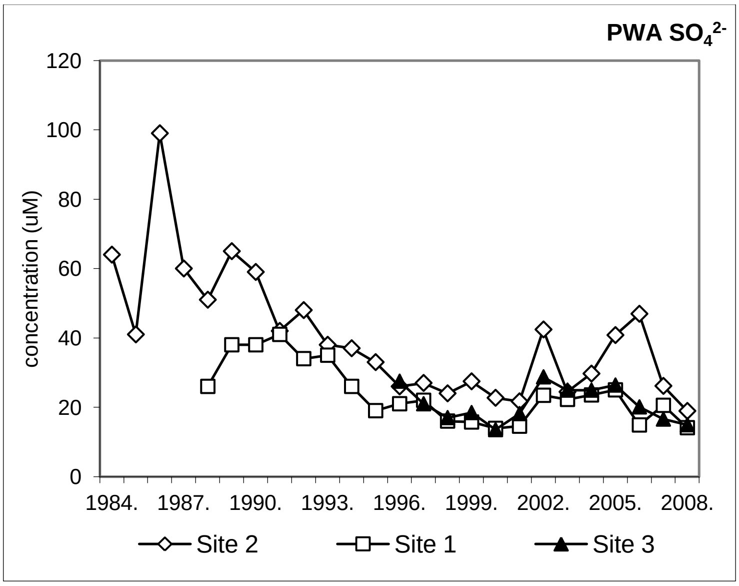

Figure 2: PWA concentrations of sulphates at urban Site 2 and remote Sites 1 and 3

Contrary to PWA concentrations, deposition of S and total N are similar and higher at urban and the highlands Site 3, with two different reasons behind: higher precipitation depths at the highlands site and local washout of the atmosphere in the urban more polluted site (Figure 3).

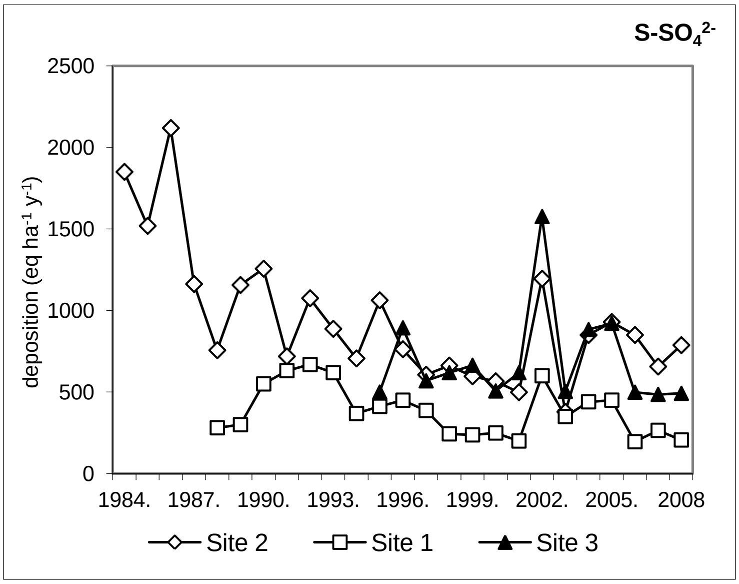

Figure 3: Deposition of sulphur as sulphates at selected sites

Dry deposition calculated as the difference between dustfall and bulk wet deposition showed a contribution of 70% to total S at urban Site 1, and only 30% to remote forest Site 4. Contrary, the contribution of dry N deposition was 30% at urban Site 1 and 45 % at remote Site 4, confirming the biogenic source of ammonia in the forest ( Micovic et al., 2010).

It should be kept in mind that the precipitation depth in this littoral-highlands area is very variable due to the complex orography. The annual precipitation depth is increasing from the island through the coast to the highlands area. The corresponding average annual values are: island: coast: highlands = 850 mm:1200 mm:1600mm, e.g. 1:1,5:2,0. Results of precipitation analyses indicate weak impact of the local emissions from the Kvarner bay area on the precipitation chemistry of the background highlands region, (Alebic-Juretic and Micovic, 2001; Alebic-Juretic, 2008) as previously assumed, and also confirm the predictions of some early modelling that estimated to < 3% the local contribution to the S and N wet deposition ( EKONERG, 1997).

The contribution of N-NH$_4$ to Total-N was initially found to be 2/3 at all three sites studied, suggesting possible regional transport to be the cause of, since neither there is big industrial source nor agriculture is important economic activity in the region (Alebic-Juretic and Micovic, 2001; Alebic, 2008). The N-NH$_4^+$/N-total ratio shows a declining tendency to approx ½ since 2004, due to increase of N-NO$_3^-$ contribution (Alebic-Juretic, 2012a). Since the emissions from the Rijeka bay do not affect the highlands area, and the same trend is observed at the remote island site, the increase of N-NO$_3^-$ might be due to incresed traffic of diesel vehicles in the wider transboundary area.

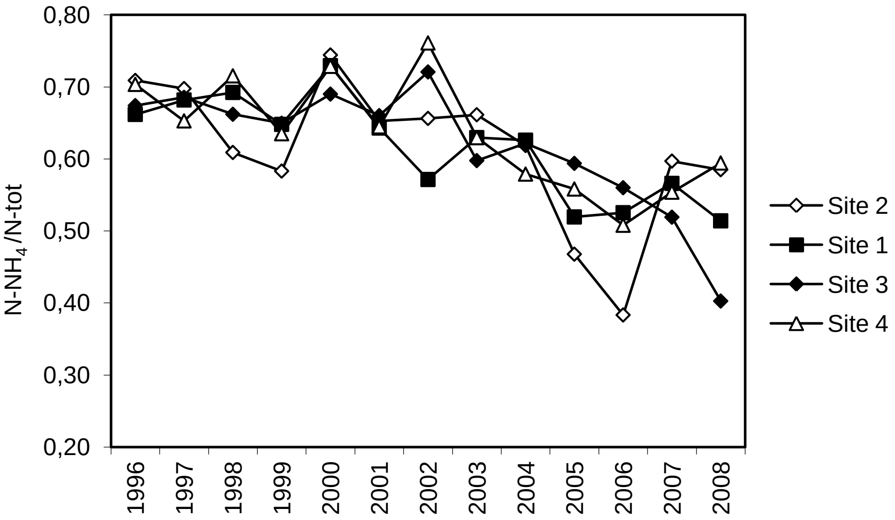

Figure 4: The ratio N-$NH_4^+$/N-tot in bulk deposition (Alebic-Juretic, 2012a)

## 2.2. Saharan sand episode

As seen from Fig 2., the highest PWA concentration and deposition of sulphates, but also nitrates and ammonium, was found in 2002. This year was exceptional fot two facts: the highest number of rainy days (172) and high precipitation depth ( cca 1700 mm) at urban Site 1, but also three times more frequent „yellow rains“, bringing Saharan sand to this area. An exceprionally intense Saharan sand episode was recorded on April, 12th 2002, over the whole Littoral-highlands County, except the southermost island of Losinj.

Synoptic situation behind was as follows: from 7th till 9th of April there was a small cyclone over Croatia, with circulation of moist and unstable air along the vertical. It was rainy in plains and valleys and snowy in mountainous areas. Over the Adriatic Sea severe gusts of scirocco were recorded first and, as the cyclone was moving, severe gusts of bora later. The next day (10th of April) was less rainy due to the influence of branch of the anticyclone over northern Europe. However, a new large cyclone, originated from the western Mediterranean, approached from the south-western Mediterranean. The high altitude wind was southwest. Due to this synoptic situation it was mainly cloudy from 11th till 15th of April, with severe scirocco in some places. Frontal passages brought heavy rain and thunderstorms, especially in the night from 12th to 13th of April. The greatest amount of precipitation fell over northern Adriatic Sea and mountainous areas (Spoler Canic et al., 2009), the very same for that the quantity of deposited Saharan sand was estimated.

„Yellow rains“ containing Saharan sand are characterized with high content of sulphates, nitrates and ammonium, but also calcium and iron, resulting with high pH (>6.5) From the dust samples collected in the polyethylene buckets used for dustfall sampling, the deposition of Saharan sand was estimated to 11000 t over the whole county area (1320 km$^2$). Analyses of insoluble (acidic extract) and soluble estimated total deposition of predominating ionic species as: 432 t of Fe, 2.06 t of $SO_4^{2-}$, 0.21 t $NO_3$, 0.16 t $NH_4^+$ and 1.23 t of $Ca^{2+}$ (Alebic-Juretic, 2005). Similar Saharan sand episode, though weaker ( 0,18 g m$^{-2}$ vs 8,2 g m$^{-2}$, recent ), was registered in Rijeka (Fiume) in March 1901 (Barac. 1902).

## 2.3. Ozone

Though air pollution monitoring dates back to mid seventies, the continuous ozone monitoring started in the city of Rijeka only in 1999, while the ozone analyzer was incorporated in the air quality monitoring network in mid-2000. The first analysis of ozone levels within Rijeka Bay area was done recently. Unusual diurnal profiles at more elevated and cleaner locations were explained by sea-breeze circulation of ozone rich air (Alebic-Juretic, 2012).

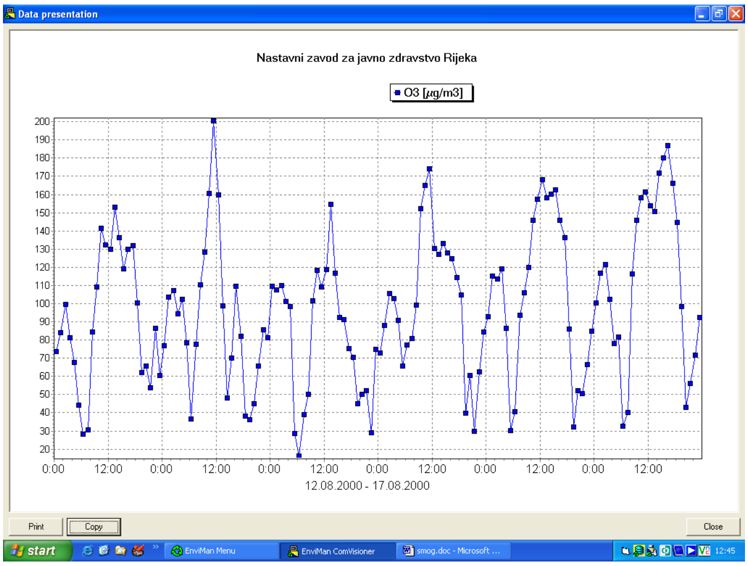

Figure 4: Elevated ozone epizode in August 2000 at urban Site 2 (Rijeka).

In the period 13th-19th August 2000, an unusually high ozone concentrations were observed, with maximum hourly afternoon concentrations exceeding the ozone information level of 180 µg m$^{-3}$, while nocturnal levels were well above 100 µg m$^{-3}$.

As that was the only monitoring station measuring ozone in the wider area, the comparison with other results was not possible.

Available ozone and meteorological data were analyzed along with supplemental numerical simulations and trajectories. Atmospheric conditions were favourable to ozone production because of high air temperatures (and consequently high insolation) associated with (i) Exchange of two dominant ( although relatively weak) large scale flows: southwesterly versus northeasterly bora winds, and (ii) local thermal circulation. Although the bora dilluted the atmosphere above the northern Adriatic region and carried the polluted air in the direction of the western Adriatic coast, the southwesterly flow returned ozone rich air towards the Alps, thus contributing to the overall pollution over the northern Adriatic Sea. Models revealed the superosition of the southwesterly wind and local, thermally induced wind that caused the regional transport pf ozone toward the Alps and the eastern Adriatic coast. While the regional transport of ozone from the Northern Adriatic enhanced somewhat the afternoon ozone concentrations in Rijeka ( especially towards the end of the period studied), its surrounding emission sources, uniform local thermal circulation system and recircularion of pollutants were crucial factors in the fo of the large daytime and nocturnal ozone levels observed in Rijeka ( Talisman et al., 2012)

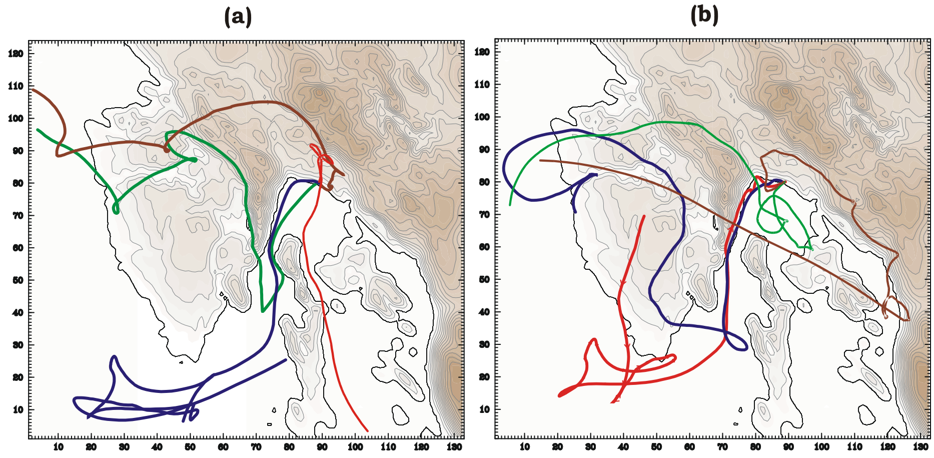

Figure 5: Air mass trajectories and ozone for a. 18.08.2000. and b. 19.08.2000., that brought elevated ozone concentrations in the Rijeka Bay (Talisman et al, 2009).

## 3. CONCLUSION

Long-term monitoring of air pollution in the Northern Adriatic area indicated the impact of transboundary pollution. The most likely source of such pollution is the Po Valley regarding precipitation, deposition and ozone. More detailed study of this phenomenon would be very appreciated.

In spite of their natural origin, the Saharan sand episodes might be connected to the global warming phenomenon. Increased frequency of „yellow rains“ in the last two decades prove the more frequent outbreak of warm air from the African continent to Europe, causing the air temperature rise.

## ACKNOWLEDGMENT

A long-term technical assistance of the Environmantal Health Department stuff is gratefully acknowledged. This work is the result of work on two projects supported by the Croatian Ministry of Science, Education and Sport (grants No. 062-0621341-0308 and No. 098-0982915-2947)

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# ADVANTAGES & BENEFITS OF USING OPEN-PATH DIFFERENTIAL OPTICAL ADSORPTION SPECTROSCOPY (DOAS) IN AMBIENT AIR & SOURCE EMISSION MONITORING PROGRAMS

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## ABSTRACT

This paper presents a general technical explanation of the principle behind the open-path Differential Optical Adsorption Spectroscopy (DOAS) technology and how this technology has been successfully applied to the measurement of sub-ppm ambient air pollutant levels, and gaseous pollutants found at much higher concentrations in the exhaust stacks and ducts of industrial facilities. The paper provides a brief history of the development of this technology and the reasons why this technology has steadily become the major alternative to conventional monitoring techniques over the past decade or so in many parts of the world. Technical differences as well as similarities of open-path DOAS technology versus conventional single-pollutant, single-analyzer approach are addressed for ambient air monitoring with an examination of the inherent problems associated with conventional ambient air monitoring techniques when a comprehensive quality assurance program is not followed. Environmental compliance benefits for a company or organization using open-path DOAS to generate an expanded database of ambient air pollutant concentration levels is also presented. The application of open-path DOAS technology to the measurement of gaseous emissions under high temperature, high humidity, and high particulate conditions is also covered. The technical advantages and cost-effective benefits of DOAS in source emission monitoring is compared to conventional stack monitoring techniques such as Continuous Emission Monitoring Systems (CEMS). The paper concludes with a summary view of the overall cost savings and technical benefits of an open-path DOAS ambient air monitoring station versus typical conventional air monitoring station, and an in-stack DOAS system versus typical CEMS.

**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# COMPILATION OF AN INDUSTRIAL EMISSION INVENTORY FOR TURKEY

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## ABSTRACT

The broad objective of this study is to examine $CO_2$, PM, $SO_2$, CO, $NO_x$, NMVOC, VOC, $CH_4$, and $N_2O$ emissions of petroleum refining, chemical, cement, metallurgical, pulp and paper, sugar industries of Turkey. Each of the industry is separated into two parts regarding to their emission emitting sources; process emissions and fuel combustion emissions. However only process emissions are considered in this study for both of controlled and uncontrolled conditions. Regarding to results of the study, the most emission emitting sector is determined as mineral industry and iron& steel industry. Respectively, petrochemical, petroleum refining, and pulp & paper industries have serious contributions to turkey’s air pollutants emission inventory.

**Keywords :** air pollution, emission inventory, industry, Turkey

## INTRODUCTION

Turkey as a candidate of European Union has to harmonize its legislation with EU legislation. Related with this subject, studies on National Emissions Ceilings Directive (NECD) are being conducted nowadays. Emission inventories and emission projections, regulatory impact assessments, establishing long term air quality strategies, and generating procedures for corporate structure, technical capacity are being conducted.

Also there are some annual reporting requirements of national total emissions of greenhouse gases and air pollutants in response to obligations under international conventions and protocols; United Nations Framework Convention on Climate Change (UNFCCC) for greenhouse gases and to the UNECE Convention on Long-Range Transboundary Air Pollution (LRTAP) for air pollutants. 2010 emission inventory is submitted on 13 April 2012 by Turkish Statistical Institute (TurkStat, 2012) to the UNFCCC. Additionally the last submitted emission inventory to LRTAP is prepared for 2009.

## METHODOLOGY

The method is applied in four steps. In the initial step, key categories were determined by investigating former studies, other countries’ emission inventories and national emission inventory (NIR) of Turkey which is prepared by TurkStat every year. Some of the sectors are not included in NIR Turkey 2010; therefore a detailed study is maintained for Turkish industry. In the second step activity data and other important specific data were collected by using either of top-down and bottom-up approaches. Generally top-down approach is used. The third stage is emission factor analyzing. Emission factors are derived from numerous sources. If emission factor does not exist in main EF sources or not compatible with Turkish industry, than an emission factor is generated using mass balances by using the manufacturing process details of the industry. If it is possible Tier-2 /3 methods are used, otherwise Tier-1 is used for calculations. The fourth stage is the calculation of both controlled and uncontrolled emissions. For controlled emissions, abatement technologies are decided by using the information gathered from industries and open sources otherwise assumption method is used by considering general approaches sector by sector. If the controlled condition emission factor did not exist, it was calculated by using abatement efficiency and uncontrolled emission factors or vice versa.

The basic method depicted by the following Eq. (1) for uncontrolled conditions and Eq. (2) for controlled conditions;

$$E = AD \times EF \tag{1}$$

$$E = AD \times EF \times (1-AE\%) \tag{2}$$

where E presents the emission of each species from different sources; AD presents activity data of product; EF presents the average emission factor; AE% presents abatement efficiency percentage; the activity data sources and emission factors used for compiling the emission inventory are briefly introduced below, sector by sector.

There are some other studies about emission inventories generally about energy industries or industrial emissions for a region or for large emission emitting sources. Up to now, there is no actual study investigates air pollutions of sub-sectors for all of these parameters for both of controlled and uncontrolled conditions. Unlike other studies, uncontrolled condition is investigated for each of the sub-sector and existing and/ or possible abatement technologies are used for the calculations of controlled emissions.

## RESULTS

Uncontrolled process emissions are calculated to show the effectiveness of the controlling technology. Process emissions do not include emissions of public electricity and heat production. Emissions are given in Table 1.

$CO_2$ emissions accounts 83% of all emissions (Figure 1) by contribution of mineral industry (cement, lime, glass, carbide) as 60% of all $CO_2$ emissions. The other sources of $CO_2$ emissions are 36% of from iron and steel industry, 3% from inorganic chemicals industry, 1% from non-ferrous metals and 0.3% from organic chemicals industry. No controlling technology is assumed for $CO_2$ emissions, therefore there is no difference between controlled and uncontrolled $CO_2$ emissions. $CO_2$ emissions account 99% of all controlled emissions (Table 2) emitted from industrial processes because controlling technologies are applied to other pollutants except $CO_2$.

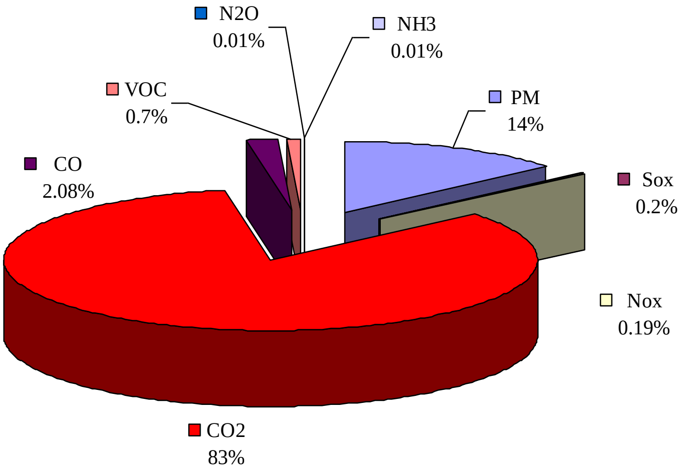


Figure 1: Uncontrolled process emission distribution

PM emissions account 14% of uncontrolled emissions. However, mineral industry accounts 81% of all industries' PM emissions under uncontrolled conditions. The industry reduces its PM emissions up to 36% under controlled conditions because of the usage of effective PM control technologies in the cement factories such as ESPs and fabric filters which have nearly 99% abatement efficiencies. Iron and steel industry accounts 9% of PM emissions under uncontrolled conditions and 45% under controlled conditions despite of reducing PM emissions from 809,696 ton to 20,723 ton, the sector share is affected from high reduction amounts in mineral industry.

SOx process emissions are mainly emitted by petroleum refining industry catalytic cracking systems, iron and steel industry furnaces, pulp and paper production by sulphite method. These three industries cover 86% of SOx emissions emitted by all industry processes under uncontrolled conditions. SOx abatement methods such as flue gas desulphurisation, scrubbing, feedstock hydrodesulfurization are used to calculate controlled SOx emissions; finally 80-85% SOx reduction is achieved. Thus the SOx amount is reduced to 25,154 from 147,567 ton.

Process related NOx emissions are mainly emitted by mineral industry (76%) inorganic chemicals (11%) and iron and steel industry (8%) and pulp and paper industry (4%) under uncontrolled conditions. 10,762 ton of the uncontrolled NOx process emissions come only from nitric acid production in the inorganic chemicals industry. Nitric acid production related NOx emission is also calculated for LRTAP convention as 7,080 ton for 2002, and Petroleum and glass industry process related NOx emissions are calculated in NIR 2010 Turkey. NOx control technologies are considered for each of the industries. Generally staged combustion (20-30% abatement efficiency), catalytic reduction (approximately 50% abatement efficiency), low excess air combustion (15-20 % abatement efficiency) [156] techniques are accepted to be used by industries for the control of the NOx emissions; finally emissions are reduced by 40%.

Uncontrolled CO emissions are mainly emitted from catalytic cracking units of petroleum refining processes (65%), pulp and paper production by kraft method (16%), non-ferrous metals (12%), and others. CO emissions are generally sent to flare. Thermal cracking or oxidative oxidation techniques are used to control CO emissions. In this study thermal cracking method is used with the assumption of approximately 95% abatement efficiency. Finally industrial processes originated, controlled CO emission is found 40,320 ton which is reduced from 1,378,593 ton.

Totally 3000 ton $CH_4$ emissions are emitted by aromatics, ethylene oxide and acrylonitrile production in organic chemicals industry (46%), coke production in integrated iron and steel plants (40%), and carbide production in mineral industry (14%) for uncontrolled conditions.

Table 1. Uncontrolled Process Emissions of the Industries

| **Paramaters** | **TOTAL** | Petroleum refining | **Chemical Industry** | | Mineral Industry | **Metallurgical Industry** | | Pulp and Paper | Sugar |
|---|---|---|---|---|---|---|---|---|---|
| | | | Organic Chemicals | Inorganic Chemicals | | Iron and Steel+EAF | Non Ferrous Metals | | |
| PM | 8,966,190 | 36,827 | 94,271 | 244,131 | 7,226,854 | 809,696 | 55,293 | 498,779 | 340 |
| $SO_x$ | 147,567 | 32,403 | 187 | 6,192 | 48,073 | 19,975 | 8,922 | 31,815 | |
| $NO_x$ | 124,878 | 1,700 | | 13,266 | 94,452 | 10,404 | 510 | 4,545 | |
| $CO_2$ | 55,123,087 | | 163,199 | 1,825,078 | 32,927,740 | 19,915,996 | 291,073 | | |
| CO | 1,378,593 | 57,805 | 19,591 | 12,516 | 130,029 | 805,857 | 154,104 | 198,690 | |
| $CH_4$ | 3,000 | | 702 | | 1,831 | 468 | | | |
| VOC | 285,362 | 88,136 | 48,186 | 150 | | 41,291 | 307 | 75,001 | 24,386 |
| $N_2O$ | 6,921 | | | 6,671 | 250 | | | | |
| $NH_3$ | 8,920 | 201 | 19 | 8,672 | | 28 | | | |

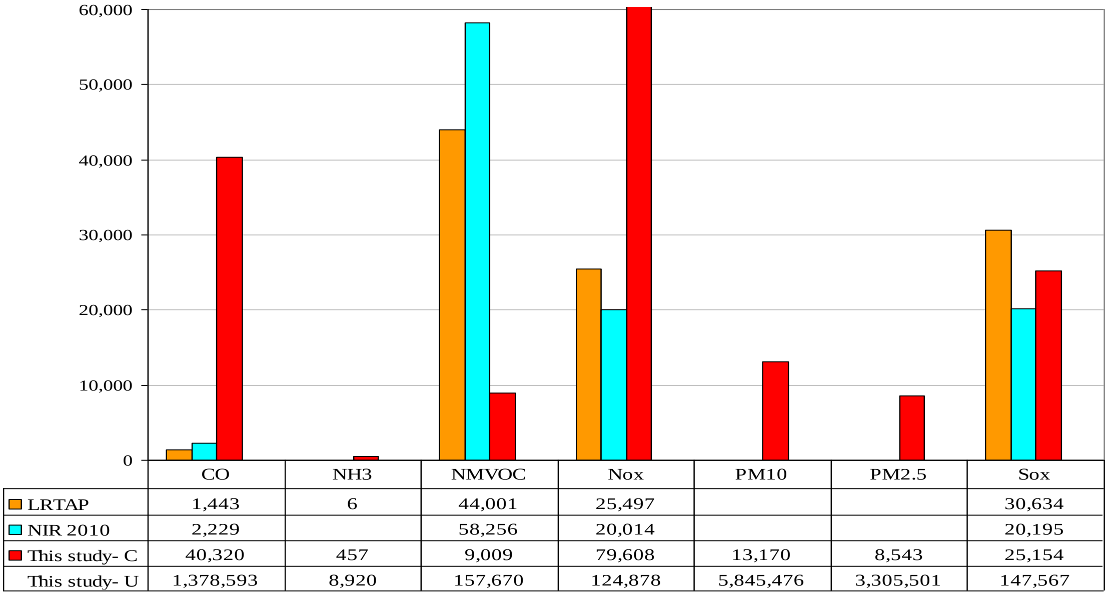
Table 2. Controlled Process Emissions of the Industries

| **Paramaters** | **TOTAL** | Petroleum refining | **Chemical Industry** | | Mineral Industry | **Metallurgical Industry** | | Pulp and Paper | Sugar |
|---|---|---|---|---|---|---|---|---|---|
| | | | Organic Chemicals | Inorganic Chemicals | | Iron and Steel+EAF | Non Ferrous Metals | | |
| PM | 45,736 | 1,841 | 1,424 | 1,903 | 16,219 | 20,723 | 1,115 | 2,494 | 17 |
| $SO_x$ | 25,154 | 4,860 | 187 | 438 | 7,211 | 5,648 | 446 | 6,363 | |
| $NO_x$ | 79,608 | 510 | | 2,431 | 66,117 | 7,283 | 86 | 3,182 | |
| $CO_2$ | 55,123,087 | | 163,199 | 1,825,078 | 32,927,740 | 19,915,996 | 291,073 | | |
| CO | 40,320 | 2,890 | 927 | 146 | 2,601 | 16,117 | 7,705 | 9,935 | |
| $CH_4$ | 133 | | 101 | | 8 | 23 | | | |
| VOC | 41,758 | 32,254 | 3,283 | 22 | | 1,214 | 15 | 3,750 | 1,219 |
| $N_2O$ | 2,264 | | | 2,252 | 12 | | | | |
| $NH_3$ | 457 | 20 | 3 | 433 | | 1 | | | |

The almost entire amount of $N_2O$ emissions (6,921 ton for uncontrolled conditions) is emitted from nitric acid production in inorganic chemicals industry. Controlled conditions' emission is calculated by considering catalytic reduction technology for some of the industries,

$NH_3$ emissions are mainly emitted from soda ash, fertilizer and ammonia production in the inorganic chemicals industry. 85-95% abatement efficiency is accepted for scrubbers when calculating controlled $NH_3$ emissions and the emission is reduced to 457 ton from 8,920 ton.

Some of the pollutants are calculated in other studies such as NIR 2010 Turkey and European Environment Agency LRTAP Convention. Comparison of the results is given in Figure 6.34. Only current emission inventories are considered in the chart for comparison. LRTAP emissions are calculated for 2009, NIR is calculated for 2010.



| | CO | NH3 | NMVOC | Nox | PM10 | PM2.5 | Sox |
|---|---|---|---|---|---|---|---|
| 🟧 LRTAP | 1,443 | 6 | 44,001 | 25,497 | | | 30,634 |
| 🟦 NIR 2010 | 2,229 | | 58,256 | 20,014 | | | 20,195 |
| 🟥 This study- C | 40,320 | 457 | 9,009 | 79,608 | 13,170 | 8,543 | 25,154 |
| This study- U | 1,378,593 | 8,920 | 157,670 | 124,878 | 5,845,476 | 3,305,501 | 147,567 |

**Figure 6.4 :** Process emissions comparison with other studies

$NH_3$ emissions are not calculated for the industrial processes in NIR, but it is calculated in LRTAP as very low as 6 ton for only nitric acid production. This value seems not realistic for the Turkish industry which has large fertilizer production plants.

CO emissions are very high when compared to other studies, despite of controlled emissions are evaluated in this chart. Because CO emissions are calculated only for mineral and petroleum refinig industries in NIR 2010, but 45% of CO emissions comes from metallurgical industry even though under controlled conditions.

$NO_x$ emissions are calculated by all of the studies. The result of this study (79,608 ton) which represents controlled conditions seems higher when compared with NIR (20,014 ton by including only petroleum refining and glass industry) and LRTAP (25,497 ton by excluding cement, non ferrous metals, pulp and paper industries). But Cement industry fuel combustion related $SO_x$, $NO_x$ and NMVOC emissions are evaluated as process emissions in this study.

## CONCLUSIONS

This study, using the best available data and knowledge, presents a detailed emission inventory of Turkish process industry. The inventory shows the largest contributors of the air pollution from industrial processes are respectively mineral industry and iron and steel industry.

Turkey should determine a ceiling for the emissions originated from energy industries and industrial processes. This is an obligation because of the harmonisation of Turkey's legislation with NEC directive which is applied for 15 years in European countries and Turkey is under preparation for the harmonisation of this directive. Development potential, resources, technologies, the quality of natural resources and economic power should be considered for determining ceilings for the parameters of the NEC Directive.

The share of the pollutants generated from industrial processes in the 'process + energy' emissions is summarized like that; process related PM emissions account 28% of all PM (energy + process) emissions, $SO_x$ is 1%, NOx and $CO_2$ are 3%, CO is 9%, $N_2O$ is 56%, NMVOC is 23%.

Despite of accounting 1% of all emissions (process+energy) under controlled condition, 147,567 ton SOx emission is emitted from industrial processes contributes to acidification, with potentially significant impacts including adverse effects on aquatic ecosystems in rivers and lakes, and damage to forests. Also 3% NOx emissions emitted from only industrial processes, which is a greenhouse gas, have same symptoms with SOx emissions.

Further studies can include future projections with scenario analyzing by considering development rate and planned measurements of the country up to 2050. Same studies should be maintained for transportation, residential heating, waste management, agriculture sectors. Sound databases should be reached easily for public usage and to be used in emissions calculations and specific emission factors should be generated for Turkey.

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# DEFINING SOCIALLY OPTIMAL EMISSION STANDARDS FOR THERMAL POWER PLANTS IN CHILE

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## ABSTRACT

In Chile, fossil fuel power plants account for the biggest share of electricity matrix, with up to 60% of the installed capacity in 2009. Air pollutant emissions from these power plants contribute to increase the already high ambient air pollutant concentrations, with the consequent welfare losses for the population. Due to increased concern about the impacts of thermoelectricity, and because of the expected high growth in the fossil fueled plants capacity, in 2010 Chile set standards for emissions of particulate matter (PM), SO2 and NOx from power plants. We present a cost-benefit analysis to establish the optimal emission level for each energy facility from 50 MWt in the country (77). Our approach intends to maximize the net social benefit, including health risk reductions and agriculture crops improvements, and pollution control measures costs. We also evaluated the net social benefit of several alternative standards for PM, SO2 and NOx such as the Chilean regulation, the World Bank recommendation and European Union emission standards. Using a simple dispersion model, we made an estimation of the marginal damage for each emitted ton of the analyzed pollutants, for every Chilean thermoelectrical facility (2009 US dollars). The mean marginal damage estimated amounts US$ 1 900, 13 000, 213 per ton for NOx, PM and SO2, respectively. The net social benefit present value obtained in an optimized regulated scenario was US$ 400 million, US$ 100 million higher than World Bank recommendation. However, when compared to the Chilean and EU regulation, it reaches even higher revenues that amount s US$ 800 and US$ 760 million higher net benefits respectively. These results can be related to the more stringent limits set for SO2 and the lower marginal damage estimated for this pollutant. Finally, we discuss the advantages and disadvantages of the propose methodology.

**Keywords:** Cost-benefits analysis, optimizing, marginal damage, externalities, fine particulate matter, power plants

**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# PAPER ON RISK ASSESSMENT METHODOLOGY TO MINIMISE THE IMPACT OF POLLUTION & REDUCING THE ROAD CRASHES

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## Objective

The purpose of this procedure is to define process for hazard Identification, risk assessment and control of risks associated to transportation and development of operating control procedures to minimize the impact of pollution & reduce the risk of accidents.

## Scope

In any plant or a premises, there are multiple vehicle operations which are required to run & manage the operations efficiently. This becomes more complex in large manufacturing units where multi scale operations are performed to optimize the efficiency.

The hazard identification process related to transportation covers all the factors in & around a plant/ office/ area. The hazards could be related to movement of non motorized & motorized vehicles & equipments such as:

**a. Non Motorized**

Handcarts, Bicycle,

**b. Motorized**

2W : Moped, Motorcycle, Scooter

4W: Car, Light Motor Vehicle, Heavy Motor Vehicle, Bus, Dumper, Fire Tender, Tractor

Equipment: Crane, Drilling Machine, Excavator, Forklift,

The operation covers all types of activities related to these vehicles including routine, non routine & emergency operations. The details are captured activity wise as per the activity flow charts. When these operations are evaluated suitable evaluation of risk is done as per defined risk assessment methodology.

## Activity Risk Assessment

i) Identify the activities carried out in each departments related to transportation. Following inputs shall be considered while identifying the activities:

   a. Up to date site layout diagram/ process flow sheets for identification of complete transportation activities

   b. All the transportation operations including motorised & non motorised vehicles.

   c. All activities having previous records of Incidents & accidents

   d. Inputs from regular Plant & Management Review meetings/ Safety inspections/ records. Details of training conducted for the drivers & operators.

e. All routine activities *(those activities which are scheduled & carried out frequently) &* All non-routine activities *(those activities which are not done in scheduled time or done occasionally)*

f. Examination of all existing safety procedures and practices used for transportation activity which includes training records & maintenance data for the vehicles

g. Activities of all personal having access to work place (including sub contractors & visitors).

h. Equipment Manufacturers Documents / IS codes for to follow correct maintenance procedure for each vehicle/ equipment

i. Identification of pollution levels at various locations

ii) Break the activities into sub-activities. The process is very important for the hazards identification & using appropriate controls. For example the cement is filled in the bags & then transported out of the plant. For this activity, the sub activities could be:

a. Identification of correct vehicle for loading

b. Checking the documents & vehicle road worthiness before loading the finished goods ( cement)

c. Preparation of gate pass for allowing the vehicle inside

d. Check pollution level for the vehicle entering the plant

e. Explaining the driver to use the Personal Protective Equipment & follow all the rules laid down as per road safety policy

f. Follow a specific path for in & out movement

g. Waiting & parking procedure at the finished goods ( cement) loading area

h. Finished Goods loading

i. Preparation of correct documents for finished goods

j. Leaving the plant on the designated route.

iii) Identify all relevant hazards related to each sub-activity. Consider who might be harmed, what might be damaged. Consider the time lapse & procedures so that the vehicle & driver stays in the plant for the optimum time. Refer to the annexure for categorisation of hazards and their subcategories.

iv) Identification of the hazards can be done through:

a. Consultation with managers, supervisors, employees, safety Representatives and others;

b. Reviewing hazard reports;

c. Records of past incidents involving injury and illness highlight sources of potential harm. Check SOT reports

d. Review of plant and equipment maintenance records;

e. Workplace/ site inspections;

f. Data for pollution levels inside the plant at various locations

g. External sources of data and information;

## Assessment of Risk

a. Each hazard identified shall be estimated for the risk, taking into consideration the existing controls. Likelihood of occurrence of the event and severity level (i.e consequence rating ) shall be identified as per the adopted matrix.

b. Assess the level of risks related to the identified hazard as per the risk classification matrix.

c. Risks shall also be assessed with respect to the prevailing motor vehicle rules.

## Control of Risk

i. Depending upon the risk level, plan shall be prepared to control the risk.

ii. Risks shall be controlled as per the hierarchy of controls.( Refer Annexure III)

1. Elimination of the hazard
2. Substitution/ Minimisation
3. Engineering controls
4. Segregation
5. Administrative (Including reduction in Personnel/ Time Exposure)
6. Personal Protective Equipment

d. As per the hierarchy identified, Management shall prepare Management program to deal with the identified hazard and the risk associated with it.

e. There shall be a review mechanism developed to assess the progress on the Management programs.

f. Risk assessments conducted of all the activities will be documented.

g. The results of risk assessment shall be considered in setting OH&S objectives and targets/ Operating control procedures/ measurement and monitoring, Training and any other relevant control measures.

## Review of the risk assessments

i. Risks shall be reviewed after the recommended controls are implemented and same shall be updated in the risk assessments.

ii. Risk assessments shall be reviewed annually or whenever there is any introduction of new process/ project/ activities/ raw materials/ personnel/ equipment.

## Methodology:

The site visit is carried out for a period of 2-5 days depending on the size of the plant & process of observation of complete operations involving transportation of vehicles. During the site visit, the entire route mapping for each category of vehicle is carried out separately. The route mapping is required to understand the flow of the particular class of vehicle or material. The mapping includes the process flow chart, operational procedure ,possible deviations & analyzing routine & non routine activities. Thus if a raw material truck is entering the plant the process such as generation of documents & gate pass, presentation of the documents, verification of vehicle & driver details, weighment procedure, route followed for unloading the raw material in the designated area, weighment procedure, collecting the final documents & leaving are some of the major features which needs to be analyzed. The points mentioned above are termed as routine activities. However there could be non routine activities such as if the vehicle breaks down, if the raw material is not matching as per specifications or any deficiency in the documents which leads to returning the loaded truck, the driver is feeling sick, process to be followed in case of any accident or mishap on the road. This list could be endless. But all operational process needs to be observed & documented with possible hazards. Thus in case of a breakdown in the vehicle the driver may get down on the road, try & repair the vehicle with the help of a mechanic or just rest around the vehicle till he gets suitable support are some of the hazards observed & can be documented. Such process needs to be followed for all the routine & non routine activities. If the activities covers multiple areas of operations, obviously the observations would be more complex & overlapping other activities.

The whole road network or the area where the vehicles are being operated needs to be scrutinized. It is necessary to check that the infrastructure inside the plant in terms of road conditions, width, road furniture & illumination levels are adequate. Suitable observations on such conditions need to be documented. The base for such observations could be the road safety policies of the company or the government guidelines whichever are stringent.

In addition to observation of the operations & various activities, the team is supposed to meet various stake holders related to transportation. Thus it is necessary to plan & meet the team from the corporate who is responsible to select, operate & control these vehicles inside a plant. If the truck is owned & managed by an external agency, the discussions should also include the agency selection, driver selection & journey management procedures. Many hazards are highlighted during such observations which might allow a vehicle in poor condition or a driver in drunken state. Pollution levels to be checked at various locations as well as for the vehicle entering the plant. In addition to the corporate side, it is necessary to meet & interview the drivers & operators who are driving inside the plant on a regular basis. Their feedback on road infrastructure, various driving concerns & bottlenecks should be vital cog to understand the operational hazards & risks associated. Some pedestrians can also be asked about the observed operational deficiencies. It is important to mention here that more detailed the observations & hazard identification, better the risk analysis for transportation. Some of the observations are likely to get substantiated thru Safety Observation tours & data of accident/ incident reporting collected from the management.

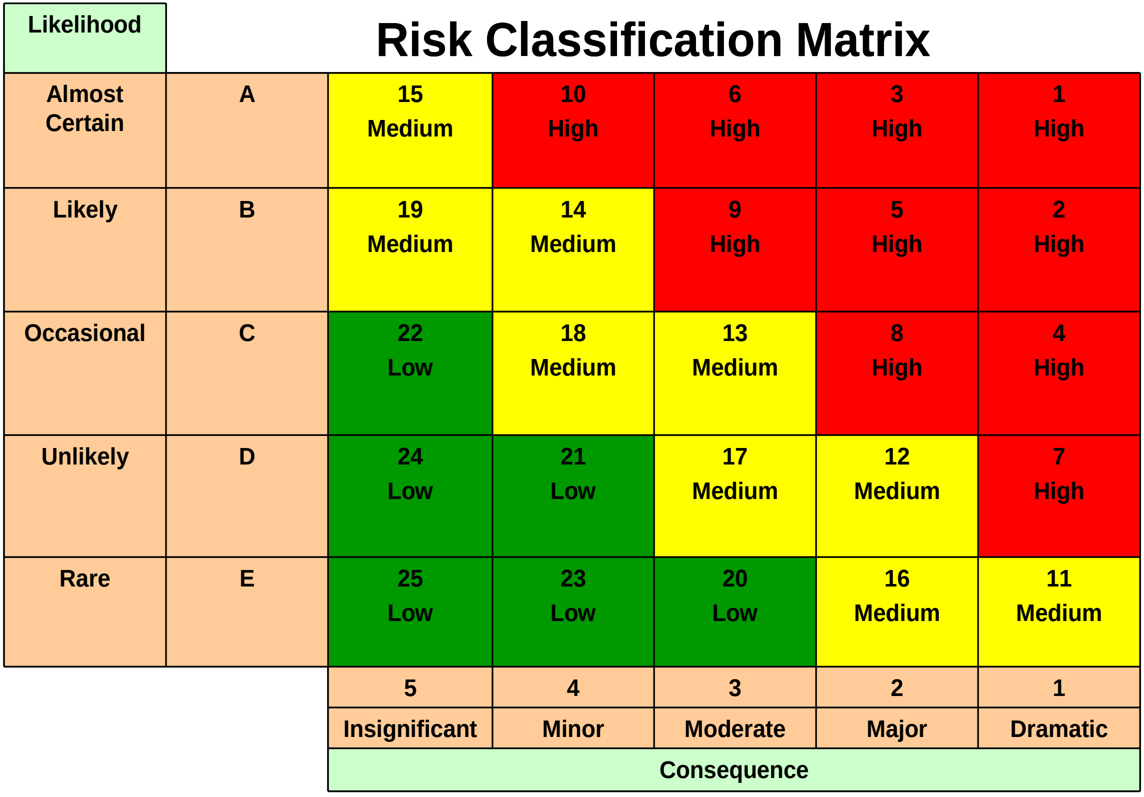
The team needs to meet & analysis all the hazards identified related to each activity. Caution should be taken to ensure that different class of vehicles will have different levels of hazards associated with it. Thus there could be hazard for wrong parking or reversing without co drivers support for a truck the bicycle rider can face the hazard of no or poor visibility, incorrect parking or driving the bicycle along with a heavy vehicle. Again all the permutations for cross operations need to be checked & analyzed.

The data collated needs to be tabulated with detailed discussion & anticipation of hazard. The hazards thru identified should be assessed for the risk associated with the same. These risk identified should be evaluated & tabled to the most serious consequences.

## Risk Classification Matrix

i) Risk assessment shall be conducted on the basis of risk classification matrix.

Table A – Example Matrix for Determining the Level of Risk



**Risk Classification Matrix**

| Likelihood | | | | | | |
|---|---|---|---|---|---|---|
| Almost Certain | A | 15<br>Medium | 10<br>High | 6<br>High | 3<br>High | 1<br>High |
| Likely | B | 19<br>Medium | 14<br>Medium | 9<br>High | 5<br>High | 2<br>High |
| Occasional | C | 22<br>Low | 18<br>Medium | 13<br>Medium | 8<br>High | 4<br>High |
| Unlikely | D | 24<br>Low | 21<br>Low | 17<br>Medium | 12<br>Medium | 7<br>High |
| Rare | E | 25<br>Low | 23<br>Low | 20<br>Low | 16<br>Medium | 11<br>Medium |
| | | 5 | 4 | 3 | 2 | 1 |
| | | Insignificant | Minor | Moderate | Major | Dramatic |
| | | Consequence | | | | |

ii) This is the recommended risk classification matrix in order to ensure standardisation across all operations.

## RISK RANKING METHOD

Risk is the combination of the likelihood of a specific unwanted event and the potential consequences if it should occur. The rankings to be given are as under:

### i) Qualitative parameters for likelihood

| Level | Descriptor | Description |
|---|---|---|
| A | Almost Certain | The event is expected to occur in most circumstances |
| B | Likely | The event will probably occur in most circumstances |
| C | Occasionally | The event should occur at some time |
| D | Unlikely | The event could occur at some time |
| E | Rare | The event may occur only in exceptional circumstances |

### ii) Qualitative parameters for consequences

| Level | Descriptor | Description |
|---|---|---|
| 1 | Dramatic/ Catastrophic | Fatality, toxic release off site with detrimental effects, huge financial loss, consistent regular intervention or prosecution |
| 2 | Major | Permanent disability, extensive injuries, loss of production capacity, off site release with no detrimental effects, major |

| | | |
|---|---|---|
| | | financial loss, consistent adverse attention by media |
| 3 | Moderate | LTI Serious, on site release contained without outside assistance, high financial loss, major client aggrieved |
| 4 | Minor | MTI; On site release immediately contained; medium financial loss; some client dissatisfaction |
| 5 | Insignificant/ Negligible | First Aid treatment, On site treated injuries; low financial loss; no significant change; no media attention |

### iii) Consequence rating matrix

| | Dramatic/ Catastrophic (1) | Major (2) | Moderate (3) | Minor (4) | Insignificant/ Negligible(5) |
|---|---|---|---|---|---|
| Consequence type | | | | | |
| People (Injury related) | Fatality | Permanent Disability | LTI | MTI | Minor injury |
| Production/ Compensation Loss (in Lakhs) | Rs.120 L-Rs.200 L | Rs.35 L-Rs.120 L | Rs.7 L-Rs.35 L | Rs. 3.5 L-Rs.7 L | <Rs. 3.5 L |
| Environment | Catastrophe | Wide spread Impact - Long Term | Wide spread Impact - Short Term | Localised Impact | Minimal Impact |
| Reputation/ Media | Prosecution | Consistent | Major | Some | Nil |

iv) Guidelines for taking actions on risk classification:

a. High- Take Immediate Action ( with in next 7 Days)
b. Medium- Take action within one month
c. Low- Manage by routine practices

**Risk Assessment Proforma**

i) Findings of the risk assessment shall be recorded in a template which shall cover various aspects as per annexure.

**Operation Control Procedures**

i. After application of the control measures as per the hierarchy of controls, the applied control should be reflected in the existing Operational control procedures. Operational Control Procedures specify the way to carry out an activity or a process.

ii. Written operating procedures assist operations personnel to manage safety by setting standards against which operational practices can be measured.

iii. Operational Control Procedures shall provide clear instructions for safe operation of the facility.

iv. Operational Control Procedures shall be prepared by the respective dept. heads for the main equipments and processes and also for the following:

   a. Initial start up
   b. Normal operation
   c. Temporary operations
   d. Emergency operations including emergency shutdown
   e. Normal shutdown & Start up following a shutdown or turnaround

## Appendices

- Annexure I- Template for Risk Assessment

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- Annexure II- Categories and sub-categories of hazards
- Annexure III- Hierarchy of controls

**Key Word:** Road Safety, Training, Risk Analysis, Hazard Identification, Pollution Control

## ANNEXURE II

## CATEGORIES AND SUBCATEGORIES OF HAZARDS

Hazards in the workplace can be divided into following groups. These include:

- Physical hazards.
- Hazardous substances./ Chemical hazards
- Ergonomic hazards.

## ANNEXURE III

## HIERARCHY OF CONTROLS

### 1. ELIMINATION

Does the task need to be done?

- Check the process. Check if some points can be eliminated to shorten the vehicle movement inside the plant. Plan the activities where the driver's interface in minimal.
- Can the material be transported thru another bulk system ?

### 2. SUBSTITUTION

Can something else be used to reduce the risk?

- Can there be GPRS to control the movement of truck inside the plant
- Can there be RFID card to get the vehicle / driver details which are pre stored in the system.

### 3. SEGREGATION

Can distance / barriers/guards be used to prevent personnel exposure to hazard?

- Access controls
- Distance
- Time

### 4. ENGINEERING CONTROLS

Can equipment be used to reduce the risk?

- Loading equipment
- Having proper illumination
- Isolations of Transportation path

### 5. ADMINISTRATIVE

- Operational control procedures
- Reduction in Personnel/ Time exposure
- Limit the number of personnel exposed to the risk and control the time they are exposed.
    - Hazardous Work carried out at low activity periods e.g nights/ weekends
    - Workplace design
- Training

### 6. PERSONAL PROTECTIVE EQUIPMENT

Suitable and sufficient PPE, appropriate for the task?

- Helmet,
- Safety Harness
- Respiratory Protective Equipment
- Goggle

# SPATIAL DISTRIBUTION OF $CO_2$ EMISSIONS IN TURKEY ON DISTRICT AND PROVINCE BASIS

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## ABSTRACT

Generally, total $CO_2$ emissions in Turkey are reported on annual basis; however the spatial distributions of the emissions are ignored. The spatial distribution of $CO_2$ emissions inTurkey at province and district levels with respect to its sources and sinks were investigated in this study for the years between 1990 and 2010. The basic source of the $CO_2$ is combustion of fuels in households, in manufacturing industries, thermal power plants and road vehicles. $CO_2$ emission is important, because it is responsible for about 60% of the “Greenhouse Effect”. To estimate the $CO_2$ emissions with respect to its sources IPCC Method is used. The carbon content and emission factors of the fuels are the starting point for the estimation of $CO_2$ emissions. $CO_2$ uptakes by sinks were also calculated. The annual increment of biomass is the basis for the estimation of $CO_2$ uptake. There is no fuel consumption data available for the provinces and districts of Turkey. However, the emissions at province and district levels were estimated by using the population, the number of industries and thermal power plants and the number of registered cars. Finally, scaled maps were prepared by using GIS software. Then the inventories were linked to the GIS maps of the districts’ and provinces’. Results of this study have shown that there are regional, provincial and district level changes in the $CO_2$ emission in Turkey for a period of 21 years between 1990 and 2010. The lowest $CO_2$ emissions in different regions were observed in 1990 and the highest in 2010. Istanbul province has emitted the highest $CO_2$ amount throughout the study period. As far as $CO_2$ emissions in districts are considered, Iskenderun district of Hatay province, Afşin district of K.Maraş province and Üsküdar district of Istanbul province emit the highest quantity of $CO_2$ in Turkey.

**Keywords:** $CO_2$ Emission, Spatial distribution on province basis, Sources, Sinks, IPCC Methods, GIS mapping

**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
**4th International Symposium and IUAPPA Regional Conference**
**10-13 September 2012 Istanbul -Turkey**

# THE "DOOMSDAY" EFFECT
# HOW THE WINDOW OF OPPORTUNITY FOR POLITICAL ACTION ON EMISSION REDUCTIONS IS CLOSING

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There are growing scientific evidences for the existence of tipping points in climate dynamics, and non linearity effects in climate damages that may happen when temperatures' increase overshoots some thresholds. It is also commonly accepted that beyond a 2◦C increase, uncertainty about climate responses in-creases drastically and climate changes might become uncontrollable. Standard Integrated Assessment Models (IAMs), combining an economic and a climate modules, usually represent climate damage by means of a smooth quadratic function incurring costs of a few percentage points of GDP at most. Given this representation of damages, optimal response to climate change is always likely to overshoot the 2◦ C target (Stern2006, Nordhaus2008). It seems that no economic model based on traditional Cost Benefit Analy-sis (CBA) has been designed to seriously take into account the possibility of a tipping point and thus of a dramatic climate catastrophe (Weitman2007). We change the usual quadratic function with a threshold effect damage function (or sigmoidal function) which makes it possible to account for the existence of a tipping point in climate dynamics by considering thresholds in temperature increase beyond which damages rocket significantly although they remain bounded. Depending on their worldviews (set of beliefs on economic growth, abatement costs, pure time preference, climate sensitivity, and technical progress, size of the damage once the threshold is passed), economic agents either find it optimal to overshoot the threshold ("doomsday effect") or on the contrary to fight against it. We especially focus on the description of the overshooting strategies resulting from what we interpret as a "doomsday effect" that look odd at a first glance but fits rather well with current climate policy orientations. Indeed, there is apparently a contradiction between the 2 ◦ C target that has been confirmed many times in international climate negotiations as the critical threshold not to overshoot and actual climate policies which are not likely to be sufficient to meet this objective. We thus empirically validate the assumption that decision-makers are actually struck by a "doomsday effect" and are carrying out mitigation policies which are gradually closing the window of opportunity for meeting the target with a reasonable chance of success. In particular our results show that the extent of this effect is increasing with time and that the number of "doomists" will significantly rise between 2010 and 2020 if no strong action is taken quickly.

**Keywords:** Climate change, Emissions reduction, Integrated assessment model, Mitigation strategies, Non-linear climate dynamics

**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# INVENTORY OF AIR POLLUTANT EMISSIONS FROM DOMESTIC HEATING IN RESIDENTIAL AREAS OF IZMIR

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## ABSTRACT

Air pollution in cities is a major environmental problem principally in the developing countries. Emission inventories are basic requirement to assess the human influence to the atmosphere. The aim of this study is to quantify the amount of domestic heating emissions for particulate matter ($PM_{10}$), sulfur dioxides ($SO_2$), nitrogen dioxides ($NO_2$), volatile organic compounds (VOC) and carbon monoxide (CO) together with greenhouse gases which are carbon dioxide ($CO_2$), nitrous oxide ($N_2O$) and methane ($CH_4$) in İzmir for 2008-2009 winter season. Emissions were estimated by using USEPA, CORINAIR and IPCC emission factors. The results indicated that the highest emissions were released from Karabağlar and Konak where a greater proportion of households use coal for domestic heating. Three methods were used to estimate greenhouse gases and the results estimated by using IPCC's emission factors were higher than those calculated by using CORINAIR and USEPA's emission factors. Air quality modeling is a great tool for assisting policy makers how to decrease emissions and improve air quality. At the second part of the study, calculated emissions were modeled by using CALMET/CALPUFF dispersion modeling system and plotted in the form of air pollution maps by using geographical information system.

**Keywords**: Air Pollution, Greenhouse Gases, Emission Inventory, Air Quality Modeling, CALPUFF

## 1.INTRODUCTION

Urban areas are broadening each day in today's society as economic growth leads to higher income and better living conditions. However, urban development also causes an increase in energy demand which produces air pollution. Population growth in the metropolitans, however, is a major reason for the air-quality problems and change in land use (Mayer, 1999). Air pollution has become an actual problem in İzmir due to rapid urbanization and increase in the polluted sources. The amounts of pollutants, emitted from these sources, are estimated by using fuel consumption data and suitable emission factors (Elbir, 2003). Generally European CORINAIR database (CITEPA, 1992), US Environmental Protection Agency emission factors catalogue (USEPA, 1998a) and Intergovernmental Panel on Climate Change Guidelines (IPCC) are widely used emission factors catalogues (Lin et.al., 2005; Zeydan, 2008; Müezzinoğlu et. al., 2001). European emission factors were insufficient to indicate the industrial subcategories so usually USEPA emission factors are chosen (Elbir & Müezzinoğlu, 2004). The significance of emission inventories in air quality modeling had been indicated by many researchers (Zoraset. al., 2006). Moreover, inventories used in modeling studies must gather the model input necessities, namely the spatiotemporal resolution and chemical speciation, according to the model setup (Borge et. al. 2007). In order to obtain that, modern tools such as GIS techniques can be executed. The latter tools which are increasingly been used for environmental modeling studies and air pollution analysis, provide an integrated system for quantification of emissions and spatial data analysis (Symeonidis et. al., 2008).

This study focused on the estimation of domestic heating emissions and air quality modeling of the emissions in İzmir in 2008-2009's winter season. A local emission inventory in the city center of İzmir was prepared to estimate emissions of main pollutants ($SO_2$, CO, PM, $NO_2$ and VOC) as well as greenhouse gases ($CO_2$, $CH_4$ and $N_2O$). At the next stage of the study, calculated emissions were modeled in the study area using the CALMET/CALPUFF dispersion modeling system. The system contains three main programs: the meteorological model CALMET, the dispersion model CALPUFF, and the post processing model CALPOST. The meteorological data were obtained from four meteorological stations. Surface data were taken from İzmir, Aliağa, Seferihisar, and Manisa Meteorological Stations and upper air data was taken from İzmir Meteorological Station. The meteorological data were then processed by CALMET Meteorological Model, and wind fields which are used as input for CALPUFF were produced. The emission data required by CALPUFF were obtained from prepared emission inventory. Geographical information system (GIS) was used to show the results for both emission inventory and air quality predictions.

## 2.MATERIALS AND METHODS

### 2.1 Characteristics of the study area

The city of İzmir is situated at the west side of Turkey with longitude between 26.228° E and 28.459° E, and latitude between 37.833° N and 39.471° N, covering a total area of 11973 $km^2$. The city center of İzmir is located with longitude between 26.814° E and 27.372° E, and latitude between 38.287° N and 38.573° N, the third biggest urban agglomeration of Turkey and the acknowledged industrial and commercial capital of the Aegean Region. In winter the daily mean temperatures were observed in the range of 1.2–24.8 °C in İzmir. Winter season wind roses were plotted for four stations in İzmir and its surroundings using hourly wind speed and direction data from November 2008 to March 2009 (Figure 1).

Coal is the most common used fuel in İzmir with 74% of households using import or local coal on a typical winter's night (Figure 2). Data of coal sales in 2008 – 2009 winter season was provided by the authorities of İzmir Provincial Directorate of Environment and Forestry. According to the sales rates taken from the approved coal resellers, 1142688 tons of coal was consumed in the city center of İzmir in this winter season. Coal consumption per building was assumed around 1 tons due to sales figures and surveys in literature. Wood isn't the main fuel in the city center of İzmir, since it is used with coal. So the wood consumption wasn't included to emission calculations. In addition the sums of monthly natural gas consumption per a district in 2008 and 2009 were obtained from İZMİRGAZ.

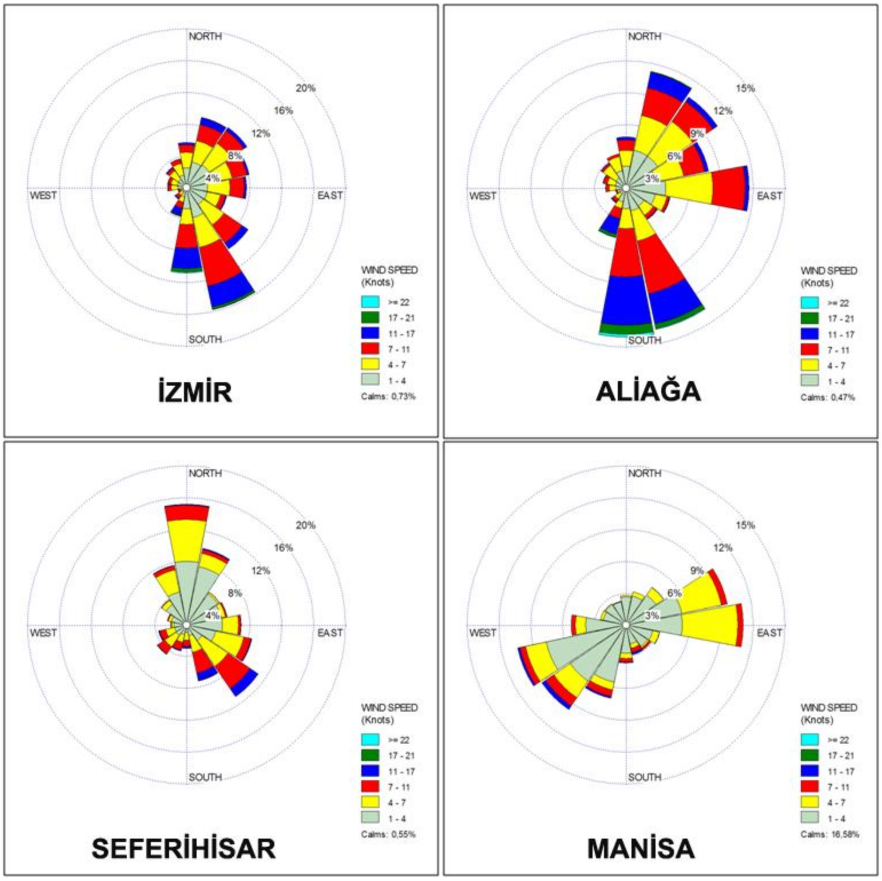

Figure 1. The wind rose in Aliağa, İzmir, Seferihisar and Manisa in 2008-09 winter season.

As in “Turkey’s Energy and Energy Efficiency Studies – Passing to the Greener Economy” Report suggested, which is prepared by Energy Efficiency Association in 2010, 25% of the buildings in Turkey uses electricity for air conditioning purposes while 72% of those is also use it for heating (Energy Efficiency Association, 2010). Roughly 206000 houses, which are nearly 18% of all houses in the city and reside within the borders of İzmir city center, uses electricity for domestic heating, as accepted so in this study and those are excluded in emission calculations. In “İzmir Region Status Report” of 2008 prepared by İzmir Development Agency, the amount of houses using liquid fuel for central heating was 1404 in 2007 (İzmir Development Agency, 2008). When the number of houses which resides within the study area is regarded, the amount of liquid fuel usage (which stays extremely lower than 1% of all houses) was excluded from emission calculations, too.

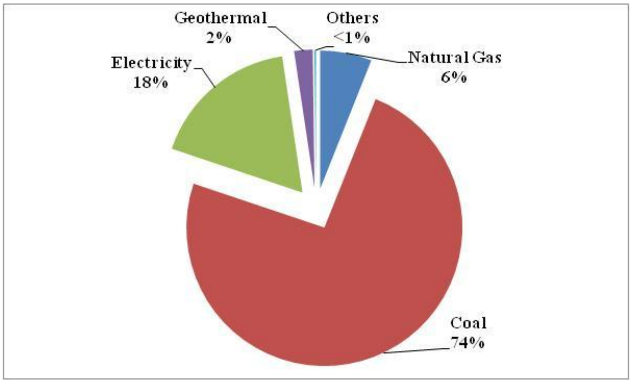

Figure 2. The distribution of fuel consumption for residential heating in 2008-09 winter season.

## 2.2 Calculation of Emissions

Emissions from house heating units were evaluated with the help of fuel use data apportioned all over district in the city center of İzmir. Quantities of fuels burned by the area sources per unit time were multiplied by suitable emission factors suiting the type of the fuels to give the total quantity of pollutant emissions over the area. Use of only two major fuel types; coal and natural gas were assumed for calculation of domestic heating emissions. Emissions of main contaminants from domestic heating activities were estimated by using the emission factors of USEPA given in Table 1 (Elbir et. al., 2009).

Table 1.Emission factors used to calculate residential heating emissions.

| | **Unit** | **$SO_2$** | **$NO_2$** | **$PM_{10}$** | **CO** | **VOC** |
|---|---|---|---|---|---|---|
| **Coal** | g/kg | 10.89 | 1.33 | 4.89 | 55.69 | 5.86 |
| **Natural Gas** | g/m3 | 0.02 | 1.85 | 0.02 | 1.01 | 0.27 |

In this study the USEPA and CORINAIR emission inventory guidelines to examplify classical air pollutants ($SO_2$, $NO_2$, etc.) with the IPCC Guidelines for National Greenhouse Gas Inventories were used. Emissions of greenhouse gases from domestic heating activities were estimated using the emission factors of USEPA, CORINAIR and IPCC given in Table 2 and compared the emission factors and greenhouse gas emissions. For calculating $CO_2$ emissions the percentage of carbon is assumed 57% in coal (Zeydan, 2008).

Table 2. Emission factors used to calculate greenhouse gas emissions.

| | | **USEPA** | **CORINAIR** | **IPCC(2006)** |
|---|---|---|---|---|
| **Coal** | **$CO_2$** | 30.1 * %C (kg/tons) | 94000 (g/GJ) | 94600 (g/GJ) |
| | **$CH_4$** | 2.27 (kg/tons) | 450 (g/GJ) | 300 (g/GJ) |
| | **$N_2O$** | 0.018 (kg/tons) | 1.4 (g/GJ) | 1.5 (g/GJ) |
| **Natural Gas** | **$CO_2$** | 1.922 (kg/m$^3$) | 56000 (kg/TJ) | 56100 (kg/TJ) |
| | **$CH_4$** | 0.037 (g/m$^3$) | 2.5 (kg/TJ) | 5 (kg/TJ) |
| | **$N_2O$** | 0.035 (g/m$^3$) | 0.1 (kg/TJ) | 0.1 (kg/TJ) |

## 2.3 Air Quality Modeling

In the second part of the study, calculated emissions were modeled to estimate air quality levels in the area by using the CALMET/CALPUFF dispersion modeling system. The system contains three main programs: the meteorological model CALMET, the dispersion model CALPUFF, and the post processing model CALPOST. The meteorological data were obtained from four meteorological stations. Surface data were taken from İzmir, Aliağa, Seferihisar, and Manisa meteorological stations, and upper air data was taken from İzmir meteorological station. The meteorological data were then processed by CALMET meteorological model, and wind fields which are used as input for CALPUFF were produced. The emission data required by CALPUFF were obtained from prepared emission inventory. Geographical information system (GIS) was used to show the results for both emission inventory and air quality predictions. In this study for calculating the air pollutant emissions from residential areas, a local emission inventory was prepared within an area of 50 km by 40 km centered at the study area in İzmir. For meteorological modeling, much wider study area (160 km x 120 km) was selected. The grid system with 4 km resolution was used for meteorological modeling domain. But for dispersion modeling domain the grid system was nested to 1 km resolution. The modeling domains are shown in Figure 3.

Figure 3.Meteorology and dispersion modeling domains.

## 3.RESULTS AND DISCUSSIONS

Like other cities, the pollutant with the most potential for air quality problems from domestic heating in İzmir is particulate. During the winter approximately 4365 tons $PM_{10}$ were released to air from households in the city. The important contaminants likely to be of concern in İzmir were $PM_{10}$ and potentially $SO_2$. The majority of the $PM_{10}$ emissions were from the burning of coal on uncontrolled burners and the main source of $SO_2$ emissions were fuel oil and lignite due to sulphur content of the fuel (Ağaçayak, 2007). Nearly 9720 tons $SO_2$ was released to atmosphere from households in İzmir during the study period. According to emission inventory results, 1250 tons/year $NO_2$ and 46700 tons/year CO were released to atmosphere from domestic heating in 2008-09 winter season. CO emissions had a strong seasonal variation configured mostly by emissions from domestic heating (Symeonidis et. al., 2008). In addition, the major source of VOC emissions for residential sources is the coal and wood combustion (Klimont et. al., 2000). The total VOC emissions of İzmir in 2008-09 winter season was approximately 5240 tons (Table 3).

Table 3. The total $SO_2$, $NO_2$, $PM_{10}$, CO and VOC emissions of İzmir in 2008-09 winter season.(tons/year)

| **DISTRICTS** | **$SO_2$(t/yr)** | **$NO_2$(t/yr)** | **$PM_{10}$(t/yr)** | **CO(t/yr)** | **VOC(t/yr)** |
|---|---|---|---|---|---|
| Bayraklı | 1001.6 | 129.0 | 449.8 | 5125.2 | 539.9 |
| Bornova | 1425.3 | 183.4 | 640.1 | 7293.6 | 768.3 |
| Buca | 1393.1 | 176.8 | 625.6 | 7127.5 | 750.6 |
| Çiğli | 595.7 | 77.3 | 267.5 | 3.048.7 | 321.2 |
| Gaziemir | 311.5 | 45.6 | 139.9 | 1596.7 | 168.7 |
| Güzelbahçe | 113.6 | 13.9 | 51.0 | 580.8 | 61.1 |
| Karabağlar | 1708.7 | 211.0 | 767.3 | 8739.4 | 919.8 |
| Konak | 1772.7 | 217.4 | 796.0 | 9066.0 | 954.0 |
| Karşıyaka | 1061.6 | 161.1 | 476.9 | 5444.5 | 575.7 |
| Balcova | 138.8 | 17.0 | 62.3 | 709.9 | 74.7 |
| Narlıdere | 197.7 | 24.1 | 88.8 | 1010.8 | 106.4 |
| **Total** | **9720.3** | **1256.6** | **4365.2** | **46694.4** | **5240.3** |

Perhaps a better indicator of the potential for ambient air quality issues is the representation of emissions in ton per $km^2$. Konak is the central district of İzmir had the highest area adjusted emission rates for $SO_2$ with 74.4 tons/$km^2$, for $NO_2$ with 9.1 tons/$km^2$, for $PM_{10}$ with 33.4 tons/$km^2$, for CO with 380.3 tons/$km^2$ and for VOC with 40 tons/$km^2$. But Güzelbahçe which is located in south-eastern of the city, had the least area adjusted emission rates for $SO_2$ with 1.8 tons/$km^2$, for $NO_2$ with 0.2 tons/$km^2$, for $PM_{10}$ with 0.8 tons/$km^2$, for CO with 9.1 tons/$km^2$ and for VOC with 0.9 tons/$km^2$. While this provides an indicator of the emission density, it is also not an ideal expression, as the housing density within the study areas will vary. Because, not residential areas which include quantities of rural land can be reduce the overall ton per $km^2$ emission rate. In the south part of the city (Balçova and Narlıdere) a house's stack released nearly 0.005 tons/year $SO_2$, 0.001 tons/year $NO_2$, 0.002 tons/year $PM_{10}$, 0.023 tons/year CO, 0.002 tons/year VOC. But in the north part of the city (Bayraklı, Bornova and Karşıyaka) closely 0.01 tons/year $SO_2$, 0.001 tons/year $NO_2$, 0.005 tons/year $PM_{10}$, 0.052 tons/year CO, 0.005 tons/year VOC were released to atmosphere from a house's stack. The highest emissions were 0.011 tons/year $SO_2$, 0.001 tons/year $NO_2$, 0.005 tons/year $PM_{10}$, 0.056 tons/year CO, 0.006 tons/year VOC per a house's stack in the center districts (Konak, Karabağlar and Buca) of the city owing to dense population in 2008-09 winter season. According to results of the study, a person in İzmir caused 3 kg $SO_2$, 1.3 kg $PM_{10}$, 0.4 kg $NO_2$, 15.1 kg CO and 1.6 kg VOC for domestic heating in 2008-09 winter season. Kecebaş calculated a release of 39.6 kg PM and 8.33 kg $SO_2$ per a person in Afyon (Kecebaş et.al., 2010). In 1995 Atımtay determined 2.4 kg $SO_x$ and 2 kg PM emissions per a person for domestic heating in Ankara (Atımtay et.al., 1995). Turalıoğlu achieved a similar study for Erzurum in 2005. It is estimated that a person who lives in Erzurum, released 21.2 kg $SO_2$ and 27.9 kg PM to atmosphere (Turalıoğlu, 2005).

By the study, the results of the study were compared with the outputs of similar project in Table 4. In conclusion of this comparison, it is observed that especially $SO_2$ and $PM_{10}$ values were decreased almost 80% from 2000. The most important fact is that coal consumption was also decreased and quality of the consumed coal was also increased at the same time. Besides, when winter emissions originated from traffic and domestic heating sources are compared, it is seen that domestic heating sources were higher.

Table 4.Comparison of the city center of İzmir emissions in 2008-09 winter season to other cities emissions (tons/year)

| LOCATION | YEAR | SOURCE | $SO_2$ | $PM_{10}$ | $NO_2$ | CO | VOC | Reference |
|---|---|---|---|---|---|---|---|---|
| **İzmir** | 2008-09 | DH | 9720 | 4365 | 1257 | 46694 | 5240 | |
| **İzmir** | 2000 | DH | 45419 | 26213 | 20536 | 48320 | 10268 | *Müezzinoğlu et.al., 2000* |
| **İzmir** | 2008 | T | 126 | 966.4 | 37.2 | 2160 | | *Elbir et. al. 2010* |
| **Zonguldak** | 2008 | DH | 1703 | 426 | 625 | 18885 | 687 | *Zeydan, 2008* |
| **Sakarya** | 2007 | DH | 3428 | 857 | 265 | 9451 | | *Odabaş, 2009* |
| **İzmir** | 2001 | DH | 8200 | 38433 | 887 | 1517 | 1216 | *Elbir et. al., 2001* |
| **İstanbul** | 2007 | DH | 10983 | 13631 | 7014 | 123510 | 18351 | *Elbir et. al., 2009* |
| **Yalova** | 2003-04 | DH | 1050 | 1448 | 192 | 3203 | | *Irmak, 2005* |

DH: Domestic heating, T: Traffic

GHGs emissions of study area for domestic heating were 2250018 tons/year $CO_2$, 33 tons/year $N_2O$ and 10427 tons/year $CH_4$ according to the calculations made by using CORINAIR's emission factors in 2008-09 winter season. Although, 1603465 tons/year $CO_2$, 17 tons/year $N_2O$ and 2027 tons/year $CH_4$ were calculated with using USEPA's emission factors, 2264046 tons/year $CO_2$, 35 tons/year $N_2O$ and 6956 tons/year $CH_4$ were calculated with using IPCC's emission factors in the study area. The three methods were compared for estimating greenhouse gases and the results calculated with IPCC's emission factors turn out to be higher than those calculated with USEPA and CORINAIR (Table 5).

Table 5. Greenhouse gases emissions of study area for domestic heating in 2008-09 winter season.

| | $CO_2$(tons/year) | $N_2O$(tons/year) | $CH_4$(tons/year) |
|---|---|---|---|
| **USEPA** | 1603465 | 17 | 2027 |
| **CORINAIR** | 2250018 | 33 | 10427 |
| **IPCC(2006)** | 2264046 | 35 | 6956 |

Emissions from residential sources, too small and difficult to be measured, were considered in a group as area sources. Consequently, domestic sources comprise area sources. Number of inhabitants, number of residences, types of fuels used, fuel consumption statistics and combustion characteristics are necessary for calculating the residential heating emissions. For the modeling air pollutant emission from domestic heating in the city center of İzmir with CALPUFF dispersion model, the residential areas were represented as polygons. 657 polygons for the residential areas in the study area were drawn (Figure 4).

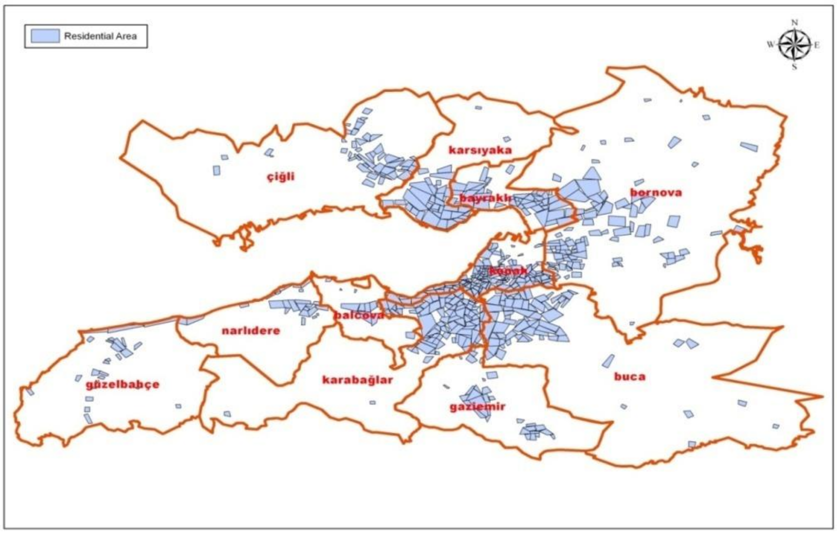

Figure 4. 657 residential areas in the city center of İzmir.

Seasonal variations on meteorology and differences in fuel consumption can affect the transportation of air pollutants. According to the model results the maximum monthly concentrations for all pollutants in January and the maximum daily concentrations in 13 January 2009 was calculated. The maximum annual, monthly, daily and hourly average concentrations and 2009 limit concentrations of Turkish Standards named Air Quality Assessment and Management Regulations was given Table 6. The maximum daily $SO_2$, $PM_{10}$ and VOC concentrations and the maximum hourly $SO_2$ and VOC concentration for this sampling day is higher than the daily limit value according to the Air Quality Assessment and Management Regulations. The maximum daily concentrations were calculated on 13 January 2009 when inversion thickness was measured as 288 meter. The beginning elevation of inversion was 41 m. The severity of inversion was estimated with using meteorological data as 55, or namely middling inversion.

Table 6. The maximum annual, monthly, daily and hourly average concentrations in İzmir

| **Maximum Concentrations** | **Annual** | **Monthly** | **Daily** | **Hourly** | **2009 Limit Concentrations of Turkish Standards * (Daily)** | **2009 Limit Concentrations of Turkish Standards * (Hourly)** |
|---|---|---|---|---|---|---|
| **$SO_2$ (µg/m$^3$)** | 87 | 159 | 1200 | 3487 | 370 (µg/m$^3$) | 900 (µg/m$^3$) |
| **$PM_{10}$ (µg/m$^3$)** | 39 | 71 | 539 | 1728 | 260 (µg/m$^3$) | - |
| **$NO_2$ (µg/m$^3$)** | 11 | 21 | 153 | 485 | 300 (µg/m$^3$) | - |
| **CO (µg/m$^3$)** | 443 | 815 | 6141 | 19683 | 26 (mg/m$^3$) | - |
| **VOC (µg/m$^3$)** | 47 | 86 | 648 | 2073 | 126 (µg/m$^3$) | 280 (µg/m$^3$) |

*Air Quality Assessment and Management Regulations

The maximum monthly average concentrations for five pollutants ($PM_{10}$, $SO_2$, $NO_2$, VOC and CO) during the winter of 2008-2009 were seen at Gulf of İzmir in January. The results showed that the most affected region was Karabağlar, Konak and Karşıyaka which are central districts in the city from domestic heating emissions. According to the model results the eastern part of the city was the less polluted than other areas.

## 4.CONCLUSIONS

In this study the contribution of emissions from domestic heating to air quality of İzmir in 2008-2009's winter was investigated. The results showed that Konak was the most polluting district in the city center of İzmir contributing to about 18% of total emissions. Nearly 9700 tons $SO_2$, 1250 tons $NO_2$, 4350 tons $PM_{10}$, 46700 tons CO and 5200 tons VOC were released to atmosphere from the city center of İzmir in 2008-09 winter season. Greenhouse gases emissions of study area for domestic heating were 1603465 tons/year $CO_2$, 17 tons/year $N_2O$ and 2027 tons/year $CH_4$ according to the calculations made by using USEPA's emission factors, 2250018 tons/year $CO_2$, 33tons/year $N_2O$ and 10427 tons/year $CH_4$ according to the calculations made by using CORINAIR's emission factors and 2264046 tons/year $CO_2$, 35 tons/year $N_2O$ and 6956 tons/year $CH_4$ according to the calculations made by using IPCC's emission factors in 2008-09 winter season. When the three methods were compared, emission factor of IPCC were higher than of USEPA and CORINAIR. According to 2008 national inventory reports and tables of Turkey 48223916 tons $CO_2$, 1264 tons $N_2O$ and 146350 tons $CH_4$ reached to atmosphere from residential in 2008. İzmir is contributing with about 5% of total greenhouse gases emissions like as total population of Turkey. According to model results, the monthly average concentrations were found higher around Gulf of İzmir in 2008-2009 winter season. The results showed that the most affected residential areas were Karabağlar, Konak and Karşıyaka which are central districts in the city center from domestic heating emissions due to their dense population. Outputs of the model showed that the eastern part of the city was the less polluted than other areas.

According to the results of this study, authorities can prepare an action plan for decreasing effects of domestic heating, hence will be able to have a better air quality in future. To prevent the negative effects of air pollution, high quality coal which has lower sulfur and ash content has to be used and use of the natural gas, geothermal or solar energy must be supported in the suitable region. In addition all present outputs of this study such as the results and maps of emission inventory with air quality modeling can be used to determine the locations and estimate the effects of the new residential areas that will be established in the city.

## ACKNOWLEDGMENTS

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# COMPARATIVE STUDY OF BRIQUETTES MADE FROM DIFFERENT RAW MATERIALS ON THE BASIS OF EMISSION

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## ABSTRACT

Indoor air pollution (IAP) represents the fourth most important health risk factor after malnutrition, unsafe sex and unsafe drinking water and sanitation in the developing world. The main objective of this study is to assess the IAP caused by briquette burning; compare the briquettes on its basis and analyze the performance of the briquettes made from the currently used raw materials and waste. Particulate matter of size less than 2.5 micron ($PM_{2.5}$), Carbon monoxide (CO), Nitrogen dioxide ($NO_2$) and Sulphur dioxide ($SO_2$) were analyzed as an indicator of IAP. $PM_{2.5}$ and CO were measured using an UCB particle monitors and HOBO CO loggers, respectively. Similarly, $NO_2$ and $SO_2$ were analyzed by using West-Gaeke spectrophotometric method and Jacob and Hochheiser modified spectrophotometer.The performance analysis was done by undergoing a customized water boiling test. The study shows that the $PM_{2.5}$ emission from the briquettes made by screw-press method were more than the emission from briquettes made by using the pyrolysed raw materials. Similarly, it was found that the CO emission from the screw-pressed briquettes was less compared to the briquettes made by using pyrolysed raw materials. The result shows that the $NO_2$ and $SO_2$ emission from the screw-pressed briquettes is more than the emission from the other briquettes. It was found that the briquettes made by undergoing pyrolysis method had longer burning duration and took longer time to boil water as compared to briquettes made without undergoing pyrolysis that had a short duration.. Similarly, the CO emission from the fuel wood exceeded the emission from all the briquettes. It can be concluded that the tested briquettes are better than fuel wood on the basis of CO emission. If the disadvantages are to be remedied then every briquette will be a potential source of healthy alternate fuel mainly for the rural areas.

**Keywords:** Indoor air pollution, Briquette, PM $_{2.5}$, Pyrolysis

**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# IMPACT OF REGIONAL ANTHROPOGENIC EMISSIONS AND MITIGATION ON AIR QUALITY IN THE EAST MEDITERRANEAN

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## ABSTRACT

The impacts of regional anthropogenic emissions and their potential mitigation on air quality in the East Mediterranean are investigated using a mesoscale WRF/CMAQ modeling system. In summer, regional anthropogenic emissions contribute to the domain mean levels of $O_3$ and $PM_{2.5}$ by 17% and 50%, respectively, whereas winter $O_3$ levels increase by ~4% while $PM_{2.5}$ levels decrease by 50%. An investigated potential mitigation scenario of anthropogenic emissions results in domain-mean surface $O_3$ mixing ratios increase by ~1%, being higher in winter and lower in summer. Urban increases are projected to be larger (up to 13%). Domain-mean $PM_{2.5}$ levels are projected to decrease by up to 10%.

**Keywords:** East Mediterranean, anthropogenic emissions, mitigation

## 1. INTRODUCTION

Megacities are large urban agglomerations with populations larger than 10 million. They show high demands of energy, transportation, industry and other facilities in their extended areas and impact on their surrounding environment and the regional and global air quality. They contribute to regional scale ozone ($O_3$) and secondary aerosols during long-range transport (LRT) and to peroxyacetyl nitrate (PAN) produced in the megacities extended areas and downwind (e.g. Molina et al., 2010). They emit large amounts of carbon monoxide (CO) that are transported to the downwind areas where they contribute significantly to the hydroxyl (OH) reactivity. Particulate matter (PM) levels in these urban areas can be double than in the rural areas, leading to significant human exposure (Molina et al., 2010).

Air pollution is an important environmental problem in the East Mediterranean where high $O_3$ and PM levels are observed that often exceed the limits due to transported pollution mixed with anthropogenic and natural emissions in the region and enhance photochemical production of secondary pollutants such as $O_3$ and secondary aerosols (Kanakidou et al., 2011). East Mediterranean is sensitive to climate change and expected to be exposed to higher levels of pollutants in the future (Im et al., 2011 and 2012). The region hosts important megacities, such as Istanbul, and large urban agglomerations, such as Athens, that significantly impact on the regional air quality. Urban plumes from these cities can affect remote sites in the East Mediterranean, Aegean Sea and Black Sea (Kanakidou et al., 2011). However, dedicated modeling studies on the quantitative evaluation of the impacts of the anthropogenic emissions from the region on the air quality in the East Mediterranean are missing.

The present study 1) quantifies the present-day contribution of regional anthropogenic emissions in the East Mediterranean to the air quality in the urban areas themselves and in the surrounding locations and 2) evaluates the potential impact of a country-based mitigation of anthropogenic emissions on the air quality in the region.

## 2. MATERIALS AND METHODS

### 2.1. Model system

In the present study, the Weather Research and Forecasting model (WRF-ARW v3.1.1; Skamarock and Klemp, 2008) is offline-coupled with the U.S. EPA Community Multiscale Air Quality (CMAQ) model, version 4.7 (Foley et al., 2010). The Model of Emissions of Gases and Aerosols from Nature (MEGAN; Guenther et al., 2006) is used for the calculation of biogenic emissions. The global Transport Model v.4 (TM4-ECPL; Myriokefalitakis et al., 2011) provides the monthly mean chemical initial and boundary conditions on a 3° longitude × 2° latitude spatial resolution and on 34 vertical layers up to 0.1 hPa (~65 km). The WRF-CMAQ domain extends over the East Mediterranean (from $31.89^oN$, $17.34^oE$ to $43.69^oN$, $34.46^oE$) on a 30×30 km horizontal resolution and on 23 vertical layers up to ~16 km. More details on the model configurations are provided by Im and Kanakidou (2012).

### 2.2. Anthropogenic emissions

For this study, anthropogenic emissions from Greece on 10 km, Athens on 2km (Markakis et al., 2010a and b) and from Istanbul on 2 km resolution (Markakis et al., 2012) have been incorporated into the emission inventory of the French National Institute of Industrial Environment and Risks (INERIS), which is a re-gridded product of the 50 km × 50 km European Monitoring and Evaluation Programme (EMEP) inventory. Table 1 provides the anthropogenic emissions from the region integrated over the model domain and the winter (December) and summer (July) periods.

### 2.2. Scenarios

The impact of regional anthropogenic emissions on the air quality of the region during winter (December 2008) and summer (July 2008) has been investigated by a number of scenarios employing Brute force analysis in order to zero-out the emissions. The impact of mitigating the anthropogenic emissions on a country-based approach has been evaluated by an additional simulation for each period. The initial and boundary chemical conditions specific for the months of the simulation have been identical for all investigated scenarios, thus, implicitly assuming the same air quality conditions outside the study areas for all scenarios:

a) Scenario Base: The base case simulation uses the anthropogenic emissions as described in section 2.2.
b) Scenario NoAnth: As Base but masking all anthropogenic emissions in the model domain.
c) Scenario Mitig: This scenario investigates the impact of emission mitigation following a country-based scenario developed in the frame of the CityZen project (Megacity-Zoom for the Environment; https://wiki.met.no/cityzen/start). Within the CityZen project, IIASA provided ratios of anthropogenic emissions in LowGWP climate-friendly scenario for the year 2030 to those for present day. These ratios are multiplied with the base case anthropogenic emissions for each country and pollutant. Table 1 provides the mitigated anthropogenic emissions using these ratios.

Table 1 Base case and mitigated anthropogenic (including shipping) emissions (in tons) from the East Mediterranean, integrated over the simulation periods of winter (December 2008) and summer (July 2008).

| Pollutants (tons) | Base | | Mitigation | |
|---|---|---|---|---|
| | Winter | Summer | Winter | Summer |
| CO | 590010 | 362010 | 399410 | 283700 |
| $NO_x$ | 233676 | 206891 | 213796 | 188451 |
| NMVOC | 99184 | 81710 | 83514 | 69100 |
| $SO_2$ | 334630 | 235590 | 330450 | 233900 |
| $NH_3$ | 3515 | 26105 | 3515 | 26105 |
| $PM_{10}$ | 72094 | 52981 | 58668 | 42910 |
| $PM_{2.5}$ | 54039 | 39588 | 40922 | 29503 |

## 3. RESULTS AND DICSUSSIONS

### 3.1. Impact of regional anthropogenic emissions

Domain-mean winter and summertime levels of major gaseous and particulate pollutants in the base and NoAnth cases are presented in Table 2. Simulation-averaged spatial distributions of $O_3$ and $PM_{2.5}$ are depicted in Figure 1 for winter and in Figure 2 for summer. In winter, contributions of regional anthropogenic emissions are 94% for $NO_x$, 9% for CO, 13% for PAN and 75% for $HNO_3$. In the absence of all regional anthropogenic emissions the domain-mean $PM_{2.5}$ levels also decrease to about half due to similar reductions in all major aerosol components (nss-$SO_4^{2-}$ by 48%, $NO_3^-$ by 57%, OC by 46%, and EC by 61%). On the opposite, winter $O_3$ levels increase by about 4% when regional anthropogenic emissions are masked (Table 2). In summer, larger impacts are computed: Regional anthropogenic emissions contribute to the domain mean levels of $NO_x$ by 90%, CO by 6%, PAN by 53% and $HNO_3$ by 72% while $O_3$ levels are suppressed by 17% (Table 2).

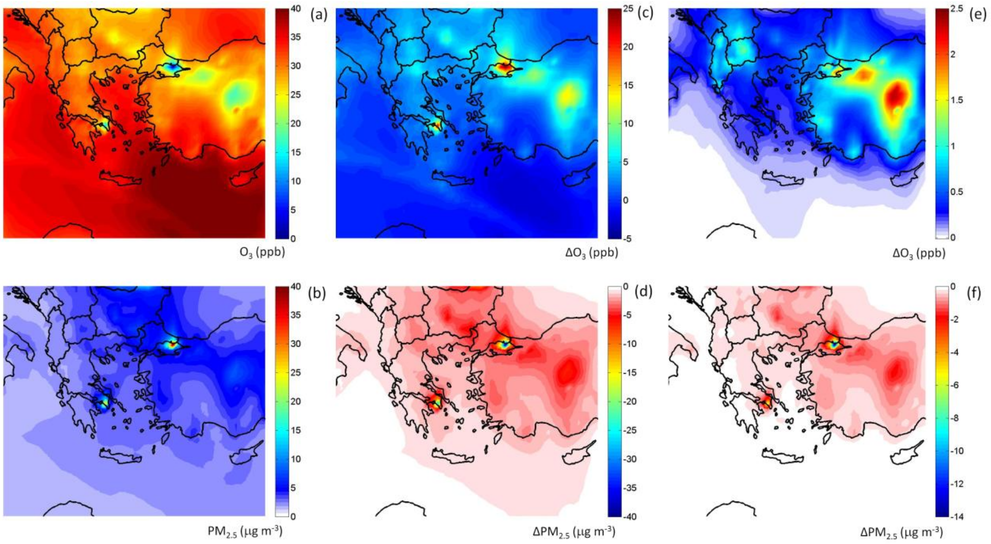

Figure 1. Wintertime $O_3$ and $PM_{2.5}$ levels (a,b) and their response to scenarios "NoAnth" (c,d) and "Mitig" (e,f), averaged over the simulation period.

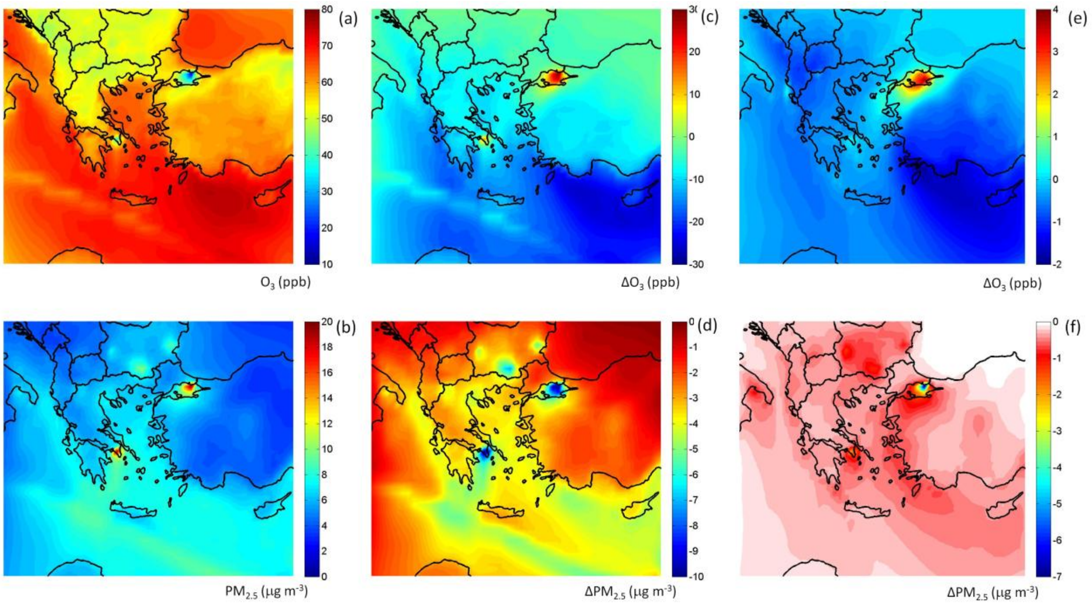

Figure 2. Summertime $O_3$ and $PM_{2.5}$ levels (a,b) and their response to scenarios "NoAnth" (c,d) and "Mitig" (e,f), averaged over the simulation period.

Overall, the regional anthropogenic emissions have a domain-mean impact up to ~90%, depending on the pollutant. $PM_{2.5}$ percent reductions in summer are also comparable with those in winter (Table 2). These contributions are of the same magnitude with the impact of boundary conditions for the region. In particular for $O_3$, the responses of the domain-mean levels of $O_3$ (30-50%) to the boundary condition perturbations are higher than those to the emission perturbations (4-17%), indicating the importance of long range transport for $O_3$ levels in the region (Im and Kanakidou, 2012).

Table 2. Domain-mean winter (December 2008) and summer (July 2008) surface levels from the 'Base', 'NoAnth' and 'Mitig' scenarios, averaged over the simulation periods.

| | Winter | | | Summer | | |
|---|---|---|---|---|---|---|
| | Base | NoAnth | Mitig | Base | NoAnth | Mitig |
| $O_3$ (ppbv) | 33.3 | 34.6 | 33.6 | 62.9 | 52.4 | 62.3 |
| $NO_x$ (ppbv) | 2.9 | 0.2 | 2.5 | 2.0 | 0.2 | 1.9 |
| CO (ppbv) | 147.4 | 134.3 | 144.2 | 124 | 116.6 | 122.1 |
| PAN (ppbv) | 0.3 | 0.3 | 0.3 | 0.3 | 0.2 | 0.3 |
| $HNO_3$ (ppbv) | 0.7 | 0.2 | 0.6 | 1.6 | 0.5 | 1.5 |
| $PM_{2.5}$ ($\mu g\ m^{-3}$) | 2.9 | 1.4 | 2.6 | 6.1 | 3.2 | 5.8 |
| nss-$SO_4^{2-}$ ($\mu g\ m^{-3}$) | 1.0 | 0.5 | 1.0 | 3.3 | 1.8 | 3.2 |
| $NO_3^-$ ($\mu g\ m^{-3}$) | 0.6 | 0.3 | 0.6 | 1.6 | 0.4 | 1.5 |
| OC ($\mu g\ m^{-3}$) | 0.5 | 0.3 | 0.4 | 0.8 | 0.4 | 0.7 |
| EC ($\mu g\ m^{-3}$) | 0.2 | 0.1 | 0.2 | 0.4 | 0.2 | 0.3 |

### 3.2. Impact of mitigation on air quality

The impacts of the mitigation scenario on the $O_3$ and $PM_{2.5}$ levels at surface are presented in Figures 1(e,f) and 2(e,f) for wintertime and summertime, respectively. Table 2 summarizes the computed changes in the main pollutants in the region. In winter, impacts are different from those in summer, particularly for $O_3$. The country-based emissions mitigation does not appear sufficient to suppress $O_3$ levels due to the non-linear chemical response of $O_3$ to $NO_x$ reductions. Surface $O_3$ levels are computed to increase domain-wide by less than 1% in winter, with changes higher than 2 ppbv over central Turkey (Figure 1e) and also in the urban areas of the cities (1.1 ppbv in Istanbul and 0.4 ppbv in Athens). In summer, however, surface $O_3$ levels are projected to decrease domain-wide except in Istanbul and Athens outflows (Figure 2e). Summertime $O_3$ increases by 2.3 ppbv over Istanbul urban area and by up to 4 ppbv over the Marmara Sea. Smaller increases (<0.5 ppbv) are calculated over southeast Attica and the Saronikos Sea downwind of Athens. Overall, a very small environmental gain of 0.5 ppbv (1%) is calculated for the domain-mean surface $O_3$. Winter levels of other gaseous pollutants are projected to decrease (Table 2).

Regarding aerosols, mitigation appears more efficient as seen in Figure 1f and 2f and in Table 2. The largest $PM_{2.5}$ reductions are computed to occur in the urban areas (8 $\mu g\ m^{-3}$: 30% in Istanbul and 4 $\mu g\ m^{-3}$: 20% in Athens). A domain-wide 0.3 $\mu g\ m^{-3}$ (10%) reduction can be achieved. Among the aerosol species, the highest percent reductions are projected for OC and EC, due to the mitigation ratios applied to their emissions that decrease by ~70% for OC and ~60% for EC in the domain (Table 1). Significant reductions in summertime $PM_{2.5}$ levels are also projected (Table 2). The largest reductions are again calculated for OC and EC (~30% for Istanbul, 20-30% for Athens and ~15% for the downwind). Since nss-$SO_4^{2-}$ are mainly of secondary origin, these changes integrate those in the emissions of their precursors and in the oxidant levels. Therefore, surface nss-$SO_4^{2-}$ are computed to decrease slightly (1% in Istanbul, 3% in Athens and 3% in the entire domain). For the same reasons, computed changes in $NO_3^-$ are larger (3% in the domain mean levels) since $NO_x$ emissions are projected to decrease significantly (Table 1).

## 4. CONCLUSIONS

In the present study, WRF/CMAQ modeling system has been used to investigate the impacts of East Mediterranean regional anthropogenic emissions on the air quality of the region for typical wintertime (December 2008) and summertime (July 2008) conditions. Results show that the impacts of regional anthropogenic emissions on the domain-mean surface pollutant levels can be significant (up to 17% for summertime $O_3$ and 52% for wintertime $PM_{2.5}$).

Mitigation of anthropogenic emissions results in domain-mean surface $O_3$ mixing ratios increase by ~1% in both seasons. On the other hand, significant reductions are calculated for pollutants dominated by primary emissions like CO. Domain-mean $PM_{2.5}$ levels are projected to decrease by ~10% in winter and ~6% in summer. The results point out improvements for some gaseous and several aerosol species in the urban areas of the cities, which could decrease the exceedences and the human exposure. Mitigation can be efficient for pollutants that are mostly of primary origin like CO and $PM_{2.5}$ but the system is more complex for secondary pollutants and in particular for $O_3$ due to the non-linear behavior of the chemistry of $O_3$-$NO_x$-NMVOC.

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AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES
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# COMBINING ENVIRONMENT AND HEALTH INFORMATION SYSTEMS FOR A FULL SCALE ASSESSMENT OF ATMOSPHERIC POLLUTION ON HUMAN HEALTH

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## ABSTRACT

The use of emerging technologies for environmental monitoring with satellite and in-situ sensors are essential instruments for assessing the impact of environmental pollution in human health especially in areas that require high spatial and temporal resolution. This was until recently a rather difficult problem. In this work a new approach for integrating monitoring data for the detection and verification of health threats attributed to environmental causes is presented. Regrettably, the reporting of spatial resolution is frequently inadequate in reporting environmental causes and health effects in the same time scale. This work refers to atmospheric pollution and examines different level of frequency and severity of health impact assessments.

The data sets needed for the integration of environment and health systems are classified against a unique nine scale pyramid of environmental consequences and against a corresponding nine scale pyramid of health effects. This work also generalizes the methodology in way that facilitates new regulatory policies and permits abatement strategies that close to real-time with innovative modelling and in-situ monitoring applications. It also allows the merging information systems for accurately describing chronic and acute environmental burdens. In addition, it facilitates a precise representation of human exposure taking into account the randomness of human activities and the accurate representation of environmental stressors of human exposure.

## 1. INTRODUCTION

For determining the status of these pollutants, monitoring stations are usually placed at the centre and periphery of urban areas as well as in surrounding rural areas. The procedure of positioning these stations is different from country to country and the measuring instruments employed vary for the different pollutants. In addition, for generalisation purposes it is essential to demonstrate the geographical representation of measurements. It is well known that this dependents greatly on the complexity of topography and the existence of nearby sources. For several European metropolitan areas these complexities prevents the establishment of representative urban background stations in most domains. Furthermore, the annual availability of these data is not usually 100%. For these reasons we have been developing in the late nineties devices that could be mobile, utilised on real-time and ideally have low cost so that could be used by a network of citizens.

At the same time we have been looking into sensors that could be deployed in satellites and can characterise the local level of atmospheric pollution with the same instrument over large geographical areas. The aim of such sensors was to have available data with instruments that can provide details in high spatial resolution and at same time characterise the air pollutants at different heights in the vertical column along the trajectory of the satellite pass.

The needs of mobile telecommunication all over the world have financed and encouraged the deployment of an intense network of ground and satellite based telematic stations which successfully remotely handle an enormous number of cells that share and relay voice or internet communication among users. These infrastructures are capable of handling more activities. In particular they can describe accurately the randomness of human behaviour. For example if there is real danger from anthropogenic emissions we need to know why a certain number of cars need to utilise a certain piece of road at a specific time of a day. Certainly we need also to know where this pollution is dispersed. But, more importantly we need to know the age and health characteristics of the persons involved, the exposure concentration, the time spent under such conditions, the possibilities for diverting these traffic flows to alternative routes and finally to successfully forecast and abate similar conditions. Efforts therefore are being made to set up information systems, which link health effects to environmental causes through a set of monitoring parameters, which are generally referred to as indicators. Unfortunately, these are usually inadequate to identify concretely the health and environment effects. Nor it was possible to characterise peak health events that occurs at specific locations (hot spots) during specific episodes. Hence, large area averaging and reporting over the whole year are not sufficient and result in doubtful conclusions or even to incorrect abatement approaches.

"Effect-assessment" has also to consider that both the human and environmental populations consist of individuals – every one of whom reacts in a unique way to a challenge or stressor. The key concept is high spatial resolution monitoring of populations susceptible to specific environmental hazards. Existing ground and remote telecommunication infrastructures can change drastically the monitoring of ambient (outdoor and indoor) air pollution and enhance the use of low cost innovative applications for the abatement of environmental pollution. The current understanding of the situation in densely populated areas should be increased, before commitments are made for reductions in total emissions as well as for assessing the effects of reduced trans-boundary fluxes. The potential benefits from the deployment of a network of sensors are already realised (Walker and Skouloudis, 2009) and knowledge of population exposure, with the use of existing tools, can lead to the accurate characterisation of health effects. Such sensor networks can be coupled with a wider use of earth observation that can assist in facilitating the monitoring and reporting requirements in high resolution and promote the development of new applications for Environment and Health protection strategies. These observations also harmonize reporting and provide a systematic warning of legislative violations.

## 2. IN-SITU SENSORS FOR ATMOSPHERIC POLLUTION

A pilot unit has been installed for a testing period of nine months and stayed operational for more than three years. This unit is equipped with five sensors for the measurement of CO, $NO_x$, $NO_2$, $O_3$ and $C_6H_6$. Contrary to conventional monitoring devices, this unit is a system capable of recording values with a frequency of a few seconds and storing the values locally for transmission to a remote based data storage system. Hence, hourly values can be real temporal average of 120 measurements made every 30 sec instead of instantaneous values obtained every 60 minutes. This frequency has been selected for the initial deployment in order to avoid costly remote interrogations.

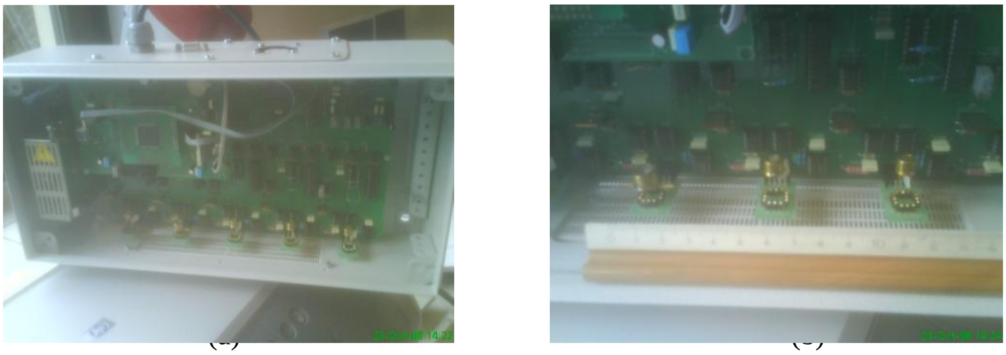

Figure 1. The inside depict of the integrated unit (a) including the telecommunication device for remote control and the five sensors for CO, $NO_x$, $NO_2$, $O_3$ and $C_6H_6$. Close up (b) of three sensors next to the inlet of the monitoring unit.

Figure 2. The deployment of a sensor unit for intensive monitoring at a port in Malta.

Such devices (figure 1) have been tested for several years at full-scale monitoring and there are several referred publications, with inter-comparisons carried out with conventional monitoring in difficult sites next to ports (figure 2) or industrial installation or in locations near to heavy traffic and street canyons (figure 3).

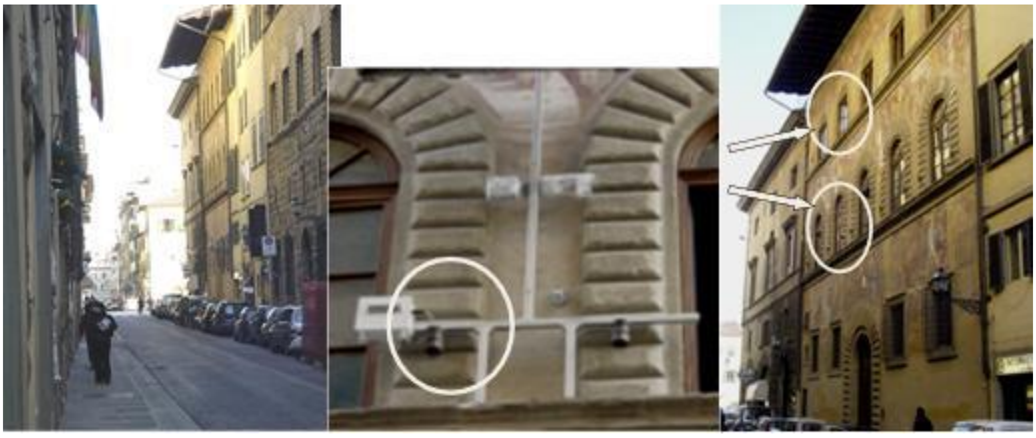

Figure 3. Intensive monitoring at narrow streets (campaign of M.C Carotta at Palazzo Mellini Fossi in Florence, http://ws.fe.infn.it/lab/ericerca_sensoristica.php)

Prior to full scale deployment a pilot unit has been utilised as a plug and play monitoring device over several months. The purpose of such deployments is not to inter-compare with conventional tools, nor the reporting for this single system for air-quality standards, but a demonstration of the capabilities of these systems to measure concentrations at a rate that other systems cannot do. Such comparison examples are shown for two of the five gases (CO and $C_6H_6$) at figure 4.

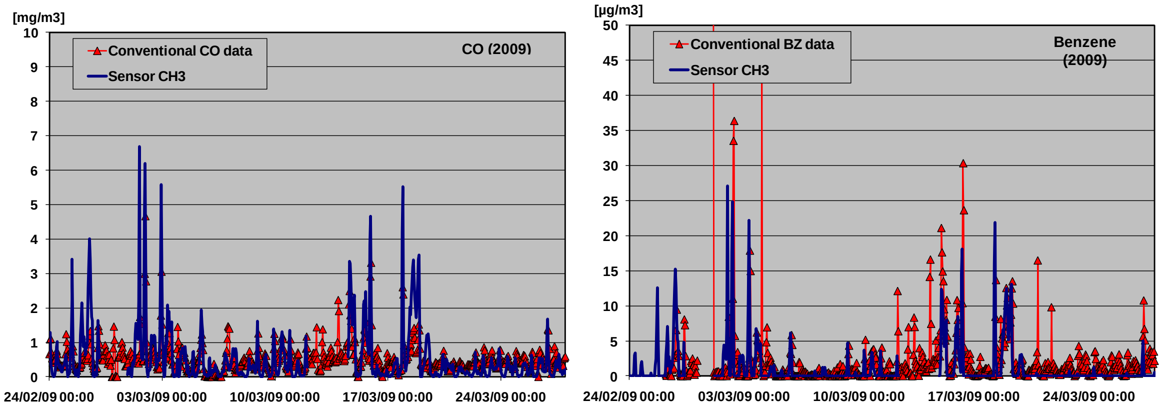

Figure 4. Comparison between conventional monitoring and the in-situ sensor measurements at the port of Malta during spring of 2009.

The monitoring was carried out during the spring of 2009. A similar graph for the same gases is shown at figure 5 for the summer of the same year. The comparison reveal not only that the unit with the multi-gas sensors is capable to reproduce the concentrations from the conventional measuring instruments, but because the sensors have a much more higher frequently of measuring these can be utilised for the real temporal for characterisation of peaks or attributing human exposure without the need to refer to exposure boxes. It should be also taken into consideration that the sensor units do not have need for calibration process. Hence, there are not black-out periods during the monitoring process.

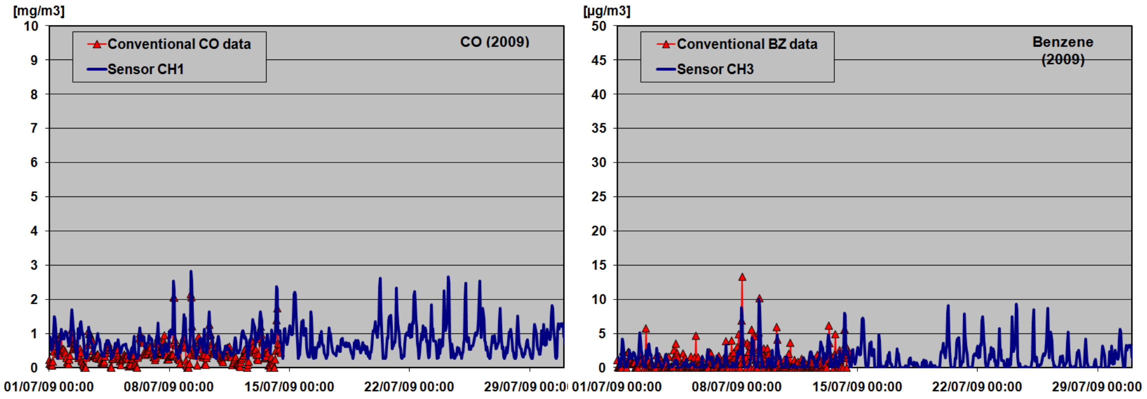

Figure 5. Comparison between conventional monitoring and the in-situ sensor measurements at the port of Malta during summer of 2009.

## 3. CITIZEN’S MONITORING NETWORKS

Nowadays, it is not rare to have health data to be closely connected to environmental conditions. Among other factors, it is essential to know, not only the environmental causes of the problems, but also the attribution of population at risk at very high spatial resolution.

Health risks from atmospheric pollution may potentially result from the various sizes of particular matter, $NO_2$ or its reaction products including $O_3$ and other volatile organic components that have been introduced in the 90ties as part of the combustion process. Oxides of nitrogen destroy organic matter such as human tissue. Animals exposed to $NO_x$ are less able to ward off bacterial infections and die more often. Their susceptibility to viral infection increases, exposure to high levels of $NO_x$ for weeks causes emphysema-like changes in the lungs of animals. Children aged 12 and younger who are exposed to $NO_x$ have more respiratory illness (Harrington and Krupnick, 1985). Those exposed to high levels of $NO_x$ outdoors had more colds that settled in their chests, chronic wheezing and cough, bronchitis, chest cough with phlegm, and episodes of respiratory illness (Hasselblad et.al, 1992).

Until now the health evidence of atmospheric pollution originate from epidemiological studies based on outdoor exposures with limited separation between direct and indirect risks. In particular, the health effects of $NO_2$ originate largely from toxicological studies and from inconclusive observational studies on $NO_2$ exposure indoors. It is therefore essential to carry out studies with sever hundreds of sensor units as described above with aim to allocate pollution hazards to individual citizen levels in order to:

- Assess $NO_2$ effects assessed in respect of exposure to other pollutants
- Characterise the effects from the combination of PM and $NO_2$, possibly indicating a potential consequence of $HNO_3$ vapour and/or PM nitrate.
- Examine if $NO_2$ can be utilised as a marker indicator for traffic and industrial-related air pollution or, if a combination of more toxic pollutants might be essential for causes of acute and chronic adverse health effects.

In addition, recent studies show that for health effects associated with environmental causes, geographical attribution has become indispensable for processing, analysing and visualising of individual cases. For certain health needs, higher resolution spatial data are required for constructing disease maps and for ecological analysis. This has also lead to more frequent updates of these spatial representations.

In other words, instead of basing the epidemiological exposure on conventional monitoring data or to uncertain modelling of exposure, we can utilise sensor units at a zone where monitoring was not possible, in areas with high population concentration where human exposure is a sensitive issue or in areas where population exposure is critical.

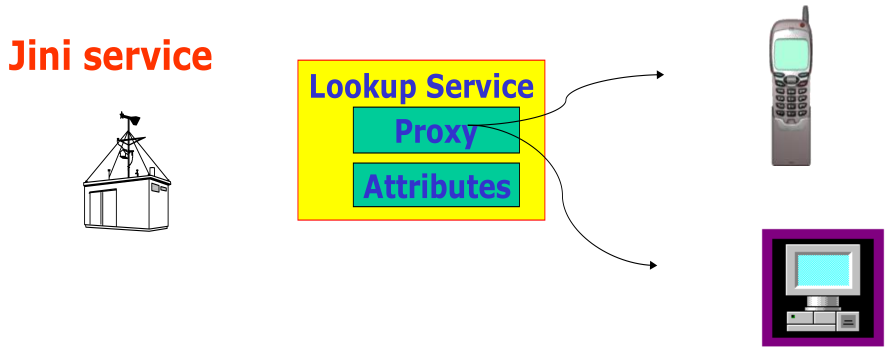

Figure 6. The creation of ad-hoc modern telematic network of devices capable to report gas concentrations on real-time (outdoors and indoor).

The sensor units described in the previous section already integrate GPS and communication devices for relaying the data under existing telematic infrastructures. Hence, there are two types of citizen's participation that could be utilised. As shown in figure 6 the data could receive information from fixed Jini type of units that measure the pollution at a fixed position or it could receive sensor signals from mobile units together with the exact location of where and when the measurements was taken. In both ways the measurements can be revealed on real-time either at the screen or through citizen's web applications.

Such applications will open the possibilities of assessing how much we have improved the life of the population, and at what cost, and we have to be sure we have not simply exported the problem to someone else's backyard. Such application will also reveal:

- The temporal trends in diseases after taking into consideration delays that occur between the exposure and the health problem as well as the interval between the onset of symptoms, the diagnosis of the problem and the eventual reporting.
- The geographic distribution of diseases or the causative exposures and the associated risks. For example, elevated blood-lead levels in children may represent exposure to heavy metal hazards or the exposure to high concentrations due to proximity in roads with heavy traffic which may require both medical and environmental intervention.
- The identification of people or groups who develop specific patterns of diseases due to their environmental or occupational exposure; eventually leading into identification of those at high risk, and targeting intervention efforts.
- The appropriateness of the abatement measures which for the time being are based on non-verifiable forecasts. This could become useful in the detection of outbreaks of rapid environmental problems with health effects.

The cost of such systems is high for the time being, but a proper deployment in medium and later at large geographical areas is going to significantly reduce this cost with a further enhancement of environmental monitoring applications (both for individual and general population exposure).

## 4. HARMONISED MONITORING WITH SATELLITE SENSORS

Although the in-situ sensors are excellent for the characterisation the effects with respect to time give suitable information on real-time they will require several hundreds of such sensors in order to describe large geographical areas especially in complex urban areas with large population density.

For such types of application the characterisation of human exposure can be carried out with observation from sensors deployed on satellites. One of the first sets of such sensors was the SCIAMACHY Vertical Column Imaging Spectrometer for the generation of maps under standardised condition all over the world for the $O_3$, $NO_2$, $H_2O$, $N_2O$, CO, $CH_4$, $H_2CO$, $SO_2$ as well as on aerosol absorption. Data could be provided at different resolutions. This was deployed on ENVISAT and was operational until very recently (May 2012) when the satellite was functioning. An example of the maps generated is shown at the figure 7 as generated by the Institute of Environmental Physics at the Ruprecht-Karls University of Heidelberg.

As shown at figure 8, measurements were carried out at nadir, limb, and solar/lunar occultation geometry. From the nadir and limb measurements total column amounts and stratospheric profiles of the aforementioned atmospheric constituents at rather coarse ground scales. However, from the dedicated limb/nadir mode will enable the derivation of tropospheric trace gas column amounts. The solar and lunar occultation measurements provide additional atmospheric profile information during sunrise and moonrise but have a restricted range of latitudes as a result of the sun synchronous orbit of ENVISAT (local equator crossing time of about 10.00 a.m. in descending node). The details of the can be consulted at the handbook of the German contribution to SCHIAMACHY (Kirchhoff et. al, 2011).

The main advantage of these observations is that the same time of instrument can standardise the levels of pollution all over the world. However, the disadvantage are because the revisiting time over the same geographical location of the satellite is several days this kind of monitoring is not suitable for real-time reporting. Another problem is the spatial resolution (figure 8). But this is addressed by the deployment of more modern sensors with significant improvements in the near future.

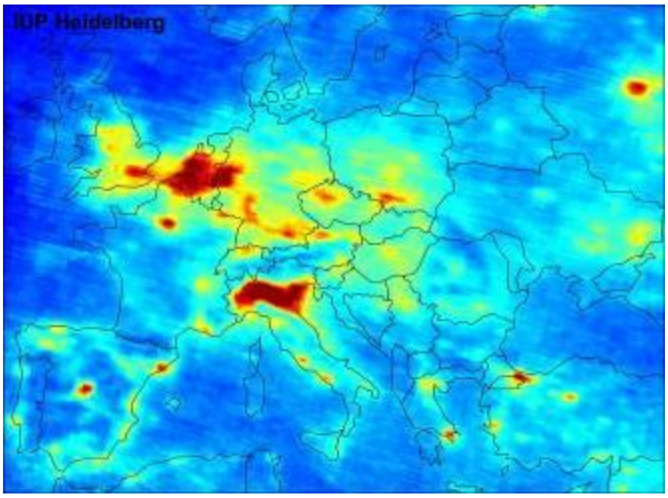

Figure 7. Vertical column $NO_2$ levels over Europe as per SCIAMACHY (European Space Agency and IUP Heidelberg 2005)

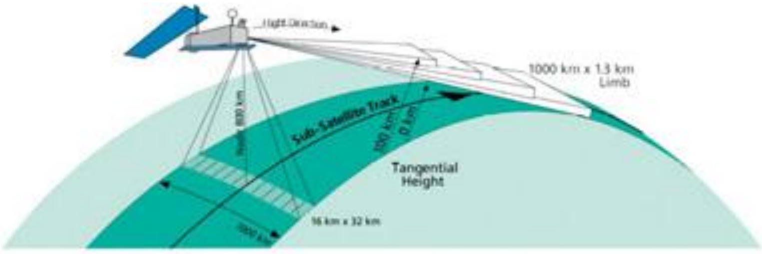

Figure 8. Measurements at nadir and limb with sensors deployed over satellites for global scale (example from the SCIAMACHY Spectrometer (ESA, 2005).

## 5. HEALTH IMPACT ASSESSMENTS

Systematic air-quality monitoring data are not easily available everywhere. However, for the purposes of this study it will be necessary to examine the consequences in one of the largest metropolitan areas in Europe. Even, if data can be considered only for the quantification of effects and not for a detailed health quality assessment. For the latter, a campaign with several in-situ sensor units must be deployed over a period of more than one year.

Nevertheless, with the ENVISAT maps and several publications on the concentration for $NO_2$ an estimate of the level of health effects could be carried out. The local concentrations for assessing health effects are taken from (Onkal-Engin et.al, 2004 and Ozkurt, 2011). In the first study, data were collected at 6 different air monitoring sites, at Kagithane, Besiktas, Esenler, Sariyer, Fatih and Bagcilar. The second study reported concentrations from the Can-Bayramic region in 2006. At these areas live approximately 30% of the total population. They are also considered to be mainly residential areas with some industrial activities. The data were collected daily and covered periods of 12-20 months. The maximum $NO_2$ concentration ranged from 10 to 65µg/m3.

Although, the concentration-response relationships are not readily established for $NO_2$ for acute effects based primarily on human exposure studies some associations have been observed only between $NO_2$ and mortality in daily time-series studies. Unfortunately, these cannot be attributed only to $NO_2$ with reasonable certainty. However, since $NO_2$ is often highly correlated with levels of other ambient pollutants emitted by the same sources or related through complex atmospheric reactions, $NO_2$ can be used as a surrogate for unmeasured traffic related pollutants such as organic and elemental carbon or freshly emitted primary ultra-fine particles (WHO 2003).

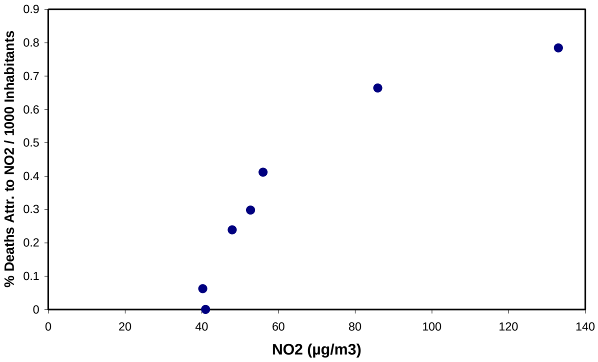

Figure 9. Deaths attributed to atmospheric pollution at Italian cities in 2004.

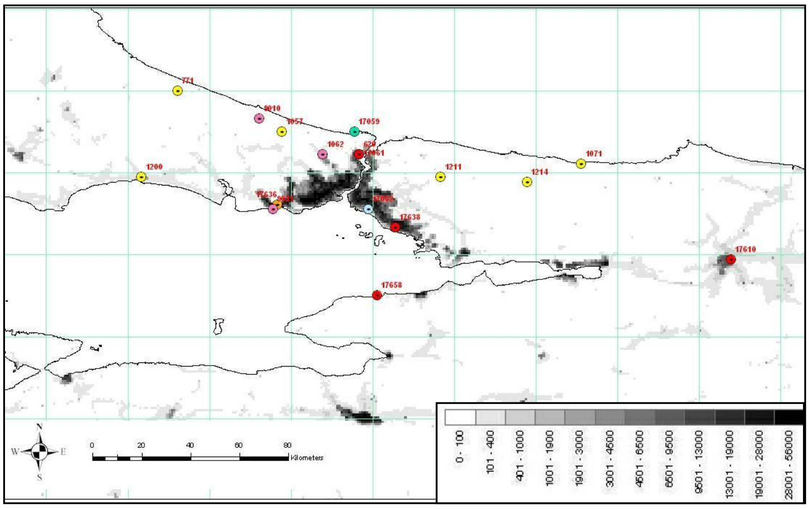

Figure 10. Population density in great area of Istanbul attributed in 1x1 $km^2$.

Based on the evidence from several Italian cities and because of the close similarity of the climatic conditions from figure 9 and with the concentration from urban measuring stations in close proximity to the kerbside it is reasonable to expect approximately 4000 deaths that could be attributed to atmospheric pollution due to $NO_2$. This number is in the range of numbers reported by several other studies (Hoek et.al. 2002 and Stieb et.al. 2002 etc).

The fact that Istanbul has regions with the highest population density in Europe together with the fact that weather conditions might allow acute pollution episodes during the year make this domain is ideal for identifying if there are health consequences from atmospheric pollution or not. These studies are beyond the scope of this introductory work. However, prior to the epidemiological studies it will be necessary to carry out detailed monitoring at various locations for several years at high spatial resolution (at least 1x1 $km^2$). This will need to be followed by a detailed source apportionment of concentrations according to the methodology developed by AutoOil-2 (Skouloudis, 2000, EC DG-ENV 2001).

## 6. CONCLUSIONS

Environmental monitoring with satellites and mobile micro-sensors can significantly enhance the consistency of reporting of environmental problems and the improvement of geographical representativeness. A suitable network of sensors can be of valuable assistance in areas where local health rates are significantly different from the macro-scale rates. It will also allow the real-time overlaying of environmental information for the identification of important acute health effects at specific population groups. Last but not least these new technologies allow the monitoring in real-time the effectiveness of local and national abatement strategies.

Integrated Environment and Health Information Systems on the other hand, provide new incentives on innovative environmental informatics projects targeted on the impact of policies for environment and public health. They provide a new perception of environment and health data-bases across time and space and allow solution to problems that were difficult to associate before to environmental causes. With this work are presented new areas of integrated applications that are based on existing infrastructures. In particular we are proposing to achieve this though the use of:

- Movable terminal communication interface with processing capabilities with wireless communication for tracking and collection of data and
- Innovative scalable network architecture with improved network management.

This work suggests that no Health and Environment Information System will be successful unless it offers benefits to all citizens along the value chain. An integrated environment and health system is the result of agreements that exist between those who provide data and the actual users of those data. This will promote data access, sharing, stimulate the reduction of burden, and resolve ethical issues related with the protection of confidentiality.

No legislatives policies are currently focusing separately on the health for specific population groups, mainly because this requires the construction of composite data sets at the same spatial and temporal resolution. With the emergence of technologies described here at high spatial and temporal resolution, such studies will become possible, allowing targeted policies for sensitive population groups, as well as for identifying problems masked within national and regional mean values.

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# HUMAN HEALTH BENEFITS OF EMISSION CONTROLS USING SINGLE AND MULTIPOLLUTANT INDICATORS OF MOBILE SOURCES

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## ABSTRACT

This work discussed a novel method to combine pollutants in a multipollutant indicator. The use of integrated mobile source indicators (IMSI) in epidemiologic modeling constitutes an alternative approach to assess the health impact of pollutant mixtures. Human health benefits, as a result of emission controls, are estimated and compared using single pollutants (EC, CO, NOx) and IMSI developing health-emission response ratios and estimating costs of emission reductions. The HHB, as a result of reduction in mobile source emissions, are estimated between 1.19-1.66 million USD per year during 1999-2004 in Atlanta, using integrated indicators. IMSI were found better surrogates of the mobile sources than single pollutants based on a larger spatial representativeness.

## 1. INTRODUCTION

In the past years, substantial progress has been made to move towards a result-oriented, risk-based multipollutant approach in air quality management. A consistent limitation of adopting this multipollutant approach has been in the identifying mixtures of pollutants in the atmosphere and the health effects of such mixtures (US-EPA, 2007; NRC, 2004; Hidy et al., 2010). Statistical tools such as factor analysis (FA) and principal component analysis (PCA) have been suggested to overcome this limitation. Receptor models are also useful with the constraint of conserving mass, unlike FA or PCA. However, these techniques rely on an abundant amount of air quality data including availability of specific compounds that are not routinely measured.

Multipollutant models in epidemiologic analysis have generally included two or more pollutants at a time in a model, with the goal of identifying confounders in the associations with health rather than the effects of a mixture of pollutants (Mauderly and Samet, 2009; Dominici et al., 2010; Mauderly et al., 2010; Bell et al., 2011). Multipollutant models are subject to exposure measurement error in the same way that single pollutant models are, but can also have differential errors (e.g., where the pollutant measured with the least amount of error is the one with the strongest signals) and reduced statistical power (when more than one pollutant at a time is included) (Vedal and Kaufman, 2011). Moreover, the mixtures included in multipollutant models do not always represent an actual or unique source of emissions which complicates designing effective measures to improve public health (Lenters et al., 2010; Metzger et al.,2004; Franklin et al.,2008; Peng et al.,2009; Hart et al.,2011)

Mobile source emissions have been identified as a key urban air pollution component adversely affecting public health (Beelen et al.,2008; Tonne et al.,2007). In the Atlanta area, elevated $NO_2$, CO, $PM_{2.5}$, organic carbon (OC) and EC concentrations, pollutants traditionally related to traffic, have been associated with Emergency Department (ED) visits for cardiovascular disease (CVD) (Metzger et al.,2004; HEI, 2010). Results from using receptor models in epidemiologic analysis provide further support that combustion-related sources are associated with CVD (Sarnat et al., 2008).

In this work we present the development and assessment of outcome-based, multipollutant indicators for mobile sources here called Integrated Mobile Source Indicators (IMSI) from our novelty manuscript (Pachon et al., 2012). IMSIs are simple to construct and calculate from readily available data and are for use in air quality and epidemiologic analyses. The use of IMSI in epidemiologic modeling constitutes an alternative approach to assess the health impact of pollutant mixtures. The HHB, as a result of reduction in mobile source emissions, are estimated between 1.19-1.66 million U$ per year during 1999-2004 in Atlanta, using integrated indicators. IMSI were found better surrogates of the mobile sources than single pollutants based on a larger spatial representativeness.

## 2. METHODS

The development of emission-based integrated mobile source indicators (EB-IMSI) follows the approach presented in our previous work (Pachon et al., 2012). Briefly, EB-IMSI uses ratios of mobile-source-to-total emissions as weighting coefficients in the combinations of ambient EC, CO and $NO_x$. The rate of change in pollutant concentrations as a result of the change in emissions is estimated as the regression slope between long-term concentrations and emissions for EC, CO and NOx (‘m’). Similarly, the rate of change in integrated mobile source emissions (IMSE) is regressed against the rate of change in ambient values of EB-IMSIs.

*Estimation of human health benefits using single and multipollutant indicators in Atlanta*

We have obtained the CVD-ED risk per change of pollutant concentrations (EC, CO, NOx) and multipollutant indicators (EB-IMSI) in Atlanta during 1999-2004. This concentration-response function (β) along with the concentration-emission relationship, ‘m’, is used to model the influence of changing emissions and corresponding incidences on adverse health impacts (here called ‘h’):

$$h\left(\frac{risk}{emissions}\right) = \beta\left(\frac{risk}{conc}\right) * m\left(\frac{conc}{emissions}\right) \tag{1}$$

where ‘risk’ is a unitless variable.

Estimates of HHB are expressed as the number of CVD-ED visits avoided per year during 1999-2004 as a result of reductions in mobile source emissions of EC, CO and NOx. The HHB is estimated as the product of ‘h’ $(ton/yr)^{-1}$ and emission reduction from 1999 to 2004 in ton/yr.

$$HHB = h\left(\frac{risk}{ton/yr}\right) * \Delta E\left(\frac{ton}{yr}\right) * 25{,}000\frac{visits}{yr} \tag{2}$$

The factor 25,000 accounts for the average number of CVD-ED visits per year in Atlanta during 1999-2004 (Tolbert et al., 2007).

The annual savings in costs of HHB (S) can then be estimated applying the typical cost of treating one CVD visit. Our calculations are based on the cost of illness (COI) for CVD provided by US-EPA (2004), which considers only direct expenditures (costs of treating or mitigating the health effect) and not the value of avoided pain and suffering or premature mortality, which are considered in more comprehensive cost-benefit analyses of air pollution.

$$S\left(\frac{\$}{yr}\right) = HHB\left(\frac{visits}{yr}\right) * COI(\$) \tag{3}$$

with respective uncertainty estimated as $\sigma_S = COI * \sigma_{HHB}$.

## 3. RESULTS

Ambient concentrations of CO, NOx and EC are plotted versus CO, NOx and EC emissions respectively in Atlanta from 1999 to 2007 observing high correlation coefficients ($R^2$=0.94 for CO, $R^2$=0.68 for $NO_X$, $R^2$=0.60 for EC) (Fig. 1). Concentration-emission regression slopes are statistically significant at the 95% confidence interval (CI), but regression intercepts are not. The rate of change in ambient concentrations of CO as a result of change in CO emissions is 1.51 ± 0.17 ppm/$10^3$ tons/yr/km$^2$, which is equivalent to $7.2\text{x}10^{-6} \pm 8.1\text{x}10^{-7}$ ppm/(ton/yr) when de-normalized by the area of Fulton County. For $NO_X$, the rate of change in ambient concentrations as a result of change in emissions is 0.54 ± 0.14 ppm/$10^3$ tons/yr/km$^2$ ($2.6\text{x}10^{-6} \pm 6.7\text{x}10^{-7}$ ppm/ton/yr). The rate of change in ambient CO is greater than the rate of change in ambient $NO_X$ as a result of change in emissions, which is explained by higher CO concentrations in the atmosphere than $NO_X$ (1.05ppm CO and 0.11ppm $NO_X$ averages during 1999-2007).

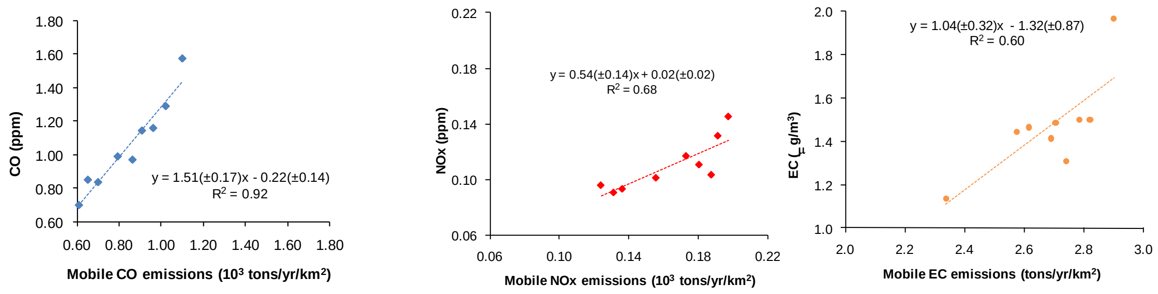

Figure 1 Ambient pollutants vs. emissions in Atlanta for 1999-2007

The rate of change in ambient concentrations of EC as a result of change in EC emissions is 1.04 ± 0.32 (μg/m$^3$)/(tons/yr/km$^2$), which is equivalent to $5.9\text{x}10^{-3} \pm 1.5\text{x}10^{-3}$ (μg/m$^3$)/(ton/yr). The relative uncertainty (uncertainty/slope) of the regression slopes is larger for EC and NOx (approx. 30%) than CO (10%).

The rates of change in ambient concentrations of EB-IMSIs as a result of change in IMSEs, after de-normalizing by the area, are: $4.36\text{x}10^{-6}\pm7.1\text{x}10^{-7}$ EB-IMSI/(ton/yr), $5.2\text{x}10^{-6}\pm5.2\text{x}10^{-7}$ EB-IMSI-GV/(ton/yr), $4.5\text{x}10^{-5}\pm1.6\text{x}10^{-5}$ EB-IMSI-DV/(ton/yr), which denotes a larger response in EB-IMSI-DV per ton of integrated pollutants reduced than EB-IMSI and EB-

IMSI-GV. The similarity in the rate of changes for EB-IMSI and EB-IMSI-GV is explained by the weight of CO and NOx in both indicators and suggests that most of the vehicles source impacts are from GV. The relative uncertainties in the regression slopes are about 20% for EB-IMSI, 10% for EB-IMSI-GV and 30% for EB-IMSI-DV.

*Human health benefits of emission controls using single and multipollutant indicators of mobile sources*

The changes in incidences on adverse cardiovascular impacts associated with the increase in mobile emissions ‘h’ (ton/yr)$^{-1}$ is substantially larger for EC than CO or NOx (Table 1), due to the greater health signal per μg/m$^3$ (β) observed for EC compared to that for CO (7.41x10$^{-6}$ (μg/m$^3$)$^{-1}$) or NOx (6.1x10$^{-5}$ (μg/m$^3$)$^{-1}$), though signal for EC was borderline significant at the 95% CI (Table 1).

Table 1 Savings in CVD visits avoided by reduction in emissions of CO, NOx and EC in Atlanta

| | **CO** | **NOx** | **EC** |
|---|---|---|---|
| β estimate for CVD outcomes<br>(p-value) | 0.0085 ± 0.004 ppm$^{-1}$<br>(0.033) | 0.095 ± 0.04 ppm$^{-1}$<br>(0.018) | 0.0078 ± 0.004 (ug/m$^3$)$^{-1}$<br>(0.054) |
| Rate of change in ambient conc. to change in emissions ‘m’ | 7.2x10$^{-6}$ ± 8.1x10$^{-7}$ (ppm/ton/yr) | 2.6x10$^{-6}$ ± 6.7x10$^{-7}$ (ppm/ton/yr) | 5.0x10$^{-3}$ ± 1.5x10$^{-3}$ (μg/m$^3$)/(ton/yr) |
| Risk per ton of emission ‘h’ (ton/yr)$^{-1}$ | 6.1x10$^{-8}$ ± 2.9x10$^{-8}$ | 2.4x10$^{-7}$ ± 1.2x10$^{-7}$ | 3.9x10$^{-5}$ ± 2.3x10$^{-5}$ |
| Average emission reduction 1999-2004 (ton/yr) | 10,690 ± 5,000<br>(5.4%)$^{\&}$ | 1,450 ± 330<br>(3.8%)$^{\&}$ | 7.3 ± 4.7<br>(1.3%)$^{\&}$ |
| HHB (CVD-ED visits avoided/yr) from 1999-2004 | 16<br>(5-27) | 9<br>(4-14) | 7<br>(1-13) |
| Annual savings in costs of CVD visits avoided from 1999-2004 ‘S’ (million $) | 0.30<br>(0.10-0.50) | 0.16<br>(0.07-0.25) | 0.13<br>(0.02-0.24) |
| Savings in CVD per ton of emissions (S’) ($/ton) | 28<br>(15-41) | 112<br>(56-168) | 17,800<br>(7200-28400) |

* Cost of Illness (COI) for all-cardiovascular diseases estimated at $18,387 per unit (US-EPA, 2004) $^{\&}$ (percentage with respect to average emissions during 1999-2007)

The savings in costs of CVD visits avoided per ton of pollutant reduced (S’) ($/ton) is the largest for EC. Fann et al. (2009) also found larger health benefits ($/ton) in the reduction of directly emitted carbonaceous particles over gases ($NO_x$, $NH_3$, $SO_x$ and VOC) in the US. They suggested that particles are more stable in the atmosphere and emitted more closely to the population than gases, resulting in larger health effects.

However, reduction in emissions of EC (average of 8 tons/yr from 1999-2004) is much less than the reduction in emissions of CO and NOx (averages of 10,000 tons/yr and 1,500 tons/yr from 1999-2004 respectively). When this reduction in emissions is taken into account, the number of CVD visits saved per year (HHB) and the respective annual savings (S) are larger for CO than NOx or EC. The largest HHB for CO is explained by the greater reduction in emissions of CO in comparison of NOx and EC. Given that CO was found to be a good indicator of GV impacts, the HHB associated with CO can be interpreted as result of the controls in GV emission from 1999-2004. Similar analysis for DV impacts is difficult since EC was not found a robust indicator of DV and NOx is significantly emitted by both GV and DV in Atlanta. With these limitations, the HHB associated with NOx and EC are similar in magnitude and can be partially explained by the controls in DV emissions from 1999-2004.

The comparison of HHB among pollutants suggest that emission reductions in CO, likely explained by emission controls on GV, have been more effective for improving public health than emission reductions in NOx or EC, partially explained by emission controls on DV. However, improvements in public health should consider further reductions in NOx and EC emissions, and therefore controls on DV, since health benefits per ton of emission are much larger for these two pollutants than for CO.

*Analysis using multipollutant indicators*

The CVD risk associated with the increase in IMSE ‘h’ $(\text{ton/yr})^{-1}$ is larger for IMSE-DV than IMSE-GV or IMSE (Table 2) because the EB-IMSI-DV has a larger health signal per unit of IMSI ($\beta$) than EB-IMSI and EB-IMSI-GV. The association of EB-IMSIs and CVD outcomes is statistically significant in all cases ($p\text{-value}<0.05$). Integrated emission reductions from 1999-2004 are larger for EB-IMSI and EB-IMSI-GV than EB-IMSI-DV, because the first two indicators include reductions of CO, which are larger than reductions in NOx or EC (Table 1). Nonetheless, reductions in integrated emissions are between 5-6% of their average emission for the integrated indicators, a range that is smaller than the range of reductions for single pollutants (1-6%).

Using the integrated indicators, the calculated human health benefits (HHB) during 1999-2004 vary between 11 and 14 visits avoided per year, equivalent to $0.20-0.25 million annually, as a result of reductions in mobile source emissions (Table 2). EB-IMSI, as an indicator of the overall fleet, has a larger HHB than EB-IMSI-GV or EB-IMSI-DV. Although, integrated emissions for EB-IMSI are the sum of the integrated emissions for EB-IMSI-GV and EB-IMSI-DV (Equations 5.4-5.6), the HHB are not expected to be additive, since the health response of EB-IMSI is not the sum of health signals for EB-IMSI-GV and EB-IMSI-DV.

Similar to the analysis using single species, the calculated HHB associated with the reduction in GV emissions were observed to be greater than the benefits accrued from reducing DV emissions. Using CO finds similar results than using EB-IMSI-GV (5-27 vs. 4-22 avoided CVD visits per year respectively). The slightly smaller HHB using EB-IMSI-GV is explained by the presence of NOx in the integrated indicator leading to a lower value of ‘h’ in comparison to CO alone. Previously, we have suggested EB-IMSI-GV as a better indicator of GV than CO, based on a larger spatial representativeness of EB-IMSI-GV that is consistent with emissions from GV spread around the metro Atlanta area (Pachon et al., 2011).

Table 2 Savings in CVD visits avoided by reduction in integrated emissions and assessed through EB-IMSI

| | **EB-IMSI** | **EB-IMSI-GV** | **EB-IMSI-DV** |
|---|---|---|---|
| β estimate for CVD outcomes<br>(p-value) | 0.0103 ± 0.0048<br>(0.029) | 0.0088 ± 0.0042<br>(0.018) | 0.0115 ± 0.0054<br>(0.022) |
| Rate of change in ambient conc. to change in emissions ‘m’ (IMSI/ton/yr) | $4.3\text{x}10^{-6} \pm 7.1\text{x}10^{-7}$ | $5.2\text{x}10^{-6} \pm 5.2\text{x}10^{-7}$ | $4.5\text{x}10^{-5} \pm 1.6\text{x}10^{-5}$ |
| Risk per ton of emission ‘h’ $(\text{ton/yr})^{-1}$ | $4.5\text{x}10^{-8} \pm 2.2\text{x}10^{-8}$ | $4.6\text{x}10^{-8} \pm 2.3\text{x}10^{-8}$ | $5.2\text{x}10^{-7} \pm 3.0\text{x}10^{-7}$ |
| Average emission reduction 1999-2004 (ton/yr) | 12,150 ± 5,000<br>(6.0%)$^{\&}$ | 11,300 ± 5,000<br>(4.5%)$^{\&}$ | 830 ± 170<br>(6.0%)$^{\&}$ |
| HHB (CVD-ED visits avoided/yr) from 1999-2004 | 14<br>(5-23) | 13<br>(4-22) | 11<br>(4-18) |
| Annual savings in costs of CVD visits avoided from 1999-2004 ‘S’ (million $) | 0.25<br>(0.09-0.41) | 0.24<br>(0.08-0.40) | 0.20<br>(0.08-0.32) |
| Savings in CVD per ton of emissions (S’) ($/ton) | 21<br>(11-31) | 21<br>(11-31) | 240<br>(100-380) |

* Cost of Illness (COI) for all-cardiovascular diseases estimated at $18,387 per unit (US-EPA, 2004)

On the other hand, using EC resulted in less HHB than using EB-IMSI-DV as indicator of DV impacts (1-13 vs. 4-18 avoided CVD visits per year respectively). The larger HHB using EB-IMSI-DV is explained by the presence of NOx in the integrated indicator leading to greater average emission reductions from 1999-2004, even though the value of ‘h’ is substantially smaller for EB-IMSI-DV than EC. Similarly to EB-IMSI-GV, our previous work suggested EB-IMSI-DV as a better indicator of DV than EC, based on a larger spatial representativeness of EB-IMSI-DV (Pachon et al., 2011). Additionally, while the association of EC with CVD outcomes was only border line significant, EB-IMSI-DV was found significantly associated with CVD outcomes in an epidemiologic model.

NOx has been suggested as an indicator of mobile sources, without distinction between GV and DV, and it has been used to study associations between mobile source impacts and cardio-vascular health in several studies (Brook et al., 2007; Burnett et al., 2004; Metzger et al., 2004). In previous work, we found NOx as the species most significantly associated with CVD outcomes, probably due to its larger spatial representativeness over CO and EC (Pachon et al., 2011). The calculation of HHB using NOx resulted in less number of CVD visits avoided than EB-IMSI (4-14 vs. 5-23). The larger HHB using EB-IMSI is explained by the presence of CO in the integrated indicator leading to greater average emission reductions from 1999-2004, even though the value of '$\beta$' is substantially smaller for EB-IMSI than NOx.

## 4. CONCLUSIONS

We presented a method to assess human health benefits of emission controls using single and multipollutant indicators of mobile sources. We found that using EC, as a tracer of heavy-duty vehicles, resulted in larger savings in costs of CVD visits avoided per ton of pollutant reduced. However, reduction in EC emissions is much less than reduction in CO and $NO_x$ emissions. When this reduction in emissions is taken into account, the number of CVD visits saved per year (HHB) and the respective annual savings (S) are larger for CO than $NO_x$ or EC. Using integrated indicators, we observe that EB-IMSI, as an indicator of the overall fleet, has a larger HHB than EB-IMSI-GV or EB-IMSI-DV.

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# HEALTH EFFECTS OF URBAN AIR POLLUTION IN TIRUCHI CITY,CENTRAL TAMIL NADU

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## ABSTRACT

Currently, in India, air pollution is widespread in urban areas where vehicles are the major contributors except in a few other areas with a high concentration of industries and thermal power plants. Attributed to location of industries in non residential areas and enforcement of air pollution standards by the Pollution control board, industrial air pollution could be considered less deleterious than vehicular pollution. Rapid urbanisation and modernisation has led to an unprecedented increase in the number of vehicles in the city. Against 1.9 million vehicular populations in 1990 in Delhi, it rose to nearly 3.6 million in the year 2001. During the same period, Delhi’s population has increased by only 43 per cent and road-length by merely 14 per cent respectively. Similar increase in vehicles in all the urban centres of India is a reality, leading to deleterious effect on the health of the people. Ambient air quality was monitored along with micrometeorological data and the results are discussed. The status of air pollution in the area has been evaluated and a questionnaire survey was conducted to estimate the allergic symptoms and exposure to assess the respiratory disorders. The data are analysed to evaluate the critical situation arising out of the emission of air pollutants and the impact on human health due to respirable diseases.The present research paper deals with the human health effects of urban air pollution in Tiruchi city,the central part of Tamil Nadu.

**Keywords**: health effects , urban air pollutants, tiruchi city, toxic substances

# SPATIAL DISTRIBUTION OF VOC CONCENTRATIONS AND CANCER RISK AROUND AN INDUSTRIAL REGION AT WESTERN TURKEY

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## ABSTRACT

Spatial distribution of VOC concentrations are measured at 46 sampling points at Aliağa region, which is a heavily industrialized area (including a petrochemical complex, petroleum refinery, ship-dismantling industry, several iron and steel plants and a gas-fired powerplant). Weekly passive sampling campaign was carried out in March 2006 and collected samples were analyzed by thermal desorption (TD) and gas chromatography/Flame Ionization detector (GC/FID). A total of 55 VOCs, including aromatics, olefins, paraffin and halogenated compounds were identified. Concentrations of VOCs were generally high at the stations located close to the refineries and gradually decreased with distance from industrial area, indicating that industrial activities are the main sources for measured VOCs at least in the close proximity of industries. The cancer risk potential is also calculated at each sampling points. The spatial distribution map of cancer risk indicated high levels along the major roads and around the petrochemical industrial areas and decreasing with distance from these sources. Consequently, the industrial activites and vehicle emissions are the principal sources of air pollution-related cancer risk in the Aliaga airshed. Furthermore, multivariate statistics, namely, principle component analysis (PCA) was applied to the VOC data. Four factors with eigenvalues >1.0, representing four sources, were extracted. These six factors accounted for 83% of the system variance. Identified VOC sources in the study area included 1) vehicular exhaust, 2) refinery emissions, and 3) industrial sources 4) heating source. Distribution of factor scores demonstrated our earlier hypothesis that VOC levels in the Aliağa airshed are determined by the industrial activities, particularly by petrochemical complex and the refinery. Traffic sources become also significant at the peripherals of the study area.
**Keywords:** Volatile Organic Compounds, Factor Analysis, Passive Sampling, Health Effects

## 1. INTRODUCTION

Aliağa region, which is located approximately 60 km to the north of Izmir is a heavily industrialized area. Although there are a large number of industries located in the region, the most important pollutant sources are the petroleum refinery, the petrochemical complex and a number of iron-steel plants. High concentrations of volatile organic compounds (VOC) have been especially emitted from the refinery and petrochemical complex. The other important characteristic of the region is the close the popular coastal area, Foça. The transit roads and the heavily industrialization has also contribute mobile emissions source in the region.

VOCs have been known to contribute to some of the most serious health problems (Parra et al.,2006); consequently people suffering from illnesses in Aliağa region are expected due to high concentrations of these pollutants in the atmosphere. VOCs also play a significant role in the formation and fate of airborne toxic chemicals and, in the presence of NOx, they react with OH radicals to form ozone (Ohura et al., 2006; Atkinson, 2000). Accordingly, the measurement of VOCs in ambient atmospheres, especially in heavily industrialized cities, becomes a crucial issue for the development strategies to mitigate affects on human health and urban air quality. To obtain effective results from action plans to mitigate VOCs, firstly the levels and sources of VOCs need to be properly determined; and consequently, understanding the sources of emissions and determining the respective sources of VOCs is essential.

Passive (diffusive) sampling has been widely used to measure VOCs in urban air (Hoque et al., 2008; Kume et al., 2008). The technique is suitable for both personal sampling and urban/rural measurements. The approach has found extensive use in air quality determinations, because samplers are rather cheap, they do not require electricity or battery powered pumps. Since VOCs concentrations changes with time and space, the determination of spatial distribution VOCs is very crucial. Hence passive sampling technique is preferred to measure VOCs for multi point samplings due to its advantages.

The aims of the study were to investigate sources of VOCs with the help factor analysis techniques and associated health effects. Spatial variability of the cancer risk was also evaluated to determine source contribution on the potential health risk. In the current study, ambient concentrations of VOCs were weekly measured at 46 sampling points, at Aliağa industrial area, using passive samplers in March 2006.

## 2. MATERIAL AND METHODS

### 2.1. Study Site

Study area is the Aliaga industrial region which is 60 km north of the metropolitan city of Izmir, Turkey. Aliaga is the high industrialized district of Izmir city, with refinery, ship breaking, and iron steel industry. The climate of the region is Mediterranean, with warm and rainy winters and dry and hot summers. Meteorological data during the sampling periods were obtained from the meteorological station located in the area that belongs to Turkish Meteorological Institute.

An important task of this study was the selection of the passive sampling points. In order to investigate the spatial distribution of VOCs in different areas which have different sources, 50 passive sampling points were selected based on their different landuse categories, populations and traffic and industrial densities. Figure 1 shows the passive sampling points in study area.

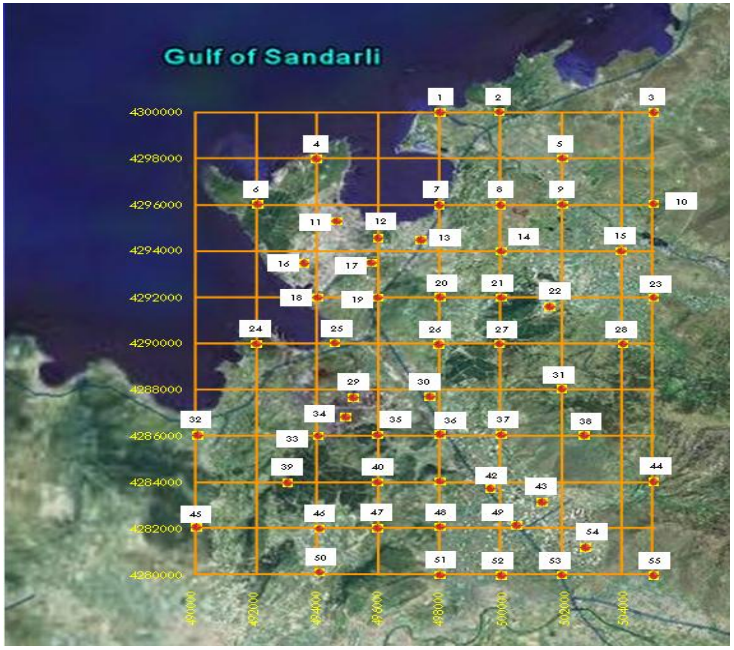

Figure1. Distribution of passive sampling points on the study area

## 2.2 Sampling and Analyzing of VOC

Samples were collected from 21 to 28 on March, 2006. Samplings were performed at 50 selected points within a sampling grid composed of about 600 km$^2$ which cover the whole urban and industrial region of Aliaga district. VOCs were measured with stainless steel tubes obtained from Gradko (6.35 mm O.D.×88.9 mm) and filled with Chromosorb 106 adsorbent (160 mg).measurement.

All VOC tubes before using were conditioned by purging them with 50 ml/min of pure nitrogen gas while heating them at 250 $^0$C, max allowable condition temperature for Chromosorb 106, in 15 min to remove any possible organic contaminants during storage.

VOC measurements were made using GC-FID (Agilent 6990) dual column coupled with Markes Unity Thermal Desorption System.. GC oven was programmed for 40 °C hold for 5 min and ramped to 195 °C at a rate of 5 °C/min with 10 min hold at 195 °C. Nitrogen was used as carrier gas with flow rate of 2.8 mL min−1 and 5.2 ml/min.

The external calibration standard mixture supplied by Environment Technology Center, Environment Canada (Ottawa, Canada) was used for the calibration Surrogate standard, 4-Bromofluorobenzene, was used to detect if any problem was encountered during sampling period or not.

Uptake rate used for concentration calculation was obtained from simultaneously measurements of passive and active sampling results conduted in the same point. The uptake rate was then calculated by formula derived from the Fick's law.

## 2.3 Factor Analysis Definition and model Implementation

Factor analysis is a widely used multivariate statistical tool in source apportionment studies (Leuchner and Rappenglück, 2010; Guo et al., 2004, Odden and Parth, 2000). Although it is very frequently used for time-series data generated in active monitoring stations, its application to spatially distributed data is very limited. FA bases on covariance of measured parameters. And co-variances are generally attributed to similar sources or similar chemistry or similar transport. This is generally understood as covariance of species in time-series of data at a single monitoring station. However, covariance of spatially distributed species has also same effect and in principle such data can be used in source apportionment. The application of multivariate techniques in spatially distributed passive VOC data actually emerged from that particular study. In this sense, this part of the study is fairly unique use of multivariate techniques in passive sampling of VOCs.

The FA was applied to data from a the data set. The data were analyzed using the Statistical Package for the Social Sciences (SPSS Inc. Chicago.USA. Version 17).The geometric means values and LOD/2 values were used to fill in missing data.16 out of 57 VOCs below the filling 80% were excluded from the data sets. 14 VOCs had no missing points. The number and percentage of missing points in the remaining 27 VOCs varied between 1 (2%) and 6 (9%). These indicate a reasonably small number of data points that should be inserted in the data set.Last pretreatment step is to evaluate communality value. 7 VOCs which have low communalities (<80%) were excluded from the input data set .

We have used a criterion known as Kaiser's criteria to determine the number of factors that should be included in FA results. This widely used approach to finding the number of factors to be extracted suggested that factors with eigen values >1.0 should be extracted for FA. A Varimax rotation was also applied to the data set to minimize the complexity of the components.

## 2.4. Health Risk Assesment

Benzene is evaluated for risk assessment associated with inhalation exposure in order to quantify the potential carcinogen health effects.

Cancer risk for the compounds have classified as carcinogen by the International Agency for Research on Cancer (IARC), is calculated based on the following equation:

$$R = I \times SF \tag{1}$$

Where;

R:Estimated inhalation cancer risk from pollutant (unitless),I: contamination intake (mg $kg^{-1}day^{-1}$), SF=Unit risk or slope factor of dose-response curve (mg $kg^{-1}day^{-1})^{-1}$.

The slope factoris unique for each chemical. The value of thes parameter was obtained from USEPA, IRIS (2009).

The following equation is advised by USEPA (2009) to estimate the contamination intake (I) via inhalation route for each compound:

$$\mathrm{I} = \frac{C \times CU \times IR \times EF \times ED}{BW \times AT} \tag{2}$$

Where;

I: contamination intake (mg $kg^{-1}day^{-1}$), C ($\mu gm^{-3}$): concentration of chemical measured in personal sampling, IR: Inhalation rate ($m^3day^{-1}$), EF: Exposure frequency (days/year) ED: Exposure duration (year), BW: Body weight (kg), AT: averaging life time (days), CU conversion unit ($10^{-3}$ mg $\mu g^{-1}$)

Inhalation rate used for risk assessment was calculated by using the activity data obtained from the questionnaires which were applied on the participants living in Aliağa.. The activity levels were categorized as light, moderate, or heavy according to the criteria developed by the U.S. EPA Office of Environmental Criteria and Assessment for the Ozone Criteria Document (USEPA, 1985)

## 3. RESULT AND DISCUSSION

### 3.1. Factor Analysis Result:

In the study, PCA was applied to analyze the treated data set. Six factors with eigen values >1.0 were extracted from the data set. Some VOCs were detected in more than one factor, indicating emissions from more than one source [Guo et al., 2004]. The extracted factors were defined using reported profiles in previous literature and the USEPA SPECIATE database (USEPA, 2006). Six factors which is a reasonable number extracted accounted for about 83% of the system variances for sampling campaigns. Factor loading values, which are a bar graph, are presented in the Figure3. Sector averages of factor scores, which includes average factor scores in “refinery”, “industrial”, “residential”, “rural” and “road” sampling stations are represented with red dots and given in Figure 2.

Factor 1 has high loadings of parafins, such as 2-methylheptane, n-decane. The factor also includes aromatics (BTEX, 2-ethyltoluene, 3-ethyltoluene, 4-ethyltoluene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene+p-cymene, 1,4-diethylbenzene) with a significantly higher loadings. High concentrations of BTEX and paraffins indicate major contributions from vehicle exhausts (Liu et al., 2008; Han and Naeher, 2006). The factor score averages at refinery, residential and road stations are comparable. If VOCs have comparable concentrations at traffic and industry or residential impacted stations, its source is probably traffic rather than industry, because industrial and residential areas also include traffic emissions. Factor one explains 27% of the system variance, which has highest variance explained in this study

Factor 2 has high loadings of light parafins and olefins, such as n-hexane, 2-methylhexane, 3-methylhexane, n- heptane+cis-3-heptene, octane etc. The factor also includes heavy hydrocarbons but with a significantly smaller loadings. It is obvious that factor two is not characterized with heavy VOCs. The main source of these VOCs is evaporative emissions (Srivastava et al., 2005; Qin et al. 2007). The factor score averages have higher values at refinery stations confirming that this is a refinery evaporative source. Factor 2 explains fairly high percent of the system variance (20%).

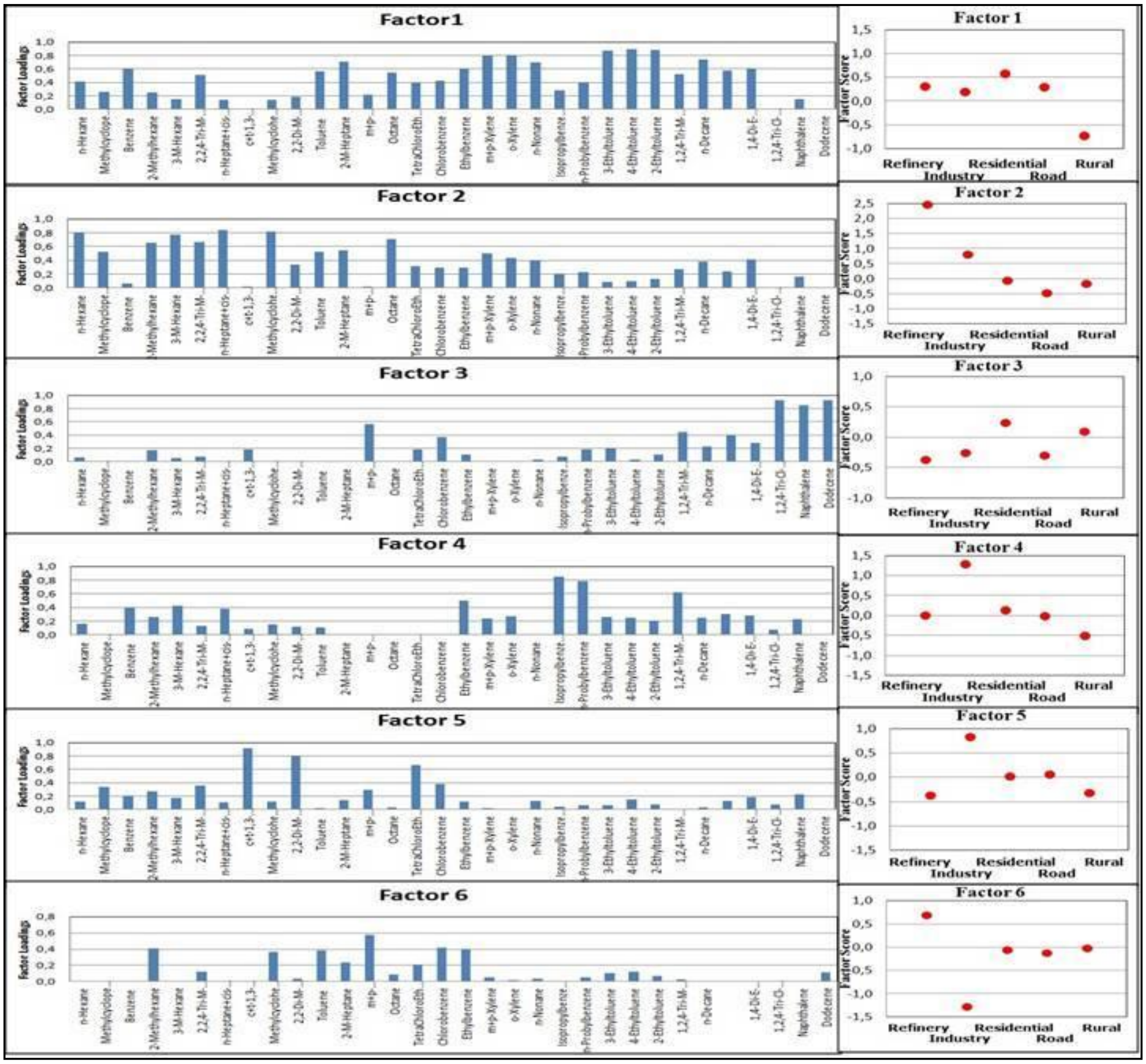

Figure 2: Factor profiles and factor scores for the data set

Factor 3 is an interesting one. It has fair loadings of halogenated compounds like m+p-chlorotoluene, 1,2,4-trichlorobenzene. The factor also explains large fraction of the variances of relatively heavy hydrocarbons such as naphthalene and dodecene. The burning of coal released significant amounts of naphthalene (Liu et al., 2008) while combustion of paper releases dodecene (USEPA, 2006). Beside average factor scores in residential and rural are higher than the average scores calculated for other microenvironments. BTEX that were identified as vehicular emission markers does not occur in this factor. Therefore this factor is not regarding to traffic related factor. The average temperature was recorded as 12.7 $^{0}$C and figure 4 depicts the hourly temperature measured in the sampling period in Aliaga region. Generally stoves or other equipments are used for heating purposes when the ambient temperature goes down below 15 $^{0}$C in İzmir and its peripherals. As it can be seen in the figure the temperature recorded during half of the sampling duration was below 15 $^{0}$C. Hence this factor may represent heating source. Factor 3 explains approximately 12% of the system variance.

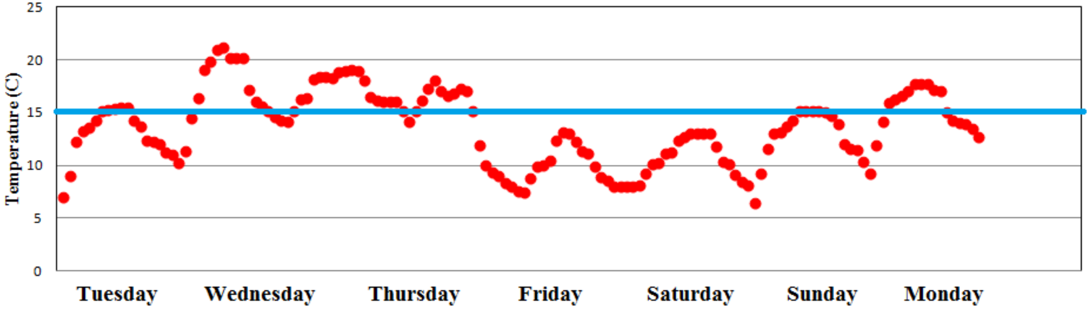

Figure 3: The hourly temperature measured in the sampling period in Aliağa region

Factors 4 and 5 have different profiles. The common feature in these two factors is that their average scores in industrial stations are higher than their averages found for the other stations. These two factors are identified as different industrial emissions from the different type of industrial plants located in the region. These two industrial factors account for 19% of the system variance.

The last factor is characterized by m+p-chlorotoluene, 2-methylhexane, toluene, ethylbenzene. The VOCs mentioned above, particularly toluene, are indicators of evaporative emissions (Qin et al. 2007; Ho et al.. 2004; Rappenglück and Fabian. 1998). The factor score averages which have higher values at refinery stations similar with that of Factor2. Factor 6 is defined as “refinery evaporative source.”

The calculated contributions including six sources of ambient VOCs by PCA are illustrated in Figure 4. From those results, vehicle exhaust and refinery evaporative source were the largest contributor to total VOC concentration with 27% and 25% of the system variance, respectively. Vehicle exhaust and refinery are the predominant pollution source in the region. Other factors, which accounted for 19% and 12% of the variability, are explained as being a result of industrial emissions and heating sources, respectively. Since the measurement was conducted in winter season, the heating source is also defined. The factor analysis indicates that traffic and refinery are significant source of VOCs for Aliağa region.

The impact of the both traffic sources and refinery emissions on the urban air quality concluded from the current study might provide a new point of view to air quality manegement to develop pollution control strategies.

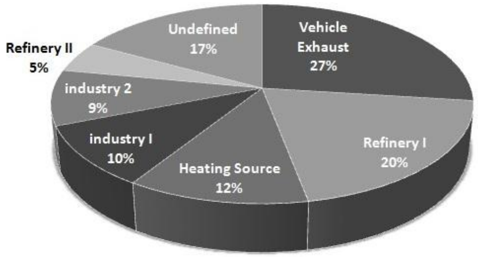

Figure 4: Contributions of different sources in the sampling campaign

### 3.2. Health Risk Assessment

Time – activity and demographic – personal data collected by a questionnaire survey in the Aliağa industrial region. Table 1 illustrates the distribution of population between downtown and its villages, number of questionnaires collected .A health risk assessment was conducted for the measured benzene concentrations.

Table 1: Population of Aliağa and the number of participants

| | **Downtown** | **Villages** | **Total** |
|---|---|---|---|
| Population | 38.225 (%67) | 18.967 (%33) | 57.192 |
| Participant number | 20 (%60) | 13 (%40) | 33 |

Cancer risk associated with inhalation exposure was estimated for benzene at each sampling point. The range of cancer risk was varied from $1\times10^{-12}$ to $1\times10^{-9}$. The spatial distribution of cancer risk of the region is depicted in Figure 5.

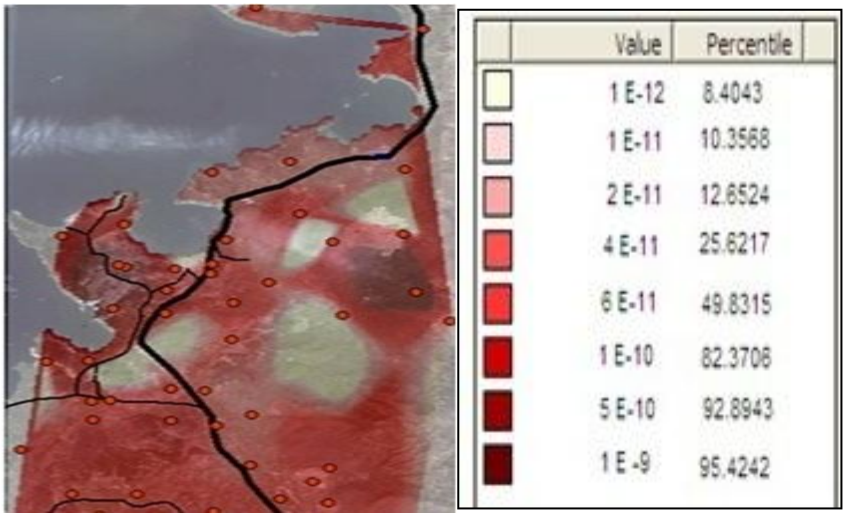

Figure 5: The spatial distribution of the cancer risk acroos the region

Even if the spatial distribution map of cancer risk indicated high levels along the major roads and around the petrochemical industrial areas and decreasing with distance from these sources, the estimated lifetime cancer risks for all points were not exceeded the acceptable level ($1\times10^{-6}$) advised by USEPA (2012).

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
**4th International Symposium and IUAPPA Regional Conference**
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# AN OPERATIONAL INFORMATION SYSTEM FOR WILDLAND FIRES FORECAST OVER SPAIN WITH WRF-FIRE

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## ABSTRACT

Spain is plagued by forest and brush fires every summer, when extremely dry weather sets in along with high temperatures. A new operational information system for wildland fire forecast has been developed based on WRF-Fire. The goal is used the system to simulate real wildland fires over Spain and the information can be used to plan and respond to fires. The meteorological information, fuel moisture content a behavior of the active fires are displayed in a web information system. To create a database for "fuel category" data, Corine Land Cover 2006, 100 meters resolution, dataset have been translated from landuse to 13 fuel models of Anderson. A new fuel moisture content model has been developed. The new module allows each time step to calculate the fuel moisture content of the dead fuels (1hr, 10hr, and 100hr) and live fuels. The system was applied and evaluated with collected data from a wildland fire in the Murcia region. The results have shown that the designed system has really the ability to simulate wildland fires.

**Key Words:** WRF-FIRE, Fire Behavior Model, Fuel Moisture Content

## 1. INTRODUCTION

One of the main causes of destruction of the vegetation in the last years is wildfire. Wildfires are responsible for an important share of global greenhouse gas emission and soil degradation. Forest fires are problem in most of the south European countries. In Spain the number of self-ignited fires has been increased, also high temperatures and dry winds and vegetation help the fire propagation.

The new computer systems can help to the fire fighters to the stop the fires if they know a priory where the fire will be in some time. Early intervention is very important issue in wildfires. If the propagation of fire can be known beforehand, the deployment of the fire fighters and the equipment can be made effectively. The fast development in computer sciences makes available the development of these automatic systems.

To get detailed meteorological information we have used the mesoscale meteorological model Weather & Research Forecasting system (WRF) developed by NCAR and others (Michalakes et al., 2001;Skamarock et al., 2005). WRF model is combined with a spread model by the level set method and the final system is called WRF-Fire, which is the core of our system.

WRF-Fire is the successor to the CAWFE model (Clark et al. 1996). The algorithms for fire spread and fuel combustion in WRF-Fire are based on the model of Rothermel (1972), using the fuel descriptors of Anderson (1982). Description of the WRF-Fire physical model with the numerical algorithms used is presented in Mandel et al. (2011).

In order for the propagation model to be efficient, forest fuels must be described in a particular way, in which the fuel characteristics are represented by certain average values. The set of these representative values is called “fuel model”. We have used the 13 fuel models of Anderson (1982)

Fuel moisture content (FMC), defined as the proportion of water over dry mass, has been the most extended measure of fire propagation, since the fuel water content has a clear impact on ignition delay and fire rate of spread. So estimation of FMC values is key in the fire propagation models.

## 2. MAIN TEXT

This paper describes an operational information system for wildland fires forecast over Spain with Wrf-Fire and the results of preliminary simulations of a real fire. The core of the system is the WRF meteorological model, to fire behavior we have the Sfire model, integrated into the WRF model. We use the WRF assimilation capability to ingest measurement data. Finally a new Fuel Moisture Content (FMC) model has been developed and integrated into the WRF-Fire system. The FMC mode will be described in the next part. A summary of the system architecture is presented in the Figure 1

A mother domain has been setup with 86 x 71 grid cells and 15 Km. resolution over Iberian Peninsula.. One nested domains are required to scale the simulation down from the atmospheric mother domain to the atmospheric domain of 3 Km. with 30 x 30 grid cells, this domain is centered on the fire ignition line. The meteorological information of the inner domain is interpolated to 200 m. resolution. Finally meteorological information is interpolated to the fire grid resolution with 20 m. The meteorological domains have 23 vertical layers. The global meteorological conditions are downloaded automatically from the Global Forecasts System (GFS) website, four times by day corresponding with the 4 initializations of the GFS (00, 06, 12, 18). The objective is always to have the most recently data available. GFS data have a 6 hour output frequency. This domain architecture is based on the CPU time restrictions. In a more powerful computational platform the resolution can be improved without problems.

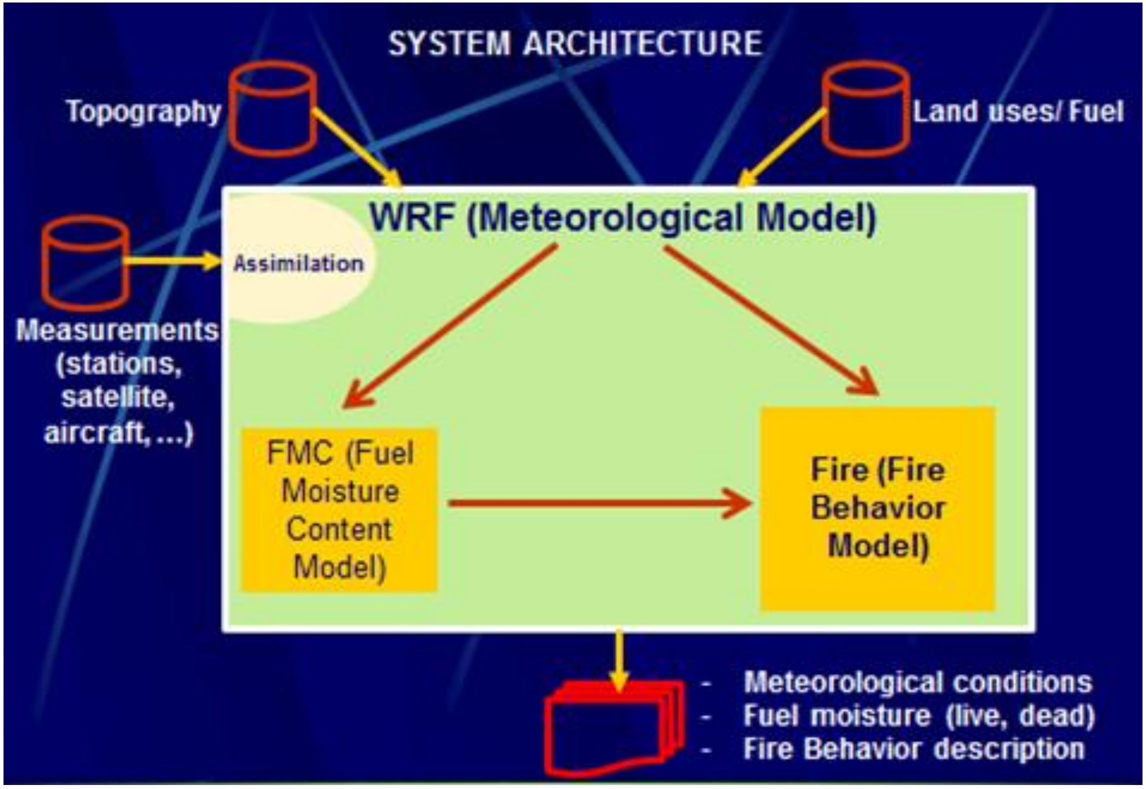

SYSTEM ARCHITECTURE

Figure 1: Basic system architecture with the main modules.

The system runs 4 times by day, starting at 00, 06, 12, 18 hours GMT, waiting for a fire notification. Simulations are run for 72 hours, with 24 hours of past time to make available the assimilation of measurement data. After 4 hours the results are available with a forecast period of 44 hours. Temporal schedule is showed in Figure 2

The information is supplied through a web interface where users can view FMC data, temperature, winds, and fire evolution, Figure 3. The web interface shows the last 4 simulations available, from the right panel the user can select several options: geographic information, winds, domain, product, time period, color scale. The user can also download the data in a TIF file. Zoom capabilities can be used to focus over an specific area and it is possible to exec temporal queries for a specific point, showing the temporal evolution of the product selected. The computer platform is composes of 2 dual core and the system has been designed to be capable of running applications in robust, automatic model and with great reliability.

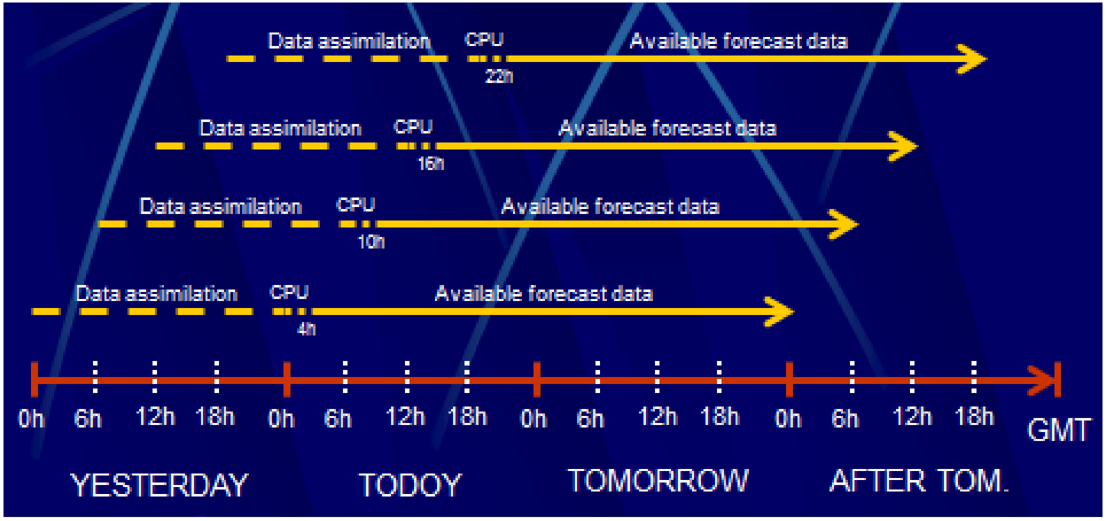
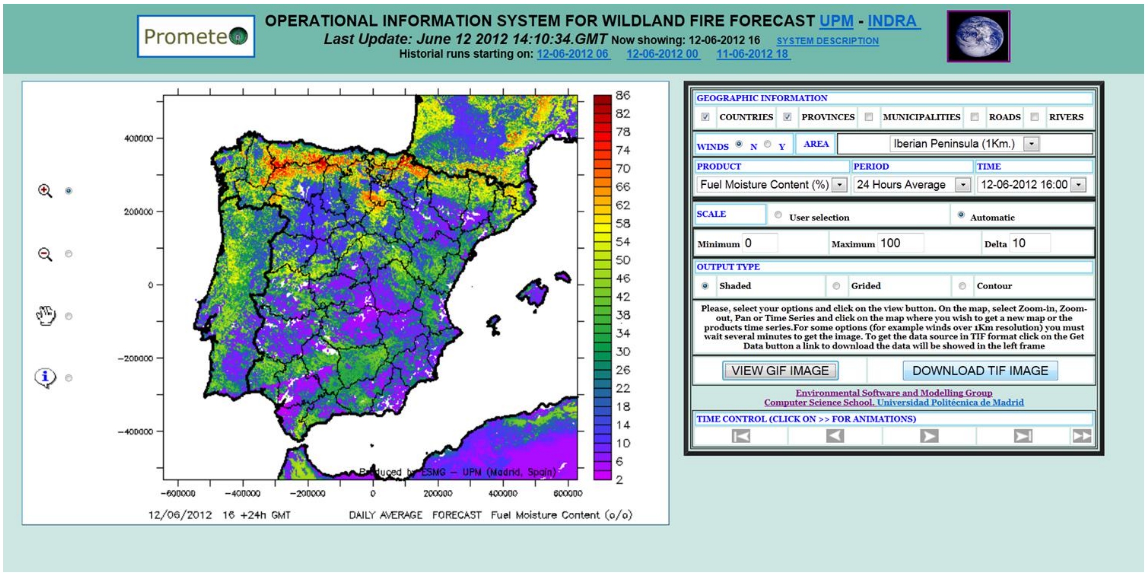


Figure 2: Temporal schedule of simulations



*Last Update: June 12 2012 14:10:34.GMT* Now showing: 12-06-2012 16
Historial runs starting on: 12-06-2012 06 12-06-2012 00 11-06-2012 18

☑ COUNTRIES ☑ PROVINCES ☐ MUNICIPALITIES ☐ ROADS ☐ RIVERS
WINDS ● N ○ Y
AREA: Iberian Peninsula (1Km.)
PRODUCT: Fuel Moisture Content (%)
PERIOD: 24 Hours Average
TIME: 12-06-2012 16:00
SCALE: ○ User selection ● Automatic
Minimum 0 Maximum 100 Delta 10
OUTPUT TYPE: ● Shaded ○ Grided ○ Contour

Please, select your options and click on the view button. On the map, select Zoom-in, Zoom-out, Pan or Time Series and click on the map where you wish to get a new map or the products time series.For some options (for example winds over 1Km resolution) you must wait several minutes to get the image. To get the data source in TIF format click on the Get Data button a link to download the data will be showed in the left frame

Figure 3: Web interface showing FMC (%) map over Iberian Peninsula, 1 Km. resolution. 24 hours average (12/06/2012 16:00 – 13/06/2012 16:00)

Developing operational methodology of FMC estimation is a key factor for fire propagation assessment. In the first test the fire appears to propagate too fast compared to observations, but the inclusion of a moisture model alleviate this problem. We have implemented a operational FMC model, integrating into the WRF-Fire.  This module allows knowing forecast the FMC values in case a fire ignition. In dead fuels, their water content is highly related to atmospheric conditions, however, in live fuels, species physiological characteristics are also important.

McArthur developed a monogram for predicting the moisture content of cured grass, as part of his Grassland fire Danger Meter (GFDM) (McArthur, 1966). The GFDM was converted to equations by Noble et al.(1980), where the prediction of fuel moisture is given by equation (1). This equation is used as base of our FMC calculations for fine dead fuel (1 hour dead fuel)

$$m=\frac{97.9+4.06H}{T+6}-0.00854H_{surf}+\frac{3000}{C}-30 \tag{1}$$

H and $H_{surf}$ are the air humidity at 1.5 meters and surface levels, T is the temperature at 1.5 meters and C is the degree of curing (%) and is considered as 100% for the calculation of dead FMC. This equation has now become more accepted that the original meters of McArthur. The GFDM has been found to perform well in predicting moisture content of aerial fuels in pine forest, mallee-heath and buttongrass moorlands.

One of the problems was the lack of consideration of the effects of condensation was a major shortcoming in the prediction of FMC, to solve this, we use the physical model to quantify the effects of nocturnal condensation on the moisture content of leaf litter (Viney and Hatton, 1990). Although the model is complex, because contain many parameters, these input data can be get from the meteorological model WRF. Here is the equation:

$$\Delta m=\frac{100}{W}\int_{\Delta t}\frac{G-N}{L+C_p(T-T_{surf})/(Q-Q_{surf})}dt \tag{2}$$

where W is the surface fuel mass, G is the soil heat flux, N is the ne all-wave radiation flux, L is the latent heat of vaporization or sublimation, Cp is the specific heat of air at constant pressure, T and $T_{surf}$ are the temperature at 1.5 meters and surface levels and Q y $Q_{surf}$ are the specific humilities at 1.5 meters and surface levels respectively.

In case of not fine dead fuel, as 10 hours and 100 hours dead fuel, we have implemented into WRF-Fire the Nelson model (Nelson, 2000) modified to make operational (Belvis and Colins, 2004). Nelson equations describing the transfer of heat and moisture at the surface and within a stick are derived and then solved numerically. The model simulated change in moisture content and temperature to cylindrical wood sticks of any practical size.

FMC in live fuels is a critical factor driving wildfire susceptibility and wildfire behavior. Live FMC is calculated following the correlation between vegetation greenness and its moisture content, consequently the Normalized Difference Vegetation Index (NDVI) can be used in estimating live FMC. Live FMC estimations can be improved by including the Land Surface Temperature (LST), because LST would be expected to increase in drier plants on account of reduced evapotranspiration. Specifically the ratio NDVI/LST was found to be very useful (Sawarvanu et al., 2005).

The FMC module produces 5 FMC values, 3 for dead fuels (1, 10, 100 hours) and 2 for live models (wood and herbaceous fuels). These 5 values are aggregated based on a weight average. Weight factor are taken from other fire models as BehavePlus, Farsite and FlamMap. This aggregation use information from the fuel model. The fuel model classification is made with information about landuses from Corine Land Cover (CLC 2000) with 100 meters of spatial resolution. The final fuel load map was derived by assigning a fuel class to each land uses. The allocation matrix is given in Table 1

Table 1: Equivalents between fuel model classes and land uses from Corine Land Cover classification (CLC 2000)

| FUEL MODEL | CLC LANDUSES |
|---|---|
| 1-Short grass | 18,22,26,32,36,12,19,20 |
| 2-Timber grass and understory | 21,24,29,33,35 |
| 4- Chaparral | 25,27,15 |
| 6- Dormant brush | 22 |
| 8- Compact timber litter | 23 |

A preliminary model validation was tested on a real case of forest fire in the territory of Murcia (Spain). We have used our operational system based on WRF-Fire to simulate a real wildland fire using our data sources in order to evaluate its ability to predict fire´s propagation in real time.

The fire ignited in a region of Murcia (Spain) on September 07, 2010 19:09. The final burned area is 7Km by 1 Km after 9 hours. We have only the fire perimeter at the end of the fire event. In addition, it is known that fire-fighters have made numerous attacks on the fire in order to constrain the fire. As there is no precise data available to these attacks, we ran the simulation without taking into account the effect of the fire-fighters.

The simulated area was discretized by a matrix of 350 x 100 cells, the cell resolution was 20 m. The simulation was started at 19:00, 9 minutes before the estimated ignition points and stopped at 04:00 of the next day, so the time total o simulation was 9 hours.

We have the following data available: topography available from local authorities at up to 4 meters resolution. Land uses datasets available from Corine Land Cover (CLC 2000) at up to 100 meters resolution. The landuses were translated into fuel model, according to the Table 1.

Figure 4 represents the superimposition of the real fire and simulated fire at 1 hour, 3 hours, 6 hours and 9 hours after ignition. Real fire contour after 9 hours from ignition is displayed as green, and simulated contour fire is represented as brown color. Arrows indicate the simulated winds from the meteorological model WRF. The fire was increase rapidly after the 3 first hours. The fire was propagating according the wind direction and taking into account the fuel available.

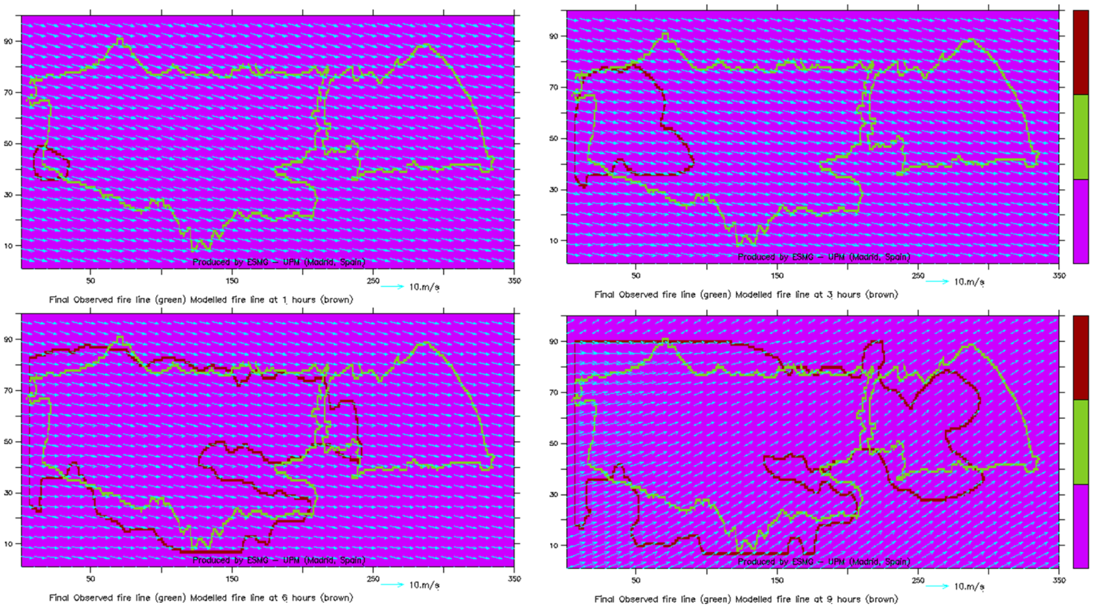


Figure 4: Observed fire line after 9 hours after ignition (green) to the modeled fire line (brown) at 1 (upper-left),3 (upper-right) ,6 (bottom-left), and 9 (bottom-right) hours and simulated vector winds

The results of the simulation looks good since few areas of the real fire don´t appear to be burnt in the simulation and few areas, which were not burnt, are computed to be “burnt”. Some differences are probably due to the attack of the fire fighters, because these actions are not modeled. The results of the simulation show a significant fit with the real data.

## 3. CONCLUSIONS

We have developed an operational and integrated simulation forecasting system for fires based on WRF-Fire. Results show that the proposed system can produce realistic simulations using the geographical information available of the fire in a real case scenario. A graphical approach is used to compare the fire perimeters and burned areas. The comparisons show that simulation results are consistent with that real data, so the system perform adequately in predicting the of the fire physics. The validation of the accuracy of the current fire propagation models is a big problem. The effect of external factors such as human interventions on the model cannot be accurately estimated.

Further enhancements to the simulation system are planned based on more test of real fire scenarios. For example we will try to improve the meteorological information because the interpolation from 3 km to 20 meters cannot capture accurate local atmospheric features, but this is the only possibility to run the system quick and an operational way at this time.

## ACKNOWLEDGEMENTS

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# THE MEASUREMENTS NOx EMMISSIONS AND EFFECTS OF THE HAMITABAT POWER PLANT-LÜLEBURGAZ/TURKEY

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## ABSTRACT

Hamitabat gas cycle Power Plant is located in Lüleburgaz-Turkey and consists of 4 combined cycle units (Each unit has 2 gas turbines and 1 steam turbine). This work was carried out at three different sites; Eskitaşlı village, Turgutbey village and Forest-Fidanlık district in Lüleburgaz. Hamitabat Power Plant cause the large amount of NO and $NO_2$ emissions. Combination with sunlight, and warm temperatures, lead to the production of ozone and are linked $N_2O_5$ and with reaction by water vapor in air, occur acidic components such as nitric acid. The power plant emissions cause air pollution and damage to the vegetation and agricultural fields.

## 1. INTRODUCTION

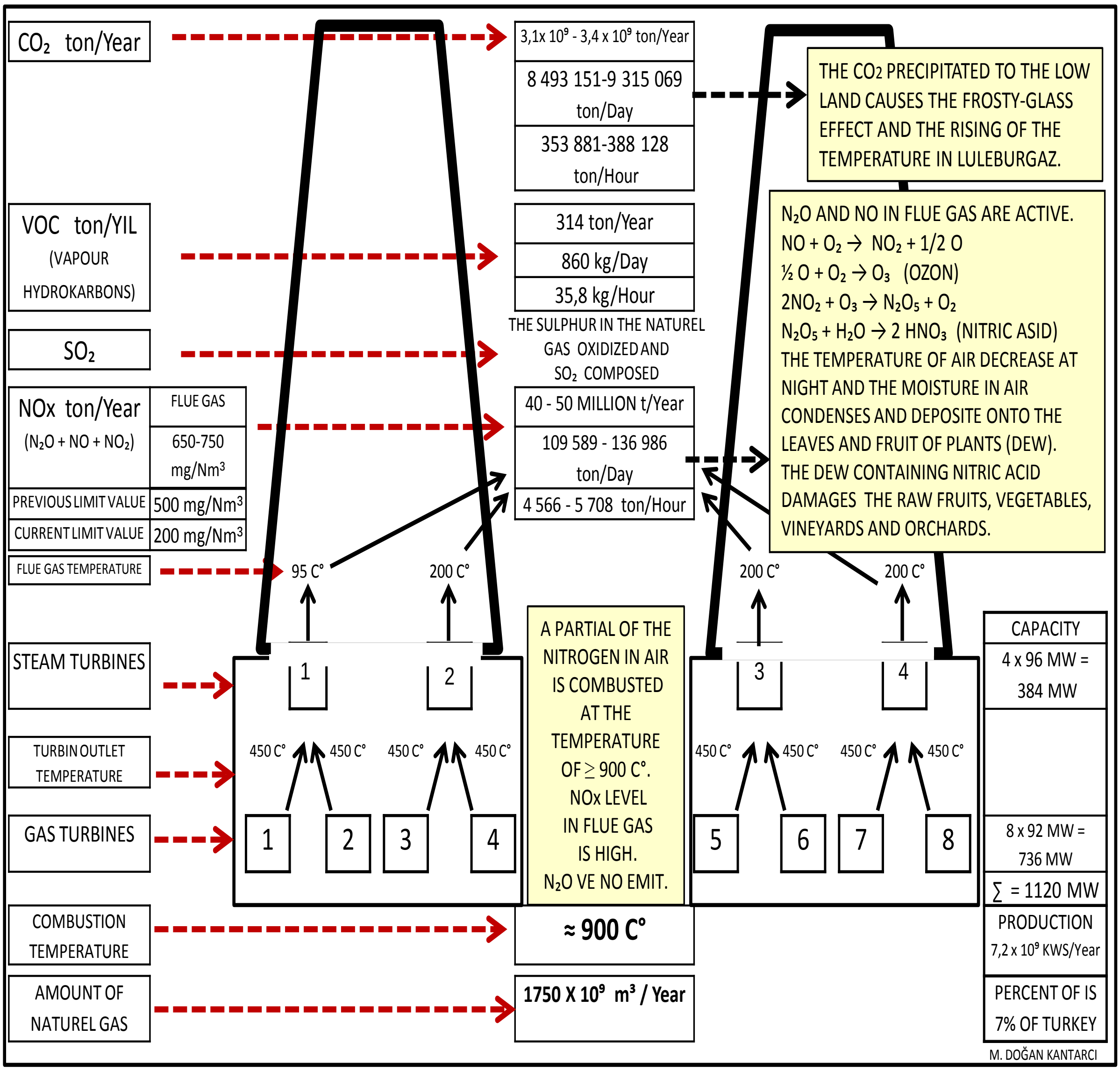
Hamitabat gas cycle plant had been planned to be built in 1983 and the construction was commenced in 1985, the first production unit of it was launched on 24.11.1985 and the last of which was launched on 13.09.1989. Power plant consists of 4 combined cycle units. Each unit has 2 gas turbines and 1 steam turbine. The hot air generated out of the natural gas burned in the gas turbines at the temperature of around >900 $^0$C is transferred to the steam turbines at the temperature of ≈ 500 C$^0$ , and then it is converted into electricity energy and finally is emitted to the atmosphere at the temperature of ≈ 200 C$^0$ The gas turbines and steam turbines have the powers of 736 MW (92x8), and 384 MW (4x96) respectively, and the total established power of the thermal power station is 1120 MW. Hamitabat Thermal Power Station generates average annual electricity energy of 7.2 Kw/per hour. The energy thus generated amounts to 7.2% of Turkey's total electricity production. Hamitabat Thermal Plant uses approximately 1750 billion m$^3$ natural gas per year (Figure 1.).

## 2. METHODS

The scope of this study is to investigate the effects of the Hamitabat power plant which is located in Lüleburgaz-Turkey. This work was carried out at three different sites; Eskitaşlı village, Turgutbey village and Forest-Fidanlık district in Lüleburgaz. Sampling stations were located around the Hamitabat power plant and the air sampling campaign was done simultaneously at three sites with a period of 8-10 hours a day for the daytime and night samples (Table 1-4). The rain and dew samples collected at three sites in the March, April, May, June and July 2012.

The samples in air was sampled using impinges with absorbing reagent of solution of sodium hydroxide and sodium arsenide and its oxides of nitrogen ($NO_2$ and $NO_3$) values was determined by ion chromatography (IC) in Lab. Environmental Engineering Dept. of Istanbul University (Gökhale, S. 2009). Anions in the rain and dew samples were analyzed by IC.

FIGURE 1. THE EFFECT OF HAMİTABAT POWER PLANT FLUE GAS.



## 3. RESULTS

**$NO_2$ and $NO_3$ amounts in dew, rain, and air samples are noteworthy**.

**(1) Highest values of $NO_2$ and $NO_3$ in dew samples;**

- $NO_2$ values in Eskitaşlı Village is 3.78 mg/lt (27-28.IV.2012), $NO_3$ is 16.97 mg/lt (27-28.IV.2012) (Table 1.1.),
- $NO_2$ values in Turgutbey Village is 18.73 mg/lt (4-5.V.2012) (Table 2.2.), $NO_3$ is 16.41 mg/lt (29-30.IV.2012) (Table 2.1.),
- $NO_2$ values in Forest Nursery is 0.18 mg/lt (24-25.V.2012), $NO_3$ is 9.54 mg/lt (28-29.IV. 2012) (Table 3).
- Highest values of $NO_2$ and $NO_3$ in rain samples;
- $NO_2$ values in Eskitaşlı Village is 0.67 mg/lt (22.IV.2012), $NO_3$ is 9.34 mg/lt (18.IV.2012) Table 1.1.),

- $NO_2$ values in Turgutbey Village is 1.65 mg/lt (27.VI.2012), $NO_3$ is 8.76 mg/lt (7.VII.2012) (Table 2.3.),
- $NO_2$ values found in Forest Nursery is 0.15 mg/lt (24.V.2012), $NO_3$ is 5.30 mg/lt (24.V.2012) (Table 3).

(2) **Reactions of dew and rain waters** were found to be ranging generally between 5.7-7.5 pH (Table 1, 2, 3). The dusts being scattered from the nearby lime soils, as well as $CaCO_3$ dusts being emitted from the cement factories (Limestone pits, and chimney) in the north escalate ($PM \leq 10\ \mu m$) reaction.

TABLE 1.1. THE VALUES OF pH , $NO_2$, $NO_3$ AND NOx MEASURED IN AIR, DEW AND RAIN SAMPLES IN LÜLEBURGAZ –ESKİTAŞLI VILLAGE IN MARCH AND APRIL 2012

| ESKİTAŞLI | DEW | | | RAIN | | | AIR | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MARCH-APRIL 2012 DATE | pH | $NO_2$ mg/lt | $NO_3$ mg/lt | pH | $NO_2$ mg/lt | $NO_3$ mg/lt | DAYTIME $NO_2$ (µg/m³) | DAYTIME $NO_3$ (µg/m³) | NIGHT $NO_2$ (µg/m³) | NIGHT $NO_3$ (µg/m³) | DAYTIME NOx (µg/m³) | NIGHT NOx (µg/m³) |
| 30.III.2012 | | | | | | | 0,0000 | 85,9581 | | | 85,9581 | |
| 30-31.III.2012 | | | | | | | | | 3,7009 | 40,3451 | | 44,046 |
| 31.III.2012 | | | | | | | 4,0606 | 30,7609 | | | 34,8214 | |
| 31.III- 1.IV.2012 | 7,1 | 3,4402 | 12,2549 | | | | | | 3,2551 | 19,6691 | | 22,9242 |
| 1.IV.2012 | | | | 7,4 | 0,065 | 1,8856 | 7,0419 | 26,1825 | | | 33,2244 | |
| 1-2.IV.2012 | 6,8 | 2,1277 | 3,8269 | | | | | | 0,0000 | 24,6853 | | 24,6853 |
| 2.IV.2012 | | | | 7,5 | 0,064 | 1,0598 | | | | | | |
| 2-3.IV.2012 | 7,0 | 0,3301 | 2,3638 | | | | | | | | | |
| 3-4.IV.2012 | 6,8 | 0,8688 | 0,4260 | | | | | | | | | |
| 4-5.IV.2012 | 7,0 | 1,0696 | 7,3008 | | | | | | | | | |
| 6.IV.2012 | | | | 6,8 | 0,112 | 1,5561 | | | | | | |
| 6-7.IV.2012 | 6,9 | 0,0534 | 2,0668 | | | | | | | | | |
| 8.IV.2012 | | | | 6,9 | 0,002 | 0,124 | | | | | | |
| 9.IV.2012/8.00 | | | | 7,4 | 0,034 | 0,4126 | | | | | | |
| 9.IV.2012/20.00 | | | | 7,3 | 0,041 | 0,3638 | | | | | | |
| 9-10.IV.2012 | 7,2 | 0,0964 | 0,1164 | | | | | | | | | |
| 11-12.IV.2012 | 7,1 | 0,0020 | 0,6318 | | | | | | | | | |
| 12-13.IV.2012 | 7,2 | 0,0020 | 0,0829 | | | | | | | | | |
| 13-14.IV.2012/Ş.1 | | | | 8,5 | 0,048 | 1,4575 | | | 0,0000 | 17,7062 | | 17,7062 |
| 13-14.IV.2012/Ş.2 | | | | 8,4 | 0,051 | 1,7389 | | | | | | |
| 14.IV.2012/Ş.1 | | | | 8,3 | 0,129 | 2,7054 | 4,6993 | 14,0424 | | | 18,7417 | |
| 14.IV.2012/Ş.2 | | | | 7,8 | 0,253 | 3,5938 | | | | | | |
| 14-15.IV.2012/Ş.1 | | | | 7,8 | 0,002 | 1,8851 | | | 0,0000 | 5,9917 | | 5,9917 |
| 14-15.IV.2012/Ş.2 | | | | 7,7 | 0,195 | 2,7044 | | | | | | |
| 15-16.IV.2012 | 7,3 | 1,1220 | 1,1953 | | | | | | | | | |
| 16-17.IV.2012 | 7,2 | 0,0020 | 0,0901 | | | | | | | | | |
| 18.IV.2012/15.00 | | | | 6,7 | 0,517 | 9,3417 | | | | | | |
| 19.IV.2012/7.30 | | | | 7,7 | 0,04 | 0,8656 | | | | | | |
| 19-20.IV.2012 | 6,7 | 0,0020 | 0,0799 | | | | | | | | | |
| 20-21.IV.2012 | 6,6 | 0,0072 | 0,2800 | | | | | | | | | |
| 21-22.IV.2012 | | | | | | | | | | | | |
| 22.IV.2012/8.00 | | | | 6,9 | 0,675 | 4,9665 | | | | | | |
| 22-23.IV.2012 | 6,8 | 0,0020 | 0,0578 | | | | | | | | | |
| 23-24.IV.2012 | 7,0 | 0,0020 | 0,1333 | | | | | | | | | |
| 24-25.IV.2012 | 6,5 | 0,0020 | 0,0416 | | | | | | | | | |
| 25-26.IV.2012 | 6,6 | 0,0020 | 0,4757 | | | | | | | | | |
| 27.IV.2012/8.00 | | | | 6,3 | 0,002 | 0,0248 | 0,0000 | 40,1637 | | | 40,1637 | |
| 27-28.IV.2012 | 6,7 | 3,7795 | 16,9706 | | | | | | 13,5422 | 38,8825 | | 52,4247 |
| 28.IV.2012 | | | | | | | 0,0000 | 9,0106 | | | 9,0106 | |
| 28-29.IV.2012 | 6,5 | 0,0070 | 0,0604 | | | | | | 3,0247 | 98,8800 | | 101,9047 |
| 29.IV.2012 | | | | | | | 4,9142 | 14,1842 | | | 19,0984 | |
| 30.IV-1.V.2012 | 6,6 | 0,0020 | 0,1778 | | | | | | | | | |

TABLE 1.2. THE VALUES OF pH , MEASURED $NO_2$, $NO_3$ AND NOx IN AIR, DEW AND RAIN SAMPLES IN LÜLEBURGAZ –ESKİTAŞLI VILLAGE IN MAY 2012.

| ESKİTAŞLI | DEW | | | RAIN | | | AIR | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MAY 2012 | pH | NO2 | NO3 | pH | NO2 | NO3 | DAYTIME | DAYTIME | NIGHT | NIGHT | DAYTIME | NIGHT |
| DATE | | mg/lt | mg/lt | | mg/lt | mg/lt | NO2 (µg/m³) | NO3 (µg/m³) | NO2 (µg/m³) | NO3 (µg/m³) | NOx (µg/m³) | NOx (µg/m³) |
| 1-2.V.2012 | 6,6 | 0,0020 | 0,0527 | | | | | | | | | |
| 2-3.V.2012 | 6,5 | 0,0020 | 0,1297 | | | | | | | | | |
| 3-4.V.2012 | 6,4 | 0,0020 | 0,0832 | | | | | | | | | |
| 4-5.V.2012 | 6,8 | 0,1465 | 0,1437 | | | | | | | | | |
| 5-6.V.2012 | 6,5 | 0,0020 | 0,0694 | | | | | | | | | |
| 6-7.V.2012 | 6,6 | 0,0020 | 0,0724 | | | | | | | | | |
| 7-8.V.2012 | 7,8 | 0,0020 | 0,1135 | | | | | | | | | |
| 8-9.V.2012 | 6,6 | 0,0020 | 0,0704 | | | | | | | | | |
| 9-10.V.2012 | 6,6 | 0,0020 | 0,0523 | | | | | | | | | |
| 10-11.V.2012 | 6,6 | 0,0020 | 0,0716 | | | | | | | | | |
| 12-13.V.2012 | 6,7 | 0,0020 | 0,0529 | | | | | | | | | |
| 13-14.V.2012 | 6,6 | 0,0020 | 0,0020 | | | | | | | | | |
| 15.V.2012/15.15 | | | | 7,3 | 0,002 | 1,0408 | | | | | | |
| 16.V.2012/7.30 | | | | 7,9 | 0,041 | 3,0396 | | | | | | |
| 16-17.V.2012 | 6,5 | 0,0020 | 0,0576 | | | | | | | | | |
| 17.V.2012/21.00 | | | | 7,1 | 0,051 | 2,832 | | | | | | |
| 18.V.2012/7.00 | | | | 7,9 | 0,002 | 1,8218 | | | | | | |
| 19.V.2012/7.00 | | | | 7,9 | 0,002 | 2,3269 | | | | | | |
| 19-20.V.2012 | 6,5 | 0,0020 | 0,0470 | | | | | | | | | |
| 22-23.V.2012 | 7,3 | 0,1356 | 3,2369 | | | | | | | | | |
| 23.V.2012/20.10 | | | | 7,5 | 0,008 | 1,6102 | 0,0000 | 9,4651 | | | 9,4651 | |
| 23-24.V.2012 | 7,4 | 0,1488 | 2,5709 | | | | | | 0,0000 | 17,1386 | | 17,1386 |
| 24.V.2012/19.45 | | | | 7,7 | 0,125 | 1,2684 | 3,1037 | 4,8226 | | | 7,9263 | |
| 24-25.V.2012 | 7,5 | 0,1619 | 1,9049 | | | | | | 1,0969 | 18,5613 | | 19,6581 |
| 25.V.2012/17.00 | | | | 7,4 | 0,012 | 0,4263 | 0,0000 | 30,1071 | | | 30,1071 | |
| 25-26.V.2012 | 6,6 | 0,0020 | 0,0681 | | | | | | | | | |
| 26-27.V.2012 | 6,5 | 0,0020 | 0,0716 | | | | | | | | | |
| 27.V.2012/21.30 | | | | 7,0 | 0,006 | 2,3622 | | | | | | |
| 28.V.2012/7.00 | | | | 7,1 | 0,002 | 0,998 | | | | | | |
| 28.V.2012/19.00 | | | | 7,2 | 0,002 | 0,5994 | | | | | | |
| 29.V.2012/7.30 | | | | 7,1 | 0,116 | 0,3931 | | | | | | |
| 31.V.2012/15.30 | | | | 6,7 | 0,007 | 0,5504 | | | | | | |
| 31.V.2012/16.00 | | | | 7,0 | 0,002 | 0,7426 | | | | | | |
| 031.V- 1.VI.2012 | 6,5 | 0,0298 | 0,9642 | | | | | | | | | |

**(4) Highest $NO_2$ values in air samples;**

- 8,99 µg/m³ (14.VI.2012) Tabelle 1.3.) during daytime in Eskitaşlı, 13,54 µg/m³ (27-28.IV.2012) (Table 1.1.) nighttime.
- 6,37 µg/m³ (28.IV.2012) during daytime in Turgutbey,17,32 µg/m³ (13-14.IV.2012) nighttime (Table 2.1.)

- 5,33 $\mu g/m^3$ (1.IV.2012) during daytime in Fidanlık, 11,68 $\mu g/m^3$ (1-2.IV.2012) nighttime (Table 3).

TABLE 1.3. THE VALUES OF pH, MEASURED NO$_2$, NO$_3$ AND NOx IN AIR, DEW AND RAIN SAMPLES IN LÜLEBURGAZ –ESKİTAŞLI VILLAGE IN JUNE AND JULY 2012.

| ESKİTAŞLI | DEW | | | RAIN | | | AIR | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| JUNE - JULY 2012 | pH | NO2 | NO3 | pH | NO2 | NO3 | DAYTIME | DAYTIME | NIGHT | NIGHT | DAYTIME | NIGHT |
| DATE | | mg/lt | mg/lt | | mg/lt | mg/lt | NO2 ($\mu g/m^3$) | NO3 ($\mu g/m^3$) | NO2 ($\mu g/m^3$) | NO3 ($\mu g/m^3$) | NOx ($\mu g/m^3$) | NOx ($\mu g/m^3$) |
| 1-2.VI.2012 | 6,3 | 1,8861 | 1,1110 | | | | | | | | | |
| 2-3.VI.2012 | 6,2 | 0,3404 | 0,6178 | | | | | | | | | |
| 3-4.VI.2012 | 6,2 | 0,2168 | 0,6364 | | | | | | | | | |
| 7-8.VI.2012 | 6,1 | 0,0020 | 0,0612 | | | | | | | | | |
| 13-14.VI.2012 | 6,5 | 0,0020 | 0,5470 | | | | | | 6,3925 | 27,1501 | | 33,5426 |
| 14.VI.2012 | | | | | | | 8,9955 | 33,7085 | | | 42,7039 | |
| 14-15.VI.2012 | 6,1 | 0,3860 | 0,0388 | | | | | | 3,7676 | 21,0282 | | 24,7958 |
| 15.VI.2012 | | | | | | | 0,0000 | 15,6577 | | | 15,6577 | |
| 15-16.VI.2012 | 6,2 | 0,0020 | 0,0714 | | | | | | 1,2434 | 10,9145 | | 12,1579 |
| 16.VI.2012 | | | | | | | 0,0000 | 8,1108 | | | 8,1108 | |
| 16-17.VI.2012 | 5,8 | 0,7185 | 0,0514 | | | | | | | | | |
| 17-18.VI.2012 | 5,5 | 0,8022 | 0,0020 | | | | | | | | | |
| 20-21.VI.2012 | 6,0 | 0,6442 | 0,0411 | | | | | | | | | |
| 21-22.VI.2012 | 6,1 | 1,2858 | 0,0465 | | | | | | | | | |
| 22-23.VI.2012 | 6,0 | 0,0408 | 0,0335 | | | | | | | | | |
| 23-24.VI.2012 | 5,8 | 0,9207 | 0,0020 | | | | | | | | | |
| 24-25.VI.2012 | 5,8 | 1,3726 | 0,0020 | | | | | | | | | |
| 25-26.VI.2012 | 5,8 | 0,4434 | 0,0563 | | | | | | | | | |
| 26.VI.2012/17.00 | | | | 5,8 | 0,05 | 2,5679 | | | | | | |
| 27.VI.2012/7.30 | | | | 6,0 | 0,032 | 2,0766 | 0,0000 | 4,4208 | | | 4,4208 | |
| 27-28.VI.2012 | 6,0 | 0,0020 | 0,0020 | | | | | | 0,6122 | 0,3537 | | 0,966 |
| 28.VI.2012 | | | | | | | 0,2811 | 1,4645 | | | 1,7456 | |
| 28-29.VI.2012 | 6,0 | 0,4817 | 0,0020 | | | | | | 0,6522 | 1,8445 | | 2,4967 |
| 29.VI.2012 | | | | | | | 1,5766 | 1,0000 | | | 2,5766 | |
| 29-30.VI.2012 | 5,9 | 0,5558 | 0,0020 | | | | | | 0,0799 | 0,6858 | | 0,7656 |
| 30.VI- 1.VII.2012 | 5,7 | 0,4637 | 0,0552 | | | | | | | | | |
| 01-2.VII.2012 | 5,8 | 0,5328 | 0,0020 | | | | | | | | | |
| 2-3.VII.2012 | 6,1 | 0,6018 | 0,0020 | | | | | | | | | |
| 3-4.VII.2012 | 5,8 | 0,4242 | 0,0020 | | | | | | | | | |
| 5-6.VII.2012 | 6,4 | 0,9163 | 0,0020 | | | | | | | | | |
| 6-7.VII.2012 | 6,0 | 0,8915 | 0,0020 | | | | | | | | | |
| 7.VII.2012/18.30 | | | | 6,0 | 0,002 | 2,2559 | | | | | | |
| 7.VII.2012/18.40 | | | | 6,0 | 0,002 | 2,0078 | | | | | | |
| 7.VII.2012/19.00 | | | | 6,2 | 0,002 | 1,8047 | | | | | | |
| 7-8.VII.2012 | 6,2 | 0,1253 | 0,0663 | | | | 0,0000 | 41,2762 | | | 41,2762 | |
| 8-9.VII.2012 | 6,2 | 0,5328 | 0,0020 | | | | | | 5,9858 | 51,5745 | | 57,5603 |
| 09.VII.2012 | | | | | | | 15,1844 | 76,8298 | | | 92,0142 | |
| 9-10.VII.2012 | 6,3 | 0,7722 | 0,1579 | | | | | | 3,4336 | 25,4825 | | 28,9161 |
| 10.VII.2012 | | | | | | | 3,8662 | 12,1549 | | | 16,0211 | |
| 10-11.VII.2012 | 5,9 | 3,0489 | 0,0349 | | | | | | 0,0000 | 15,9231 | | 15,9231 |

### (5) Highest NO$_3$ values in air samples;

- 85.95 $\mu g/m^3$ (30.III.2012) during daytime in Eskitaşlı, 98,88 $\mu g/m^3$ (28-29.IV.2012) nighttime (Table 1.1.),

- 73.91 µg/m³ (30.III.2012) (Table 2.1.) during daytime in Turgutbey,38.39 µg/m³(9-10.VII.2012) (Table 2.3.) nighttime,
- 88.91 µg/m³ (27.IV.2012) during daytime in Fidanlık, 81.17 µg/m³ (8-9.VII.2012) nighttime (Table 3.).

TABLE 2.1. THE VALUES OF pH , $NO_2$ AND $NO_3$ MEASURED IN AIR, DEW AND RAIN SAMPLES IN LÜLEBURGAZ –TURGUTBEY VILLAGE IN MARCH AND APRIL 2012.

| TURGUTBEY | DEW | | | RAIN | | | AIR | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MARCH-APRIL 2012 DATE | pH | NO2 mg/lt | NO3 mg/lt | pH | NO2 mg/lt | NO3 mg/lt | DAYTIME NO2 (µg/m³) | DAYTIME NO3 (µg/m³) | NIGHT NO2 (µg/m³) | NIGHT NO3 (µg/m³) | DAYTIME NOx (µg/m³) | NIGHT NOx (µg/m³) |
| 30.III.2012 | | | | | | | 0,0000 | 73,9095 | | | 73,9095 | |
| 30-31.III.2012 | | | | | | | | | 5,2203 | 29,6929 | | 34,9132 |
| 31.III.2012 | | | | | | | 1,6885 | 32,0777 | | | 33,7662 | |
| 31.III- 1.IV.2012 | | | | | | | | | 4,2980 | 30,5049 | | 34,8030 |
| 1.IV.2012 | | | | 7,1 | 0,0379 | 4,3885 | 0,0000 | 37,0184 | | | 37,0184 | |
| 1-2.IV.2012 | 6,7 | 0,9665 | 6,8906 | 7,5 | 0,0921 | 0,9329 | | | 12,1459 | 35,2691 | | 47,4150 |
| 3.IV.2012/7.00 | | | | 7,1 | 0,0791 | 1,1207 | | | | | | |
| 3-4.IV.2012 | 7,2 | 1,0593 | 3,4842 | | | | | | | | | |
| 4-5.IV.2012 | 7,2 | 0,3104 | 2,3807 | | | | | | | | | |
| 6.IV.2012/7.00 | | | | 7,2 | 0,1178 | 2,5712 | | | | | | |
| 6-7.IV.2012 | 6,9 | 0,4857 | 7,8748 | | | | | | | | | |
| 8.IV.2012/7.45 | | | | 6,6 | 0,0485 | 3,5661 | | | | | | |
| 9.IV.2012/7.00 | | | | 6,7 | 0,0559 | 0,844 | | | | | | |
| 10.IV.2012/7.00 | | | | 7,2 | 0,0363 | 0,9626 | | | | | | |
| 11-12.IV.2012 | 6,7 | 3,0089 | 0,5427 | | | | | | | | | |
| 12-13.IV.2012 | 6,9 | 0,8084 | 0,5756 | | | | | | | | | |
| 13-14.IV.2012/8.25 | | | | 7,5 | 0,1046 | 2,1308 | | | 17,3184 | 15,4029 | | 32,7213 |
| 14.IV.2012/7.30 | | | | 7,0 | 0,1241 | 1,5194 | 0,7961 | 3,0237 | | | 3,8198 | |
| 14-15.IV.2012/Ş.1 | | | | | | | | | 0,0000 | 4,3636 | | 4,3636 |
| 15.IV.2012/6.45-1 | | | | 7,0 | 0,168 | 3,3978 | | | | | | |
| 15.IV.2012/6.45-2 | | | | 6,6 | 0,0296 | 9,21 | | | | | | |
| 15.IV.2012/6.45-3 | | | | 6,7 | 0,0297 | 5,2442 | | | | | | |
| 15.IV.2012/6.45-4 | | | | 6,9 | 0,0271 | 2,6322 | | | | | | |
| 15.IV.2012/6.45-5 | | | | 6,9 | 0,0966 | 3,8892 | | | | | | |
| 15-16.IV.2012 | 6,6 | 2,5688 | 0,944 | | | | | | | | | |
| 16-17.IV.2012 | 6,4 | 0,002 | 0,16 | | | | | | | | | |
| 18.IV.2012/20.00-1 | | | | 7,6 | 0,0657 | 1,2866 | | | | | | |
| 18.IV.2012/20.00-2 | | | | 6,9 | 0,0918 | 3,1347 | | | | | | |
| 18.IV.2012/20.00-3 | | | | 6,6 | 0,0803 | 3,9285 | | | | | | |
| 18.IV.2012/20.00-4 | | | | 6,3 | 0,192 | 3,8181 | | | | | | |
| 18.IV.2012/20.00-5 | | | | 6,9 | 0,0521 | 3,5125 | | | | | | |
| 19.IV.2012/7.10-1 | | | | 8,2 | 0,0324 | 1,0515 | | | | | | |
| 19.IV.2012/7.10-2 | | | | 6,6 | 0,0218 | 1,3377 | | | | | | |
| 19.IV.2012/7.10-3 | | | | 6,3 | 0,0179 | 1,2976 | | | | | | |
| 19.IV.2012/7.10-4 | | | | 7,0 | 0,0095 | 0,3847 | | | | | | |
| 19-20.IV.2012 | 6,7 | 0,0414 | 0,0789 | | | | | | | | | |
| 20-21.IV.2012 | 6,9 | 0,0085 | 0,0512 | | | | | | | | | |
| 22.IV.2012/7.00 | 6,6 | 0,002 | 0,0878 | 6,8 | 0,0396 | 0,2238 | | | | | | |
| 22-23.IV.2012 | 6,5 | 0,007 | 0,0934 | | | | | | | | | |
| 23.IV.2012 | | | | 6,8 | 0,1602 | 3,7051 | | | | | | |
| 23-24.IV.2012 | 6,8 | 0,0034 | 0,0595 | | | | | | | | | |
| 24.IV.2012/ 1 | | | | 6,8 | 0,0224 | 1,1705 | | | | | | |
| 24.IV.2012/ 2 | | | | 7,0 | 0,0254 | 1,3949 | | | | | | |
| 24.IV.2012/ 3 | | | | 6,9 | 0,0226 | 1,0857 | | | | | | |
| 24.IV.2012/ 4 | | | | 6,7 | 0,0202 | 1,3229 | | | | | | |
| 24-25.IV.2012 | 6,9 | 0,003 | 0,1488 | | | | | | | | | |
| 25-26.IV.2012 | 6,5 | 0,0214 | 0,1089 | | | | | | | | | |
| 26-27.IV.2012 | 6,1 | 4,3813 | 1,4199 | | | | | | | | | |
| 27.IV.2012 | | | | | | | 3,7705 | 33,3255 | | | 37,0960 | |
| 27-28.IV.2012 | 6,4 | 0,0149 | 0,105 | | | | | | 3,5014 | 19,3923 | | 22,8936 |
| 28.IV.2012 | | | | | | | 6,3734 | 19,4850 | | | 25,8584 | |
| 28-29.IV.2012 | 6,4 | 0,0138 | 0,244 | | | | | | 2,5606 | 17,4470 | | 20,0076 |
| 29.IV.2012 | | | | | | | 3,4424 | 12,2121 | | | 15,6545 | |
| 29-30.IV.2012 | 6,8 | 4,553 | 16,413 | | | | | | | | | |
| 30.IV - 1.V.2012 | 6,5 | 0,2652 | 0,7458 | | | | | | | | | |

TABLE 2.2. THE VALUES OF pH , $NO_2$ AND $NO_3$ MEASURED IN AIR, DEW AND RAIN SAMPLES IN LÜLEBURGAZ –TURGUTBEY VILLAGE IN MAY 2012.

| TURGUTBEY | DEW | | | RAIN | | | AIR | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MAY 2012 | pH | $NO_2$ | $NO_3$ | | $NO_2$ | $NO_3$ | DAYTIME | DAYTIME | NIGHT | NIGHT | DAYTIME | NIGHT |
| DATE | | mg/lt | mg/lt | pH | mg/lt | mg/lt | $NO_2$ (µg/m³) | $NO_3$ (µg/m³) | $NO_2$ (µg/m³) | $NO_3$ (µg/m³) | $NO_x$ (µg/m³) | $NO_x$ (µg/m³) |
| 1-2.V.2012 | 6,7 | 0,154 | 0,1188 | | | | | | | | | |
| 2-3.V.2012 | 6,9 | 16,517 | 11,093 | | | | | | | | | |
| 3-4.V.2012 | 7.0 | 4,302 | 2,76 | | | | | | | | | |
| 4-5.V.2012 | 7,1 | 18,736 | 15,53 | | | | | | | | | |
| 5-6.V.2012 | 6,5 | 0,002 | 0,0395 | | | | | | | | | |
| 6-7.V.2012 | 6,5 | 0,002 | 0,002 | | | | | | | | | |
| 7-8.V.2012 | 6,6 | 1,2419 | 1,8169 | | | | | | | | | |
| 8-9.V.2012 | 6,4 | 0,002 | 0,0304 | | | | | | | | | |
| 9-10.V.2012 | 6,4 | 0,0939 | 0,0434 | | | | | | | | | |
| 11.V.2012 | | | | 7,2 | 0,0135 | 1,1024 | | | | | | |
| 14-15.V.2012 | 6,5 | 0,8614 | 11,434 | | | | | | | | | |
| 15-16.V.2012 | 6,6 | 0,0659 | 0,1776 | | | | | | | | | |
| 23.V.2012 | | | | | | | 0,0000 | 11,4989 | | | 11,4989 | |
| 23-24.V.2012 | 6,3 | 0,0554 | 0,0135 | | | | | | 0,0000 | 8,3750 | | 8,3750 |
| 24.V.2012 | | | | | | | 0,0000 | 8,8108 | | | 8,8108 | |
| 24-25.V.2012 | 6 | 0,0622 | 0,002 | | | | | | 0,0000 | 17,6014 | | 17,6014 |
| 25.V.2012 | | | | | | | 0,0000 | 19,0827 | | | 19,0827 | |
| 25-26.V.2012 | | | | | | | | | | | | |
| 26.V.2012/ 1 | | | | 6,8 | 0,0261 | 2,1337 | | | | | | |
| 26.V.2012/ 2 | | | | 6,9 | 0,0295 | 0,9803 | | | | | | |
| 26.V.2012/ 3 | | | | 6,7 | 0,0884 | 1,2198 | | | | | | |
| 31.V.2012/ 1 | 6,2 | 0,002 | 0,002 | 7,0 | 0,0133 | 0,7172 | | | | | | |
| 31.V.2012/ 2 | | | | 7,0 | 0,0467 | 0,7434 | | | | | | |
| 31.V.2012/ 3 | | | | 7,0 | 0,0096 | 0,7439 | | | | | | |
| 031.V- 1.VI.2012 | 6,3 | 1,8861 | 1,1110 | | | | | | | | | |

## (6) Highest $NO_x$ values in air samples;

- 85.95 µg/m³ (30.III.2012) during daytime in Eskitaşlı,101.90 µg/m³(28-29.IV.2012) nighttime (Table 1.1.),
- 73.91 µg/m³ (30.III.2012) during daytime in Turgutbey, 47.41 µg/m³ (1-2.IV.2012) nighttime (Table 2.1.),
- 103.82 µg/m³ (2.IV.2012) during daytime in Fidanlık, 81.17 µg/m³ (8-9.VII.2012) nighttime (Table 3.),
- $NO_x$ values frequently exceed the limit value of 30 µg/m³ in air samples (Figure 2).

TABLE 2.3. THE VALUES OF pH , NO$_2$ AND NO$_3$ MEASURED IN AIR, DEW AND RAIN SAMPLES IN LÜLEBURGAZ –TURGUTBEY VILLAGE IN JUNE AND JULY 2012.

| TURGUTBEY | DEW | | | RAIN | | | AIR | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| JUNE-JULY 2012 DATE | pH | NO2 mg/lt | NO3 mg/lt | pH | NO2 mg/lt | NO3 mg/lt | DAYTIME NO2 (µg/m³) | DAYTIME NO3 (µg/m³) | NIGHT NO2 (µg/m³) | NIGHT NO3 (µg/m³) | DAYTIME NOx (µg/m³) | NIGHT NOx (µg/m³) |
| 1-2.VI.2012 | 6,2 | 0,002 | 0,002 | | | | | | | | | |
| 2-3.VI.2012 | 6,2 | 0,002 | 0,002 | | | | | | | | | |
| 3-4.VI.2012 | 6,2 | 0,002 | 0,002 | | | | | | | | | |
| 5-6.VI.2012 | 5,9 | 0,002 | 0,002 | | | | | | | | | |
| 5-6.VI.2012 | 5,8 | 0,0423 | 0,002 | | | | | | | | | |
| 6-7.VI.2012 | 5,8 | 0,1191 | 0,002 | | | | | | | | | |
| 7-8.VI.2012 | 5,9 | 0,1148 | 0,0627 | | | | | | | | | |
| 9-10.VI.2012 | 5,5 | 0,002 | 0,002 | | | | | | | | | |
| 10-11.VI.2012 | 5,7 | 0,002 | 0,002 | | | | | | | | | |
| 11-12.VI.2012 | 5,5 | 0,0894 | 0,002 | | | | | | | | | |
| 12-13.VI.2012 | 6,0 | 0,0493 | 0,002 | | | | | | | | | |
| 13-14.VI.2012 | 6,0 | 0,0286 | 0,002 | | | | | | 1,3431 | 1,8467 | | 3,1898 |
| 14.VI.2012 | | | | | | | 1,8449 | 0,5271 | | | 2,3720 | |
| 14-15.VI.2012 | 6,1 | 0,0381 | 0,002 | | | | | | 0,3664 | 1,0719 | | 1,4383 |
| 15.VI.2012 | | | | | | | 0,4836 | 1,1979 | | | 1,6815 | |
| 15-16.VI.2012 | 6,1 | 0,0198 | 0,002 | | | | | | 0,6471 | 3,8889 | | 4,5359 |
| 16.VI.2012 | | | | | | | 0,0000 | 1,7494 | | | 1,7494 | |
| 16-17.VI.2012 | 6,4 | 0,0531 | 0,002 | | | | | | | | | |
| 17-18.VI.2012 | 6,4 | 0,0927 | 0,002 | | | | | | | | | |
| 18-19.VI.2012 | 5,1 | 0,4847 | 0,002 | | | | | | | | | |
| 20-21.VI.2012 | 6,2 | 0,2355 | 0,002 | | | | | | | | | |
| 21-22.VI.2012 | 6,3 | 0,1033 | 0,002 | | | | | | | | | |
| 22-23.VI.2012 | 6,2 | 0,0323 | 0,002 | | | | | | | | | |
| 23-24.VI.2012 | 6,2 | 0,0813 | 0,002 | | | | | | | | | |
| 24-25.VI.2012 | 6,1 | 0,124 | 0,002 | | | | | | | | | |
| 25-26.VI.2012 | 7,2 | 0,1188 | 0,002 | | | | | | | | | |
| 26-27.VI.2012 | 6,0 | 0,1484 | 0,0385 | | | | | | | | | |
| 26.VI.2012/17.00 | | | | 6,5 | 0,3945 | 2,1036 | | | | | | |
| 27.VI.2012/7.30 | | | | 6,7 | 1,654 | 1,5548 | | | | | | |
| 27.VI.2012/17.00 | | | | 6,4 | 0,505 | 4,2765 | 0,0000 | 4,8452 | | | 4,8452 | |
| 27-28.VI.2012 | 6,2 | 0,1145 | 0,002 | | | | | | 0,0000 | 1,0000 | | 1,0000 |
| 28.VI.2012 | | | | | | | 0,0000 | 2,2802 | | | 2,2802 | |
| 28-29.VI.2012 | 6,0 | 0,002 | 0,002 | | | | | | 0,0000 | 1,1939 | | 1,1939 |
| 29.VI.2012 | | | | | | | 0,0000 | 2,2165 | | | 2,2165 | |
| 29-30.VI.2012 | 6,8 | 0,0268 | 0,002 | | | | | | 1,1889 | 1,1625 | | 2,3514 |
| 01-2.VII.2012 | 5,2 | 0,0595 | 0,0262 | | | | | | | | | |
| 2-3.VII.2012 | 5,7 | 0,0865 | 0,002 | | | | | | | | | |
| 3-4.VII.2012 | 5,5 | 0,1932 | 0,002 | | | | | | | | | |
| 4-5.VII.2012 | 6,1 | 0,136 | 0,002 | | | | | | | | | |
| 5-6.VII.2012 | 6,0 | 0,1919 | 0,002 | | | | | | | | | |
| 6-7.VII.2012 | 6,0 | 0,2304 | 0,002 | | | | | | | | | |
| 7.VII.2012/1 | | | | 5,9 | 0,0964 | 5,5898 | | | | | | |
| 7.VII.2012/2 | | | | 6,2 | 0,1084 | 8,7661 | | | | | | |
| 7.VII.2012/3 | | | | 6,3 | 0,0481 | 3,3274 | | | | | | |
| 7-8.VII.2012 | 6,2 | 0,0231 | 0,903 | | | | | | | | | |
| 8.VII.2012 | | | | | | | 4,9757 | 49,8854 | | | 54,8611 | |
| 8-9.VII.2012 | 6,0 | 0,0677 | 0,002 | | | | | | 2,1978 | 24,0360 | | 26,2338 |
| 09.VII.2012 | | | | | | | 3,8831 | 65,0346 | | | 68,9177 | |
| 9-10.VII.2012 | 5,8 | 0,1173 | 0,002 | | | | | | 1,2254 | 38,3873 | | 39,6127 |
| 10.VII.2012 | | | | | | | 2,4097 | 12,1667 | | | 14,5764 | |
| 10-11.VII.2012 | 5,9 | 0,0318 | 0,002 | | | | | | 2,4003 | 9,2503 | | 11,6506 |

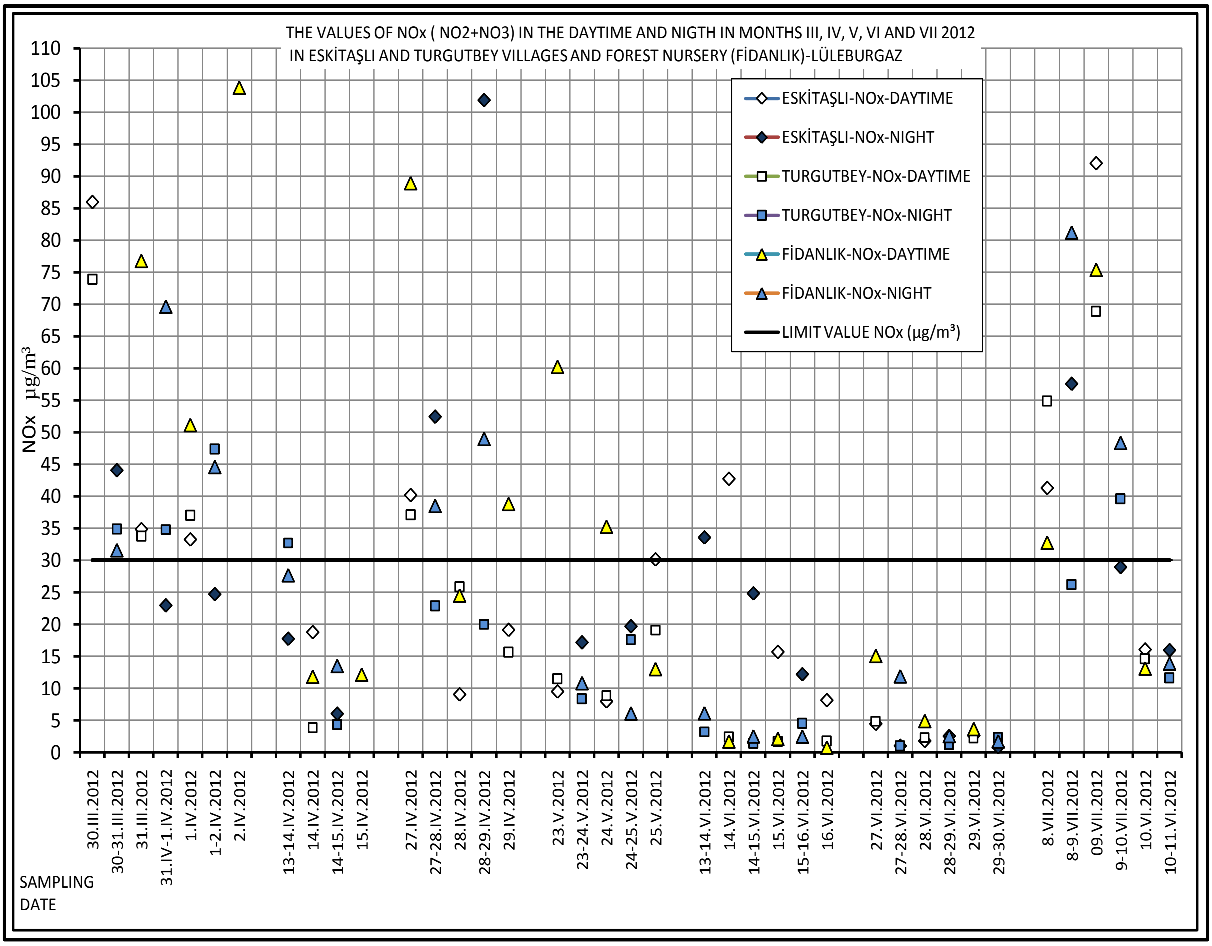
TABLE 3. THE VALUES OF pH , $NO_2$ AND $NO_3$ MEASURED IN AIR, DEW AND RAIN SAMPLES IN LÜLEBURGAZ – ORMAN FİDANLIĞI (Forest Nursery) IN MONTHS III, IV, V, VI AND VIII 2012

| FİDANLIK | DEW | | | RAIN | | | AIR | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (Forest Nursery) DATE | pH | $NO_2$ mg/lt | $NO_3$ mg/lt | pH | $NO_2$ mg/lt | $NO_3$ mg/lt | DAYTIME $NO_2$ (μg/m³) | DAYTIME $NO_3$ (μg/m³) | NIGHT $NO_2$ (μg/m³) | NIGHT $NO_3$ (μg/m³) | DAYTIME NOx (μg/m³) | NIGHT NOx (μg/m³) |
| 30-31.III.2012 | | | | | | | | | 1,5068 | 30,0257 | | 31,5325 |
| 31.III.2012 | | | | | | | 0,0000 | 76,7529 | | | 76,7529 | |
| 31.III- 1.IV.2012 | | | | | | | | | 9,8197 | 59,7831 | | 69,6028 |
| 1.IV.2012 | | | | 7,3 | 0,0633 | 2,5405 | 5,3350 | 45,7682 | | | 51,1031 | |
| 1-2.IV.2012 | | | | 7,6 | 0,0483 | 0,6731 | | | 11,6852 | 32,8548 | | 44,54 |
| 2.IV.2012 | | | | | | | 0,0000 | 103,8256 | | | 103,8256 | |
| 13-14.IV.2012/9.04 | | | | 7,4 | 0,0621 | 0,1877 | | | 0,4518 | 27,1679 | | 27,6197 |
| 14.IV.2012 | | | | | | | 0,0000 | 11,7631 | | | 11,7631 | |
| 14-15.IV.2012/9.20 | | | | 6,8 | 0,002 | 0,0452 | | | 0,0000 | 13,4434 | | 13,4434 |
| 15.IV.2012/6.45-1 | | | | | | | 0,0000 | 12,0823 | | | 12,0823 | |
| 27.IV.2012 | | | | | | | 0,0000 | 88,9132 | | | 88,9132 | |
| 27-28.IV.2012 | 8,0 | 0,1776 | 3,4805 | | | | | | 2,8915 | 35,5713 | | 38,4628 |
| 28.IV.2012 | | | | | | | 0,0000 | 34,4494 | | | 24,4391 | |
| 28-29.IV.2012 | 7,9 | 0,1743 | 9,5443 | | | | | | 8,6693 | 40,2696 | | 48,9389 |
| 29.IV.2012 | | | | | | | 5,1259 | 33,6453 | | | 38,7712 | |
| 23.V.2012/19.20 | | | | 7,6 | 0,002 | 0,0495 | 0,0000 | 60,2034 | | | 60,2034 | |
| 23-24.V.2012 | 7,4 | 0,1099 | 0,9389 | | | | | | 0,0000 | 10,7523 | | 10,7523 |
| 24.V.2012/17.00 | | | | 7,5 | 0,1495 | 5,3022 | 0,0000 | 35,2060 | | | 35,206 | |
| 24-25.V.2012 | 7,2 | 0,1868 | 4,8794 | | | | | | 3,0109 | 3,0109 | | 6,0219 |
| 25.V.2012/16.00 | | | | 8,0 | 0,0191 | 1,2085 | 0,0000 | 12,9588 | | | 12,9588 | |
| 13-14.VI.2012 | | | | | | | | | 2,5641 | 3,4887 | | 6,0528 |
| 14.VI.2012 | | | | | | | 0,0000 | 1,6406 | | | 1,6406 | |
| 14-15.VI.2012 | | | | | | | | | 1,9967 | 0,4424 | | 2,439 |
| 15.VI.2012 | | | | | | | 0,0000 | 2,0521 | | | 2,0521 | |
| 15-16.VI.2012 | | | | | | | | | 2,0513 | 0,3419 | | 2,3932 |
| 16.VI.2012 | | | | | | | 0,0000 | 0,6838 | | | 0,6838 | |
| 27.VI.2012 | | | | | | | 4,1667 | 10,8494 | | | 15,0161 | |
| 27-28.VI.2012 | | | | | | | | | 0,0000 | 11,8203 | | 11,8203 |
| 28.VI.2012 | | | | | | | 0,0000 | 4,8383 | | | 4,8383 | |
| 28-29.VI.2012 | | | | | | | | | 0,0000 | 2,4952 | | 2,4952 |
| 29.VI.2012 | | | | | | | 0,0000 | 3,5903 | | | 3,5903 | |
| 29-30.VI.2012 | | | | | | | | | 0,0000 | 1,6509 | | 1,6509 |
| 8.VII.2012 | | | | | | | 0,0000 | 32,7141 | | | 32,7141 | |
| 8-9.VII.2012 | | | | | | | | | 0,0000 | 81,1702 | | 81,1702 |
| 09.VII.2012 | | | | 6,8 | 0,0000 | 1,4972 | 0,0000 | 75,3671 | | | 75,3671 | |
| 9-10.VII.2012 | | | | | | | | | 0,0000 | 48,3118 | | 48,3118 |
| 10.VII.2012 | | | | | | | 0,0000 | 13,0460 | | | 13,046 | |
| 10-11.VII.2012 | | | | | | | | | 0,0000 | 13,8194 | | 13,8194 |

## 4. CONCLUSION AND DISCUSSION

Power plants lead to important environmental problems in their particular area. The power plant emissions cause air pollution and damage to the vegetation and agricultural fields. Electric power generation cause the large amount of NO and $NO_2$ emissions. NOx emissions, in combination with VOCS, sunlight, and warm temperatures, lead to the production of ozone ($O_3$), the primary component of photochemical smog. NO and $NO_2$ emissions are linked $N_2O_5$ to acid deposition and precipitation and to atmospheric particulate formation. The NOx emissions are emitted by power plant stacks and with reaction by water vapor in air, occur acidic components such as nitric acid (VDI-1978, WHO-1985, Kantarcı, M.D.1996).

FIGURE 2. THE VALUES OF NOx (NO2+N03) OF AIR SAMPLES MEASURED IN THE DAYTIME AND AT NIGTH IN LÜLEBURGAZ-ESKİTAŞLI AND TURGUTBEY VILLAGES AND FOREST NURSERY (FİDANLIK) IN MONTHS III, IV, V, VI AND VII. 2012 AND LIMIT VALUE (30 µg/m³)



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# RESPONSES OF ADULT OLIVE TREE TO AIR FLUORIDE POLLUTION UNDER ARIDE CLIMATE IN THE SOUTH OF TUNISIA: LEAF ANTIOXIDANT DEFENSE SYSTEM AND OIL QUALITY CHARACTERISTICS

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## ABSTRACT

This study's purpose was a comparison of the characteristics of some leaf antioxidative enzymes activities and oil quality of two adult olive orchards (*Olea europaea* L. cv. Chemlali) grown under two different environmental circumstances. The first is located around the main industrial factory in Sfax city, the Industrial Society of Phosphoric Acid and Fertilizers (polluted area) and the second is placed at 40 km from the industrial unit and chosen as the control one (Control). Results of this study showed that polluted olive leaves displayed a significant increase in the malondialdheyde (MDA) content, if compared to control ones. This increase was at more than 1.5 times if compared to T0 plants. This increase was accompanied with those of catalase (CAT) and superoxyde dismutase (SOD) activities. These increments were at 68 and 55 %, respectively for SOD and CAT activity, in comparison to control plants. On the other hand, olive production and oil content have decreased under polluted conditions. This decrease was accompanied with that of total phenol, oxidative stability, total chlorophyll and carotenoids. Nevertheless, this decrease was significant for only the photosynthetic pigments contents. For the acid composition of polluted olive plants, a significant decrease was observed in the case of oleic acid in parallel with an increase of the palmitic and linoleic acids. Nevertheless, this increase was significant only for the linoleic acid and oil samples of both treatments were classified as "extra virgin".

**Key Words:** Air pollution; Antioxidative enzymes; Fatty Acid Composition; *Olea europaea* L.; Phenolic Compounds.

## 1. INTRODUCTION

Environmental stresses such as extreme temperature, salinity, drought, flooding, heavy metals and air pollutants greatly affect plant metabolism and productivity. In Tunisia, along several decades ago, the main constraints for plant growth was the limitations of water resources and the urgent use of marginal water quality. Nowadays, face to the increase of the industrial activities, the plant development is facing to the combined effects of arid climate and air pollution. Nevertheless, in Sfax city, the main industrial region in Tunisia, it has been observed that recently the landscape around the main industrial factory "The Industrial Factory of Phosphoric Acid and Fertlizers (Société Industrielle d'Acide Phosphorique et des Engrais "SIAPE") is characterized by the progressive degradation of natural vegetations and the extension of cultivated olive tree (*Olea europaea* L. cv. Chemlali). Fluroide is among the most phytotoxic air pollutant emitted from this industry. Indeed, analysis of the air surrounding the factory showed that fluoride air contents oscillate between 3 and 12 µg dm$^{-3}$ day$^{-1}$ (Ben Abdallah et al., 2006).

Plant injury caused by pollutants released into the environment is most common near large cities and industrialized regions. Fluorides, the most stable of all chemical elements, result from the combination of fluorine with most chemical compounds (Fornasiero, 2001). Likewise, Klumpp et al. (2000) reported that fluoride pollutants taken up via root uptake and / or via direct foliar absorption are responsible of very acute damaging effects on vegetation.

The most common air pollutants are oxides of sulphur (especially SO2), fluorides (especially HF), oxides of nitrogen, ozone, peroxyacetyl nitrate (PAN) and particulates (Ben Abdallah et al., 2006). Nevertheless, the effects of air pollutants on plants have been mainly studied in annual or forest species; and information on the response of woody plants is scarce. Furthermore, major investigations have been interested in the pattern of accumulation of toxic ions and physiological and morphological responses of plants (Eleftheriou and Tsekos, 1991; Ben Abdallah et al., 2006). Nevertheless, one of the important biochemical changes occurring in plants subjected to biotic or abiotic stresses is the production of reactive oxygen species (ROS) (Fornasiero, 2001; Sofo et al., 2005; Ben Ahmed et al., 2009a). Plants use enzymatic and nonenzymatic antioxidative defense mechanisms to scavenge ROS. According to Kuwabara and Katoh (1999), among antioxidants enzymes, superoxide dismutase (SOD; EC 1.15.1.1) is the major scavenger of superoxide. With catalase (CAT; EC 1.11.1.6), SOD catalyses the dismutation of superoxide to $H_2O_2$ and $O_2$.

A great deal of research has been performed to evaluate visible symptoms and / or to examine the fluoride concentrations in the different plant parts, however, few works deal with the changes in some biochemical traits resulting from alterations induced by this toxic substance. Indeed, to our best of Knowledge, there is no study on the antioxidative responses and oil quality characteristics of adult olive tree subjected to air fluoride pollution under natural environmental conditions of arid climate in the south of Tunisia. This report attempts to characterize biochemical traits of adult olive tree in response to air fluoride pollution under natural environmental conditions of arid climate in the south of Tunisia. In particular, we are interested in some antioxidative enzymes activities of olive leaves and oil quality characteristics (fatty acid composition, phenolic composition and chlorophyll and carotenoid contents) of oil produced under these circumstances.

## 2. MATERIALS AND METHODS

### 2.1. Plant material and experimental design

The region is characterized by an arid climate of Mediterranean type. The annual rainfall and temperature averages over a 52-year period were 250 mm and 23°C, respectively (Ben Ahmed et al., 2009b). The studied olive tree (*Olea europaea* L. cv. Chemlali), were marked in land plots close to “Société Industrielle d’Acide Phosphorique et d’Engrais” (SIAPE) factory near to Sfax city. They consist of 35 years old trees planted on a loamy sand soil and served as the polluted trees. The control area is located in El Hencha region, at 40 km from the factory. The olive plants of both sites (polluted and control) were chosen to be similar in old and canopy. For each experimental site, ten trees from two adjacent rows (total 20 trees per treatment), with four replications of 5 trees each, were selected to be similar in potential yield and canopy.

The SIAPE factory constitutes the main pollution source in Sfax city. It is a phosphate fertilizer producing factory, located in the southern suburb of Sfax, that converts crude phosphate with a high fluoroapatite $[Ca_5(PO_4)_3F]$ content into a granule phosphate fertilizer easily assimilated by plants. During the phosphate attack by sulphuric and phosphoric acids, fluoride compounds such as HF, $H_2SiF_6$, and $CaF_2$ are given off by the factory chimney (Azri et al., 2002). In addition, analysis of the air surrounding the factory showed that fluoride air contents oscillate between 3 and 12 $\mu g\ dm^{-3}\ day^{-1}$ (Ben Abdallah et al., 2006). These concentrations exceeding the standard tolerated by sensitive vegetation (0.25 $\mu g.m^{-3}$ according to Doley, 1988), clearly show that olive trees used in this study are constantly exposed to an atmosphere contaminated by fluorine.

### 2.2. Enzyme activities analysis

The total superoxide dismutase (SOD) catalase (CAT) activities were determined as activity was determined as described by Ben Ahmed et al. (2009a). The determination of leaf protein content was realized according to the procedure described by Bradford (1976). The lipid peroxidation level in leaves under stressed conditions was evaluated by the measurement of malondialdheyde (MDA) content via the Thiobarbituric Reactive Species Test (TBARS).

### 2.3. Oil mechanical extraction process and quality analysis

For oil analyses, three samples of 4 Kg of fruits each per treatment were harvested at mid-December. Olive oil used for analysis was extracted using a laboratory olive Bench Hammer Mill (Abencor Analyzer, MC2 Ingenierias y Sistemas, Sevilla, Spain). Oil samples were filtered, transferred into amber glass bottles and stored at 4°C in darkness until analysis.

### 2.3.1. Oil quality indices, photosynthetic pigments contents and fatty acid composition

Free acidity (% oleic acid) and peroxide value (meq $O_2$ / kg) were measured following the analytical method as described in the European Regulation EEC 2568/91 (1991). Extinction coefficients $K_{232}$ and $K_{270}$ were measured at 232 and 270 nm, respectively.

The chlorophyll fraction at 670 nm and the carotenoid fraction at 470 nm were evaluated from the absorption spectrum of each oil sample (7.5 g) dissolved in cyclohexane as described by Mínguez - Mosquera et al. (1990).

Fatty acid composition was determined based on the European Regulations EEC 2586/91 method (1991) as described by Ben Ahmed et al. (2009b).

### 2.3.2. Total phenols, phenolic compounds and oxidative stability

The concentration of total polyphenols was estimated with Folin-Ciocalteu reagent at 725 nm as described by Ben Ahmed et al. (2009b). Results were expressed as mg of caffeic acid per kg of oil.

The different phenolic compounds analysed were determined from virgin olive oil according to Patumi et al. (1999) method. They were identified according to their order of elution and their retention times compared to those of the standard ones.

Oxidative stability is evaluated using a 679 Rancimat apparatus (Metrohm, Switzerland) at 120 °C and 20 l $h^{-1}$ air flow. The oil stability is expressed as the induction time (hours) of hydroperoxide decomposition.

### 2.4. Statistical Analysis

Statistical analyses were performed using the SPSS 10. Windows and treatment means were compared using Least Significant Difference (LSD) test at $p < 0.05$. At least three replicates were used for each analysis.

## 3. RESULTS AND DISCUSSION

### 3.1. Activities of Antioxidative Enzymes

The exposition of the Chemlali olive tree to fluoride polluted air resulted in significant changes in the pattern of both the malondialdheyde (MDA) content, the catalase (CAT) and the superoxide dismutase (SOD) activities, in comparison to leaves of non polluted site. Indeed, in polluted plants, the increases of MDA content, CAT and SOD activities were of

1.6, 2.2 and 3.3-fold higher than those recorded in the case of leaves of non polluted area (**Fig. 1**) and differences among experimental sites were significant ($p < 0.05$). The higher level of MDA content revealed the important damage affecting the lipid peroxidation caused by the reactive oxygen species generated in the case of the studied olive tree under polluted environmental conditions as reported by Shalata and Tal (1998). This increase was accompanied with the reduction of photosynthetic activity to more than 50% in comparison to control ones as well as the chlorophyll content (data not shown). In fact, as any abiotic stress, the limitation of photosynthetic activity by high air fluoride pollution would induce oxidative stress resulting from the imbalance between light capture and its utilization (Foyer et al., 2004; Ben Ahmed et al., 2009a).

Changes in the phytochemistry of the chloroplasts in leaves of polluted plants resulted in dissipation of excess energy, thus, generating active oxygen species, which are potentially dangerous to plant health under stressed conditions. The decrease of leaf chlorophyll content (data not shown) and the increase of SOD and CAT activities in leaves of polluted plants exhibits the oxidative stress induced by fluoride accumulation and suggests that the antioxidant defense system would play an important role in the air fluoride tolerance response of olive tree. The increase of MDA content, the CAT and SOD activities in polluted plants could be also due to the water deficit induced by fluoride accumulation in leaves. Nevertheless, although the important biochemical alterations, the polluted olive trees have maintained their evergreen landscape and continue to grow and produce even in low rates if compared to non polluted ones. According to Büssis et al. (1998), these strategies could be related to the ability of expanded leaves to mobilize photosynthetic resources, via the degradation of their photosynthetic apparatus, for the new acclimated leaves which allow the preservation of the evergreen landscape of the polluted plants.

## 3.2. Olive yield and oil quality characteristics

### 3.2.1. Olive yield, free acidity, peroxide values, extinction coefficients and total chlorophyll and carotenoids contents

The average olive production of polluted plants during the experimental period (12.5 kg tree$^{-1}$) was much lower (52%) than that of control ones (26 kg tree$^{-1}$). This yield reduction could be due, at the same time, to the negative effects of pollutants on fruit development process, via limitation of water availability, and also to the alternate bearing phenomenon characterizing the olive tree production and/or to the effects of climatic conditions characterizing the experimental site. Generally, fruit development phase (from June to December) coincides with period of high temperature and radiations which can affect fruit growth, and hence, olive yield.

During the experimental period, the free acidity varied from 0.45 to 0.65 %, respectively, in control and polluted area and the peroxide value oscillated between 12.73 and 16.54 meq $O_2$ kg$^{-1}$, respectively (**Table 1**). The registered values were lower than the upper limits (0.8 % as oleic acid and 20 meq $O_2$ kg$^{-1}$ as the peroxide value) established by the EU legislation for extra virgin olive oil. More to the point, these oil quality indices were influenced by the air fluoride pollution, since differences between both treatments were statistically significant ($p < 0.05$).

According to Boskow (1996), the increment of free acidity value under polluted conditions could be due to the increase of enzymatic activity of some lipolytic enzymes characterizing the damaged olive tissues. The increment of the peroxide value of oil from the polluted area could be explained, in accordance to Gutierrez et al. (1999), by the increase of the lipoxygenase activity. On the other hand, these values were higher than those recorded for the same olive cultivar irrigated with saline water by Ben Ahmed et al. (2009b). These differences showed clearly the effects of the different surrounding environmental circumstances on the responses of the olive tree (climatic conditions, plant age).

The comparison of spectrophotometric absorption characteristics in the UV region at 232 and 270 nm between oils from the two treatments did not show significant differences. Taking into account the values of free acidity, peroxide value and $K_{232}$ and $K_{270}$, the oil samples obtained from both treatments met the European Union requirements for the virgin olive oil category.

Total chlorophyll and carotenoids contents in the virgin oils were enormously affected by the air pollution level around the industrial society. Indeed, both of the photosynthetic pigments contents were reduced at more than 50% in oil coming from plants exposed to air pollution if compared to the control ones (**Table 1**) and differences between both treatments were significant. This reduction could be attributed to the pigments' degradation by pollutants particularly the fluoride one. Furthermore, the decrease of these pigments contents confirms the oxidative stress induced by the pollutants and could be considered as a toxicity sign caused by environmental stress.

### 3.2.2. Fatty acid composition

Results displaying the fatty acid composition of VOO characterizing both of the experimental sites are represented in **Table 2**. For both oil samples, the most abundant acid was the oleic one with values recorded in oil obtained from polluted plants were statistically lower ($p = 0.0031$) than those in oil of control ones. The unsaturated- saturated acid ratio did not appear to be influenced by the air pollution characterizing the polluted experimental site. However, the oil obtained from control plants would be nutritionally better than that obtained in the case of polluted ones. According to Salvador et al. (2001), the reduction of oleic acid and the slight increase of the palmitic one in the case of polluted plants could be due to disturbance occurring in the triacylglycerol biosynthesis induced by the air pollutants characterizing the polluted area. On the other hand, the higher amounts of linoleic acid recorded in polluted plants and the low level of oleic acid found in the case of Chemlali olive oil, in comparison to other cultivars such as Arbequina (José-Motilva et al., 2000) and Cornicabra (Gomez-Rico et al., 2007) may be due, according to Sanchez and Harwood (2002), to the transformation of oleic acid into linoleic one by the oleate desaturase activity and / or probably to the disturbance of the activities of enzymes involved in the oleic acid synthesis chain by fluoride pollution characterizing the SIAPE site.

### 3.2.3. phenolic compounds, total phenols and oxidative stability

Table 3 reports the concentrations of the major phenolic compounds, total phenols and oxidative stability of VOO samples under both environmental conditions. Total phenols contents of VOO were not significantly influenced by the air pollution level. They were of 281 and 277 mg / kg, respectively in control and polluted plants. The three phenolic compounds in highest concentrations in both oil samples are hydroxytyrosol, tyrosol and glycoside oleuropein. The maintenance of high phenols contents in polluted oil samples could be involved in the antioxidative mechanisms developed by the olive tree in response to oxidative stress induced by air pollution as was suggested by several papers under different environmental constraints (Wiesman et al., 2004; Servili et al., 2007).

On the other hand, the higher polyphenol contents recorded in oils of stressed plants could be due to the acceleration of maturation of the olives which could account for the higher levels of phenols. Furthermore, as it is known, the air pollution could result in both water deficit and pollutants accumulation. Per consequent, the increase of phenols contents in stressed plants might be due to the effects of water deficit on the activation of Phenylalanine ammonia-lyase

(PAL), a key enzyme in the biosynthetic pathway of phenolic compounds, which is directly involved in the accumulation of polyphenols in the virgin olive oil (Romero et al., 2002) as recently reported in cv. Leccino olive by Servili et al. (2007). Moreover, periods of severe conditions could influence PAL activity in olive fruit (Tovar et al., 2002).

The oxidative stability of VOO samples did not show a significant variation between treatments. Furthermore, values recorded were comparable to those obtained by José-Motilva et al. (2000) in the case of Arbequina olive cultivar but lower than those characterizing the Cornicabra virgin olive oil (Salvador et al., 2001). The same authors have stated that oxidative stability of VOO depends on a multitude of factors such as the extraction system, climate, latitude and stage maturity of collected olive fruits. Moreover, the higher oxidative stability of VOO obtained in polluted plants could be due to the higher phenols contents as has been suggested by several papers (José-Motilva et al., 2000, Salvador et al., 2001).

In conclusion, it appears that olive tree tolerance to air fluoride pollution under field conditions is dependent on the performance of different adaptive mechanisms. Among them, the positive evolution of antioxidative enzymes activities is further evidence of direct implication of antioxidant defense system in improving olive tolerance to air fluoride pollution.On the other hand, our results are further evidence of direct effects of such stress on qualitative parameters of olive oil, particularly the fatty acid and phenolic composition of virgin olive oil. Overall, the Chemlali olive tree used in this study displayed a great ability for extension in polluted area in the south of Tunisia. So, in addition to the benefits of olive oil produced, its extension would to preserve green landscape in industrial zone of arid region in the south of Tunisia (Sfax).

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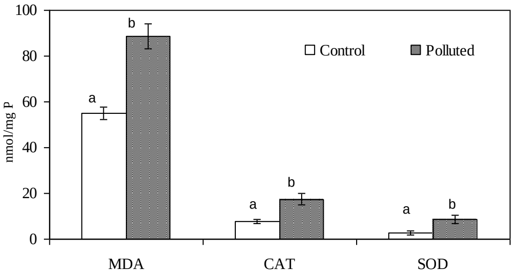

**Figure 1:** Malondialdheyde (MDA) content, catalase (CAT) and superoxide dismutase (SOD) activities in leaves of olive trees (Cv. Chemlali) grown under non polluted (control) and fluoride polluted area. Values are means of three different measurements (n = 3) ± standard deviations. Different letters (a, b) indicate significant differences ($p < 0.05$) between treatments.

**Table 1.** Free acidity, peroxide values, extinction coefficients, total chlorophyll (Chl) and carotenoids (Car) contents of oils and olive yield of olive trees (Cv. Chemlali) grown under non polluted and fluoride polluted area.

| | Free Acidity (%) | Peroxide Value (meq $O_2$ / kg) | K232 | K270 | Chl (mg/ kg) | Car (mg/kg) | Olive yield (Kg/tree) |
|---|---|---|---|---|---|---|---|
| Control | $0.45±0.05^a$ | $12.73±1.21^a$ | $2.33±0.21^a$ | $0.25±0.08^a$ | $27.30±2.45^a$ | $12.05±1.85^a$ | $26±3.85^a$ |
| Polluted | $0.65±0.09^b$ | $16.54±1.56^b$ | $2.27±0.25^a$ | $0.24±0.06^a$ | $13.27±1.76^b$ | $5.89±1.01^b$ | $12.5±2.65^b$ |

Values are means of three samples (n = 3) ± standard deviations. Different letters (a, b) indicate significant differences ($p < 0.05$) between treatments.

**Table 2.** Fatty acid composition (%) of virgin olive oils from olive trees (Cv. Chemlali) grown under non polluted and fluoride polluted area.

| | Control area | Polluted area |
|---|---|---|
| Palmitic acid (C16) | $20.45 \pm 1.40^a$ | $21.88 \pm 1.38^a$ |
| Palmitoleic acid (C16’) | $2.69 \pm 0.49^a$ | $3.54 \pm 0.46^a$ |
| Heptadecanoic acid (C17) | $0.14 \pm 0.01^a$ | $0.17 \pm 0.03^a$ |
| Heptadecenoic acid (C17’) | $0.19 \pm 0.02^a$ | $0.16 \pm 0.02^a$ |
| Stearic acid (C18) | $3.08 \pm 0.28^a$ | $2.94 \pm 0.21^a$ |
| Oleic acid (C18’) | $66.48 \pm 5.03^a$ | $55.74 \pm 4.78^b$ |
| Linoleic acid (C18’’) | $14.15 \pm 3.46^a$ | $20.16 \pm 3.02^b$ |
| Linolenic-eicosanoic acid (C18’’’) | $0.86 \pm 0.08^a$ | $0.84 \pm 0.06^a$ |
| Eicosanoic acid (C20) | $0.69 \pm 0.09^a$ | $0.64 \pm 0.05^a$ |
| Eicosenoic acid (C20’) | $0.37 \pm 0.04^a$ | $0.30 \pm 0.04^a$ |
| Insat / Sat ratio | $3.49 \pm 0.64^a$ | $3.14 \pm 0.42^a$ |

Values are means of three samples (n = 3) ± standard deviations. Different letters (a, b) indicate significant differences ($p < 0.05$) between treatments.

**Table 3.** phenolic composition concentrations (mg / Kg of oil), total phenols contents (mg/kg of oil) and oxidative stability (h) of olive oils from olive trees (Cv. Chemlali) grown under non polluted and fluoride polluted area.

| | Control area | Polluted area |
|---|---|---|
| Tyrosol | 41.53 ± 2.36$^a$ | 48.27±3.21$^b$ |
| Hydroxytyrosol | 79.52±3.56$^a$ | 81.36±2.06$^a$ |
| Oleuropein | 10.23±2.84$^a$ | 11.45±2.56$^a$ |
| glycoside oleuropein | 23.23±2.56$^a$ | 22.49±2.47$^a$ |
| Vanillic | 10.62±1.56$^a$ | 19.09±1.04$^a$ |
| Caffeic | 7.87±1.24$^a$ | 9.37±1.03$^b$ |
| Syringic | 10.27±1.2$^a$ | 9.26±1.24$^a$ |
| p-coumaric | 6.12±1.32$^a$ | 5.56±1.42$^a$ |
| o-coumaric | 5.19±1.02$^a$ | 6.76±1.25$^a$ |
| Ferulic | 4.27±0.43$^a$ | 4.88±0.65$^a$ |
| Total phenols (mg/kg) | 281.74±4.96$^a$ | 277.09±4.45$^a$ |
| Oxidative stability (h) | 16.02±1.02$^a$ | 15.61±1.45$^a$ |

Values are means of three samples (n = 3) ± standard deviations. Different letters (a, b) indicate significant differences ($p < 0.05$) between treatments.

**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# DETERMINATION OF SOURCES OF PM2.5 PARTICULATE MATTER IN A FORESTRY BASED INDUSTRY CITY IN CANADA

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## ABSTRACT

Quesnel is sustained by the forestry industry, although mining, ranching and tourism are also important. Seven fine particulate matter (PM2.5) sources were identified using Positive Matrix Factorization (PMF) receptor modelling. Three-year PM2.5 sampling results from the National Air Pollution Surveillance program were analyzed. Sources identified were the plywood industry, wood combustion, Kraft processes, mining, road and crustal dust. Surprisingly, natural gas related combustion was found to be the highest contributing factor to PM2.5. Although use of natural gas as a heating fuel at the location of the air monitoring station may possibly explain this anomalous finding, further investigation is required.

**Key Words:** PMF, source apportionment, receptor modeling, PM2.5, Quesnel, Canada

## 1. INTRODUCTION

Human exposure to ambient fine particulate matter (PM2.5) is associated with increased cardiovascular and respiratory morbidity (Miller et al., 2007). Numerous studies have found an association between increased mortality and exposure to PM2.5 (Miller et al., 2007). Particulate matter pollution is also a factor in reduced visibility and it affects the radiation balance of the Earth (Watson, 2002).

Quesnel is located in a valley at the confluence of the Fraser and Quesnel Rivers in British Columbia, Canada. At the north and south ends of the valley, there are local plateaus which are at higher elevations than the downtown area. This creates a bowl which encompasses the downtown area. The local topography inhibits air circulation which can lead to frequent stagnation periods and the subsequent buildup of air pollutants in the valley bottom (Plain, 1998).

Throughout the past two decades, Quesnel attracted attention of the researchers and local authorities due to high particulate matter levels in the region. There have been many attempts to reduce the PM levels in the area. However previous studies have not shown a reduction in PM levels to meet British Columbia air monitoring standards.

The present study attempted to identify sources contributing to PM2.5 in Quesnel, BC using a receptor oriented method known as Positive Matrix Factorization (PMF).

## 2. MATERIALS AND METHODS

### *2.1. Sample Collection and Analysis*

Samples in this study were collected at a downtown site in Quesnel, BC (52.98$^o$N, 122.49$^o$W). The sampling site is one of the National Air Pollution Surveillance sites (NAPS S101701) and is operated by the British Columbia Ministry of Environment. This air monitoring station is located on the roof of Quesnel Secondary School. It's location is identified on the map together with the locations of the principle industries in the area (Figure 1).

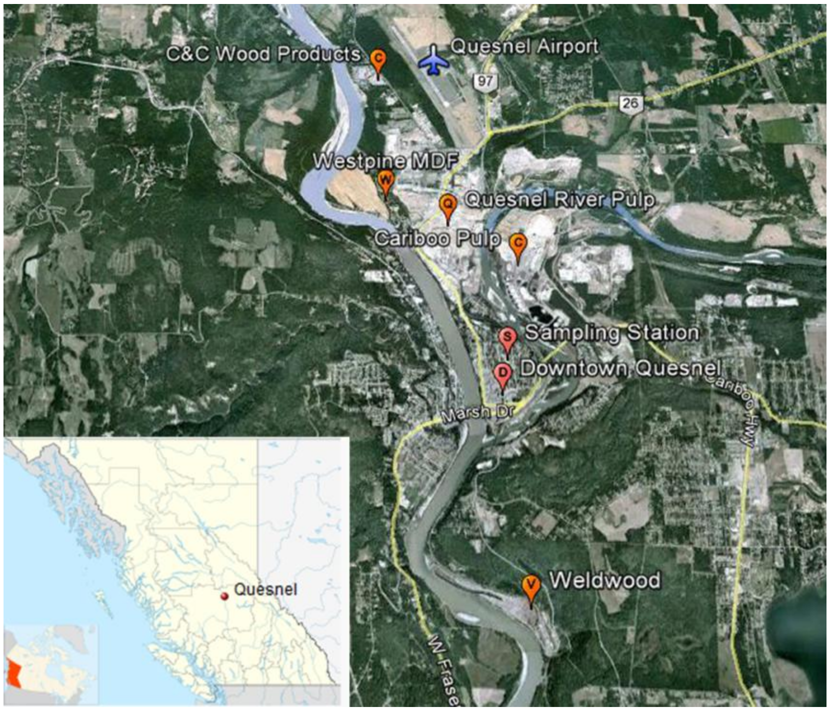

Figure 1. The air monitoring site and major industries (Quesnel, B.C., Canada)

Integrated 24-hr ambient aerosol samples were collected in co-located dichotomous sequential (PartisoPlus 2025D) and speciation samplers (Partisol 2300-Ruppercht & Patashnick Co., Inc.) between June 2007 and March 2009 with a 1-in-3-day sampling frequency. A total of 154 samples were collected during this period and analyzed by Environment Canada's Analysis and Air Quality Section in Ottawa, Canada.

Teflon filter samples obtained by the Partisol-Plus 2025D sequential sampler were used for the analyses of trace metals (Al, Sb, Ba, Br, Ca, Cd, Cr, Co, Fe, Pb, K, Mn, Ni, Rb, S, Se, Sr, Si, Sn, Ti, V, and Zn) by energy dispersive X-ray fluorescence (XRF). The Partisol 2300 speciation sampler was equipped with three Harvard-designed Chemcomb cartridges. These cartridges included honeycomb-type annular denuders and filter packs consisting of Teflon and Nylon filters. The filters were extracted and analyzed by ion chromatography (IC) to quantify water-extractable anions and cations: sulfate, nitrate, ammonium, calcium, chloride, potassium, magnesium, sodium, acetic acid, formic acid, and oxalic acid. The aqueous extracts of PM2.5 were also analyzed for water-soluble species (Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Se, Ag, Sr, Ti, Sn, Ti, V, and Zn) by inductively coupled plasma mass spectrometry (WICPMS). Acid extracted results (ICPMS) were not available for this study. Concentrations of organic carbon (OC) and elemental carbon (EC) were determined from the analysis of PM collected on quartz fibre filters using a DRI Model 2001 thermal/dual-optical carbon analyzer (Atmoslytic Inc.) and the Interagency Monitoring and Protected Visual Environments (IMPROVE) protocol. Quartz filter samples were heated stepwise at temperatures of 120$^oC$ (OC1), 250$^oC$ (OC2), 450$^oC$ (OC3), and 550$^oC$ (OC4) in a non-oxidizing helium (He) atmosphere, and 550$^oC$ (EC1), 700$^oC$ (EC2), and 800$^oC$ (EC3) in an oxidizing 2% $O_2$/98% He atmosphere. Pyrolyzed organic carbon (POC) was reported as the carbon evolved from the filter after oxygen was introduced, but before the reflectance achieved its original value. The eight fractions, OC1, OC2, OC3, OC4, EC1, EC2, EC3, and OP obtained by the reflectance method. Positive artifacts of OC were estimated by measuring OC fraction concentrations on a backup quartz filter positioned behind a Teflon filter. These positive OC artifacts were subtracted from the concentrations of each OC fraction measured on the directly exposed quartz filters (Evans and Jeong, 2007). A more detailed description of the sampling and analytical methods can be elsewhere (Dabek-Zlotorzynska et al., 2011).

### *2.2. Positive Matrix Factorization*

Positive Matrix Factorization (PMF) produces strictly nonnegative factor loading and factor scores with less rotational ambiguity. PMF uses a weighted least-squares fit with the known error estimates of the elements of the data matrix used to derive the weights, and provides a solution that minimizes an object function, Q, based upon uncertainties for each observation (Polissar et al., 1998). This function is defined as

$$Q = \sum_{i=1}^{I} \sum_{j=1}^{J} \left| \frac{x_{ij} - \sum_{n=1}^{N} g_{in} f_{nj}}{s_{ij}} \right|^2$$

In the above equation, $x_{ij}$ refers to a measured variable j in sample i, $g_{in}$ refers to the contribution of source n to sample i, $f_{nj}$ refers to the contribution of variable j to this source profile n and $s_{ij}$ are estimates of the uncertainties in the $j^{th}$ variable measured in the $i^{th}$ sample.

The success of PMF is strongly dependent on good estimates of overall measurement uncertainties for each data value. The uncertainty estimation provides a useful tool for decreasing the weight of missing and below-detection limit data in the solution and to account for the variability in the source profiles. NAPS data do not include overall measurement uncertainty, only analytical uncertainty. Therefore, analytical uncertainties and, where these were missing, 10% of the concentration values were used instead (Polissar et al., 1998). Below detection limit (BDL) values were replaced by half of the detection limit values, and their overall uncertainties were set at 5/6 of the detection limit values. Imputation, using the geometric mean of the measured values, was used to replace missing values and their accompanying uncertainties were set at four times the geometric means. The EPA PMF 3.0 modelling software was used for the analysis.

## 3. RESULTS AND DISCUSSION

Positive Matrix Factorization analyses were performed using 30 species. Descriptive statistics of the data are provided in Table 1. Formate (IC), $Cl^-$ (IC), Zn (XRF), Mn (ICP-MS), Ar (ICP-MS), Cd (ICP-MS), Ba (ICP-MS) and Pb (ICP-MS) had residuals greater than three times the uncertainties even when the number of factors was increased. These species categories were set to ‘weak’ and the remaining species categories were set to ‘strong’. Four to eight factor solutions were investigated. A 7-factor solution was found to be the optimum solution. Explained variances and source contributions of seven factors are shown in Figure 2. This paper reports the preliminary results of the study.

The first factor explained most of the variances of Al, Si, Ca (XRF), and Fe. Also, moderate contributions of Mg, Ca (IC) and Mn were observed. These elements are markers of crustal dust. Therefore, this factor is attributed to crustal dust. This factor explains 8% of the total PM2.5 mass in Quesnel.

The second factor accounted for most of the variances of Na, K and Ca (IC) were explained in the second factor. Magnesium, oxalate, formate, $Cl^-$ and some heavy metals also contributed to this factor. Sodium, K, Ca and Mg are used as a road salt in Canada. While sodium chloride (NaCl) is by far the most frequently used road salt, other inorganic salts used in Canada include calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$) and potassium chloride (KCl) (Environment Canada and Health Canada, 2001). Heavy metals in this factor may be result of the abrasion of breaks and tires. Therefore this factor was attributed to road dust. Chlorine was expected to be present in higher concentrations, but there may have been losses due to chloride depletion (Yaou & Zhang, 2012). This factor explained 10% of PM2.5 mass.

Factor three explained most of the variances of the OCs, EC1 and nitrate. Contributions of formate, oxalate and K were also observed in this factor. EC is a primary pollutant, and the product of incomplete combustion of carbon-based materials and fuels, whereas OC can be directly released into the atmosphere or produced via secondary gas-to-particle conversion processes (Lonati et al., 2007). Relatively low EC contributions in

Table 1. Summary of 29 PM2.5 species mass concentrations used for PMF analysis[a]

| | **Concentration (ng/m³)** | | | | | | |
|---|---|---|---|---|---|---|---|
| **Species** | **Arithmetic Mean** | **Geometric Mean** | **Minimum** | **Maximum** | **n** | **% BDL Values** | **% Missing Values** |
| **Formate_IC[b]** | 22 | 17 | 5.2 | 105 | 117 | 24 | 0 |
| **Oxalate_IC** | 69 | 54 | 5.2 | 354 | 145 | 6 | 0 |
| **Na_IC** | 227 | 153 | 1.7 | 2846 | 152 | 1 | 0 |
| **K_IC** | 185 | 133 | 3.1 | 907 | 152 | 1 | 0 |
| **Mg_IC** | 8.1 | 6.4 | 1 | 34 | 143 | 7 | 0 |
| **Ca_IC** | 36 | 24 | 1 | 195 | 146 | 5 | 0 |
| **Cl_IC** | 29 | 18 | 5.2 | 190 | 102 | 34 | 0 |
| **Sulphate_IC** | 925 | 639.6 | 70 | 4153 | 154 | 0 | 0 |
| **Nitrate_IC** | 479 | 336 | 13 | 3454 | 152 | 1 | 0 |
| **Ammonium_IC** | 678 | 522 | 0.7 | 2355 | 152 | 1 | 0 |
| **OC1_TOR[c,d]** | 76 | 13 | 0.9 | 1017 | 91 | 41 | 0 |
| **OC2_TOR[c,d]** | 567 | 253 | 1.1 | 2385 | 140 | 9 | 0 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **OC3_TOR**[c,d] | 1100 | 899 | 69 | 3579 | 154 | 0 | 0 |
| **OC4_TOR**[c,d] | 666 | 587 | 27 | 1571 | 154 | 0 | 0 |
| **POC_TOR**[c,d] | 584 | 426 | 12 | 1957 | 149 | 3 | 0 |
| **EC1_TOR**[c,d] | 1225 | 988 | 122 | 4034 | 154 | 0 | 0 |
| **EC2_TOR**[c,d] | 489 | 440 | 112 | 1174 | 154 | 0 | 0 |
| **EC3_TOR**[c,d] | 41 | 6.9 | 0.1 | 272 | 106 | 31 | 0 |
| **Al_XRF**[e] | 32 | 21 | 0.6 | 176 | 108 | 12 | 18 |
| **Si_XRF** | 101 | 59 | 0.6 | 699 | 112 | 9 | 18 |
| **S_XRF** | 351 | 258 | 0.2 | 2814 | 125 | 1 | 18 |
| **Ca_XRF** | 33 | 25 | 0.5 | 135 | 117 | 6 | 18 |
| **Fe_XRF** | 36 | 23 | 0.1 | 201 | 119 | 5 | 18 |
| **Zn_XRF** | 15 | 9.6 | 0.4 | 66 | 116 | 7 | 18 |
| **Mn_WICPMS**[f] | 1.8 | 1.3 | 0.1 | 12 | 145 | 2 | 4 |
| **Ar_WICPMS** | 0.1 | 0.1 | 0 | 0.8 | 106 | 27 | 4 |
| **Cd_WICPMS** | 0.1 | 0 | 0 | 1.1 | 129 | 12 | 4 |
| **Ba_WICPMS** | 1.1 | 0.7 | 0 | 12 | 145 | 2 | 4 |
| **Pb_WICPMS** | 0.4 | 0.2 | 0.1 | 4.3 | 100 | 31 | 4 |

[a] Below detection limit (BDL) values were replaced by 1/2 of the reported detection limits.

[b] IC, results of Ion Chromatography analysis of water soluble species.

[c] TOR, results of Thermal/dual-Optical Reflectance analysis.

[d] OC values corrected using a dynamic blank measuring positive organic artefacts. EC values were not blank corrected.

[f] WICPMS, results of ICPMS analysis of water soluble species.

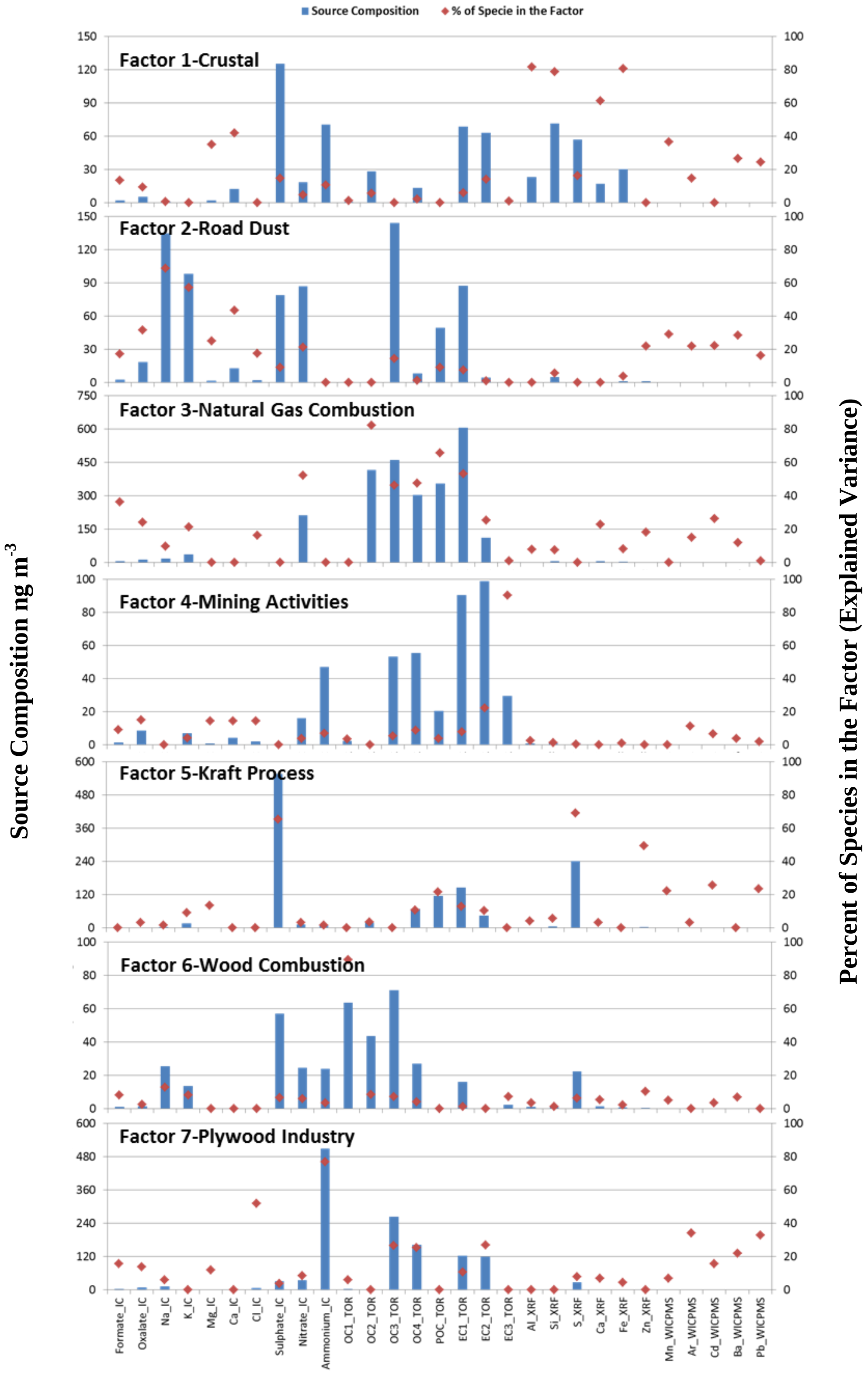

Figure 2. Concentration profiles and percent of species explained in each factor

factor three were likely due to restricted use of high EC emitting fuels such as fuel oil and coal. Relatively high OC concentrations were likely due to secondary formation by condensation processes fostered by low winter temperatures and by the low boundary layer height typical during the winter. In fact, low temperatures enhance condensation of semi-volatile gaseous precursors, whereas temperature inversions limit their dilution and allow for super-saturation conditions with exceedance of the equilibrium vapour pressures. Other processes that can contribute to elevated cold season OC levels are the adsorption of semi-volatile OCs onto existing solid particles and the dissolution of soluble gases that can undergo reactions in particles (Odum et al., 1996). Natural gas is a low EC emitting fuel. This factor explained 35% of the total PM2.5 mass. Based on the discussion above, this factor was tentatively attributed to natural gas combustion. This is a very surprising and difficult to accept finding, since natural gas is a clean burning fuel.  However, the School Board uses natural gas for heating and, since the location of the air monitoring station on the roof of a school may explain this anomalous finding. Further investigation is required to resolve this issue.

The fourth factor explained most of the variance of EC3. Reasonable contributions of EC1, EC2, OC3, OC4, ammonium, nitrate, Mg, Ca (IC) and $Cl^-$ were also observed in this factor. As discussed above for factor three, EC would be encountered with high EC emitting fuels like fuel oil or a product of incomplete combustion. Ammonium and nitrate concentrations also contributed to this factor. Ammonium and nitrate with fuel oil is found in the mining industry as an explosive (Ministry of Justice, 2012). Therefore this factor is tentatively identified as emissions from mining activities, but further investigation of this finding is necessary.

Factor five accounted for most of the variances of sulphate and sulphur. Malodorous emissions of reduced sulphur compounds, measured as total reduced sulphur, including hydrogen sulphide, methyl mercaptan, dimethyl sulphide, and dimethyl disulphide, are emitted in Kraft pulping processes. This factor also exhibited a statistically significant correlation with $SO_2$. Factor five was thus attributed to the pulp & paper Kraft process.

In the sixth factor, species contributing to the source profile were sulphate, OCs, nitrate, ammonium, Na, K and sulphur. Potassium is an indicator of wood combustion, and previous studies have demonstrated that OC is a dominant component of residential wood smoke emissions. According to profiles given in the literature, this factor is attributed to wood combustion due to space heating (Kim et al., 2004).

Ammonium and chloride were dominant species in the seventh factor. There were also contributions from OCs, ECs, formate, oxalate and heavy metals. Ammonium chloride ($NH_4Cl$), is a clear white water soluble crystalline salt added as a hardener to glue used in plywood industry. There were also some OC and EC contributions indicating residuals of combustion processes. Therefore, this factor was attributed to emissions from the plywood industry.

## 4. LIMITATIONS OF THE STUDY AND FUTURE WORK

Although the PMF analysis identified meaningful sources, there are some limitations to this study. These include: absence of overall measurement uncertainty; use of less accurate XRF data instead of acid soluble ICPMS data for metals, hence, fewer variables than optimal number of variables. In order to finalize this work, the following require further study: possible seasonal effects in the variations of sources; possible effect of natural gas emissions close to the air sampling station; factors attributed to mining activities; and, dataset validation in relation to results from neighbouring sites and in the broader context of overall NAPS dataset validation.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# MORPHOLOGICAL AND ANATOMICAL RESPONSES OF PEAR AND ALMOND TREES EXPOSED TO AIR FLUORIDE POLLUTION

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## ABSTRACT

Leaves of almond (*Prunus dulcis*) and pear (*Pyrus communis)* growing in the vicinity of a phosphate fertilizers producing factory were used to study the effects of fluoride pollution on the morphology and the anatomy of their leaves.

Regular field observations in the polluted area allowed us to recognize various expressions of damage caused to almond and pear trees. In almond, damages appear from the beginning of the growing season. They consist of apical brick-yellow necroses that extent to leaf margins. On pear leaves, necroses were not frequent and appeared later as apical burns but however, the lower leaf surface seems to be covered by a layer of white dust difficult to remove.

Chemical analysis of dust deposited on the leaf lower surface of pear, as a whitish layer, would to confirm the existence of a mechanism regulating $F^-$ content by its exclusion outside the leaf followed by its removal through leaching. The chemical analysis of both peripheral and central necrotic leaf round slices, revealed the occurrence of an isolation mechanism of $F^-$ allowing the plant to maintain the photosynthetic integrity of its remaining leaf area. On the other hand, our results demonstrate the role of $Ca^{++}$ in trapping $F^-$ ions in the form of $CaF_2$. Damages seem to appear when $Ca^{++}$ ions are no more available. In comparison with controls, the anatomical sections of polluted leaves revealed several structural changes induced in response to air fluoride pollution such as: (i) an elongation in mesophyll palisade cells (ii) a disruption in mesophyll spongy cells being more pronounced in pear leaves (iii) a decreasing in epiderm cells size associated with a cuticle thickening.

**Keys words:** Almond; Pear; Leaf Morphology; Anatomy; Fluoride, Calcium

## 1. INTRODUCTION

Nowadays, the (SIAPE) factory constitutes the main pollution source. It is a phosphate fertilizer producing factory, located in the southern suburb of Sfax, that converts crude phosphate with a high fluoroapatite [$Ca_5(PO_4)_3F$] content into a granule phosphate fertilizer easily assimilated by plants. During the phosphate attack by sulphuric and phosphoric acids, fluoride compounds such as HF, $H_2SiF_6$, and $CaF_2$ are given off by the factory chimney (Ben Abdallah & Boukhris, 1990; JICA, 1993; Azri et al., 2002). In addition, analysis of the air surrounding the factory showed that fluoride air contents oscillate between 3 and 12 μg $dm^{-3}$ $day^{-1}$ (Mezghani et al., 2005).

Since the installation of the SIAPE, the agrosystems in its surroundings have undergone increasing degradation. In the vicinity of the factory, some local fruit species, such as pear and almond trees, grow in a naked landscape and are daily subjected to fluorine air pollution. For the almond tree, which has often been considered as sensitive to fluoride pollution (Mezghani, 2001; Ben Abdallah et al., 1994), we did not observe any flowers or fruit within a radius of 1.5 km from the factory. However, for the pear tree, classified among tolerant fruit species to fluoride pollution (Ben Abdallah et al., 1994), some ecotypes thrive and fructify in the most polluted area. In an attempt to explore some adaptation strategies adopted by resistant as well as sensitive fruit species to survive in such fluoride polluted area, and to explain different plant responses to air pollutants, we studied the distribution of calcium and fluoride in healthy and necrotic leaf areas.

By another way, anatomical sections were performed to (i) identify plant tissues affected by air pollution and (ii) to explore some morphological reactions adopted by these species still surviving in such restrictive conditions (aridity, high temperatures ranging from 35 to 40°C, low rainfall etc…, (Elloumi et al., 2003)).

## 2. MATERIAL AND METHODS

Plant material consists of 2 fruit species indigenous to Sfax area: almond (*Prunus dulcis*) and pear (*Pyrus communs*) trees.

To study the distribution of leaf Ca and Fluoride, sampling was done during the growing season. Each sampling was repeated 3 times. Leaf samples from each species were taken from several branches of tree side exposed to the factory fume. For F and mineral analyses of necrotic and healthy leaf area, only almond leaves exhibiting marginal necroses and occupying the middle of the shoots were selected during July. Scissors were used to separate necrotic and central (healthy) leaf areas from each other and then analyzed within 24h. Control samples were gathered in non polluted land plots situated at a distance of 45 km from the factory. Dust and particle, deposited on pear leaves were removed by gentle hand shaking. Leaves were washed with tap water and subsequently dipped into 0.01M HCl for 5 mn followed through washing with deionised water.

Damaged leaf areas were cut off carefully in such a way that central (healthy) leaf surfaces remain attached on mother plant shoots for photosynthesis measurements. Leaf photosynthesis was measured using a portable infrared gas analyzer (CID 301 PS, Vancouver USA) on attached leaves in the field, between 9:30 and 10:00 am. Only the central leaf area was introduced in the leaf chamber. Leaf surface as well as leaf percentage necroses were estimated as reported by the method of Mabrouk and Carbonneau (1996). In order to avoid the effect of light intensity variation, all measurements were taken on sunny days, with Photosynthetic Active Radiation (PAR) being higher than 1600 $\mu molm^{-2}s^{-1}$, by orienting the leaf chamber to obtain maximum light absorption. The PAR was measured directly by the infrared gas exchange analyser system. The average leaf temperature was 34ºC ±2.55º C.

For analysis of F and Ca, different plant tissues (leaf blade, leaf stalk, and internodes) were dried at 80ºC for 48 h and ground to pass through a 40-mesh sieve in a Willey hammer mill. Leaf powder was re-dried for 1 to 2 h prior to weighing sub-samples for analysis at either 80ºC for F or 105ºC for Ca. Fluoride concentrations were determined using the potentiometric technique described by the Association of Official Analytical Chemists (AOAC, 1975) **.**
After digesting plant powder with nitric and perchloric acids (2v/1v), Ca was determined by the atomic absorption spectrophotometry technique with polarized Zeeman (HITACHI, Z-6100).

For anatomical sections, fresh polluted and non polluted leaves were gathered and fixed for 24 hours in Formalin-Acetic-Alcohol mixture (FAA) according to Sass (1958) fixation procedure. The fixed material is rinsed with water and then divided into two plots. The first one was deshydrated in alcohol and included in paraffin, cut and stained by the triple stain (Safranin, Heidenhain’s and blue anilin (Sass, 1958)). The second plot is cut by a freezing microtome and stained with aceto-carmin (Locquin & Langeron, 1978). Freezing and serial cross sections were observed under a light Reichert LKB microscope equipped with a camera.

Statistical analyses were performed with the SAS package (Statistical Analysis System, version 6.12, Cary, NC, USA) using both Duncan multiple range and Student Tests at the 5% significance level.

## 3. RESULTS AND DISCUSSION

### 3.1 Morphological responses of plants to air fluoride pollution

The regular monitoring in the polluted area allowed us to recognize various expressions of damage caused to almond and pear trees. In almond, damage appears on leaf tips and margins from the beginning of the growing season. They consist of apical brick-yellow necroses that extent to leaf margins **(Figure 1)**.

Miller (1993) and Fornasiero (2001) reported that gaseous fluorides enter the leaf by diffusion through the stomata, and dissolve in the humid space of substomatal cavity; the ions are carried with the transpiration stream to sites of greatest evaporation, which are usually leaf margins and tips where concentrated $F^-$amounts cause the first signs of damage.

As shown in figure 1, necrotic tissues are limited by a dark violet borderline. It consists of anthocyanin pigments secreted by plant leaf cells when subjected to any stress (Ezzilli et al., 1999). The secretion of anthocyanins along a waved line seems to show a primary defense reaction developed by the plant in order to limit damage at leaf extremities. By another way, the follow-up of the status of some ecotypes of pear trees exposed to the fume given off by the polluting factory allowed us to identify damages caused to these species.

Regarding the necroses exhibited on almond leaves, those on pear leaves were infrequent and appear later as burns occupying leaf margins **(Figure 2)**. Our results are in agreement with our previous work (Ben Abdallah et al., 2006) considering this species as tolerant to air fluoride pollution since resistant fruit species are those accumulating fluoride without showing symptoms either of F toxicity or growth restrictions.

### 3.2 Evidence of plant survival mechanisms in the polluted area

The high levels of fluorine in unwashed leaves of pear tree (Table 1) and the presence of a whitish layer of dust covering the lower leaf surface (Figure 2) confirm the existence of a particulate pollution already reported by Azri et al. (2002). The chemical analyses of dust deposited on pear leaves showed high Ca and fluoride contents (Table 1). Thus suggesting the existence possibility of fluoride ions regulatory mechanism, by which fluorides excess may be excreted on the outside of the leaf, followed probably by their removal through leaching. According to Elloumi et al., (2003), the particle cover, which was difficult to be removed after washing, seems to be related to the plant specificity on the one hand and the direction of prevailing winds on the other one.

In the absence of rain, particles deposited on the surface of the leaves may obstruct the stomata and cover assimilatory surfaces. Such particles are not phytotoxic: it is a latent pollution. However, in the rainy season, if a portion of fluoride particulate is leached, another part may be dissolved and then enter the leaf tissue (Ben Abdallah, 2007).

Our data acquired from our chemical analyses revealing (i) high fluoride and calcium contents in necrotic almond leaf tips and margins with respect to those of central leaf parts (ii) low fluoride and calcium contents in healthy leaf areas in comparison with those of non polluted leaves (iii) non significant fluoride quantities recorded in internodes and leaf stalks adjacent to polluted leaf blades **(Figure 3).**

These findings would confirm the tendency of polluted species to balance the fluoride accumulation by a parallel calcium accumulation in its leaf margins thus suggesting the trapping of fluoride in the form of $CaF_2$. Therefore, tolerant varieties accumulating high leaf fluoride content are able to sequester it, as $CaF_2$. When trapped in this form, fluoride cannot disturb the plant metabolism (Machoy-Mokrzynska 1995). Our findings are in favor of the non-translocation of fluoride, through phloem towards lower plant organs as demonstrated in previous work (Turk et al., 1993). The interaction between fluoride and calcium has also been reported with other cations such as silicon and aluminium (Konishi and Miyamoto, 1983; Charlot and Kisman, 1983). Therefore, the pear tree which could assimilate calcium ions would have the ability not only to fight $F^-$ ions toxicity through trapping them in the form of a $CaF_2$ insoluble complex, but also to delay the appearance of necroses as late as possible. Such behaviour would to explain the relative thriving and fructifying of pear despite its existence in the most polluted area. Ben Abdallah, (2007) attributed the appearance of necroses to the quantity of calcium available in leaf tips and/or margins. Accordingly, damage seems to appear in the form of necroses when calcium ions are no more available.

The separation between healthy and damaged leaf areas by anthocyanins secreted as a dark waved borderline let us suggest the existence of an isolation mechanism developed by the plant in order to avoid harmful effects of fluoride on its metabolism. By limiting damages in margins and leaf tips and owing to this mechanism, the plant is able to maintain the photosynthetic integrity of its remaining leaf area. A significant proportion of the leaf assimilatory surfaces is thereby preserved, thus explaining the ability of the plant to photosynthesize while 30 to 40 % of its leaf surface is damaged **(Table 2)**. In addition, the evidence of fluoride air pollution in the study site (Mezghani et al., 2005) suggests that damaged almond leaf can be used as a bio-indicator of fluoride pollution (Festy, 2002).

### 3.3 Plant anatomical responses

In our experimental conditions, anatomical sections performed on polluted almond (**Figure 4,** B-B’) and pear leaves (**Figure 4,** D-D’) revealed in comparison with controls (Figure 4, A-C-A’-C’) a decreasing in epidermal cells size. Furthermore, cuticle is getting thicker in both lower and upper epidermis. Cutin layers thickness is thought to be a usual response of plants subjected to abiotic stress (Asish et al. 2004; Dolatabian et al. 2011). This thickening already reported by Stevens et al., (1998) working on *Avena sativa* and *Lycopersicon esculentum*, seems to be more important at the midrib, the lower epidermis of which is folded by the collapse of some of its cells. This folding being less important in the case of pear becomes however for almond more important at the end of the growing season.

By another way, some structural changes were recorded as a case in point (i) an increase in the number of fibers at the midrib in such a way they form a multilayered ring on the side of phloem. In pear, ring fibers are increasing in number (ii) a remarkable and progressive thickening of collenchyma cell walls. Furthermore, air fluoride pollution seems to induce in both species an elongation in mesophyll palisade cells, a disruption in mesophyll spongy cells being more pronounced in pear leaves and a decreasing in epidermal cells size associated with a cuticle thickening. Our results corroborate those of Zuiazek and Shay (1987) and Miller (1993) who reported that the damage to leaves occurs first in the spongy mesophyll and lower epidermis, and then a total collapse followed up by an alteration of its architecture (Zuiazek and Shay, 1987; Miller, 1993). Such morphological and structural changes demonstrate the tendency of these species to develop a survival strategy in such restrictive conditions.

Table 1. Fluoride and calcium contents in dust covering polluted and non polluted pear leaves

| | Fluoride (µg/g DW) | Calcium (mg/g DW ) |
|---|---|---|
| Dust | 435.5 ± 31.1 | 140.3 ± 12.2 |
| Non washed leaves | 270.5 ± 14.3 | 92.0 ± 8.1 |
| Washed leaves | 86.0 ± 6.0 | 73.2 ± 7.1 |
| Non polluted leaves | 15.0 ± 1.1 | 22.0 ± 1.3 |

Values are the means ± SD of 10 replicates.

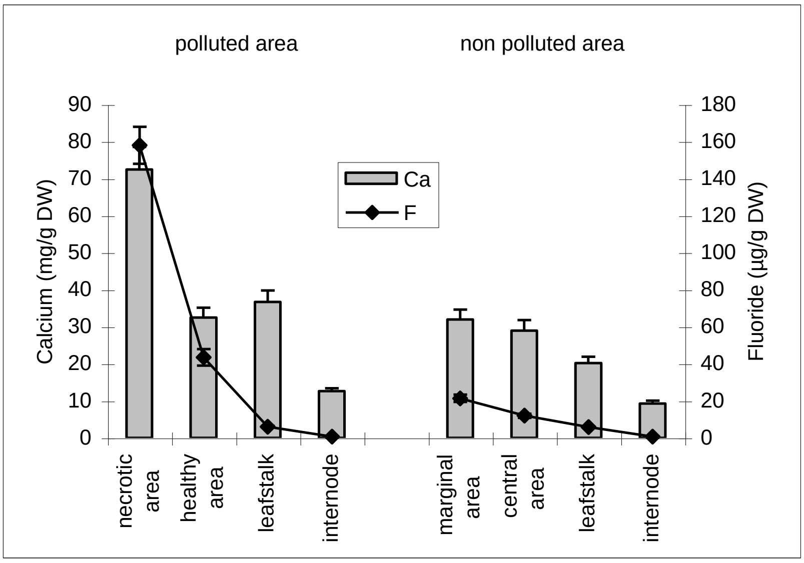

Figure 3. Distribution of calcium and fluoride contents in some organs of polluted and non polluted almond trees. Values are the means ± SD of 10 replicates.

Table 2. Net photosynthesis (μmol $CO_2$ $m^{-2}$ $s^{-1}$) of healthy leaf almond areas in function of leaf necroses percentage.

| | Leaf necroses percentage (%) | | | | |
|---|---|---|---|---|---|
| | Control | 10-20 | 30-40 | 50-60 | > 60 |
| Classes | C0 | C1 | C2 | C3 | C4 |
| Pn | 18.1 ± 1.1 | $16.9 \pm 1.2^{NS}$ | $15.16 \pm 1.34^{+++}$ | $12.24 \pm 1.17^{+++}$ | $8.0 \pm 1.0^{+++}$ |

Photosynthesis vs. controls. +++*p* ≤ 0.001, NS: non significant (*n* = 19) NS: non significant

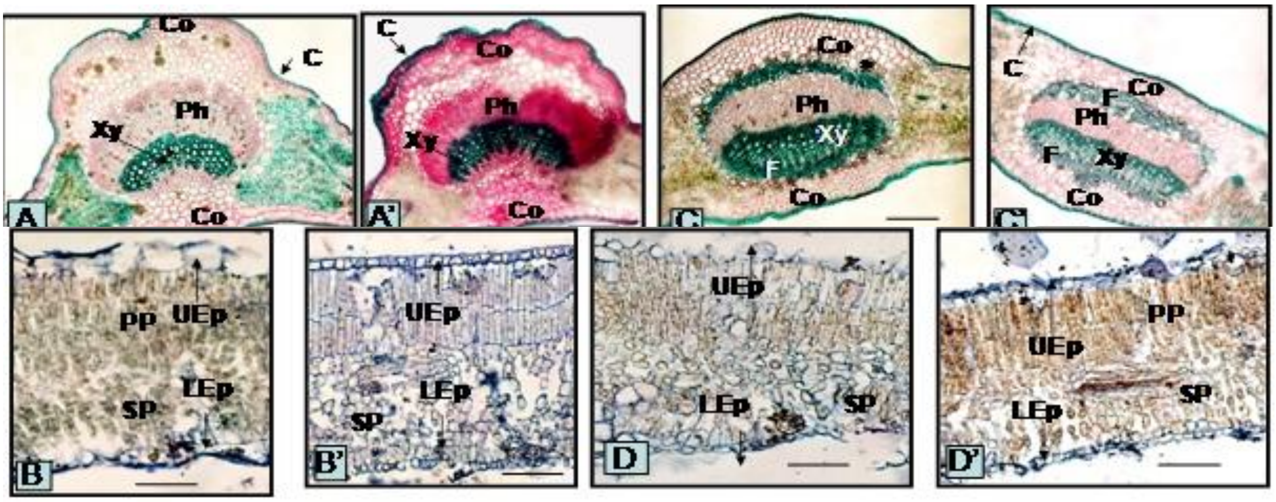

Figure 4. Transverse sections in almond and pear leaves at two leaf levels:

1) At the midrib level. (scale 1 bar= 10µm)

(A) non polluted almond leaves, ( B) polluted almond leaves, (C) non polluted pear leaves, ( D) polluted pear leave

2) At the leaf blade level. (scale 1 bar= 100µm)

(A') non polluted almond leaves, ( B') polluted almond leaves, (C') non polluted pear leaves, ( D') polluted pear leave

Abbreviations: C = cuticle; Co = collenchyma; LEp = lower epidermis; Ph = phloem; PP = palisade parenchyma; SP = spongy parenchyma; UEp = upper epidermis; Xy = xylem.

F= Fiber

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
**4th International Symposium and IUAPPA Regional Conference**
**10-13 September 2012 Istanbul -Turkey**

# EFFECTS OF AIR POLLUTION ON FLUORIDE ACCUMULATION PATTERN IN *ROSA DAMASCENA* L. CULTIVATED IN THE SOUTH OF TUNISIA

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## ABSTRACT

Fluoride damaged leaves of a rose shrub (*Rosa damascena* Mill.) growing in the vicinity of a phosphate fertiliser manufacturing plant near Sfax-Tunisia, were used to determine (i) the different steps of fluoride accumulation in this species exposed to air fluoride pollution, and (ii) so the tolerant mechanisms adopted by this species still surviving in such restrictive conditions (ii) in order to verify the possible utility of this species in environmental risk assessment. Our results showed that leaf fluoride accumulation pattern was characterized by three distinguished steps. The first one is called "an accumulation phase" during which the leaf fluoride contend tend to increase until reaching a maximum. The accumulation phase occurred in coincidence with the active vegetative growth phase of the rose shrub. The second phase is called a "comapartimentation phase of fluoride in leaf necrosis". This phase was characterized by a reduction in leaf fluoride content. This diminution was accompanied by the appearance of leaf necrosis at the marginal parts of the leaves with fluoride content at the central part of necrosis leaves similar the that of control plants. The third phase is called "a stable phase" along which the leaf fluoride content was almost similar along the time. This stability could be explained by a dynamic stability between the fluoride content in the environment air and the damaged leaves. Otherwise, despite its survival in the most polluted area, without showing growth restrictions, this plant continues to produce a rose water and oil ensuring quite large urban incomes. Our results suggest that *Rosa damascena could* be used as a bioindicator of fluoride pollution and therefore a useful tool in mapping fluoride polluted areas.

**Key words:** Air pollution, Bioindicator, Fluoride content, *Rosa damascena* L**.**

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# MEASURING THE UPTAKE RATES OF ETHYLENE BY 23 PLANT SPECIES IN TAIWAN

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## ABSTRACT

The purpose of this study is to measure and compare the uptake rates of ethylene that may be emitted from vehicle in urban areas or petrochemical industry by 23 common plant species in Taiwan. The tested species are camphor tree (*Cinnamomum camphora*), red cedar (*Bischofia javanica*), Taiwan zelkova (*Zelkova serrata* ), Chinese pistache (*Pistacia chinensis*), Honduras mahogany (*Swietenia macropnylla* ), rose wood (*Pterocarpus indicus*), flame goldrain tree (*Koelreuteria formosana* ), China berry (*Melia azedarach* ), Norfolk island pine (*Araucaria heterophylla* ), iron-wood (*Casuarina equisetifolia*), Madagascar almond (*Terminalia boivinii*), Indian almond (*Terminalia catappa* ), Cajeput tree (*Melaleuca leucadendra*), Linden hibiscus (*Hibiscus tiliaceus*), juniper Tamarisk (*Tamarix juniperina*), lemon eucalyptus (*Eucalyptus citriodora*), India laurel fig (*Ficus microcarpa* var. *microcarpa*), golden-leaf fig (*Ficus microcarpa*), Formosan nato tree (*Palaquium formosanum*), poonga-oil tree (*Pongamia pinnata*), date palm (*Phoenix hanceana* var. *formosana*), Ceylon ardisia (*Ardisia squamulosa*), and silvery Messerschmidia (*Tournefortia argentea*). A PP plastic bag branch chamber with size of 45 L was designed for measuring the ethylene uptake rates of these species. Each time a healthy shoot or branch was enclosed with the bag branch chamber and the ethylene gas was immediately introduced into the chamber and concentration changes were measured from then on by an ethylene monitor with photoionization detector (Ion Science PhoCheck 1000 ). Depletion rates and deposition velocities of ethylene by plant leaves were calculated from the net concentration change over the time, the chamber volume and the leaf areas. Results showed that ethylene is uptaken most effectively by Taiwan zelkova, Chinese pistache, red cedar, and Madagascar almond, followed by silvery Messerschmidia, iron-wood, juniper Tamarisk, and China berry. Those with lower uptake rate are poonga-oil tree, Ceylon ardisia, Indian almond, and rose wood. Generally the ethylene uptake rates were decreased when the light intensities were decreased. This indicated that most plants show higher ethylene uptake rates during daytime than those in nighttime. These results are useful for people and organizations to select the better plant species for growing in urban areas or petrochemical industry parks to mitigate the hydrocarbon air pollution.

**Key words:** ethylene; deposition velocity; ornamental trees; uptake; Taiwan

## 1. INTRODUCTION

Ethylene is emitted to the atmosphere from a variety of artificial and natural sources. Its principal sources are burning of organic materials, automobile emissions, and leaks from petrochemical complexes and polyethylene manufacturing factories (Abeles et al.,1971; Abeles and Heggested, 1973; Cheng and Sun, 2003; Kwangsam et al., 2002; Sun, 1994; Temple et al., 1998).

Ethylene, unlike other pollutants, is also a plant hormone normally made and used by the plant to control a variety of phenomena, including growth, flowering, organ initiation, tropistic response, and aging (Abeles, 1973; Abeles et al., 1992; Cheng and Sun, 2003; Mattoo and Suttle, 1991). Tonneijck, et al. (1999; 2000) had assessed the effects of atmospheric ethylene on potato (*Solanum tuberosum* L.) in the vicinity of polyethylene manufacturing plants, finding that the epinastic response of ethylene increased significantly with ethylene concentrations. Dueck, et al. (2003) also reported that potato exposed to 170 ppb ethylene in open-top chambers (OTCs) resulted in reducing flower, but atmospheric ethylene concentrations higher than 800 ppb are required to affect the yield of potato.

There was also a growing interest on ethylene as it is an important member of volatile organic compounds (VOCs), and because all of them are important precursors of photochemical air pollutants such as ozone (Derwent and Jenkin, 1991; Derwent et al., 1996; Altenstedt and Pleijjel, 2000). As ethylene accumulates close to the ground in urban areas, its capacity to produce high ozone is strongly increased (Lasry et al., 2005).

Cheng and Sun (2008) reported that in a city like Taipei, the highest ethylene concentrations were 230 ppb and most of the higher concentrations occurred during rush hour. The urban emission sources are the two-stroke motorcycles with the maximum of 8690 ppb in the exhausts. The ambient concentrations of ethylene in Taipei urban area are high and harmful for plants.

Green plants have long been proven to be able to clean the air pollutants and carbon dioxide. Plant leaves were able to uptake nitrogen dioxide, ozone and other toxic pollutants, thus they are thought as live air cleaners in urban areas (Chen and Sun, 1999; Collins et al., 1999; Cornejo et al., 1999; Hill 1971; Nowak et al., 2006; Sun, 1990; Sun and Ho, 2005; Sun et al., 2009; Thomas and Hill, 1935). It was on this purpose that Taiwan EPA initiated a series of projects to evaluate the uptake efficacies of pollutants such as formaldehyde and benzene by various plant species in various environmental and temporal conditions (Sun et al., 2009; 2010). Recently Taiwan EPA has initiated a new project to evaluate the trees around petrochemical industrial areas for their uptake efficacies of pollutants such as NOx and ethylene, and that is right the aim of this paper.

The deposition velocity concept was generally accepted for evaluating the uptake efficiency of plants and other receptors (Hanson and Lindberg, 1991; Horii et al., 2004; Sun, 1990; Sun and Ho, 2005; Sun et al., 2009; 2010). Generally there were many methods for measuring the pollutant uptake rates. For example, the continuously stirred tank reactor was used frequently to do this job (Sun, 1990). However since a lot of environmental factors could affect the uptake rates of pollutant by plants (Cornejo et al., 1999; MacLaughlin and Taylor, 1981; Meidner and Mansfield, 1968; Yoo et al., 2006), we have developed a specially designed bag branch enclosure chamber (Sun and Ho, 2005; Sun et al., 2009) that can do the measurement more naturally and quickly.

This study was so initiated by Taiwan EPA with the objective to measure the ethylene uptake rates by common plants in Taiwan. We had measured the ethylene uptake rate by a total of 23 plant species in 2010, so that the plants with higher uptake rate can be recommended to people to grow around the petrochemical industrial areas to mitigate the air pollution there.

## 2. MATERIALS AND METHODS

### 2-1. Measuring Equipments

A bag branch enclosure chamber was designed for measuring the ethylene uptake rate (Sun and Ho, 2005; Sun et al., 2009). It is made by a cylindrical plastic frame that is enclosed by a PP plastic bag with size of 45 L (Fig. 1). The diameter of the cylindrical chamber is 36 cm and the length is 42 cm to fit the size of PP bag. On the inner top of the bag chamber a mini electrical fan driven by dry battery was installed at the center to produce wind and circulate the target gas ethylene in the chamber.

Fig. 1. The bag branch enclosure chamber used for ethylene uptake rate determination.

The ethylene gas was supplied by a steel cylinder and the flow rate is adjusted by a regulator. Before a measurement was started, the plants grown in 14-cm pots were grown in a greenhouse. The healthy shoot or branch was enclosed with the bag branch enclosure chamber, and the bottom or opening of the bag was constricted and tied tightly to the stem with a plastic wire to keep the chamber in cylindrical shape and air-tied. The ethylene gas from steel cylinder was immediately introduced into the chamber from the bottom seal around the stem for about 1-2 minute to raise the ethylene concentration to the range of 1-5 ppm (v/v). Then the ethylene concentration in the chamber was continuously monitored by an ethylene detector (Ion Science PhoCheck 1000). A blank control measurement was conducted for each batch of measurement, in which the enclosure chamber was enclosed on a small tree stem without any leaves. Total leaf areas of the whole shoot or branch was measured thereafter the uptake measurement by a Licor leaf area meter (Li-3000 Portable Area Meter). The concentration change of ethylene in each plant experiment was then calculated, subtracted by blank change value, and calculated into deposition velocity by the following equation:

. $$Vd = \{[ C_2H_{4\,cp} ] - [C_2H_{4\,cb} ] \}/ [C_2H_{4\,co} ] \times S \div A \div t \qquad (1)$$

Where Vd is deposition velocity in unit of mm/sec.

$C_2H_{4\,cp}$ is ethylene concentration change when plant shoot or branch was enclosed, in unit of ppb.

$C_2H_{4\,cb}$ is blank ethylene concentration change when blank stem was enclosed, in unit of ppb.

$C_2H_{4\,co}$ is ethylene concentration at starting point, or time 0, in unit of ppb.
S is the chamber size in unit of $mm^3$.
A is the total leaf area in unit of $mm^2$.
t is the measuring time for the experiment, in unit of sec.

Fig. 2. The ethylene detector (Ion Science PhoCheck 1000) (left), and $CO_2$ monitor (right) used in this study.

## 2-2. Screening the Common Plant Species for High Ethylene Uptake

A total of 23 plant species as in Table 1 were tested for their ethylene uptake rate. Seedlings of them about 1-2 year old were grown in pots containing soil, peat moss, vermiculite, chicken manure, and No. 43 fertilizer (Taiwan Fertilizer Co.) that contains N, $P_2O_5$, and $K_2O$ in the ratio 15:15:15. They were grown in the greenhouse and exposed to 1-5 ppm of ethylene in enclosure chamber at temperatures of 25-32℃, relative humidity of 50-80 %, and normal light intensity in the greenhouse. After exposure they were kept in the greenhouse for further observation.

Table 1. Twenty-three plant species tested in this study.

| Order | Scientific name | Common name | Growing stage |
|---|---|---|---|
| | | | |
| 01 | *Cinnamomum camphora* | Camphor | Normal mature |
| 02 | *Bischofia javanica* | Red cedar | Normal mature |
| 03 | *Zelkova serrata* | Taiwan zelkova | Young-leaf stage |
| 04 | *Pistacia chinensis* | Chinese pistache | Normal mature |
| 05 | *Swietenia macropnylla* | Honduras mahogany | Normal mature |
| 06 | *Pterocarpus indicus* | Rose wood | Young-leaf stage |
| 07 | *Koelreuteria formosana* | Flame goldrain tree | Young-leaf stage |
| 08 | *Melia azedarach* | China berry | Normal mature |
| 09 | *Araucaria heterophylla* | Norfolk island pine | Normal mature |
| 10 | *Casuarina equisetifolia* | Iron-wood | Normal mature |
| 11 | *Terminalia boivinii* | Madagascar almond | Normal mature |
| 12 | *Terminalia catappa* | Indian almond | Normal mature |
| 13 | *Melaleuca leucadendra* | Cajeput tree | Young-leaf stage |
| 14 | *Hibiscus tiliaceus* | Linden hibiscus | Normal mature |
| 15 | *Tamarix juniperina* | Juniper Tamarisk | Normal mature |
| 16 | *Eucalyptus citriodora* | Lemon eucalyptus | Normal mature |
| 17 | *Ficus microcarpa* var. *microcarpa* | India laurel fig | Normal mature |
| 18 | *Ficus microcarpa* | Golden-leaf fig | Normal mature |

| | | | |
|---|---|---|---|
| 19 | *Palaquium formosanum* | Formosan nato tree | Normal mature |
| 20 | *Pongamia pinnata* | Poonga-oil tree | Normal mature |
| 21 | *Phoenix hanceana* var. *formosana* | Date palm | Normal mature |
| 22 | *Ardisia squamulosa* | Ceylon ardisia | Fruiting stage |
| 23 | *Tournefortia argentea* | Silvery Messerschmidia | Normal mature |

## 3. RESULTS AND DISCUSSION

### 3-1. Performance of the Branch Enclosure Chamber for Measuring the Ethylene Uptake

The ethylene detector (Ion Science PhoCheck 1000 ) used in this study worked pretty well and performed constantly. For each measurement it inhaled a constant volume of air and showed up the result in about 10 seconds.

When an empty PP bag chamber was enclosed and ethylene gas was introduced into the blank chamber, the concentration change was determined by continuously monitoring the ethylene concentration. Results of the blank depletion of ethylene in this PP chamber were shown in Table 2.

From data in Table 2, we found that the concentration changes of ethylene in empty bag chamber over the time of 1.5 minutes were very low and quite uniform.

Table 2. Concentration change of ethylene in empty bag enclosure chamber

| | Concentration change of $C_2H_4$ in empty bag chamber over the time of 90 seconds ( ppm ) | | | | | | | | | | Slope* (ppb/sec) | slope/ppb** ( /sec ) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time (sec) | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | | |
| Run 1 | 1.9 | 1.9 | 1.9 | 1.9 | 2 | 1.9 | 1.9 | 2 | 2 | 1.9 | 0.000667 | 0.000351 |
| Run 2 | 2.1 | 2.1 | 2.1 | 2.1 | 2.1 | 2.2 | 2.2 | 2.2 | 2.2 | 2.2 | 0.00151 | 0.000721 |
| Run 3 | 1.7 | 1.8 | 1.8 | 1.8 | 1.9 | 1.8 | 1.8 | 1.9 | 1.9 | 1.9 | 0.00176 | 0.00103 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Run 4 | 2.3 | 2.3 | 2.3 | 2.3 | 2.3 | 2.3 | 2.3 | 2.3 | 2.3 | 2.3 | 0 | 0 |
| Run 5 | 5.8 | 5.8 | 5.8 | 6 | 5.8 | 5.7 | 5.7 | 5.5 | 5.2 | 5.1 | -0.00788 | -0.00136 |
| Average | | | | | | | | | | | | 0.000148 |

* Slope = △concentration/△time ; ** slope/ppb= slope/ original concentration in ppb.

When the blank uptake measurement was finished, the same bag chamber was blown with clean air for several times. It was then used to enclose the shoot or branch for measuring the plant uptake rates of ethylene. Usually a measurement for a plant took a total of 1.5 minutes that containing nine continuous measurements of ethylene. For each species four plants were selected and conducted for uptake rate determination. Results of a typical plant species like the 2-year-old Cajeput tree were shown as Table 3. From these results we can see that the uptake rates as expressed as Vd are quite constant.

Since this method take only about 1.5 minutes for a complete course of measurement, both plant health and physical conditions can be kept at better situation. Because before and after the test period, plants were grown in natural condition without any other stresses, they were healthy and the uptake results were more constant and reliable. It means that with these advantages, this measuring system is satisfactory for the ethylene uptake measurement.

Table 3. Concentration change of ethylene and deposition velocity of 2-year-old Cajeput tree measured with bag branch enclosure method

| | Concentration change of $C_2H_4$ in empty bag chamber over the time of 90 seconds ( ppm ) | | | | | | | | | | Slope/ ppb ( /sec ) | Total leaf area ($cm^2$) | Vd* (mm/s) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time (sec) | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | | | |
| Plant 1 | 0.9 | 0.9 | 0.8 | 0.8 | 0.8 | 0.8 | 0.7 | 0.7 | 0.7 | 0.7 | -0.00269 | 576.3 | 2.74 |
| Plant 2 | 1.3 | 1.3 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 | -0.00075 | 264.7 | 2.15 |
| Plant 3 | 1.1 | 1.1 | 1.1 | 1.1 | 1.1 | 1.1 | 1.1 | 1.1 | 1 | 1 | -0.00088 | 266.3 | 2.41 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Plant 4 | 1 | 1 | 1 | 1 | 1 | 1 | 0.9 | 0.9 | 0.9 | 0.9 | -0.00145 | 394.3 | 2.38 |
| Blank | 1.9 | 1.9 | 1.9 | 1.9 | 2 | 1.9 | 1.9 | 2 | 2 | 1.9 | 0.000351 | | |
| Mean | | | | | | | | | | | | | 2.42 |

* $Vd = \{[C_2H_{4\,cp}] - [C_2H_{4\,cb}]\} / [C_2H_{4\,co}] \times S \div A \div t$

### 3-2. Screening the Common Plant Species for High Ethylene Uptake in Taiwan

A total of 23 plant species as in Table 1 were tested for their ethylene uptake rate. Seedlings of them about 1-2 year old were grown in pots in the greenhouse and exposed to 1-5 ppm of ethylene in enclosure chamber. A typical result of ethylene uptake by Cajeput tree was shown in Table 3. All the deposition velocity of ethylene by 23 common plant species measured with this method were listed in Table 4.

Table 4. Deposition velocity of ethylene on 23 common plant species measured with bag branch enclosure method

| Order | Scientific name | Common name | Vd(mm/s) |
|---|---|---|---|
| | | | |
| 01 | *Cinnamomum camphora* | Camphor | 1.92 def |
| 02 | *Bischofia javanica* | Red cedar | 10.43 b |
| 03 | *Zelkova serrata* | Taiwan zelkova | 17.95 a |
| 04 | *Pistacia chinensis* | Chinese pistache | 11.83 b |
| 05 | *Swietenia macropnylla* | Honduras mahogany | 3.37 cdef |
| 06 | *Pterocarpus indicus* | Rose wood | 1.41 ef |
| 07 | *Koelreuteria formosana* | flame goldrain tree | 3.06 cdef |
| 08 | *Melia azedarach* | China berry | 4.41 cd |
| 09 | *Araucaria heterophylla* | Norfolk island pine | 2.53 def |
| 10 | *Casuarina* | iron-wood | 5.52 c |

| | | | |
|---|---|---|---|
| | *equisetifolia* | | |
| 11 | *Terminalia boivinii* | Madagascar almond | 9.26 b |
| 12 | *Terminalia catappa* | Indian almond | 1.06 ef |
| 13 | *Melaleuca leucadendra* | Cajeput tree | 2.42 def |
| 14 | *Hibiscus tiliaceus* | Linden hibiscus | 3.73 cde |
| 15 | *Tamarix juniperina* | juniper Tamarisk | 4.44 cd |
| 16 | *Eucalyptus citriodora* | lemon eucalyptus | 1.95 def |
| 17 | *Ficus microcarpa* var. *microcarpa* | India laurel fig | 2.31 def |
| 18 | *Ficus microcarpa* | golden-leaf fig | 2.93 cdef |
| 19 | *Palaquium formosanum* | Formosan nato tree | 2.25 def |
| 20 | *Pongamia pinnata* | poonga-oil tree | 0.73 f |
| 21 | *Phoenix hanceana* var. *formosana* | date palm | 3.13 cdef |
| 22 | *Ardisia squamulosa* | Ceylon ardisia | 0.81 f |
| 23 | *Tournefortia argentea* | silvery Messerschmidia | 5.65 c |

* Vd data are mean of 4 replicates, those with the same letter were not significantly different by least significant difference test (P=0.05)

Results in Table 4 showed that ethylene is uptaken most effectively by Taiwan zelkova, Chinese pistache, red cedar, and Madagascar almond, followed by silvery Messerschmidia, iron-wood, juniper Tamarisk, and China berry. Those with lower uptake rate are poonga-oil tree, Ceylon ardisia, Indian almond, and rose wood. Generally the ethylene uptake rates were decreased when the light intensities were decreased.

All the above results indicated that most plants are useful for ethylene uptake. Thus if people grow a lot of them in urban or industrial areas, they can work as the ethylene remover as Wolverton ( 1996) reported in his book: How to Grow Fresh Air -- 50 – Houseplants that Purify Your Home or Office.  Our data, however, were more precisely to compare the uptake efficacy of common plant species found in Taiwan. We recommend that people and organizations have better to select the better plant species for growing in urban, industrial areas or even neighborhood parks to clean the air pollutants.

## 4. CONCLUSION

a. Performance of the branch enclosure chamber for measuring the ethylene uptake showed that this measuring system is satisfactory for the ethylene uptake measurement.

b. Results showed that ethylene is uptaken most effectively by Taiwan zelkova, Chinese pistache, red cedar, and Madagascar almond, followed by silvery Messerschmidia, iron-wood, juniper Tamarisk, and China berry. Those with lower uptake rate are poonga-oil tree, Ceylon ardisia, Indian almond, and rose wood.

c. All results indicated that most plants are useful for ethylene uptake. Thus if people grow a lot of them in urban or industrial areas, they can work as the ethylene remover.

d. We recommend that people and organizations have better to select the better plant species for growing in urban, industrial areas or even neighborhood parks to clean the air pollutants.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# RESPONSES OF YOUNG OLIVE TREE (*Olea europaea* L. cv. CHEMLALI) TO DIFFERENT NaF LEVELS UNDER NATURAL ENVIRONMENTAL CONDITIONS IN THE SOUTH OF TUNISIA

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## ABSTRACT

In Tunisia, as in the rest of Mediterranean countries, the olive tree cultivation has a particular interest in the agricultural activities. In arid region in the south of Tunisia (Sfax) the main extended cultivar is the Chemlali. Indeed, in addition to its great resistance to the harsh climatic conditions of the area, it displayed a great ability to well develop under increasing air pollution factors emitted from the main industrial factory. Fluroide is among the most phytotoxic air pollutant emitted from this industry. The aim of this study was to determine the effects of increasing levels of NaF supplied to the irrigation water on some physiological, biochemical and anatomical traits of young olive tree (*Olea europaea* L. cv ‘‘Chemlali’’) grown under ambient environmental conditions of arid climate in Sfax (Tunisia). Uniform two-year-old self-rooted olive trees (*O. europaea* L. cv Chemlali,) were transplanted into 10-L pots filled with sand and perlite (3:1; v/v) and irrigated for 6 months with six increasing levels of NaF ranging from 0 (control), to 20, 40, 60, 80 and 100 mM NaF. The obtained results showed that photosynthetic activity, leaf water status, transpiration, leaf area and stomatal density were markedly decreased with the increase of NaF level, but at different extent among treatments. The net photosynthesis reduction was of 28, 38 and 53%, respectively for 60, 80 and 100 mM NaF, if compared to the control. These decreases were accompanied with the increase of leaf thickness, trichomes density and diameter. To activate water uptake and accommodate the ionic imbalance, NaF-treated olive plants tend to accumulate proline and soluble sugars as well in leaves as in roots. In fact, at 100 mM NaF, for proline content, these increases were at 2.68, 2.12 times higher than the control, respectively in leaves and roots. For soluble sugars, these values were of 1.58 and 1.44 times, respectively. Face to lipid peroxidation and oxidative stress induced by NaF, a significant accumulation of malondialdheyde was recorded in leaves and roots of stressed plants. On the other hand, the positive evolution of malondialdheyde and proline content in NaF-treated plants is further evidence of direct interaction between proline accumulation and antioxidant defense system for improving olive -NaF tolerance. Overall, the olive plants irrigated for 6 months with NaF solution did not show signs of toxicity, with except for the 100 mM NaF level. Nevertheless, the different plants continue to produce olive fruits, even in low rates. Such response justified the effectiveness of the different mechanisms developed by the Chemlali olive. Furthermore, such patterns allow us to suggest the use of olive plant for phytoremediation process in polluted area particularly in area suffering the extension of desertification due to harsh climatic conditions taking into account the cultivar response under described conditions.

**Key Words:** Malondialdheyde Content; NaF; Net Photosynthesis; *Olea europaea* L.; Proline Accumulation.

## 1. INTRODUCTION

To most plants, fluoride (F) is phytotoxic through altering a series of metabolic pathways (Miller, 1993). Fluoride can be deposited into soil from several anthropogenic sources, both directly through phosphate fertilizers or indirectly through atmospheric pollution from industrial activities and burning of fossil fuels (Stevens et al., 1997; Arnesen, 1998). From the soil, F is absorbed by plant roots and then transported via xylematic flow to the transpiratory organs, mainly the leaves, where it can accumulate with adverse effects (Klumpp et al., 1996; Davison and Weinstein, 1998). The rate at which symptoms appear depends on many environmental factors, such as the type and concentration of pollutants, distance from the emission source, length of exposure, and climatic conditions. In Sfax city, agricultural soils with high fluoride contents are commonly due to long term accumulation of fluoride released from a phosphate fertilizers producing factory which represents the main source of pollution in the region where the olive tree constitutes the main cultivated crop fro several reasons.

Nowadays, face to the increase of the industrial activities, the plant development is facing to the combined effects of arid climate and air pollution. Nevertheless, in Sfax city, the main industrial region in Tunisia, it has been observed that the olive tree cv. Chemlali was able to resist and grow around the main industrial factory “The Industrial Factory of Phosphoric Acid and Fertlizers (Société Industrielle d’Acide Phosphorique et des Engrais “SIAPE”).

Actually, the olive development in arid region in Tunisia (Sfax) is faced to the combined effects of salinity (urgent use of marginal water for irrigation) and fluoride pollution resulting from emission by the main industrial unit “SIAPE”. In this report we are interested in characterizing some physiological, biochemical and anatomical responses of young olive tree irrigated with increasing levels of NaF solution and grown under ambient environmental conditions of arid climate in Tunisia.

## 2. MATERIAL AND METHODS

### 2.1. Plant material, treatments and experimental conditions

Trials were conducted at the Olive Tree Institute of Sfax, Tunisia (34° 43N; 10° 41E). Uniform two-year-old self-rooted olive trees (*O. europaea* L. cv Chemlali,) were transplanted into 10-L pots filled with sand and perlite (3:1; v/v) and subjected to the irrigation for 6 months with increasing levels of NaF ranging from 0 (control), to 20, 40, 60, 80 and 100 mM NaF. The pots were kept under ambient environmental conditions with natural sunlight and temperature and they were covered with plastic film and aluminum foil to reduce evaporation from the soil surface and to minimize temperature increases inside the containers. At the start of each month during the experimental period, all the plants were weighed early in the morning and in the evening. The weight difference allowed a calculation of the amount of water lost by transpiration. When plants developed shoots of 15-20 cm length, treatments were initiated. Each treatment consisted of nine plants divided into three blocks of 3 plants each. The amount of water used for irrigation daily during the experimental period was equal to that lost by transpiration. It was of 520, 460, 360, 420, 540, and 620 ml, respectively in November, December, January, February, March and April of 2009/ 2010 crop season.

### 2.2. Leaf water relations, shoot growth and gas exchange measurements

At the end of the experiment, measurements of leaf relative water content (RWC) were determined using the equation:

$$RWC (\%) = (Fw – Dw) / (Tw – Dw) \times 100;$$

Where, $F_W$ is the fresh weight, $D_W$ the dry weight and $T_W$ the turgid weight of leaf samples. Leaves were excised before dawn, weighed fresh ($F_W$) and placed in distilled water in the dark for 24 h. The following morning, leaf turgid weight ($T_W$) was measured and then leaves were dried at 80 °C for 48 h and dry weight ($D_W$) was determined.

At the beginning of the experiment, 2 shoots per plant × 3 plants per treatment per cultivar were selected. The initial length of each shoot was measured. The shoot elongation rate (SE) was determined two times per month as the difference between final and initial measurement for each time. The results represent the average shoot length along the experimental period. Using a portable gas exchange system (Li-CorInc. 6200), gas exchange measurements were taken from 10:00 to 11:00 am on well-exposed and fully expanded leaves from the median part of the shoot from 3 plants per treatment.

### 2.3. Proline, soluble sugars and malondialdheyde contents

The proline and soluble sugars contents were determined as described by Ben Ahmed et al. (2009). The level of lipid peroxidation, expressed as MDA content, was determined as described by Zhang (1992).

### 2.4. Total chlorophyll concentrations

At the end of the experiment, leaf discs from each treatment were taken from three fully expanded leaves per treatment. Leaf sections were ground in 80% acetone. Total chlorophyll Chl (a + b) concentrations were determined according to the method of Arnon (1949).

### 2.5. Leaf area and thickness and anatomical traits

Leaf area ($Cm^2$) and thickness (mm) were measured with an area-meter LI-3100 (Li-Cor, Lincoln, NE) coupled to a computer. The determination of stomatal and trichomes density, stomatal length and trichome diameter were determined as described by (Jones, 1998). The counting and observations were made with electronic microscope coupled to a computer.

### 2.6. Data analysis

Statistical analyses were performed using SPSS Release 10 for Windows. Significant differences between values of all parameters were determined at $p \leq 0.05$ according to Duncan's Multiple Range Tests. At least three replicates were made for each field and laboratory measurements.

## 3. RESULTS AND DISCUSSION

### 3.1. Leaf water status, gas exchanges, photosynthetic pigments contents and plant growth

Results displaying the leaf water status under the different soil NaF levels showed that relative water content (RWC) decreased with the increment of the NaF level, but at different extent among the different treatments (**Table 1**). In comparison to control plants, this decline was significant from 60 to 100 mM NaF. The highest decline was recorded in the case of 80 and 100 mM NaF. If compared to control treatment, the relative reduction of RWC was of 14 and 16%, respectively in 80 and 100 mM NaF, and differences between these latter were not significant. Similarly to RWC values, for the photosynthesis, the decrease was significant for NaF level varying from 60 to 100 mM, too. The relative reduction was of 28, 38 and 53%, respectively for 60, 80 and 100 mM NaF, if compared to the control. For stomatal conductance, the irrigation with 20 mM soil NaF was so effective to induce significant decline. In comparison to control treatment, this decline was of 8, 23, 42, 59 and 63 %, respectively for 20, 40, 60, 80 and 100 mM NaF. For transpiration rates, the registered values were low and differences with the control were significant from 40 to 100 mM NaF (**Table 1**).

The decline of shoot elongation rates was significant from 60 to 100 mM NaF. For 80 and 100 mM, among which SE differences was not significant, the decrease rate was of 35 and 39 %, if compared to control plants. Overall, plants with the highest decline in RWC (100 mM NaF) also suffered the largest loss in net $CO_2$ assimilation and shoot elongation.

Table 1. Leaf relative water content, net photosynthetic, stomatal conductance, transpiration rates, shoot elongation rate and chlorophyll a and b contents in olive tree cv. Chemllai grown under different NaF levels

| NaF (mM) | RWC (%) | Pn (µmol $m^{-2}$ $S^{-1}$) | Gs ( µmol $m^{-2}$ $S^{-1}$) | E (m µmol $m^{-2}$ $S^{-1}$) | SE (Cm) | Chl a (mg/g Fw) | Chl b (mg/g Fw) |
|---|---|---|---|---|---|---|---|
| 0 | 86.30±1.26$^{a}$ | 13.40±1.28$^{a}$ | 79.16±4.30$^{a}$ | 2.84±0.27$^{a}$ | 8.50±0.67$^{a}$ | 0,45±0,03$^{a}$ | 0,23±0,01$^{a}$ |
| 20 | 84.90±1.03$^{a}$ | 12.59±0.76$^{a}$ | 73.28±4.98$^{b}$ | 2.22±0.25$^{ab}$ | 8.53±0.94$^{a}$ | 0,43±0,03$^{a}$ | 0,22±0,01$^{a}$ |
| 40 | 82.17±1.14$^{ab}$ | 11.32±1.02$^{a}$ | 61.32±3.82$^{b}$ | 1.94±0.22$^{bc}$ | 8.10±0.82$^{a}$ | 0,38±0,02$^{b}$ | 0,19±0,01$^{ab}$ |
| 60 | 79.00±1.01$^{bc}$ | 9.67±0.61 $^{b}$ | 46.39±3.27$^{c}$ | 1.49±0.16$^{c}$ | 6.79±0.67$^{b}$ | 0,33±0,02$^{bc}$ | 0,17±0,02$^{ab}$ |
| 80 | 74.83±1.75$^{c}$ | 8.34±0.6 $^{bc}$ | 33.16±2.74$^{cd}$ | 1.30±0.13$^{c}$ | 5.60±0.79$^{c}$ | 0,31±0,02$^{bc}$ | 0,17±0,02$^{ab}$ |
| 100 | 71.33±2.30$^{c}$ | 6.37±1.10 $^{c}$ | 29.78±1.69$^{d}$ | 1.34±0.18$^{c}$ | 5.22±1.11$^{c}$ | 0,26±0,01$^{c}$ | 0,14±0,03$^{b}$ |

Values are means of at least three measurement (n = 3) ± SE. Different letters within each column (a-c) indicate significant differences ($p \leq 0.05$) between treatments.

The irrigation with water containing NaF induced the decrease of leaf chlorophyll a and b content. Nevertheless, this decrease was slow particularly in the case of the chl b for which the effect of NaF stress was significant only at the highest level (100 mM). Regardless of the treatments, the Chl a content was at almost two times higher than the Chl b.

The decrease of RWC under stressed conditions indicated a loss of turgor that resulted in limited water availability for cell expansion process. This decrease could result from the high sodium and fluoride concentration of the external solution, which caused osmotic stress and dehydration at the cellular level (Fornasiero, 2001). Nevertheless, it seems that the olive tree, as soon as it perceived water deficit resulting from sodium fluoride stress, it adjusted rapidly its stomatal movement to avoid water loss and to maintain hydration. Previous papers have correlated the decrease of net photosynthesis in stressed plants subjected to air pollution mainly to lower stomatal conductance and to toxic ions accumulation in the different plant tissues (Muppala and Meenakshi, 2008). Our data confirmed this hypothesis, whereas non stomatal limitations on photosynthetic activity might have occurred in leaves of NaF - treated plants. For instance, the lowered leaf chlorophyll content might have contributed to the decrease of net photosynthesis. Nevertheless, faced with such damage, the Chemlali olive plants tend to limit their water loss and to maintain its activity in such a way to preserve their growth and development, even in low rates if compared to control plants. According to Murphy and Hoover (1992), the decrease in photosynthetic activities under fluoride treatment could be due to the binding of fluoride with $Mg^{2+}$, limiting per consequent the availability of this element essential for enzymes activity and /or fluoride induced inactivation of $Mg^{2+}$ at sites of physiological activity.

On the other hand, the reduction in photosynthetic performances of the stressed Chemlali olive tree could be considered as a dehydration avoidance mechanism, and constitutes an adaptive mechanism of olive plants rather than a merely negative consequence of the fluoride stress. The effectiveness of such mechanism is revealed via the reasonably high values of RWC (> 70%) recorded in fluoride - stressed olive plants. Furthermore, toxicity symptoms (apical and marginal leaf necrosis) were recorded only at high NaF level; and the central part of leaves has maintained its integrity. The negative effects of fluoride stress on plant water status has been also shown in *Populus tremuloides* (Kamaluddin and Zwiazek, 2003),

The preservation of suitable leaf water status and plant growth under high soil NaF concentration could be also attributed to the development of young leaves more hydrated and photosynthetically active. In fact the differential pattern of water status and photosynthetic activity between young and old leaves (data not shown) of NaF - treated plants may result from higher RWC in young tissues and high toxic ion accumulation in the old ones, actions that seem to play a protective role for the young ones against toxic ion damage as reported previously under different abiotic stress circumstances (Ben Ahmed et al., 2008, 2009). Overall, the maintenance of photosynthetic activity in plants treated with high NaF concentrations (80 and 100 mM) and the absence of toxicity symptoms from 20 to 80 mM NaF revealed the effectiveness of the different mechanisms developed by the Chemlali olive tree to resist under described experimental conditions. These strategies were justified by the continuous olive fruit development, albeit at low rates, even in high NaF - treated plants.

### 3.2. Morphological and anatomical characteristics

The results describing some morphological and anatomical characteristics (such as leaf area and thickness, trichomes and stomatal densities) showed that leaf area, stomatal density and stomata length decreased with the increase of NaF level (**Table 2**). Furthermore, this decrease was significant for 60 and 100 mM NaF for the leaf area and for only the highest NaF level in the case of stomatal density. For stomata length, this decrease was not significant as well under low as under high NaF level. In contrast, the leaf thickness, trichomes density and diameter increased with that of the stress. What’s more, for these parameters, this increase was significant for both 60 and 100 mM NaF.

**Table 2.** Leaf area and thickness, trichomes density and diameter and stomatal density and length of olive tree cv. Chemlali under different soil NaF levels.

| NaF (mM) / Parameters | 0 | 20 | 60 | 100 |
|---|---|---|---|---|
| Leaf area (LA) ($mm^2$ ) | 685.2 ± 63 $^a$ | 682.4 ± 60 $^a$ | 582.6 ± 62 $^b$ | 504 ± 45 $^c$ |
| Leaf thickness (mm) | 544 ± 53 $^a$ | 568 ± 44 $^a$ | 642 ± 40 $^b$ | 700 ± 44 $^b$ |
| Trichomes density (trichomes/$mm^2$) | 84 ± 10 $^a$ | 87.2 ± 7 $^a$ | 102.6 ± 10 $^b$ | 129.8 ± 5 $^c$ |

| | | | | |
|---|---|---|---|---|
| Trichomes diameter (µm) | 152.8 ± 9.4 $^{a}$ | 158.2 ± 8.7 $^{a}$ | 173.4 ± 7.6 $^{b}$ | 195.6±8.4 $^{c}$ |
| Stomatal density (stomata/mm$^{2}$) | 473.8 ± 25 $^{a}$ | 471± 28 $^{a}$ | 426.2± 20 $^{b}$ | 363.2± 26 $^{c}$ |
| Stomata length (µm) | 19 ± 1.5 $^{a}$ | 19 ± 1.2 $^{a}$ | 18.1± 1.1 $^{a}$ | 17.3±1.5 $^{a}$ |

Values are means of at least three measurement (n = 3) ± SE. Different letters between values within each line (a-c) indicate significant differences ($p \leq 0.05$) between treatments.

In order to better limit water loss, the studied Chemlali olive tree developed several morphological and anatomical mechanisms. Indeed, in addition to the limitation of transpiration and stomatal aperture / closure control, the increase of leaf thickness and trichomes density in parallel with the decrease of stomatal density would to play a great role in avoiding water loss. The increase of trichomes density was accompanied with that of their diameter in such a way to limit the leaf surface exchange with the environment via stomata aperture as suggested by previous reports (Chaves et al., 2002).

On the other hand, the reduction of stomatal density and the increase in leaf thickness and trichomes density would to limit the $H_2O$ and $CO_2$ diffusion and per consequent the photosynthetic activity. It is clear that the different parameters are correlated and retrocontrolled. Similar results were registered in adult olive tree cv. Chemlali under water deficit (Ben Rouina, 2007) and salt stress (Ben Ahmed et al., 2012) and in melon plants (Kaya et al., 2007). However, in Mastoidis and Koroneiki olive cultivars grown under water deficit, Bosabalidis and Kofidis (2002) recorded an increase in stomatal density and the decrease of ostiole diameter.

On the other hand, the reduction of leaf expansion could be due to the competition between these tissues and other developing organs for the allocation of photosynthetic assimilates as suggested by Maroco et al., (2000). Such mechanism could explain the preservation of fruit development even at high NaF level (data not shown).

### 3.3. Proline, soluble sugars and malondialdheyde contents

Under the described experimental conditions, the proline content increased significantly from 40 mM NaF in both leaf and root tissues (**Table 3**). The higher the NaF stress was, the more important the proline accumulation was. In control plants, these values were almost similar for both tissues.

As well in the case of proline, in comparison to control plants, the increment in soluble sugars content in NaF-treated plants was significant from 40 mM NaF with higher amounts in roots than in leaves. At 40 mM NaF, the increase of proline content was at 1.41, 1.37 times higher than the control respectively, in leaves and roots. For the soluble sugars this increase was at 1.14 and 1.13 times, respectively. At 100 mM NaF, for proline content, these increases were at 2.68, 2.12 times, respectively in leaves and roots. For soluble sugars, these values were of 1.58 and 1.44 times, respectively.

**Table 3.** Proline and soluble sugars contents in leaves and roots of olive tree cv. Chemlali grown under different soil NaF levels.

| NaF (mM) | Proline (µmol / g Fw) | | Soluble sugars (mg / g Fw) | |
|---|---|---|---|---|
| | Leaves | Roots | Leaves | Roots |
| 0 | 0,25±0,01 $^{a}$ | 0,24±0,02 $^{a}$ | 4,31±0,35 $^{a}$ | 4,49±0,39 $^{a}$ |
| 20 | 0,29±0,01 $^{a}$ | 0,28±0,02 $^{ab}$ | 4,57±0,42 $^{a}$ | 4,82±0,42 $^{ab}$ |

| | | | | |
|---|---|---|---|---|
| 40 | 0,35±0,02 $^{b}$ | 0,33±0,01 $^{bc}$ | 4,94±0,46 $^{b}$ | 5,11±0,49 $^{b}$ |
| 60 | 0,42±0,03 $^{c}$ | 0,37±0,02 $^{c}$ | 5,52±0,51 $^{c}$ | 5,64±0,52 $^{c}$ |
| 80 | 0,59±0,02 $^{d}$ | 0,44±0,02 $^{d}$ | 6,11±0,56 $^{d}$ | 6,18±0,55 $^{d}$ |
| 100 | 0,67±0,02 $^{d}$ | 0,51±0,03 $^{e}$ | 6,82±0,55 $^{e}$ | 6,48±0,59 $^{d}$ |

Values are means of at least three measurement (n = 3) ± SE. Different letters between values within each column (a-e) indicate significant differences ($p \leq 0.05$) between treatments.

The highest accumulation of proline and sugars observed in plants with low photosynthetic performances justifies the important role of these osmoticums in photosynthesis upholding via the accommodation of ionic imbalance in the vacuole and activation of water uptake to growing tissues as reported by Ashraf and Foolad (2007). The same authors have correlated the accumulation of proline under stresses in many plants with stress tolerance. The capacity for osmotic adjustment via net solute accumulation under stressed conditions in olive tree has been also recorded in the case of water and salt stresses (Sofo et al., 2005; Ben Ahmed et al., 2009). Similar results in response to fluoride stress have been reported by Li and Ni (2009).

The distribution of malondialdheyde content (MDA) showed a clear increase in both leaves and roots of the different treatments, in comparison to control one (**Fig. 1**). For both olive tissues, this increase was significant for NaF concentration varying from 40 to 100 mM NaF and differences between them were not significant for all NaF levels.

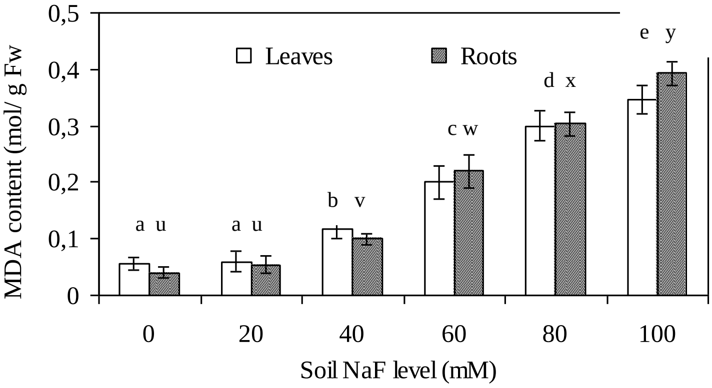

Figure 1. Malondialdheyde content in leaves and roots of olive tree grown under different soil NaF levels. Different letters (a - e) indicate significant differences ($p \leq 0.05$) between treatments in the case of leaves and different letters (u - y) indicate significant differences between treatments in the case of roots. Values represent means of three replicates ± SE.

The accumulation of MDA in stressed plants has been considered as an indicator of lipid peroxidation resulting from oxidative stress caused by toxic ions effects and water deficit (Skórzyńska-Polit and Krupa 2006). Indeed, olive plants irrigated with water containing NaF seems to be subjected to the combined effects of both $Na^+$ and $F^-$. Similar results were observed in *Bruguiera gymnorrhiza* exposed to a variety of metals (Zhang et al., 2007). According to Aziz and Larher (1998), at low NaF level (20-40 mM), the protective mechanisms developed by the Chemlali olive against lipid peroxidation seem to be effective in such a way to avoid significant accumulation of MDA as well in leaves as in roots.

## CONCLUSION

The tolerance of Chemlali olive under described circumstances and its ability to produce fruits and preserve its growth, even in low rates, at high NaF level resulted from the interaction between the different morphological, anatomical and physiological mechanisms leading to the activation of water uptake. On the other hand, the positive evolution of malondialdheyde and proline content in NaF-treated plants is further evidence of direct interaction between proline accumulation and lipid peroxidation for improving olive tolerance. To confirm better this hypothesis, further experiments focusing on effects of exogenous application of proline on antioxidative defense system of Chemlali olive tree irrigated with different NaF levels are on the way. Further, these results confirm the hypothesis of use of the Chemlali olive tree for soil phytoremediation in polluted area in the south of Tunisia.

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# INVESTIGATION OF INDOOR AIR QUALITY IN CHILDREN HOMES AT PRENATAL AND POSTNATAL PERIOD

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## ABSTRACT

Volatile Organic Compounds (VOCs) are a large group of carbon-based chemicals that easily evaporate at room temperature. Some examples of sources of VOCs are building materials, home and personal care products and behaviors. Indoor air VOCs were collected simultaneously from variety of indoors (e.g. living rooms, baby's rooms) and outdoor environments which were voluntarily selected throughout Ankara. Studies have shown that the level of indoors VOCs is generally higher than the level of outdoors. This is the first comprehensive study done in Turkey including prenatal and postnatal periods. VOCs levels were measured over 94 homes. Total VOC in the living rooms and baby's rooms varied between 71.92 to 84.85µg/$m^3$ in summer and 117.38 to 128.19 µg/$m^3$ in the winter. According to the sampled indoor environments of the study, it was found that the levels of indoor air volatile organic compounds in the baby's rooms were higher than the living rooms.

**Key words:** Indoor air quality, volatile organic compounds, baby's rooms

## 1. INTRODUCTION

There is an increase in the number of evidences indicating increase rate of health problems associated with environmental pollution. Volatile Organic Compounds (VOCs) are a large group of carbon-based chemicals that easily evaporate at room temperature. They have been associated with a number of health problems that include cancer ( Hellén et al., 2002; Ohura et al., 2006) and the induction of acute and chronic health pathologies (Park and Jo, 2004).

Indoor air pollution caused by volatile organic compounds (VOCs) is attracting international interest as many indoor materials and utilities contain VOCs (Godish, 2001). There are hundreds of VOCs in the air, which increases the complexion of indoor air pollution. (VOCs) emitted from various sources such as building materials (Haghighat et al., 2002; Lee et al., 2005; Claeson et al., 2007; Nicolle et al., 2008; Han et al., 2010; Jia et al., 2010), household materials (Kwon et al. 2008), and combusted materials (Liu et al., 2003; Ye, 2008; Fromme et al., 2009; Kabir & Kim, 2011). VOCs are widely used in many household products and are emitted by paints (Afshari et al., 2003; Wieslander & Norbäck, 2010; Chang et al., 2011), adhesives (Wilke et al., 2004), waxes, solvents, detergents, woods (Jensen et al., 2001; Kirkeskov et al., 2009), and items containing them, including carpets (Katsoyiannis et al., 2008), vinyl flooring (Cox et al., 2001 and 2002), air-conditioners (Tham et al., 2004), newspapers (Caselli et al. 2009), printers and photocopiers (Lee et al., 2006).

Previous studies show that indoor air is contaminated to various degrees by a wide variety of hydrocarbons and hydrocarbon derivatives including paraffin, olefin, aromatics, carbonyls, polycyclic aromatics, and chlorinated hydrocarbons (Guo et al., 2003; Kim et al., 2001; Lai et al., 2004; Lee et al., 2002a; Park and Ikeda, 2004, 2006; Sawant et al., 2004).

Reported indoor concentration of individual VOCs are generally below 50 mg/m$^3$ , with most below 5 mg/m$^3$ (Wolkoff et al., 2006). Combined indoor/outdoor air quality measurements have shown that there exist significant VOC sources indoors.

Several researches have demonstrated that babies and children are more sensitive to environmental pollution than adults. Babies spend about 95% of their time in indoor environment. The time spend in indoor might be more during winter times. The health effects of indoor air pollutants are not fully understood, but indoor air quality has been linked with a wide array of health outcomes including deficits in lung function, chronic respiratory disease, lung cancer, heart disease, developmental disorders, and damage to the brain, nervous system, liver, or kidneys (Grandjean et al., 2006; Wang et al., 2007).

## 2. MATERIAL AND METHOD

### 2.1. Study site and sampling strategy

The study undertook on the homes of 94 voluntary pregnant women. The sampling was conducted in summer and winter, during two periods from May 2011 and from November 2011. Indoor and outdoor levels of volatile organic compounds (VOC) were determined. The measurements are done in two periods, during the third three-master of pregnancy, and when the babies are 0-4 months old in different areas of Ankara. The air sampling tubes was placed in living and baby`s rooms in the 50cm above the floor on a horizontal surface. Also, temperature and relative humidity were measured both indoors and outdoors.

### 2.2. Sampling

The air sampling tubes was placed in the middle of the sampled rooms in the 50cm above the floor on a horizontal surface. Previously to sampling or calibration, all sampling tubes were conditioned at 280 °C by forcing pure nitrogen gas through the tubes at a flow rate of 75 mL min$^{-1}$ for 5h and then analyzed to certify that no target pollutants were present.

Samples of VOCs were collected by drawing air through a stainless steel tube containing 500 mg of Tenax TA using a personal air sampling pump (SKC Pump) at a flow rate of 80-85 mL min$^{-1}$ for a period of 45 min.

### 2.3. Chemıcal analysis

7 VOCs were selected for chemical analysis in this study. The description of sampling and species analysis methods is shown in Table 1.

Table1. Sampling and species analysis

| sampler | Active Tenax tube |
|---|---|
| Target compounds (7 compounds) | Benzene, Toluene, m,p,o-Xylene, Ethyl benzene, Naphthalene |
| Sampling method | Active sampling for 45min |
| Desorption method | Thermal desorption (Tenax disulfide) |
| Analytical method (TD-GC/MS) | Thermal Desorber-Gas chromatography/Mass Spectroscopy<br>Column: DB-1 (Agilent J&W Columns, part number 123-1063)<br>ID: 0,32mm, length:60m, film 1µm |

Air samples were collected in Tenax TA sorbent filled tubes with active sampling method and analyzed with Thermal Desorber(Tekmar Dohrmann AERO Trap6000)-Gas chromatography (Agilent 6890N)/Mass Spectroscopy (Agilent 5975C)Detector (TD-GC/MS). The sum of the concentration of the 7 target VOCs was defined as TVOC.

### 2.4. Data analysis

All statistical analyses, including correlation, one-way ANOVA and multiple sample comparison, were performed using the Stat graphics centurion statistical software package and Microsoft excel.

## 3. RESULTS AND DISCUSSION

### 3.1. Indoor concentrations

Monitoring for indoor air quality was conducted in the rooms in which the infant spends the most time for 94 homes in Ankara. Tables 2 and 3 summarize the mean, median and TVOs levels in each home in the summer and winter seasons.

Table2. Summarizes the Mean, Median and TVOCs[1] in summer (Prenatal Period)

| Area | Living + Baby`s Room[2] | | Baby`s Room | | Living Room | |
|---|---|---|---|---|---|---|
| sample | n=18 | | n=73 | | n=73 | |
| | Mean | Median | Mean | Median | Mean | Median |
| benzene | 1.15 | 0.75 | 1.04 | 0.59 | 1.02 | 0.63 |
| toluene | 31.05 | 17.36 | 41.48 | 20.45 | 33.77 | 14.37 |
| ethy benzene | 2.76 | 1.95 | 3.33 | 2.75 | 4.14 | 2.11 |
| m,p-xylene | 7.48 | 5.72 | 7.69 | 5.83 | 6.68 | 4.73 |
| o-xylene | 5.87 | 2.88 | 6.21 | 5.55 | 6.11 | 4.03 |
| Naphthalene | 24.51 | 6.40 | 25.14 | 12.90 | 20.73 | 10.62 |
| TVOCs | 72.81 | 39.14 | 84.85 | 57.65 | 71.92 | 48.72 |

1. Total Volatile Organic Compounds
2. living room and baby`s room is the same

Mean of toluene (41.48µg/m$^3$) and naphthalene (25.14 µg/m$^3$) in the baby`s rooms were highest. Warmer temperatures during the summer time will obviously increase the evaporation of VOCs from vehicle fuel tanks. Also, the decay or removal of VOCs through photochemical reactions will be more significant during the summer than during the winter (Sillman, 1999).

Table3. Summarizes the Mean, Median, TVOs in winter (postnatal Period)

| Area | Living + Baby`s Room[1] | | Baby`s Room | | Living Room | |
|---|---|---|---|---|---|---|
| sample | n=25 | | n=69 | | n=69 | |
| Winter | Mean | Median | Mean | Median | Mean | Median |
| benzene | 3.41 | 0.68 | 3.69 | 0.63 | 2.51 | 0.38 |
| toluene | 37.90 | 14.05 | 44.26 | 12.99 | 30.88 | 14.42 |
| ethy benzene | 7.57 | 5.03 | 7.46 | 5.24 | 7.46 | 5.24 |
| m,p-xylene | 15.78 | 13.82 | 16.59 | 11.00 | 16.59 | 11.63 |
| o-xylene | 10.28 | 9.98 | 11.66 | 7.85 | 11.19 | 8.16 |
| Naphthalene | 49.55 | 19.60 | 44.53 | 13.09 | 49.20 | 14.89 |
| TVOCs | 124.49 | 76.06 | 128.19 | 68.47 | 117.38 | 69.52 |

1. living room and baby`s room is the same

As it was at winter season, no mechanical ventilation systems were turned on. Mean of benzene (3.69 µg/m$^3$) and toluene (44.26 µg/m$^3$) in the baby`s rooms were highest and naphthalene in the living and baby`s room is the same was 49.55 µg/m$^3$. No national ambient air quality standards have been established for VOCs in these places, although benzene is a known human carcinogen that can induce leukemia (WHO, 2000), and toluene, ethyl benzene and xylenes may cause brain dysfunction and are suspected carcinogens ( Molhave, 1991; Tang et al., 2002; Jacquot et al., 2006). Table 4 provides air quality guidelines developed by AirAdvice using information from the U.S. EPA; the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE); World Health Organization (WHO); Leadership in Environmental and Ecological Design (LEED); Indoor Air Quality Association; California Air Resources Board; Health Canada; European Union; U.K. Department of Health; state governments; and scientific experts (AirAdivce.,2010 a ; AirAdvice.,2010 b ; Pickett et al.,2011).

Table4. Indoor air quality guidelines

| TVOCs | Indoor Air Quality Rating |
|---|---|
| ≤500 µg/m3, daily average | Acceptable |
| 501–3000 µg/m3, daily average | Action recommended for sensitive groups[1]<br>Action recommended |
| >3000 µg/m3, daily average | Action necessary |

[1] Sensitive groups are defined as: “the elderly; children under the age of 18; asthma and allergy sufferers; pregnant women and their unborn children; immuno-compromised individuals; and those with cardiovascular, respiratory, and other chronic disease conditions” (AirAdivce.,2010 a ; AirAdvice.,2010 b ; Pickett et al.,2011).

### 3.2. Seasonal variations

In order to investigate the seasonal evolution of indoor air quality and summary statistics for the indoor in winter and summer mean concentrations and standard deviation were calculated as shown in Table 5 and 6. Since the P-value of the F-test is less than 0.05, there is a statistically significant difference between the means of the 2 variables at the 95.0% confidence level.

Table5. Comparison of indoor VOC concentrations in homes with baby`s room in various seasons

| Sample | Baby`s Room(summer) | | Baby`s Room(winter) | |
|---|---|---|---|---|
| | Sample | Mean | Sample | Mean |
| benzene | 73 | 1.04* ± 1.24 | 69 | 3.69* ± 7.62 |
| toluene | 73 | 41.48 ± 51.93 | 69 | 44.26 ± 65.84 |
| ethy benzene | 73 | 3.33* ± 3.08 | 69 | 7.46* ± 9.77 |
| m,p-xylene | 73 | 7.69* ± 8.64 | 69 | 16.59* ± 21.79 |
| o-xylene | 73 | 6.21* ± 5.13 | 69 | 11.66* ± 16.25 |
| Naphthalene | 73 | 25.14 ± 33.72 | 69 | 44.53 ± 91.96 |
| TVOCs | 73 | 84.85 | 69 | 128.19 |

*Statistically significant differences ($p < 0.05$) between winter and summer

Amount of BTEX and naphthalene in the baby`s rooms in winter higher than summer. TVOCs in winter were 128.19µg/m$^3$.

Table6. Comparison of indoor VOC concentrations in homes without baby`s room in various seasons

| Sample | Living + Baby`s Room[1] (summer) | | Living + Baby`s Room[1] (winter) | |
|---|---|---|---|---|
| | Sample | Mean | Sample | Mean |
| benzene | 18 | 1.15 ± 1.00 | 25 | 3.41± 6.52 |
| toluene | 18 | 31.05 ± 37.66 | 25 | 37.90 ± 78.98 |
| ethy benzene | 18 | 2.76* ± 2.26 | 25 | 7.57* ± 7.82 |
| m,p-xylene | 18 | 7.48 ± 5.80 | 25 | 15.78 ± 15.83 |
| o-xylene | 18 | 5.87 ± 9.21 | 25 | 10.28 ± 9.00 |
| Naphthalene | 18 | 24.51 ± 52.01 | 25 | 49.55 ± 78.43 |
| TVOCs | 18 | 72.81 | 25 | 124.49 |

1. living room and baby`s room is the same.
*Statistically significant differences ($p < 0.05$) between winter and summer.

All the VOCs in the living and baby`s room was the same in summer were lower than winter. Naphthalene in winter was 2 times higher than naphthalene in summer.

Correlations between indoor VOCs concentrations in summer and winter are shown in Table 7and 8. P-values below 0.05 indicate statistically significant non-zero correlations at the 95.0% confidence level.

Table7. Correlation between indoor in summer

| | Benzene | Toluene | Eth B | m,p Xylene | o- Xylene | Naphthalene |
|---|---|---|---|---|---|---|
| Benzene | | ** | ** | ** | ** | ** |
| Toluene | ** | | ** | ** | ** | |
| Eth B | ** | ** | | ** | ** | ** |
| m,p -Xylene | ** | ** | ** | | ** | ** |
| o- Xylene | ** | ** | ** | ** | | ** |
| Naphthalene | ** | | ** | ** | ** | |

** P-values < 0.05 indicate statistically significant non-zero correlations.

Table8. Correlation between indoor in winter

| | Benzene | Toluene | Eth B | m,p Xylene | o- Xylene | Naphthalene |
|---|---|---|---|---|---|---|
| Benzene | | ** | | | | ** |
| Toluene | ** | | ** | ** | ** | |
| Eth B | | ** | | ** | ** | |
| m,p -Xylene | | ** | ** | | ** | |
| o- Xylene | | ** | ** | ** | | |
| Naphthalene | ** | | | | | |

** P-values < 0.05 indicate statistically significant non-zero correlations.

## 4. CONCLUSION

Concentration of toluene and naphthalene were higher than other VOCs. Household painting and paint, varnish and lacquer removal, tobacco smoke, and consumer products such as adhesives, floor polish, inks, coatings and solvent-thinned products may contain toluene.

In indoor air, emissions from cooking, tobacco smoking, or moth repellants are expected to be the predominant sources of naphthalene. Available data are inadequate to establish a causal association between exposure to naphthalene and cancer in humans. Adequately scaled epidemiologic studies designed to examine a possible association between naphthalene exposure and cancer was not located.

Increased levels of VOCs are generally expected during the winter ( Ilgen et al., 2001b; Schlink et al., 2004) when lower temperatures determine an enhanced heating and low indoor ventilation rates. Also, their concentrations can be affected by the chemical reactivity and the meteorological changes. Amount of BTEX and naphthalene in the baby`s rooms in winter higher than summer.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# INDOOR AIR QUALITY AND SICK BUILDING SYNDROME

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## ABSTRACT

The importance of indoor air quality (IAQ) has been recognized in the recent days. Therefore, this study attempts to provide more information about the association between IAQ and the Sick Building Syndrome (SBS) phenomenon. The indoor concentrations of $PM_{10}$ in the living rooms were measured at two multistory residential buildings during summer 2010 in the Damietta city, Egypt. Information on possible particle sources and SBS outcomes were obtained from questionnaires. The SBS score is an integrated index which indicated directly the number of different types of SBS symptoms that were analyzed on a scale of 0–6. Linear relationship between $PM_{10}$ concentration and SBS score was found. Questionnaire was also incorporating questions to evaluate the awareness of occupants towards indoor environmental conditions.

**Keywords:** Damietta, IAQ, SBS, $PM_{10}$, questionnaire, awareness.

## INTRODUCTION

Sick building syndrome (SBS) was first recognized by the World Health Organization as a medical condition (WHO, 1983). It is a collection of health problems caused by indoor chemical and biological pollution, uncomfortable temperature and humidity, or other factors in buildings (Godish, 1994). SBS is characterized by a variety of nonspecific subjective symptoms, including irritation of the eyes, blocked nose and throat, headache, dry skin, fatigue, sinus, congestion, skin rash, irritation and nausea (Lyles et al., 1991; Burge et al., 1987; WHO 1984).

A number of epidemiologic studies have been performed, and have been attributed symptoms characteristic of SBS to the physical indoor environment, especially poor indoor air quality (Samet et al., 1998; Burge et al., 1987). Many studies have investigated the association between questionnaire-based responses to SBS symptoms and measured indoor chemical exposures in houses (Takigawa et al., 2012; Sahlberg et al., 2010; Takigawa et al., 2010; Kishi et al., 2009; Sahlberg et al., 2009; Takigawa et al., 2009; Gupta 2007).

Indoor air pollution may pose greater exposure than outdoor air pollution because people spend the majority of their time indoors where dispersion of pollutants may be poor (Bruce et al., 2000). Many studies have shown the association between indoor air pollution and adverse health outcomes in developed and developing countries (Mengersen et al., 2011; Mestl et al., 2007).

Many studies have found that the concentrations of suspended particulate matter were higher indoors than outdoors (El-Batrawy, 2010; Jones et al., 2000). In addition to cooking and smoking, indoor particle concentrations also depend on housekeeping activities such as sweeping and vacuuming (Allen et al., 2003; Chao et al., 1998).

The study was conducted at Damietta City, the capital of Damietta Governorate, which locates northeast of Cairo on the eastern branch of the Nile and is surrounded by The Mediterranean Sea to the North. this study attempts to provide more information about the association between IAQ and the SBS phenomenon, two multistory residential buildings were recruited for the study; one of them located at urban area while the other located at sub- urban area. The indoor concentrations of $PM_{10}$ in the living rooms were measured at each floor of the two multistory residential buildings during summer 2010. Information on possible particle sources and SBS outcomes were obtained from questionnaires.

## MATERIALS AND METHODS

**Study Area:** The study was conducted at Damietta City, the capital of Damietta Governorate, which locates northeast of Cairo on the eastern branch of the Nile and is surrounded by The Mediterranean Sea to the North. Two multistory residential buildings were recruited for the study; each of them has four floors and therefore has four sampling sites. One of them located at urban area and their sampling sites designated as U1- U4, while the other located at sub-urban area and their sampling sites designated as S1- S4. The building (U) located in high traffic density area, whereas the building (S) located at low traffic density area. Therefore, traffic may affect sources of $PM_{10}$.

**Study design:** The indoor concentrations of $PM_{10}$ in the living rooms were measured at each floor of the two multistory residential buildings during summer 2010. Sampling was not restricted to days when the occupants were home the entire 24-h period, although since most households had young children, homes were typically occupied throughout the sampling period. Inlets for the indoor samplers were placed at breathing level for a typical adult. The residents have been instructed to keep the windows closed two hours before the measurements. The doors were opened only for entering or leaving the room. Nobody was present during the measurements and the door of the room was kept close.

Information on possible particle sources and SBS outcomes were obtained from questionnaires. The questionnaire also included queries about age, gender, number of persons living in the apartment, time spent in cooking place and smoking. If the participants were too young or old to read or write, another family member answered the questionnaires on their behalf. Participation in the study was voluntary. All subjects gave their informed consent.

**Environmental sampling of $PM_{10}$:** Indoor sampling of $PM_{10}$ was carried out for 8-h duration. Indoor samplers were placed in the middle of the living room approximately 1.5 m above the floor. The sampling equipment was housed such that it was as compact as possible and positioned indoors to cause minimal intrusion to the occupants. $PM_{10}$ concentrations were measured using the filtration method (Harrison and Perry, 1986). Particles were collected on Whatman 47 mm Teflon filters with 2µm pores size. Filters were weighed in temperature and relative humidity control. Weighing methods are detailed elsewhere (El-Batrawy, 2010).

All samples were collected in duplicate. To eliminate contamination effects, field blanks were used and analyzed simultaneously with the exposed samples for quality control during the study.

**Particle sources:** Information on possible particle sources was derived from questionnaires. Data from completed questionnaires comprised information on smoking behavior of the parents and housing conditions. Indoor $PM_{10}$ sources are mainly cooking, smoking, and cleaning activities. Only 3 homes reported indoor smoking during air monitoring.

**The SBS score**: Questionnaire data were used to assess the occurrence of respiratory symptoms and disorders. The SBS score is an integrated index which indicated directly the number of different types of SBS symptoms that were analyzed on a scale of 0–6 (WHO, 1984). It was also used by Gupta et al., 2007and Seppanen and Jaakkola, 1989. The six main symptoms of the SBS questionnaire are dry, itching or irritated eyes; headache; sore or dry throat; unusual tiredness, fatigue, or drowsiness; stuffy or runny nose, or sinus congestion; and dry or itchy skin. The answers might be Always, sometimes, or never. They were assigned the scores of 1.0, 0.5 and 0, respectively. “Always” symptoms were defined as occurring ≥3 times per week and “sometimes” symptoms as occurring once or twice per week (Gupta, 2007).

**Statistical Analysis:** All analyses were performed using SPSS, v. 17.0 (SPSS, Inc., Chicago, IL).The descriptive statistics (i.e. arithmetic means, standard deviations, maxima and minima) were used to present the data. Linear regression was performed to determine the relationships between $PM_{10}$ concentration and SBS score. In analysing the SBS symptoms, chi square test and Student's t test was used.

## RESULTS AND DISCUSSION

**The study population**: The study population comprises 37 participants. The basic description of the study population including interviewer information and particle sources is given in Table 1. The average age of participants included in the analysis was 25.6 years (range 2-80). More than half of the participants (55.6%) were aged less than 19 years. Overall, they comprised 62.2% females and 37.8% males. Approximately 37.5% of the subjects smoked.

**Table 1:** The basic description of the study population**.**

| factor | category | % N |
|---|---|---|
| **Age** | < 10 | 37.8 |
| | 10- 19 | 16.2 |
| | 20-29 | 5.4 |
| | 30-39 | 13.5 |
| | 40-49 | 10.8 |
| | 50-59 | 8.1 |
| | ≥ 60 | 8.1 |
| **Gender** | Female | 62.2 |
| | Male | 37.8 |
| **Number of persons living in the apartment** | ≤ 2 | 12.5 |
| | 3 | 12.5 |
| | 4 | 12.5 |
| | ≥5 | 62.5 |
| **Time spent in cooking place** | 1 hr | 25.0 |
| | 2 hrs | 25.0 |
| | 3 hrs | 37.5 |
| | 4 hrs | 12.5 |
| **Smoking** | Yes Daily | 37.5 |
| | No or rarely | 62.5 |
| **Dust inside a dwelling** | Always a lot | 50 |
| | Sometimes a lot | 37.5 |

| | | |
|---|---|---|
| | Never a lot | 12.5 |

**Questionnaire derived $PM_{10}$ sources:** Table 1 lists the potential sources of indoor particles according to questionnaire evaluation. Almost 37.5% of subjects were exposed to smoke inside. Almost half of the women spent between 1 and 2 h in the cooking place whilst a 37.5% of them spent 3 hours and 12.5% spent 4 hours or more in this location, although cooking was not always taking place. Approximately half of the women reported a lot of dust inside. Gas was the fuel used at building (U), while LPG was the fuel used at building (U). The apartments of building (U) were located in a street with traffic density higher than that of building (S).

**Indoor measurements of $PM_{10}$:** The indoor concentrations of $PM_{10}$ were measured in the living rooms at each floor of the two multistory residential buildings during summer 2010 and were presented in Fig. 1. The concentrations of $PM_{10}$ varied significantly. As shown in Fig. 1, the indoor concentrations of $PM_{10}$ at building U were slightly higher than that at building S. The concentrations of $PM_{10}$ may be affected by the surrounded traffic density. The concentrations of $PM_{10}$ were higher in areas with higher traffic density (El-Batrawy 2011).

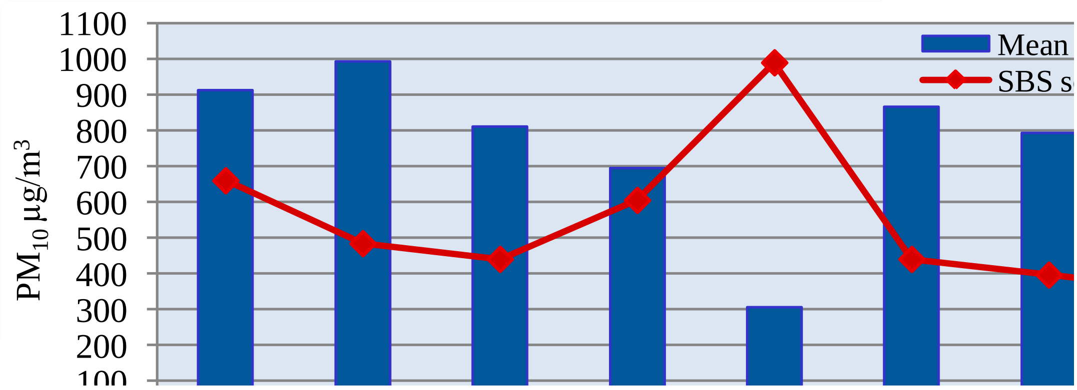

**Fig. 1:** The indoor $PM_{10}$ concentration and corresponding SBS score at each floor of the two multistory residential buildings based on occupant's response in the questionnaire.

The descriptive statistics were shown in Table 2. The median concentration of $PM_{10}$ was 801.9µg/m$^3$ whereas the mean concentration of $PM_{10}$ was 793.0µg/m$^3$. The maximum concentration of $PM_{10}$ was 992.3µg/m$^3$ were measured at U2 while the minimum concentration of $PM_{10}$ was 605.6µg/m$^3$ were measured at S1. The standard deviation was 131.0µg/m$^3$. In homes where people smoke as U2, S2 and S3, the mean indoor levels of $PM_{10}$ recorded were higher than those measured in homes with no smokers. In addition to tobacco smoking, household cleaning is a predominant indoor activity associated with increased concentrations of $PM_{10}$ within a home. It was found that higher levels of $PM_{10}$ recorded in the living areas of homes were probably associated with the infrequent housekeeping (Lee et al., 2002).

**Table 2:** The descriptive statistics of the indoor concentrations of $PM_{10}$ measured in the living rooms at each floor of the two multistory residential buildings during summer 2010.

| Mean | SD | Max | Min | Median |
|---|---|---|---|---|
| 793.0 | 131.0 | 992.3 | 605.6 | 801.9 |

**The Sick building syndrome:** Fig. 1 presents the SBS score on different floors of the two buildings. The S1 was having maximum SBS score (4.75) while U2 and S3 were having minimum (1.90). It implies that occupants of the first floor of the building (S) were having, on an average, four SBS symptoms out of six that creating an unhealthy indoor environment.

Gupta et al., 2007 studied the SBS at a multistory building in India and found that the SBS score was higher on the third floor (3.01) as compared to other floors and the control tower (0.97).

The prevalence of various SBS symptoms on different floors of the study sites based on occupant's response in the questionnaire was presented at Fig 2. The main SBS symptoms prevailing were tiredness, fatigue, or drowsiness followed by Headache and runny nose, or sinus congestion. Dry, itching or irritated eyes symptom was prevailed at U4 and S4. Headache was prevailed at U1 and S1. Unusual tiredness, fatigue, or drowsiness was prevailed at U2, S1 and S4. Stuffy or runny nose, or sinus congestion was prevailed at S2 and S3. Both Sore or dry throat and Dry or itchy skin symptoms were not prevailed at any sampling sites. Gupta et al., 2007 concluded that the main symptoms prevailing were headache (51%) and tiredness (50%).

The prevalence of SBS have been reported to be between 15% of the studied population (Takigawa et al., 2012). Bachmann and Myers, 1995 investigated the influences of SBS symptoms and reported that Eye symptoms, dry skin and sneezing were relatively common in all buildings, whereas lower respiratory tract symptoms, facial and hand rashes, dizziness and nausea were all relatively uncommon.

The prevalence's of specific symptoms were compared using Student's t test and chi square test. The results of t test (Sig. (2-tailed) = 0.737) indicated that there is no differences of IAQ of both studied urban and suburban areas. The results of chi square test ($\chi^2$= 8.222) show that the prevalence's of specific symptoms were not similar in each of the two buildings. Therefore, this may indicate that there is no direct influence of $PM_{10}$ sources on the presence of SBS symptoms in both buildings.

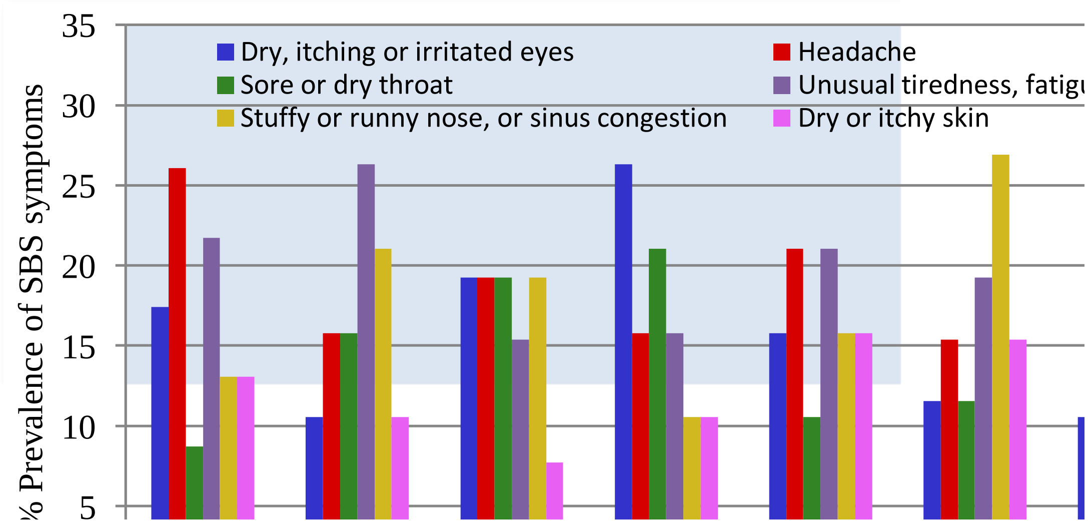

**Fig. 2:** The prevalence of SBS symptoms at the two multistory residential buildings.

**Correlation between $PM_{10}$ concentration and corresponding SBS score:** Fig. 3 shows a linear relationship between PM concentration and SBS score ($R^2$ = 0.3039), which shows less correlation between them. This implies that $PM_{10}$ is not the only influencing parameter affecting the SBS score in a building. However, The linear relationship between $PM_{10}$ concentration and SBS score shows that $PM_{10}$ may be categorized as an ‘indicator’ of IAQ, indicating likely presence of indoor air pollutants. Gupta et al. 2007 found good correlation between $PM_{10}$ concentration and SBS score ($R^2$ = 0.9499); the higher the PM concentration, the more the SBS score.

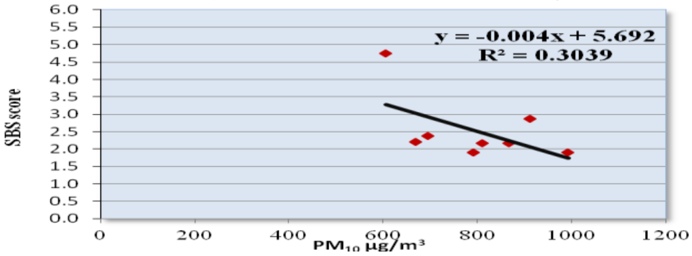

**Fig. 3:** The correlations between indoor concentrations of $PM_{10}$ and SBS score.

**Association between age and mean SBS symptoms/person:** The distribution of mean SBS symptoms per person over age groups on the two buildings is described in Fig. 4. Mean SBS symptoms per person ranged between 1.2 and 4.7 for occupants in the age groups of < 10 and ≥ 60 respectively. It was maximum for occupants in the age groups of ≥ 60 indicated that they might be having chronic health problems. Occupants in the age groups of 20–49 were more susceptible to SBS symptoms as compared to the occupants in the age group of and 50- 59. Gupta et al., 2007 found that Occupants in the age group of 20–29 were more susceptible to SBS symptoms as compared to the occupants in the age group of 50–59.

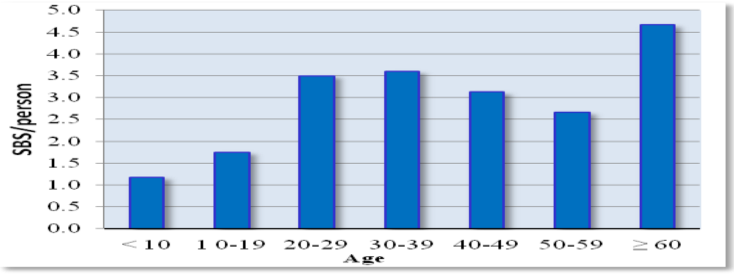

**Fig. 4:** Association between age and mean SBS per person.

**Association between gender and mean SBS symptoms/person:** Females were more susceptible to SBS symptoms than males (Fig. 5). Females show more SBS symptoms (2.5) as compared to males (2.0) on all the floors. It shows that female gender was more sensitive to SBS symptoms than male, thus needing a lesser dose of pollutants to response to the sick building symptoms. Previous investigations carried out in different countries also reported that females were more susceptible to SBS symptoms than males (Gupta et al., 2007; Bachmann and Myers, 1995; Stenberg and Wall 1995; Burge et al., 1987).

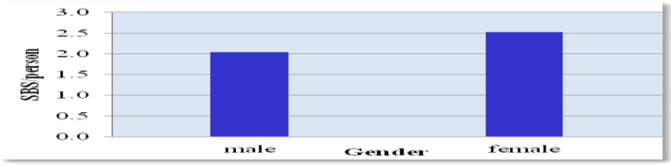

**Fig. 5:** Association between gender and mean SBS per person.

**The awareness of occupants towards IAQ:** Questionnaire was also incorporating questions to evaluate the awareness of occupants towards indoor environmental conditions. In all 35% of the occupants aware of indoor air pollution whereas 60% were not but they showed concern to know about it and a small portion i.e. of 5% was completely ignorant to it, indicating the need for awareness programmes by concerned authorities as human spend most of their daily life indoors.

## CONCULSION

This study attempts to provide more information about the association between IAQ and the Sick Building Syndrome (SBS) phenomenon. The indoor concentrations of $PM_{10}$ at building

U were slightly higher than that at building S. the SBS score on different floors of the two buildings. The S1 was having maximum SBS score (4.75) while U2 and S3 were having minimum (1.90). The main SBS symptoms prevailing were tiredness, fatigue, or drowsiness followed by Headache and runny nose, or sinus congestion. There is no differences of IAQ of both studied urban and suburban areas. Therefore, this may indicate that there is no direct influence of $PM_{10}$ sources on the presence of SBS symptoms in both buildings. a linear relationship between PM concentration and SBS score ($R^2 = 0.3039$), which shows less correlation between them. This implies that $PM_{10}$ is not the only influencing parameter affecting the SBS score in a building. It was maximum for occupants in the age groups of ≥ 60 indicated that they might be having chronic health problems. Occupants in the age groups of 20–49 were more susceptible to SBS symptoms as compared to the occupants in the age group of and 50- 59. Females show more SBS symptoms (2.5) as compared to males (2.0) on all the floors. In all 35% of the occupants aware of indoor air pollution whereas 60% were not but they showed concern to know about it and a small portion i.e. of 5% was completely ignorant to it, indicating the need for awareness programmes by concerned authorities as human spend most of their daily life indoors.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# LEVELS OF BIOAEROSOLS IN INDOOR ENVIRONMENTS IN ANKARA

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## ABSTRACT

Asthma and allergy has become more frequent worldwide during the past decades. Even though the air in many cities is much cleaner than in the past, the prevalence of allergy and asthma has increased worldwide. This study undertaken in Ankara was aimed at identifying the effects of the indoor bio-aerosols and their effects on indoor air quality. Air samples were collected from indoor and outdoor environments of 94 dwellings in 15 different districts of Ankara in winter and spring of 2012. The concentration and type of bacteria and fungi were measured by NIOSH Method-0800 with three types of agar plates (Plate -Count,Sabourad-Antibiotic and Blood Agar)and one vacuum pump with 28.3 L/min stable debi in 4 minutes. According to the sampled in-and outdoor environments of the study,the concentration of bacteria and fungi were comparede in flats without additional emission source of microorganisms, flats with persons who smoke cigarettes and flats located near traffic centre. At the completion of the study, it was observed that in general, bacteria and fungi levels were higher in the bedrooms during spring than sitting room and out environments. This explains why most people experience a lot of respiratory symptoms from acute allergic rhinitis to pneumonia during the spring months. In accordance with the sampled indoor and outdoor environments of the study, the concentration of bacteria and fungi were compared in flats without any additional emission source of microorganisms, flats with persons smoking cigarettes, and flats located near the traffic centres. It was also found that,the dominant bacteria and fungi present in the air of examined dwellings (Staphylococcus spp.(56%),Corynebacterium spp.(20%), Bacillus spp(15%))and (Penicillium spp(52%), Sporothrix spp,(43%), Stachybotrytis spp(15%)). Air samples that were taken from different sampling sites,located in Ankara showed taht,concentration of bioaerosols were high in Sincan(857 CFU/m$^3$) ,Altındağ(496.4 CFU/m$^3$), Etlik (435.3 CFU/m$^3$)and for fungi, Akyurt(459 CFU/m$^3$),Çankaya(335.6 CFU/m$^3$).

**Keywords:** Bioaerosol ,Bacteria,fungi.Indoor air pollution

## INTRODUCTION

Indoor air quality has variety of components; which mainly categorized as organics, particles, biological constituents, climate parameters. All these entire components enable to generalize the indoor air quality. Besides, several aspects of indoor environments (e.g. number of person, close to traffic source, carpet and wood products loadings, renovation application, etc.) affect the air quality themselves.

The three most commonly investigated indoor air pollution are bioaerosols (both bacteria and fungi), Volatile Organic Compounds (VOCs), and fine particulate matters which have diameter of <2.5 µm (PM2.5).

Levels and characteristics of bioaerosols in indoor environments are mainly related with microbial content of outdoor air and presence of potential indoor bioaerosol sources like moisture damage, human presence, season, humidity, temperature, ventilation and presence of indoor pets.

It is known that the health effects of indoor air pollution, bioaerosols are of concern in terms of public health and still needs to be researched.

Exposure to bio-aerosols, containing airborne microorganisms and their by-products, can result in respiratory disorders and other adverse health effects such as infections, hypersensitivity pneumonitis and toxic reactions. Fungi are common in indoor and outdoor environments and nearly 10% of people worldwide have fungal allergy (Pasanen *et al*.,1996).

Microbial damage in indoor/outdoor areas, is caused most frequently by fungi and bacteria.

Recentaly, 10-25% of the population have symptoms of hay fever or allergic asthma for the whole Earth and the incidence has more than doubled since the 1970s (Traidl-Hoffmann et al.2003).

This study was performed to investigate the weight of indoor air pollutants (bioaerosols) and their effect on health and their relationship between amount of bioaerosols and climate factors (temperature, RH, …) and building factors (distance to traffic, number of person, smoking, carpet and wood-products' loads, the last painting time, and building age).

Asthma and allergy has become more frequent worldwide during the past decades. Even though the air in many cities is much cleaner than in the past, the prevalence of allergy and asthma has increased worldwide.

## MAIN TEXT

Indoor air pollution can be as much more worses than that of outdoor air, it can cause a wide range of health problems.

In non-industrial indoor environments, the most important source of airborne bacteria is the presence of human (Stetzenbach, 2007).

Specific activities like talking, sneezing, coughing, walking, washing and toilet flushing can generate airborne biological particulate matter.

In addition food stuffs, house plants and flower pots, house dust, pets and their bedding, textiles, carpets, wood materials and furniture stuffing, occasionally release spores of Alternaria, Aspergillus, Botrytis, Cladosporium, Penicillium, Scopulariopsis into the air (Cox and Wathes, 1995; Maeir et al., 2002).

Although indoor environments are considered to be protected, they can become contaminated with particles that present different and sometimes more serious risks when their concentrations exceed recommended maximum limits than those related to outdoor exposures (Banerjee, 2008). The recommended maximum limits are : 1000 CFU/m$^3$ for the total number of bio-aerosol particles set by National Institute of Occupational Safety and Health (NIOSH); 1000 CFU/m$^3$ set by the American Conference of Governmental Industrial Hygienists (ACGIH) with the culturable count for total bacteria not to exceed 500 CFU/m$^3$ (Cox and Wathes, 1995;Jensen and Schafer, 1998).

Air sampling of microorganisms is a popular method of conducting microbial examinations, as it allows a direct toxicological evaluation.

Air samples were taken from different sampling sites (94 houses), located in Ankara in winter (24/10/2011-28/12/2011) and spring (16/04/2011 -26/07/2011).

Turkey Description of the sampling sites are : Keçiören, Etlik, Yenimahalle, Batıkent, Ostim, Etimesgut,Mamak, Dikmen, Pursaklar, Kazan, Bağlum, , Sincan, Altındağ, Çankaya, Seyranbağları, Siteler, Gölbaşı, Akyurt, Demetevler, Çubuk.

Air samples were taken from three sites of every house (sitting room-bed room-outdoor ).

The concentration and type of bacteria and fungi were measured by NIOSH Method-0800 with three types of agar plates (Plate-Count, Sabourad-Antibiotic and Blood Agar)and one vacuum pump with 28.3 L/min stable debi in 4 minutes.These results can be related to a concentration expressed in colony forming units per cubic meter.

Information regarding the micro-environments of each sampling site (number of person, , building age, smoking, and distance to traffic source) are also measured.

Fig (1). Vacuum pump and impactor for bioaerosols measuring

Plate-Count and Blood agar, stayed in incubator for 24 hours and 37 °C, For separating the Gram Positive and Gram Negative Bacteria.

Fig(2). Incubator for bacteria growth

The procedure involves staining bacteria initially with a weak alkaline solution of gentian (crystalline) violet. All bacterial cells stain blue with this dye. Subsequently these cells are treated with Lugol's iodine solution (Iodine in potassium iodide solution) and washed with alcohol. At this stage if the bacteria retain the purple colour, they are described as Gram positive bacteria and if they lose their purple colour, they are described as Gram negative bacteria. The Gram negative bacteria can be subsequently stained with saffranine for further investigations. The Gram positive and Gram negative bacteria show certain morphological and physiological differences between them.

Fig (3). Crystalline, Lugol's iodine solution, Alkaline, Saffranine for Morphological and Physiological analysing of bacteria

For analysing the types and the structure of fungi, they were put 7 days in 25°C, and then they were conducted by atlas (Morphologic Atlas).

## CONCLUSION

Statistical tests were performed using Statgraphics 3.0 software.Environmental parameters such as temperature and RH levels at indoor and outdoor air during the sampling campaigns

were measured to estimate the influence of these factors on bioaerosol levels.

Generally,because of optimum bioaerosols activity in warm places, bioarosol levels were higher in the spring than in the winter, so the season is the key factor of observed indoor TBC and TMC levels and they measured 2 folds higher bioaerosol levels in the spring than in the summer.it means that season is the key factor affecting the indoor air pollutants .Season also change the ventilation frequency of indoor environment , which causes indirect effect on indoor air quality.

Box-and-Whisker plot for seasonal is shown in Fig (4) .

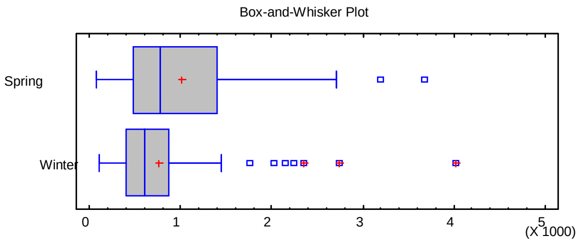


Fig (4). Amount of bioaerosols during spring and winter

Accordingly, the highest TBC and TMC (CFU/ m³ ) levels were observed in the sitting room and bed room.Box-and-Whisker plot for the positional differences is shown in Fig (5) .

In the Box-and-Whisker plot,O means sitting room, B means bed room, D means outdoor and OB means the houses with single room.

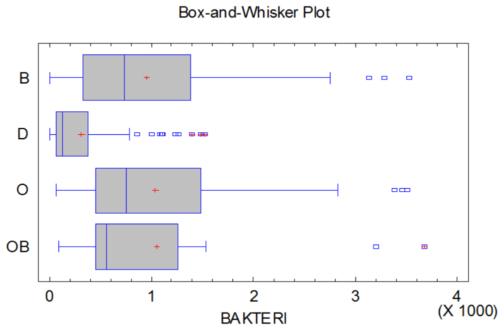


Fig (5). Amount of bioaerosols in (sitting room = O),(bed room = B),(outdoor = D), single room = OB)

This study showed that indoor bioaerosol levels varied spatially and seasonally.

When we compare the air quality of sitting room and bed room,we can see that amount of bioaerosols are higher in bed room than sitting room.it happens because of small area and limited ventilation in bed room, which resulted in higher air contaminant concentration.

TBC and TMC (CFU/ m³ ) levels were observed in the sitting room and bed room,in Fig (6)

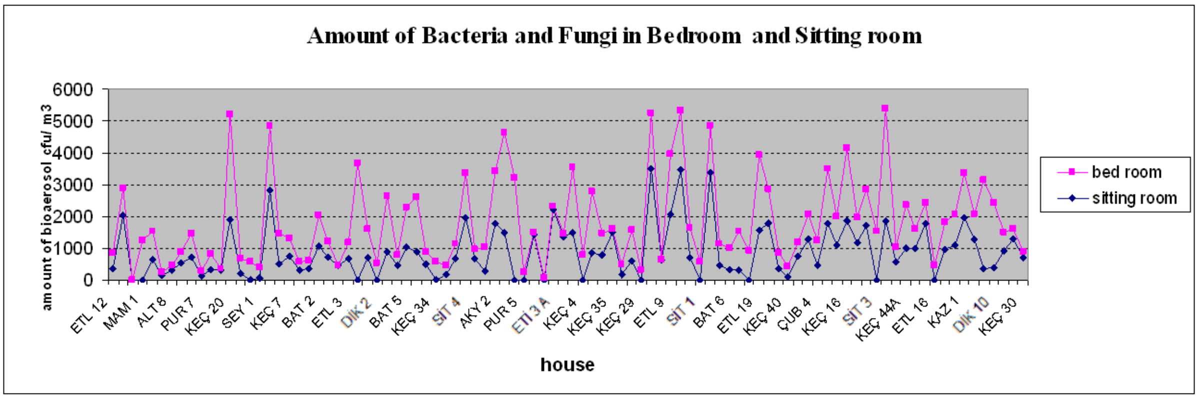


Fig (6). Amount of bioaerosols in sitting room and bed room

The outdoor and indoor levels of bioaerosols were analaysed in this study.The outdoor levels of TBC and TMC were found lower than inside .It means Indoor/Outdoor >> 1, so the human activity inside the houses are the key factor of observed indoor bioaerosol levels in the houses. Indoor/Outdoor ratio of bioaerosol levels are shown in Fig (7).

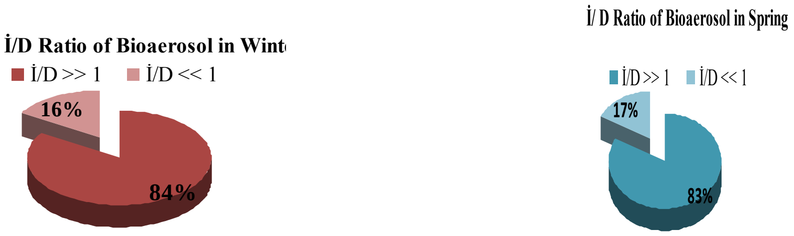


Fig (7). Indoor/Outdoor ratio of bioaerosol levels

The following microorganisms were most often present in the indoor air:

It was also found that,the dominant bacteria and fungi present in the air of examined dwellings are (Staphylococcus spp.(56%),Corynebacterium spp.(20%), Bacillus spp(15%))and (Penicillium spp(52%), Sporothrix spp,(43%), Stachybotrytis spp(15%)).

The most common microorganisms in the indoor air are presented in Fig (8).

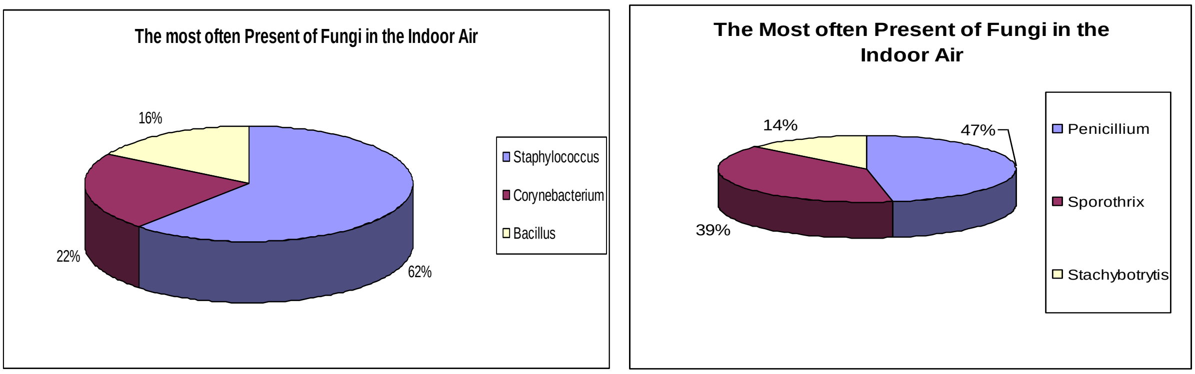


Fig (8). The most often present of bacteria and fungi in the indoor air

Amount of different types of Bacteria and Fungi are shown in Fig (9) .

Fig (9). The most common microorganisms in the indoor air

Distance to traffic sources is another important factor that influence indoor air quality.

Air samples that were taken from different sampling sites,located in Ankara showed taht,concentration of bioaerosols were high in Sincan (857 CFU/m$^3$) ,Altındağ(496.4 CFU/m$^3$), Etlik (435.3 CFU/m$^3$) and for fungi, Akyurt (459 CFU/m$^3$),Çankaya (335.6 CFU/m$^3$) during winter and spring.

Amount of bioaerosols in different districts of ankara are shown in Fig (9).

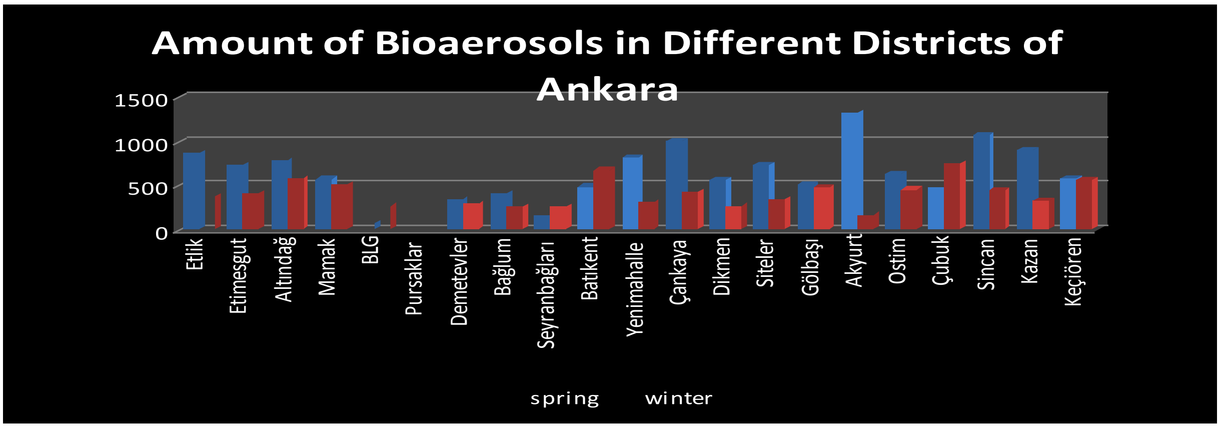


Fig (9). Amount of bioaerosols in different districts of Ankara

According to rank correlation and ANOVA results, the significant data pairs and significant good relationship between factors are shown in following tables.

Fig (10),Scatterplot shows that there is important relationship between amount of bioaerosols and distance to traffic sourses.in the Scatterplot, (1) means the dwellings near to traffic sources and (2) is the houses far from the traffic sources.

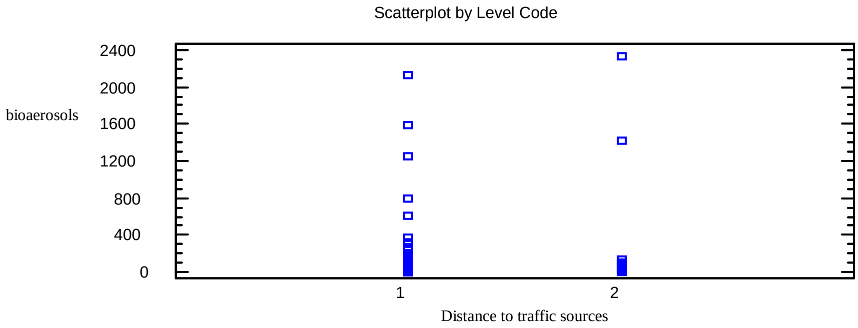


Fig (10). relationship between amount of bioaerosols and distance to traffic sourses

In ANOVA table,Since the P-value of the F-test is smaller than 0.05, there is a statistically significant difference between the distance of the dwellings to traffic sources and concentration of bioaerosols at the 95.0% confidence level.

ANOVA Table also shows ,higher amount of bioaerosols in the dwellings that are nera the traffic sources.it is shown in table (1).

Table (1). ANOVA Table for Bioaerosols and Distance to Traffic Sources

| *Source* | *Sum of Squares* | *Df* | *Mean Square* | *F-Ratio* | *P-Value* |
|---|---|---|---|---|---|
| Between groups | 567096. | 1 | 567096. | 6.08 | 0.0147 |
| Within groups | 1.51991E7 | 163 | 93245.8 | | |
| Total (Corr.) | 1.57662E7 | 164 | | | |

Fig(11),Scatterplot shows that there is important relationship between amount of bioaerosols and area of the flats.in the Scatterplot, (1) means the dwellings whose total surface more than 100 $m^2$ and (2) is the houses with total surface smaller than 100 m.$^2$

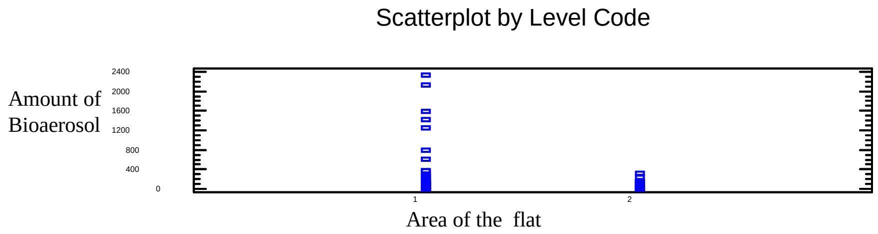


Fig (11). relationship between amount of bioaerosols and area of flats

In ANOVA table Since the P-value of the F-test is smaller than 0.05, there is a statistically significant difference between the area of the dwellings and concentration of bioaerosols at the 95.0% confidence level.

ANOVA Table also shows ,higher amount of bioaerosols in the dwellings that have total surface mora than 100 m.$^2$ ANOVA Table is shown in table (2).

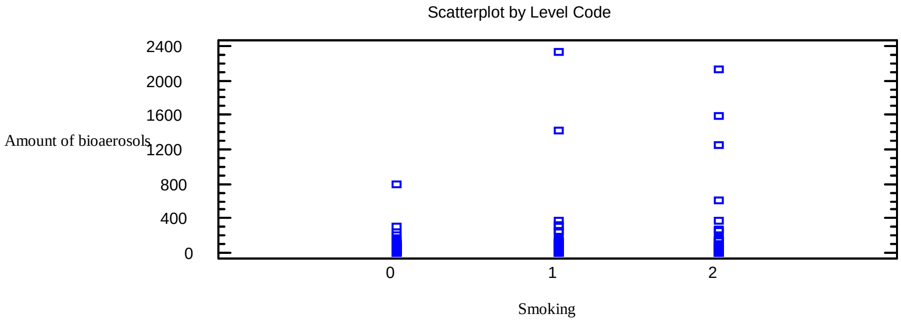
Table (2).ANOVA Table for Bioaerosols and area of flats

| *Source* | *Sum of Squares* | *Df* | *Mean Square* | *F-Ratio* | *P-Value* |
|---|---|---|---|---|---|
| Between groups | 690379. | 1 | 690379. | 7.42 | 0.0071 |
| Within groups | 1.50646E7 | 162 | 92991.1 | | |
| Total (Corr.) | 1.57549E7 | 163 | | | |

In accordance with the sampled indoor and outdoor environments of the study, the concentration of bacteria and fungi were compared in flats without any additional emission source of microorganisms, flats with persons smoking cigarettes, and flats located near the traffic centres.

Fig(12),Scatterplot shows the concentration of bioaerosols and flats without any additional emission source of microorganisms, flats with persons smoking cigarettes.

In the Scatterplot, (0) shows the houses that there isnt any cigarette smoker,(1) shows the houses that there is one smoker and (2) shows the houses that have more than one person who is smoking.



In ANOVA table ,Since the P-value of the F-test is smaller than 0.05, there is a statistically significant difference between the number of smokers inside the dwellings and concentration of bioaerosols at the 95.0% confidence level.

ANOVA Table also shows ,higher amount of bioaerosols in the dwellings that have more than one smoker. ANOVA Table is shown in table (3).

Table (3). ANOVA Table for total bioaerosols and number of smokers in the dwellings

| *Source* | *Sum of Squares* | *Df* | *Mean Square* | *F-Ratio* | *P-Value* |
|---|---|---|---|---|---|
| Between groups | 768490. | 2 | 384245. | 4.15 | 0.0175 |
| Within groups | 1.49977E7 | 162 | 92578.3 | | |
| Total (Corr.) | 1.57662E7 | 164 | | | |

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# INDOOR AND OUTDOOR CONCENTRATIONS OF PARTICULATE MATTER AT DOMECTIC HOMES

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## ABSTRACT

Among 30 homes in Ankara, the relationship between indoor and outdoor levels for particulate matter less than 10 µm ($PM_{10}$), particulate matter less than 2.5 µm ($PM_{2.5}$), particulate matter less than 1.0 µm ($PM_{1.0}$) was investigated in three different environment (living room, baby's room and outdoor). The mean concentration of $PM_{10}$ at living room is higher than baby's room (or bedroom) whereas there is no statistically significant variation of $PM_{2.5}$ and $PM_{1.0}$ levels at living and baby room. It has been found that the household activities and environmental conditions are very important for PM concentrations in the indoor and outdoor environments during the sampling periods. Smoking indoors, being near a main road or construction, use of stove, room spray or vacuum-cleaner and near a construction increased the fine PM concentration.

**Key Words:** Indoor air quality, Particulate matter (PM), $PM_{10}$, $PM_{2.5}$, $PM_{1.0}$

## 1. INTRODUCTION

The indoor air quality (IAQ) as assessed by particulate matter (PM) has become one of the most important topics of air pollution research. This is because most people spend most of their time in various indoor environments (homes, schools, offices, shopping malls and restaurants). Usually, in health studied, particulate matter (PM) has been measured as the mass of particle smaller than 10 µm, $PM_{10}$ or smaller than 2.5 µm, $PM_{2.5}$ (IEH 2000). These findings were especially pronounced for inhalable thoracic particles (particles of aerodynamic diameter less than 10 µm, $PM_{10}$) and fine particles (particles smaller than 2.5 µm, $PM_{2.5}$) (Pope & Dockery 1992; Braun et al. 1992; Dockery et al. 1993; Schwartz 1993; Seaton et al. 1995; Ackermann-Liebrich et al. 1997).

Many studies have found that the concentrations of suspended particulate matter were higher indoors than outdoors when there were sources of indoor particulate in domestic homes (Jones et al. 2000; Chao, Tung & Burnett 1998; Wallace 1996; Kamens et al. 1991; Spengler et al. 1981). Incremental concentrations of fine particles were attributed to tobacco smoking and operation of gas stoves for cooking. Spengler et al. (1981) found that concentrations of fine particle were as high as 300 µg/m$^3$ when a smoker kept smoking for up to 30 min until the cigarette had burnt out, also the 24-h average concentrations of fine particles could be elevated by 20 µg/m$^3$.

As most time is spent at indoors, information on the indoor/outdoor (I/O) relationship of particulate concentrations is important. Indoor levels can be influenced by outdoor levels and by particle generation indoors (Yocom 1982). Not only emission sources, but also human activities (e.g. cleaning, working) and even the mere presence of people at home lead to increases in particulate levels indoors (Spengler et al. 1981).

A variety of studies on I/O relationships have been conducted in the USA. Overall, the I/O ratios ranged from 0.5 to 2 and greater (Kim & Stock 1986; Lioy et al. 1990; Sexton, Spengler & Treitman 1984; Li 1994). In homes with indoor sources (e.g. gas-cooking, smoking) I/O ratios were generally found to be greater than 1, showing that the exposure of subjects to particulates can be greater than outdoors.

A dose-concentration relationship was found for fine particulates with the number of cigarettes smoked at home (Quackenboss, Lebowitz & Crutchfield 1989). Raunemmaa et al. (1989) investigated I/O relationships in Finland, where the ratios were less than 1 in homes without any indoor sources but greater than 1 in homes with smokers. For fine particulates (Monn & Schaeppi 1993) found I/O ratios between 0.6 and 2. Without indoor sources, an almost linear indoor/outdoor relationship was observed. In all homes no air conditioning is used and ventilation is conducted mechanically by opening windows.

This study demonstrates a few representative cases of I/O investigations with the emphasis on reference conditions (homes without indoor source and activity), indoor sources (e.g. smoking, heating type, nearby construction) and elevated human indoor activity in the absence of indoor sources. The objectives of this study were to: 1) compare fine and course PM exposure for the rooms, 2) determine fine and coarse PM ($PM_{10}$-$PM_{2.5}$-$PM_{1.0}$) levels for all houses at outside environment (balconies or near to the front of the homes, 3) discuss possible sources that influence PM concentrations for the homes (living and baby's room), and 4) compare PM levels of the homes to other residential homes.

## 2. MATERIALS AND METHODS

### 2.1. Sampling sites

This sampling period took place from June 11 – July 2, 2012. The measurements were selected on different neighbourhoods in Ankara. The locations of the sampling sites are shown in Fig.1.

**Fig. 1.** The Sampling locations in Ankara.

### 2.2. Methods

$PM_{10}$ and $PM_{2.5}$ are two of the six criteria pollutants that are nationally regulated by the U.S. Environmental Protection Agency (EPA). PM mass concentration ($\mu g/m^3$), the current metric of regulation, has been the topic of numerous studies that focus on

PM measurements in urban areas (Chow & Watson 2002; Cabada & Rees 2004; Kim & Hopke 2005; Demerjian & Mohnen 2008).

During the study, one handheld real-time condensation particle counters, models Grimm Environmental Dust Monitoring (EDM) 107 were used to measure the concentrations of particles. This working devices are real-time light scattering instruments.

The Indoor air IQ-410 quality probe was used to measure carbon dioxide ($CO_2$) concentrations, temperature (T), and relative humidity (RH). The concentrations of $PM_{10}$, $PM_{2.5}$, $PM_{1.0}$, temperature (T), relative humidity (RH), $CO_2$ were measured at each environment for a period of 15 min. The measurement parameters were measured non-simultaneously indoors and outdoors.

During the air measurement, some factors like domestic heating, smoking areas and near a construction were also recorded. Indoor air samples were collected both in living and baby's rooms (or bedroom). All of the outdoor air samples were taken at balconies or near to the front of the homes.

## 3. RESULTS AND DISCUSSION

Statistical calculations were performed using the Statgraphics Centurion Statistical Software. The continuous particle concentration data and other environmental parameters were initially investigated by descriptive statistics (mean and standard deviation).

All measurements were conducted for the approximately 3 weeks in Ankara. Table 1 and Fig. 2 showed the average concentrations of particulates indoors and outdoors at homes in $PM_{10}$, $PM_{2.5}$ and $PM_{1.0}$ size fractions respectively. The mean concentration of $PM_{10}$ at living room is higher than baby's room (or bedroom) whereas there is no statistically significant variation of $PM_{2.5}$ and $PM_{1.0}$ levels at living and baby's room. During the study period, average $PM_{10}$ concentration and standard deviation (SD) in indoor (living room and baby's room) and outdoor were 100,8 ± 69,6 µg/m$^3$and 67,9 ± 29,2 µg/m$^3$ and 58,3 ±3 2,6 µg/m$^3$ respectively.

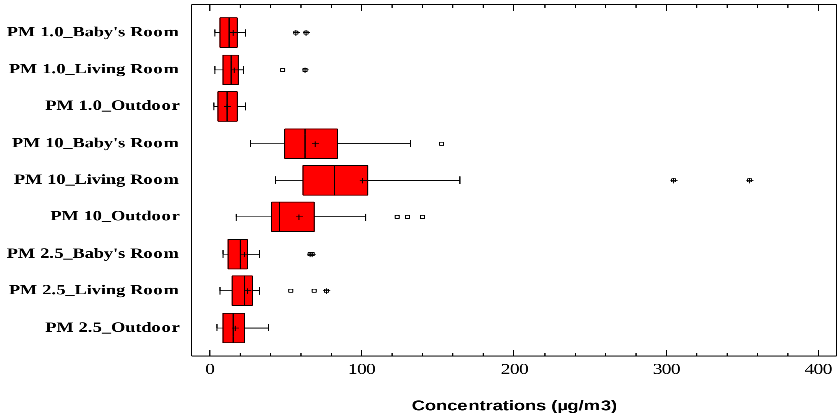

**Fig. 2.** Living room, baby's room and outdoor $PM_{10}$, $PM_{2.5}$ and $PM_{1.0}$ concentrations (µg/m$^3$)

Table 1. summarizes the results of light scattering measurements. For both two rooms, the mean indoor $PM_{10}$-$PM_{2.5}$-$PM_{1.0}$ concentrations were consistently higher than the outdoor concentrations. As shown in Table 1., higher values of I/O ratios were found for living room.

The indoor and outdoor levels of $PM_{10}$-$PM_{2.5}$-$PM_{1.0}$ concentrations obtained in the living rooms, baby's rooms, living and baby's room is the same and outdoor of residence are shown in Table 1. The mean concentrations of $PM_{10}$ and $PM_{2.5}$ at living rooms are higher than baby's rooms (or bedroom) and living and baby's room is the same. The average $PM_{10}$ concentrations in the living rooms ranged from 43,3 to 354,4 µg/m$^3$ with an average of 100,8 µg/m$^3$. These $PM_{10}$ levels did not exceed the WHO air quality guidelines and interim targets for particulate matter: 24 hour concentration Interim Target-1 (IT-1) standard of 150 µg/m$^3$, as shown in Table 2. (WHO 2005).

**Table 1.** Summary of indoor, and outdoor $PM_{10}$, $PM_{2.5}$ and $PM_{1.0}$ measurements (µg/m$^3$)

| | *n* | **$PM_{10}$** | **$PM_{2.5}$** | **$PM_{1.0}$** | **I/O ($PM_{10}$)** |
|---|---|---|---|---|---|
| **Living Room** | 30 | 100,8 ±69,6[*] | 25,1±16,2 | 16,1±12,4 | 1,7 |
| **Minimum** | | 43,3 | 7,0 | 3,3 | |
| **Maximum** | | 354,4 | 76,8 | 62,4 | |
| **Baby Room** | 28 | 67,9±29,2[*] | 22,2±14,1 | 15,5±13,4 | 1,1 |
| **Minimum** | | 26,7 | 8,5 | 3,5 | |
| **Maximum** | | 152,3 | 67,3 | 63,3 | |
| **Living room and baby's room is the same** | 2 | 58,4±4,7 | 21,6±0,2 | 17,7±0,04 | 1,0 |
| **Minimum** | | 55,1 | 21,4 | 17,6 | |
| **Maximum** | | 61,8 | 21,7 | 17,7 | |
| **Outdoor** | 30 | 58,3±32,6 | 16,7±8,6 | 11,8±6,3 | |
| **Minimum** | | 17,2 | 4,5 | 2,8 | |
| **Maximum** | | 139,6 | 39,0 | 23,5 | |
| **I/O Ratio (Living Room/Ourdoor)** | 30 | 2,2±2,2 | 1,8±1,6 | 1,3±0,9 | |
| **I/O Ratio (Baby Room/Outdoor)** | 28 | 1,5±1,3 | 1,7±1,9 | 1,4±1,8 | |

[*] Statistically significant differences ($p < 0.05$) between living rooms and baby's rooms $PM_{10}$ concentrations.

**Table 2.** WHO air quality guidelines and interim targets for particulate matter:

24 hour concentrations

| | **$PM_{10}$ (µg/m$^3$)** | **$PM_{2.5}$ (µg/m$^3$)** |
|---|---|---|
| Interim Target-1 (IT-1) | 150 | 75 |
| Interim Target-2 (IT-2) | 100 | 50 |
| Interim Target-3 (IT-3) | 75 | 37,5 |
| Air quality guideline (AQG) | 50 | 25 |

$PM_{2.5}$ levels did not exceed the 24 hour concentration Interim Target-3 (IT-3) standard of 37,5 µg/m$^3$, as shown in Table 2. (WHO 2005).

Table 3. shown the indoor and outdoor levels of $CO_2$, temperature and relative humidity obtained in the living rooms, baby's rooms and outdoor of residence. The average $CO_2$ concentration in living rooms ranged from 429 to 975 ppm with an average of 614 ppm. These $CO_2$ levels did not exceed the HKIAQO Level I standard of 800 ppm, as shown in Table 4. (EPA 1999). On the other hand, the mean $CO_2$ concentrations in the baby's rooms ranged from 410 to 1575 ppm with an average of 583 ppm.

**Table 3.** Indoor and outdoor concentrations of carbon dioxide ($CO_2$), temperature (T), relative humidity (RH) in living and baby's room and outdoor of a domestic home.

| | ***n*** | **$CO_2$ (ppm)** | **T (˚C)** | **RH (%)** |
|---|---|---|---|---|
| **Living Room** | 30 | 614,9±144,8 | 26,9±2,3 | 31,6±7,4 |
| Minimum | | 429 | 21 | 17 |
| Maximum | | 975 | 33 | 53 |
| **Baby Room** | 28 | 583,4±227,2 | 27,5±3,7 | 30,9±8,6 |
| Minimum | | 410 | 20 | 12 |
| Maximum | | 1575 | 43 | 56 |
| **Outdoor** | 30 | 441,6±37,2 | 27,7±4,1 | 26,1±7,1 |
| Minimum | | 377 | 19 | 10 |
| Maximum | | 548 | 35 | 40 |
| **Living room and baby's room is the same** | 2 | 560,5±4,9 | 28,0±1,4 | 28,0±0,0 |
| Minimum | | 557 | 27 | 28 |
| Maximum | | 564 | 29 | 28 |

**Table 4.** Recommended indoor air quality objectives for office buildings and public places in Hong Kong (Indoor Air Quality Management Group, 1999)

| **Air Parameter** | **Unit** | **8-hour average based** | |
|---|---|---|---|
| | | **Level 1** | **Level 2** |
| Carbon dioxide ($CO_2$) | ppm | <800 | <1000 |
| Respirable suspended particulate ($PM_{10}$) | µg/m$^3$ | <20 | <180 |

As shown in Fig. 3, Fig 4, and Fig 5 in homes where people smoke only at kitchen and balconies, the mean indoor levels of $PM_{10}$, $PM_{2.5}$ and $PM_{1.0}$ recorded in living and baby's rooms were higher than those measured in homes with non-smoking and smoking at balconies and doorsteps ($p < 0.05$) (Table 5). During the periods of air sampling, at least one window was ventilated with open windows.

Some studies found that increasing levels of indoor PM2.5 were associated with significantly higher measurements with smokers (Taneja, Massey & Maih 2012; Lee, Li & Ao 2002; Mohamed, Bothaina & Eman 2012) (Table 5).

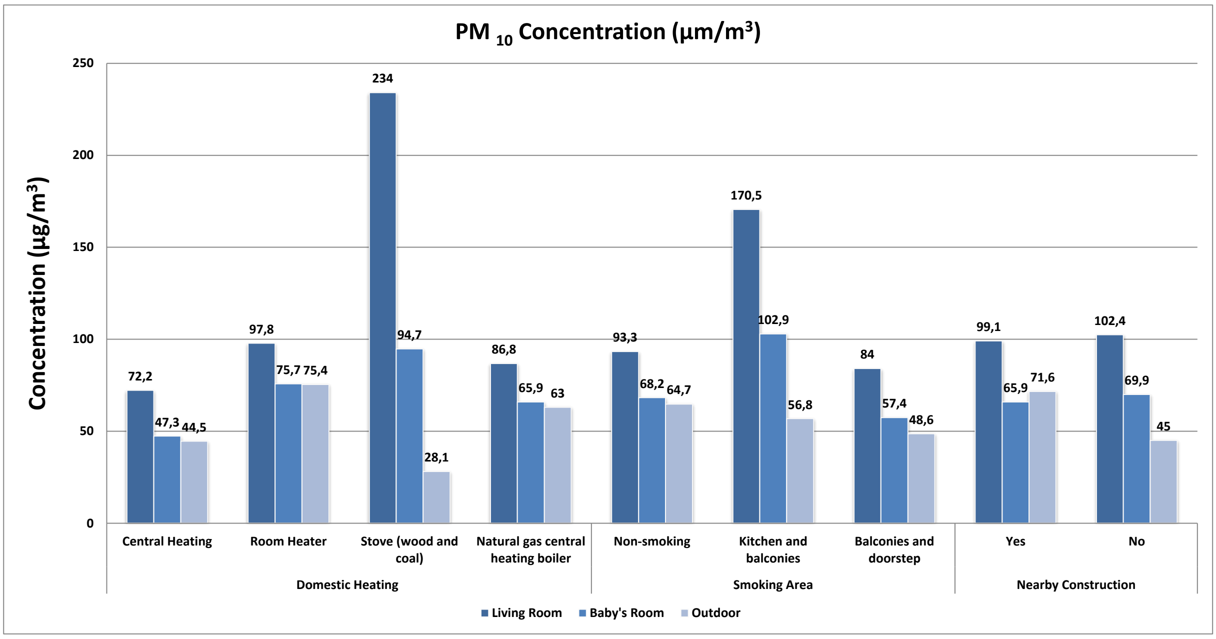

**Fig. 3.** Concentrations of PM$_{10}$ in living, baby's rooms and outdoor of domestic home.

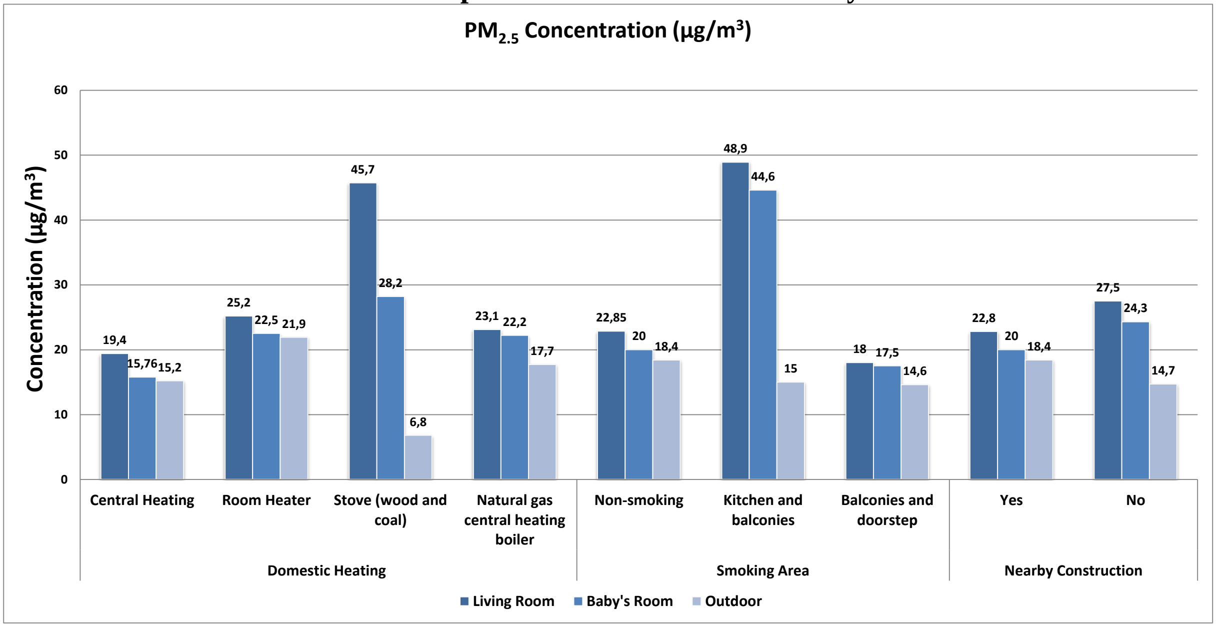

**Fig. 4.** Concentrations of $PM_{2.5}$ in living, baby's room and outdoor of domestic home.

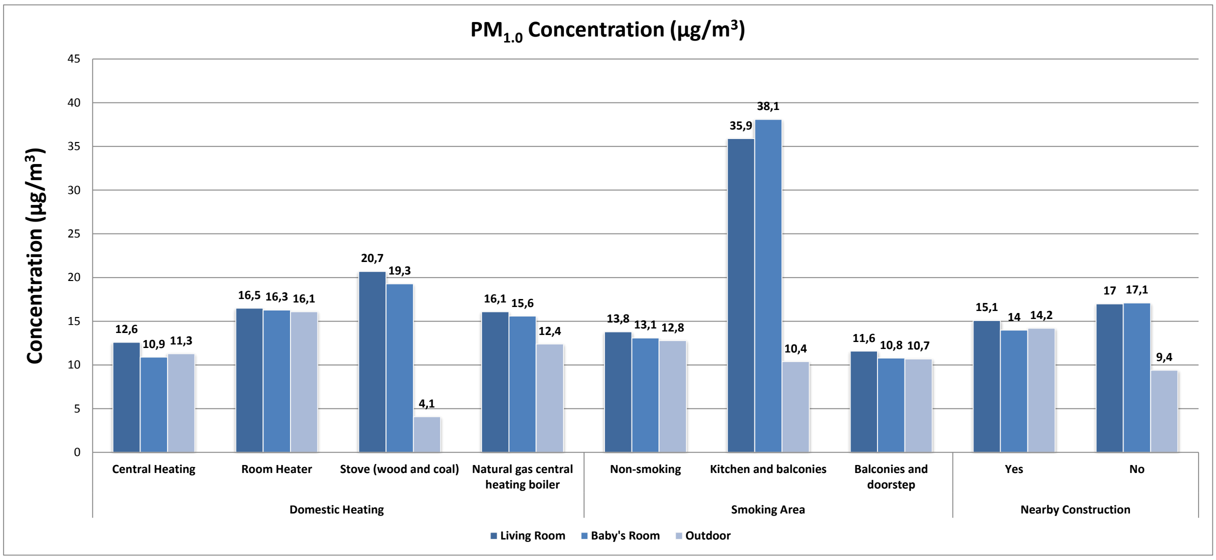

**Fig. 5.** Concentrations of $PM_{1.0}$ in living, baby's room and outdoor of domestic home.

**Table 5.** A comparison of indoor and outdoor particulate matter concentrations and range for worldwide studies at various measurement locations.

| | | | | | | | | Case | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Study sites** | **Measurement details** | **Sample number** | **PM 10 (µg/m3) Indoor** | **PM 10 (µg/m3) Outdoor** | **PM 2.5 (µg/m3) Indoor** | **PM 2.5 (µg/m3) Outdoor** | **Case Name** | **PM 10 (µg/m3) Indoor** | **PM 2.5 (µg/m3) Indoor** | **PM 2.5 (µg/m3) Outdoor** | **PM 2.5 (µg/m3) I/O ratios** | **Reference** |
| **1** | Kuwait<br>(2011) | H 1 | 6 | - | - | Livingroom: 36,06<br>Kitchen: 46,2<br>Bedroom: 31,5 | - | | - | | - | - | Mohamed F. Y. et al., 2012 |
| | | H 2 | 9 | - | - | Livingroom: 60,96<br>Kitchen: 88,15<br>Bedroom: 23,68 | - | | - | | - | - | |
| | | H 3 | 5 | - | - | Livingroom: 27,74<br>Kitchen: 59,4<br>Bedroom: 24,43 | - | Smoking | - | 54 | - | - | |
| | | H 4 | 7 | - | - | Livingroom: 22,42<br>Kitchen: 58,56<br>Bedroom: 24,02 | - | | - | | - | - | |
| | | H 5 | 9 | - | - | Livingroom: 26,98 | - | | - | | - | - | |
| | | H 6 | 4 | - | - | Livingroom: 49,4 | - | | - | | - | - | |
| | | H 7 | 6 | - | - | Livingroom: 59,4 | - | | - | | - | - | |
| | | H 8 | 6 | - | - | Livingroom: 58,55 | - | Non-smoking | - | 37,6 | - | - | |
| | | H 9 | 8 | - | - | Livingroom: 52,96 | - | | - | | - | - | |
| | | H 10 | 5 | - | - | Livingroom: 46,20 | - | | - | | - | - | |
| **2** | North-Central India<br>October 07-March 09 | five roadside homes | 64 | 247 (annual) | 255 (annual) | 161 (annual) | 160 (annual) | Smoking | 329 | 279 | | - | Taneja A. et al., 2011 |
| | | | | | - | | | Non-smoking | 188 | 163 | | - | |
| | | five urban homes | 40 | 181 (annual) | 195 (annual) | 109 (annual) | 123 (annual) | Using of stoves | 268 | 287 | | - | |
| | | | | | | | | not using of stoves | 200 | 157 | | - | |
| **3** | Birmingham, UK<br>July, 1998 | Roadside | 3 homes | 47,8±52<br>34.7±23<br>16.5±11.6 | - | 7.9±5.2 | - | - | - | - | - | - | Harrison R.M. et al., 2011 |
| | | Flats | 2 homes | 15±4.9<br>17±12<br>88±97 | - | - | - | - | - | - | - | - | |
| | | Rural | 2 homes | 34±26<br>27±11<br>45±98 | - | - | - | - | - | - | - | - | |
| **4** | Hong Kong<br>Jul-October 1999 | Home 1 (Kwum Tong) | Home 1 | - | - | - | - | Smoking | 155 | - | - | - | Lee C. S. et al., 2002 |
| | | Home 2 (Jordon) | Home 2 | | | | | | | | | | |
| | | Home 3 (Shatin) | Home 3 | | | | | | | | | | |
| | | Home 4 (Lam Tin) | Home 4 | - | - | - | | Non-smoking | 148 | - | - | - | |
| | | Home 5 (Wong Tai Sin) | Home 5 | | | | | | | | | | |
| | | Home 6 (Siu Sai Wan) | Home 6 | | | | | | | | | | |
| **5** | Switzerland<br>May- July 1996 | A: suburban | 7 | 25,8 | 38,4 | - | - | A: suburban | | 18,3 | 33,9 | - | Monn Ch. et al., 1997 |
| | | B: residential | 4 | 10,8 | 15,2 | - | - | - | - | - | - | - | |
| | | C: residential | 7 | 32,8 | 23,4 | - | - | C: residential | - | 26 | 21 | - | |
| | | D: city | 4 | 21,4 | 18,1 | - | - | - | - | - | - | - | |
| | | E: city | 4 | 24,6 | 19,7 | - | - | - | - | - | - | - | |
| | | F: residential | 4 | 26,9 | 14,6 | - | - | - | - | - | - | - | |
| | | G: residential | 4 | 26,5 | 12,8 | - | - | - | - | - | - | - | |
| **6** | Southeastern Ohio<br>January 1999-August 2000 | Koebel[1] | 251 (I)-315 (O) | - | - | 14,9 | 13,8 | School-day | - | - | - | 1,71 | Kevin C.C. et al., 2007 |
| | | | - | - | - | - | - | Non-school-day | - | - | - | 1,27 | |
| | | New Albany[2] | 270 (I)-327 (O) | - | - | 16,5 | 12,7 | School-day | - | - | - | 2,98 | |
| | | | - | - | - | - | - | Non-school-day | - | - | - | 0,82 | |
| | | Athens[3] | 298 (I)-332 (O) | - | - | 17,2 | 13,6 | School-day | - | - | - | 2,61 | |
| | | | - | - | - | - | - | Non-school-day | - | - | - | 0,8 | |

[1] Koebel Elementary School (Columbus)

[2] New Albany Elementary School (Columbus)

[3] East Elementay School (Athens)

It was found that higher levels of $PM_{10}$ and $PM_{2.5}$ recorded in the living areas of homes were probably associated with heating of stove ($p < 0.05$) (Table 6). Airborne $PM_{10}$ and $PM_{2.5}$ can originate from stove-heated (wood and coal) within a home (Fig. 3 and Fig. 4).

Outdoor particulates are an important source of indoor particulates. The calculated indoor and outdoor PM levels of the presented measurement series are given Fig.3, Fig. 4, and Fig. 5. In homes where close to the constructions, the mean outdoor levels of $PM_{10}$, $PM_{2.5}$ and $PM_{1.0}$ recorded in the outdoor were higher than those measured in homes with far away from the constructions ($p < 0.05$) (Table 6).

In addition outdoor air pollution, nearby constructions are predominant outdoor activity associated with increased concentrations of $PM_{10}$, $PM_{2.5}$ and $PM_{1.0}$.

**Table 6.** Indoor and outdoor concentrations and I/O rates of $PM_{10}$ and $PM_{2.5}$ in living and baby's room and outdoor of a domestic heating, smoking areas and near a construction (µg/m$^3$)

| | | | **PM 10** | | | | | **PM 2.5** | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Domestic Heating** | | **n** | **Living Room** | **I/O** | **Baby's Room** | **I/O** | **Outdoor** | **Living Room** | **I/O** | **Baby's Room** | **I/O** | **Outdoor** |
| | **Central Heating** | 4 | 72,2±25,1 | 1,62 | 47,3±17,2 | 1,62 | 44,5±2,1 | 19,4±5,1 | 1,28 | 15,76±5,6 | 1,03 | 15,2±2,3 |
| | **Room Heater** | 2 | 97,8±8,9 | 1,30 | 75,7±32,4 | 1,30 | 75,4±47,5 | 25,2±4,1 | 1,15 | 22,5±2,3 | 1,02 | 21,9±6,0 |
| | **Stove (Coal and wood)** | 3 | 234±167,1[*] | 8,33 | 94,7±57,2 | 8,33 | 28,1±14,7 | 45,7±35,4 | 6,72 | 28,2±25,9 | 4,14 | 6,8±2,1 |
| | **Natural gas central heating boiler** | 20 | 86,8±30,0 | 1,38 | 65,9±20,9 | 1,38 | 63,0±33,3 | 23,1±13,2 | 1,31 | 22,2±13,4 | 1,25 | 17,7±9,3 |
| **Smoking Areas** | | **n** | **Living Room** | **I/O** | **Baby's Room** | **I/O** | **Outdoor** | **Living Room** | **I/O** | **Baby's Room** | **I/O** | **Outdoor** |
| | **Non-smoking** | 15 | 93,3±62,8 | 1,44 | 68,2±25,1 | 1,05 | 64,7±35,6 | 22,85±11,7 | 1,24 | 20,0±8,3 | 1,08 | 18,4±9,3 |
| | **Kitchen and balconies** | 4 | 170,5±123,7[**] | 3,00 | 102,9±40,8[**] | 1,81 | 56,8±51,0 | 48,9±27,6[**] | 3,26 | 44,6±25,4[**] | 2,97 | 15,0±9,7 |
| | **Balconies and doorstep** | 10 | 84,0±35,6 | 1,73 | 57,4±19,8 | 1,18 | 48,6±16,5 | 18,9±7,1 | 1,29 | 17,5±7,6 | 1,19 | 14,6±7,2 |
| **Nearby Construction** | | **n** | **Living Room** | **I/O** | **Baby's Room** | **I/O** | **Outdoor** | **Living Room** | **I/O** | **Baby's Room** | **I/O** | **Outdoor** |
| | **Yes** | 14 | 99,1±62,5 | 1,38 | 65,9±302 | 0,92 | 71,6±33,4[***] | 25,3±10,6 | 1,24 | 21,6±8,5 | 1,05 | 20,4±8,8[***] |
| | **No** | 15 | 102,4±77,8 | 2,28 | 69,9±29,2 | 1,55 | 45,0±26,7 | 24,8±20,6 | 1,91 | 22,7±18,5 | 1,74 | 13,0±6,7 |

[*] Statistically significant differences ($p < 0.05$) between stove heating and others.
[**] Statistically significant differences ($p < 0.05$) between non-smoking and smoking at kitchen and balconies cases.
[***] Statistically significant differences ($p < 0.05$) between nearby construction homes and non- nearby construction homes.

## 4. CONCLUSION

This study was designed to study residential indoor and outdoor levels of particle matter mass concentrations of approximately 30 homes in Ankara. At all rooms, $PM_{10}$, $PM_{2.5}$ and $PM_{1.0}$ exposures were significantly affected by indoor $PM_{10}$, $PM_{2.5}$ and $PM_{1.0}$ presumably the result of re-suspended by human activity.

The results showed living places allowing spending most of the occupant’s time had higher I/O ratios of PM, than baby’s rooms (Table 1.).

This conclusion was supported by the consistently higher indoor $PM_{10}$ concentrations as compared to baby’s rooms $PM_{10}$ levels seen at homes heated with stove (coal and wood). Furthermore, in homes where people smoke only at kitchen and balconies, the mean indoor concentrations of $PM_{10}$ and $PM_{2.5}$ were greater than those measured in homes with no smokers and smoking at balconies and doorstep. During the periods of air sampling, at least one window was ventilated with open windows.

Other important factors, such as heating with stove (coal and wood) and smoking inside the homes resulted in increased I/O ratios, which were greater than 1 (Table 6). By far the highest outdoor levels were found in homes which are close to the constructions, where the I/O ratios were approximately twice as high as in homes far away from the constructions (Table 6).

## ACKNOWLEDGEMENTS

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# ATMOSPHERIC PARTICLES AT ANTARCTIC: PAST, PRESENT AND FUTURE OF MONITORING OF BRAZILIAN ANTARCTIC PROGRAM

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## ABSTRACT

In recent years, there has been growing recognition of the importance of the Polar Regions as a result of global and regional climate effects. Antarctica is assumed to suffer minimally from anthropogenic pollution, although the concentrations of several trace gases and particles are known to be increasing over the continent. Several studies have shown that the atmospheric transport, deposit of trace elements and gaseous reactions affect the chemistry and also the biology of the oceans. As a result of the South Atlantic Subtropical High circulation, the transport of anthropogenic emissions migrates from South America toward Antarctic continent. Our research proposes to study the aerosol dispersion from Rio de Janeiro city to the Brazilian Antarctic Station at King George Island / Antarctic Peninsula, as part of the Brazilian Antarctic Program (PROANTAR). Individual Antarctic aerosol particles in the fine and coarse fractions were analysed by low-Z EPMA and the bulk of particles by EDXRF, in order to investigate the elemental composition of individual particles and bulk samples, respectively. EPMA results shows high contributions of sulphur, sea salts particles aluminosilicates and iron rich and a few soot particles. Alongside to the cruise, the elemental concentration results revealed two main groups. The first group is originating mainly from natural sources, and the second group to be related to long-range transport of anthropogenic aerosol. Meteorological observations in Antarctica pointing to a significant increase in the trend curves of the atmosphere temperature for the West Sector of the Antarctic continent and its consequences for the Albedo, the variability of sea ice, the shrinkage of glaciers and changing patterns of ocean currents. Our actual project (2010-2012) aims to improve the understanding the impact of aerosols in the Antarctic Peninsula and Continent, based on terrestrial monitoring network, associated with satellite data and numerical modeling of dispersion.

**Keywords:** Aerosol, Antarctica, Pollution

Acknowledgment: Fundação Araucária, CNPq, Capes

**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
**4th International Symposium and IUAPPA Regional Conference**
**10-13 September 2012 Istanbul -Turkey**

# $CO_2$ EMISSIONS FROM URBAN RESIDENTIAL KITCHEN OF BANGLADESH- A CFD STUDY

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## ABSTRACT

In this study, a typical kitchen has been modelled with single open door exit. Steady simulations have been performed using 3D CFD code with appropriate boundary conditions. Two heat sources are used for modelling the kitchen that resembles the double burner gas stove. The results are presented for $CO_2$ gas emission from the stove exhaust and dispersion within the kitchen space. A comparative analysis between the ventilation (natural and forced) and no ventilation conditions is also reported in this study. The four cases that were investigated had an exhaust flow rate of 0.5 m/s and 1.5 m/s for the closed vent and open vent cases respectively. The location of the breathing zone was at a height of 73 cm and at a distance of 33 cm from the center of the two burners. Very high critical zone of carbon dioxide gas concentration was observed at the plane passing the breathing zone. At this zone the calculated $CO_2$ concentration was above 6000 PPM for the close vent case. This level was significantly higher than the normal indoor air level. By applying natural ventilation for the open vent case, there was no significant reduction of the carbon dioxide level. Similar distribution of $CO_2$ concentration was observed for the case of forced ventilation with an exhaust flow rate of 0.5 m/s. However, when the exhaust flow was increased to 1.5 m/s, the $CO_2$ concentration substantially reduced to 2000 PPM in the breathing zone. In addition, this paper discusses dispersion characteristics of the pollutant in association of air flow pattern inside the kitchen space.

**Keywords:** Kitechen, Ventilation, $CO_2$ emission

# INDOOR AIR QUALITY DURING HIGH POLLUTION EVENT DAYS IN ANTWERP

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## ABSTRACT

Many studies probing the link between air quality and health have pointed towards associations between particulate matter (PM) exposure and decreased lung function, aggravation of respiratory diseases like asthma, premature death and increased hospitalization admissions for the elderly and individuals with cardiopulmonary diseases. Of recent it is, however, believed that the chemical composition and physical properties of PM may contribute significantly to these adverse health effects. As part of a Belgian Science Policy project (Health effects of particulate matter in relation to physical-chemical characteristics and meteorology) the chemical composition (elemental and ionic composition) and physical properties (PM mass concentrations) of PM were investigated, indoors and outdoors of old age homes in Antwerp. The case reported here specifically relates to high versus normal / low pollution event periods. PM mass concentrations were determined gravimetrically after collection via impaction for PM1, PM2.5 and PM10 fractions. These same samples were hence analysed by EDXRF and IC for elemental and ionic composition. During high pollution event days PM mass concentrations inside the home reached 53.5 $\mu$g m$^{-3}$ and 31.9 $\mu$m m$^{-3}$ for PM2.5 and PM1 while outside concentrations were 100.6 $\mu$g m$^{-3}$ and 46.1 $\mu$g m$^{-3}$ for PM2.5 and PM1, respectively. The V, Ni and Fe concentrations were significantly higher during non-episode days indoors. The sum of nitrate, sulphate and ammonium accounts for 49% (69% episode days and 40% non-episode days) of the total PM2.5 mass outdoors and 28% (41% on episode days and 22% on non-episode days) of the PM2.5 indoors, with similar percentages for the PM1 fraction. The mass ratio of nitrate to sulphate was considerably higher during event days (2.1 versus 1.7). Acid-base ionic balance equations point to acidic aerosols during event days and neutral to basic aerosols during non-event days. Elevated mass and elemental concentrations, together with increased acidity experienced during episode days may contribute to adverse health effects.

**Keywords:** indoor air quality, particulate matter, mass concentration, elemental composition

# DETERMINATION AND EVALUATION OF AIR POLLUTANTS IN INDOOR AIR AT CHEMICAL ENGINEERING DEPARTMENT OF HACETTEPE UNIVERSITY

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## ABSTRACT

This study aims to quantify and define the sources of volatile organic compounds including formaldehyde, several VOCs in indoor air of Hacettepe University Department of Chemical Engineering. Besides the volatile organic compounds, some inorganics like nitrogendioxide ($NO_2$), sulphurdioxide ($SO_2$) and ozone ($O_3$) have been measured. The concentrations of seasonal variations have been evaluated. VOCs, inorganics and formaldehyde were collected seperately using passive samplers for five day long. Samplers are taken from 45 points indoor including laboratories, offices and classrooms and also corridors. To see the penetration effects, three samples taken from outdoor.

Maximum toluene concentration was detected as 1339 ug/$m^3$ in a research laboratory in winter. The concentration of n-hexane changes between 0,2-15 ug/$m^3$ respectively. Ethlybenzene range values are 0,3-10,8 ug/$m^3$. Ozone concentrations varies between 44-79 ug/$m^3$ outdoors and 1-4 ug/$m^3$ for indoors.

Eventually this study indicated that; the higher concentrations of pollutants, mostly detected in research laboratories, which are diluted as soon as leaving its source because of air circulation. For the reason that in summer period doors and windows are opened regularly; the concentration values resemble each other indoors and outdoors for VOCs.

**KEY WORDS:** indoor air, VOCs, inorganics, formaldehyde, passive method.

## 1.INTRODUCTION

The definition of indoor air pollution can be described as; the pollution that has adverse health effects to humans sourced as pollutants, allergens or microorganisms. (Soysal et al., 2007). The ratio of the pollutants indoor air depends the chemical structure of construction, the activty pattern that is taken in place, the heating system or the ventilation system of the construction. Poor ventilation, using cheap fuels for heating or strong isolation systems make indoor air less healty. The exposure to the pollutants that can be counted as volatiles usually make people sick. If the complaints are sourced from the costruction of building or the materials used in, that can be expressed as "Sick Building Syndrome" (Bahadır et al.,2009).

The most important pollutants can be counted as volatile organic compounds (VOCs) which are seen both indoor and outdoor air. Benzene and toluene are released from automobiles. The volatile organic compounds also trigger ozone formation by photochemical reactions. However there are many exposure ways to pollutants, in this study only respiratory way is taken into account. Also the concentrations $C_5$-$C_{12}$ carbons including formaldehyde were measured in this study. Through the inorganics; ozone ($O_3$), nitrogendioxide ($NO_2$) and sulphurdioxide ($SO_2$) concentrations were measured. The sources of such pollutants in indoor air can be counted as ; construction materials, general and personal hygene pruducts, furniture, some human activities and penetration from outdoor air (Harper et al.,2000). The VOCs like benzene, toluene, xylene and 1,3 butadiene are sourced from traffic emissions where formaldehyde and styrene are emitted from carpets (Murrey,2001). From dry cleaned clothes; tetrachloroetylene, from chlorinated water 1,4 dichlorobenzene and from personal care pruducts styrene and tetrachloroethane can be emitted (Daisey et al.,1996).

In this study the sampling place was chosen as Hacettepe University of Chemical Engineering Department. The most important reason of the place choice is that this study will be the first in this place. There are many research laboratories with classes and offices in the department. At the same time, many different chemicals are used in scientific studies in such laboratories and in offices there are lazer printers or in classes some materials are used during lecture times which let emissions that have unhealty effects. In literature; similar studies are taken in factories where standart production takes place, in offices, at homes or in classes. In our research area there is no regular production also not regular chemicals are used. The offices, classes with research laboratories make the place differnt from a standart place. A person in deaprtment, spends approximately 8 hour/day of his time, so in this time he exposes to various concentrations of various chemicals in one day.

The target aim of the study is that to qualify and quantify of the pollutant concentrations in the department and then to calculate the unfavorable health effects to people who spend most of their time in the department. Because there is no another study has been made before, this study will be the guide similar prospective studies.

## 2.MAIN TEXT

The sampling period was realesed as two parts. Winter and summer parts compose the sampling. Summer part is 2010 June and winter part is 2011 January time

The Chemical Engineering Department of Hacettepe University places in Beytepe where it is on Ankara-Eskiseşir way 14th km far away from city center. The vicinity of the campus is become forest areas. One side there is a pulp and paper factory. The Chemical Engineering deparment is in the neighbourhood of Chemistry Department. The building age is nearly 25 years old. The floor of the building is made of concrate and the area of its is nearly 3500 $m^2$. In the research laboratories at least one hood exist. Except three of them they have not any other ventilation system. In one laboratory there exists an air conditioning system, the others has not. The heating of the building is provided by natural gas. The cleaning of the building is made daily and domestic products are being used.

The optimisation has been made to decide the sampling numbers to get pregnant results and capasity of opportinities. In figure 2.1 a sampler is seen in a research laboratory.

The samplers indoor air are placed on the respiration height and outdoor samplers are placed 1,5 m height.

The average temperature was measured 24 $^0$C in summer period and 21 $^0$C in winter.

There are many sampling methods to observe air pollutants. Because it is cheap, not require quailified person and needs small area; passive method is selected in this study. The stainless steel tubes used for organics sampling had been got from Gradko (England). However the tubes were not first hand, it is cleaned and prepared for samling firstly. The stainless steel tubes have 8,89 cm length, 6,35 cm outer diameter and they were filled with Tenax TA absorbent material. The schemmatic representation of stainless tube can be seen on Figure 2.1.

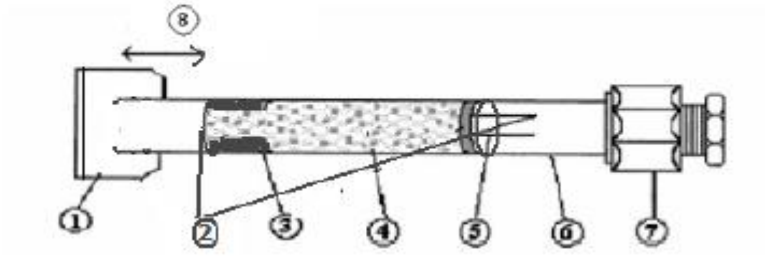

Figure 2.1 Schemmatic representation of a passive tube (Roche, 1999)

1. Diffusion cap
2. statinless stell screen
3. screen gauge (home made)
7.swagelock storage cap

4. adsorbent
5. back screen gauge
6. sample tube
8. diffusion lengt

In the study, to support the passive method, at one point, active sampling has been made in the winter period.

The analysis of VOCs sample tubes have been made on Gas Chromatograpy-Mass Spectrum System (Agilent Technologies Inc, Palo Alto, CA, USA). The analiysis of formaldehyde has been made on HPLC (Schimadzu) with UV dedector. The anaysis of inorganics have been made by Anadolu University Department of Enviromental Engineering -Eskişehir. The VOCs which concentrations have been measured can be seen on Table 2.1.

Table 2.1 Detected Volatile Organic Compounds

| **Detected Volatile Organic Compounds** | | |
|---|---|---|
| n-Hexane | Dimethylcyclohexane | 4 Ethyltoluene |
| Methylcyclopentane | Chlorobenzene | 2 Ethyltoluene |
| Benzene | Ethylbenzene | n-decane |
| Cyclohexane | m,p xylene | Benzylchloride |
| 1 Heptane | Styrene | 1,2,3 Trimethylbenzene |
| 2,2,4 Trimethykpentane | 1 nonane | 1,2 Dichlorobenzene |
| n-Heptane | o-xylene | 1 Undecene |
| 1,3 Dichloropropane | n-nonane | Undecane |
| Methylcyclohexane | İzopropylbenzene | 1,2,4 Trichlorobenzene |
| Toluene | Alpha pinene | Naphtalane |

| | | |
|---|---|---|
| 1 Octane | n-propylbenzene | Dodecane |
| Octane | Champane | Formaldehyde |

## 3.CONCLUSION

In research laboratories, solvents are being used freuently, because of this the maximum concentrations were observed as toluene, benzene and xylene . Also in the research laboratories, the concentrations are higher than other places. This can be explained with source effect. Because of strong air circulation , the concentration values become smaller. Also summer values are smaller than winter ones. The cause of this situation is in research laboratories experimental studies are denser in winter if compared with summer. The maximum toluene concentration is observed as 1339,2 ug/m3 in winter period in a research laboratory. The used solvents in research laboratories are generally toluene based, so this result is not a surprise to us. Also toluene is a dominant hydrocarbon in the atmosphere and the penetration effect can play a role in the observed higher toluene concentartion. In summer period; sampling and whitewashing was being done at the same time, as a result, in some points toluene concentration is higher in summer, than in winter period. Ethylbenzene has the potential of to convert styrene, so where average ethylbenzene concentration is 2,69 ug/m3 and styren of it is 4,38 ug/m3. The maximum benzene concentration is observed as 129,2 ug/m3 in winter period in a research laboratory. In one class, benzene is relatively high value with 42 ug/m$^3$ in winter period. That class's window is opened the general ventilation system of department and during the sampling time the door of the class is closed, this can bring about accumulation. In table 3.1 the maximum, minimum and median values of organics can be seen. In that table, N is the sample point number. ND is the "not detected" values. The minimum values of some pollutants are below zero, so these are expressed by "0".

If the source is in the ground floor, the concentration value is diluted on the upwards. However, for benzene, cyclohexane, m,p xylene, styrene and o xylene the concentration values become higher upwards. The 75% of measured concentrations of pollutants have the smaller value on the ground floor that is near to the main door. This can be explained by the dilution effect from outdoor air. The results gap between floors for benzene and toluene krustal walllis graphs can be seen on Figure 3.1 and 3.2.

The concentartions of inorganics are higher than indoor for outdoor. The concentration of ozone varies between 44-79 ug/m$^3$ , sulphur dioxide ($SO_2$) and nitrogendioxide ($NO_2$) values varies between 43-47 ug/m$^3$ for outdoors.

In this study we achieved that the qualification and quantification of mostly organic indoor air pollutants by passive sampling method. To understand the photochemical reactions and conversion factors between organics and inorganics we also measured the concentrations of some important inorganics. Because there is no similar study made before in our sampling area we will be a guide for the following studies.

Table 3.1 Statistical values of pollutants

| | N | Minimum | Maximum | Avarage | Median | Std. Deviation |
|---|---|---|---|---|---|---|
| n-hegzane | 45 | 1,00 | 134,7 | 16,96 | 10,1 | 22,9 |
| methylcyclopentane | 45 | ND | 21,7 | 3,3 | 0,1 | 6,1 |

| | | | | | | |
|---|---|---|---|---|---|---|
| benzene | 45 | ,60 | 60,2 | 10,3 | 5,7 | 12,2 |
| cyclohexane | 45 | ND | 42,8 | 9,1 | 7,0 | 8,0 |
| heptane | 45 | ND | 10,1 | 2,0 | 1,6 | 2,0 |
| trimethylpentane | 45 | ND | 6,7 | 0,6 | 0 | 1,3 |
| n-heptane | 45 | ND | 32,6 | 5,8 | 3,3 | 7,2 |
| dichloropropane | 45 | ND | 9,4 | 0,5 | 0 | 1,8 |
| methylcyclohexane | 45 | ND | 54,5 | 8,6 | 1,5 | 14,9 |
| toluene | 45 | 1,10 | 142,2 | 19,9 | 7,5 | 28,6 |
| octene | 45 | ND | 6,8 | 0,5 | 0 | 1,3 |
| octane | 45 | 15,5 | 2492,5 | 206,8 | 67,9 | 488,3 |
| dimethylcyclohexane | 45 | ND | 2,8 | 0,2 | 0 | 0,6 |
| kchlorobenzene | 45 | ND | 14,9 | 2,8 | 1,3 | 4,1 |
| ethylbenzene | 45 | 0,5 | 15,5 | 3,1 | 2,2 | 2,9 |
| m,pxylene | 45 | 0,2 | 7,7 | 1,9 | 1,8 | 1,4 |
| styrene | 45 | 0,2 | 41,0 | 7,6 | 4,1 | 9,9 |
| nonane | 45 | 0,1 | 22,2 | 8,6 | 8,6 | 4,8 |
| oxylene | 45 | 0,2 | 22,7 | 5,5 | 3,6 | 5,3 |
| n nonane | 45 | ND | 30,1 | 8,2 | 4,2 | 8,1 |
| izopropylbenzene | 45 | 0,1 | 9,0 | 2,1 | 1,2 | 1,7 |
| Alpha pinene | 45 | ND | 6,5 | 1,2 | 0,8 | 1,3 |
| n-propylbenzene | 45 | ND | 11,8 | 2,0 | 1,5 | 2,5 |
| camphen | 45 | ND | 14,6 | 2,8 | 1,6 | 3,2 |
| 4 ethyltoluene | 45 | ND | 65,4 | 28,4 | 29,5 | 16,3 |
| 2 ethyltoluene | 45 | ND | 99,1 | 20,4 | 14,0 | 20,5 |
| n-decane | 45 | ND | 7,9 | 1,9 | 1,4 | 1,9 |
| Benzylchloride | 45 | ND | 17,7 | 3,4 | 2,5 | 4,1 |
| trimethylbenzene | 45 | ND | 28,2 | 2,5 | 0 | 5,4 |
| dichlorobenzene | 45 | ND | 23,4 | 4,6 | 3,1 | 5,4 |
| undecene | 45 | ND | 23,5 | 3,2 | 1,5 | 4,4 |
| undecane | 45 | ND | 23,7 | 3,7 | 2,3 | 5,4 |
| trichlorobenzene | 45 | ND | 17,2 | 3,5 | 1,3 | 5,0 |

| | | | | | | |
|---|---|---|---|---|---|---|
| naphtaline | 45 | ND | 21,2 | 6,9 | 6,6 | 4,8 |
| dodekan | 45 | ND | 21,7 | 4,5 | 2,5 | 5,4 |
| Valid N (listwise) | 45 | | | | | |

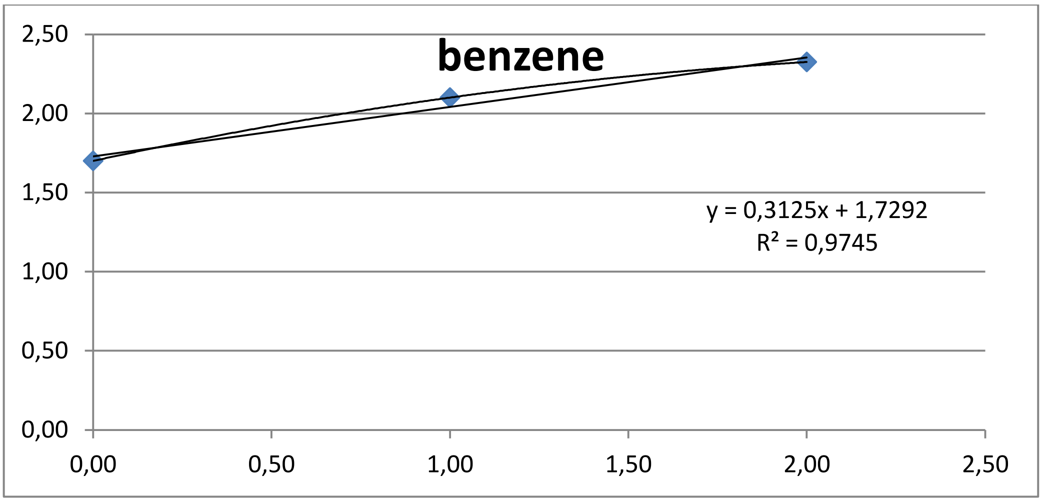

Figure 3.1 Krustal walllis graph for benzene

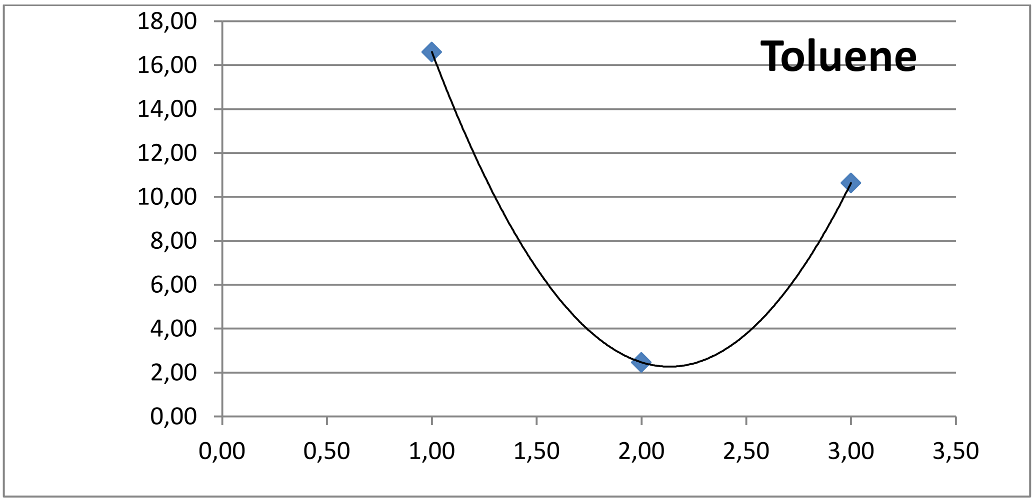

Figure 3.2 Krustal walllis graph for benzene

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# DETERMINATION OF PARTICULATE MATTER CONCENTRATIONS IN DIFFERENT MICROENVIRONMENTS

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## ABSTRACT

In this study, particulate matter (PM) sampling was carried out in two microenvironments (photocopy centers and restaurants performing cooking with charcoal, which is used frequently in Turkey) from May-2010 to May-2011 and PM samples were collected on PTFE filters with 5-stage Sioutas Cascade Impactor and Leland Legacy Pump. Mass concentrations of particles was determined and the independent sample T-test was performed on experimental data to determine the statistical significance of difference in $PM_{2.5}$ concentrations between photocopy centers and restaurants. It was concluded that $PM_{2.5}$ mean concentrations were higher in restaurants ($p<0.05$, 95% confidence interval) than $PM_{2.5}$ mean concentrations in the photocopy centers.

**Keywords:** indoor air, particulate matter, Kocaeli.

## 1. INTRODUCTION

Particulate matter causing lung and heart diseases because of its sizes (smaller than 10 µm) and organic or inorganic compositions is a crucial topic requiring serious research in order to determine the relationship between air pollution and human health. It is estimated that approximately 76% of all global particulate matter air pollution occurs indoors in the developing world (Fullerton et al., 2008). Therefore, determining the indoor particulate matter sources and taking precautions against related hazards are very important for protecting human health.

Levels of particulate matter in indoor air are a function of outdoor activities (motor vehicles, fuel usage, hazardous and municipal waste), indoor activities (smoking, cooking, photocopying, dusting, movement of people, building materials, animals, air conditioning systems and heating systems), the fraction of ambient air penetrating indoors, filtration, air exchange rate, decay rates and resuspension rates (CEPA, 1999). A US EPA particle total exposure assessment methodology (PTEAM) study showed that cooking is the second largest identified source of indoor particles (Lai et al., 2008).

Most of the studies on cooking aerosol emissions were based on a study of the influence of the cooking activities on the indoor $PM_{10}$ or $PM_{2.5}$ concentration ($\mu g/m^3$) in houses or restaurants (Gehin et. al., 2008). Restaurants can be considered to public indoor environments where many local and foreign people tend to spend a lot of their time. Therefore, a health and comfortable indoor environment of a restaurant not only enhances the enjoyment of the restaurant surroundings, but also protect the health of restaurant workers and customers from exposure to harmful air pollutants (Lee et. al., 2001). Cooking stoves fueled by coal or biomass, which are major sources of indoor combustion, release respiratory irritants such as particulate matter (PM), carbon monoxide (CO), sulfur dioxide ($SO_2$), nitrogen dioxide ($NO_2$), and organic toxins (Jie et. al., 2011).

Electronic equipments (laser printers, photocopiers and multi-task devices) are also identified as well known sources for particulate matter at the indoor environment (Horemans and Grieken, 2010). Laser printers and photocopiers can emit small amounts of dust, volatile organic compouns (VOC) and ozone. Particles emitted by laser printers or photocopiers may consist of paper dust as well as toner dust. Toners consist of very small particles (diameter is about 2 – 10 µm) and is heated up 170 $^0$C (Ewers and Nowak, 2006).

Health effects of PM have examined in numerous studies (Polichetti et. al., 2009; Langkulsen et al., 2006; Franck et al., 2011; Scapellato et al., 2009) and PM was associated with a variety of health effects such as cardiovascular and respiratory diseases (Jahn et al., 2011;). In Europe, the APHEA (Air Pollution and Health: a European Approach) studies have provided many new insights. The APHEA-2 hospital admission study showed that Hospital admissions for asthma and chronic obstructive pulmonary disease (COPD) among people older than 65 years were increased by 1.0% (0.4–1.5) per 10 µg/m$^3$ PM$_{10}$, and admissions for cardiovascular disease (CVD) were increased by about 0.5% (0.2–0.8) per 10 µg/m$^3$ PM$_{10}$ (Brunekreef and Holgate, 2002). Ewers and Nowak (2006) have described the health effects associated with operating laser printers are persistent rhinitis, sore throat, cough, asthma as well as inflammations of the eye and skin.

The objective of this study is to determine the mass concentrations of particles performed in two microenvironments; restaurants where open fire occurs and photocopy centers including photocopiers and laser printers. And the differences between two microenvironments were evaluated with in this context.

## 2. MATERIAL AND METHOD

In this study, particulate matter sampling was carried out in Kocaeli, which is the second most populated city in Turkey (TurkStat, 2011). A total of 14 sampling in restaurants and 9 sampling in photocopy centers were performed in May-2010 and May-2011. Ten-twelve hour PM samplings were performed in each sampling point. All restaurants use charcoal as cooking fuel.

Particulate matter samples were collected on Teflon filters (37-mm PTFE filters with a 2.0-µm pore size and 25-mm PTFE filters with a 0.5-µm pore size) with a 5-stage Sioutas Cascade Impactor. The filters were stored in desiccator for 24 hours before and after each sampling; and were weighted with an analytical balance (Sartorius CP225D - 0.01/0.1 mg precision). The size fractions (which is defined as Stage A, B, C, D and F) of Sioutas Cascade Impactor are >2.5 µm, 2.5-1.0 µm, 1.0-0.5 µm, 0.5-0.25 µm and <0.25 µm. For Stage A, B, C and D, 25-mm collection filters were used; and for stage F, 37 mm collection filters were used. The pump flow rate was calibrated at 9 L/min with a BIOS DryCal DC-2 calibrator. The stages of Sioutas cascade impactor was presented in Fig.1.

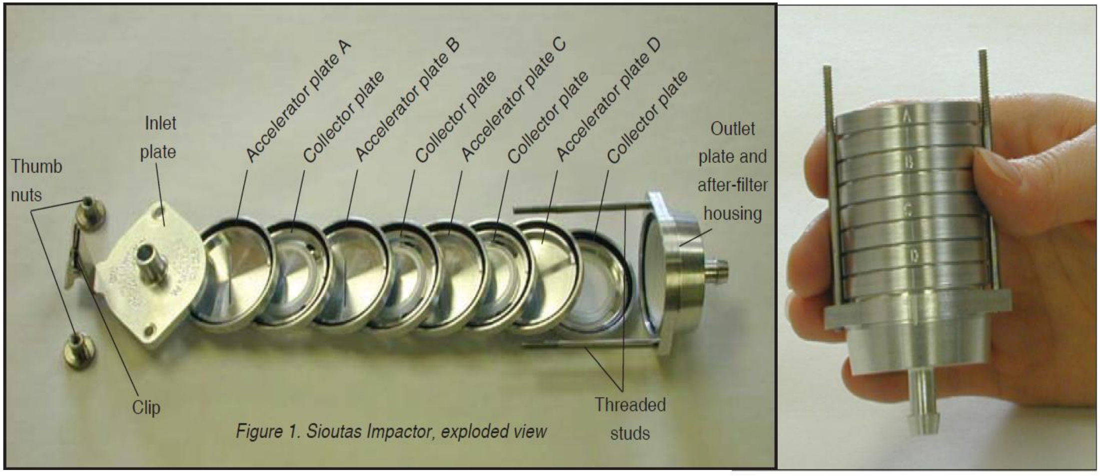

Figure 1. Stages of Sioutas Cascade Impactor

For sampling, sampling devices were placed at a height of 1.5 m and at point near the stove and the employee's workplace.

Descriptives statistics (including mean concentrations and standard deviations) and T-test were performed with SPSS software (v.14).

## 3. RESULTS AND DISCUSSIONS

Minimum, maximum, mean concentrations and standard deviations of particulate matter determined in restaurants and photocopy centers were presented in Table 1.

According to the Table 1, average particle concentrations determined in restaurants was higher than in photocopy centers. Average $PM_{2.5}$ concentrations and standard deviations were found as 235 ± 158 µg/m$^3$ and 89.1 ± 48.6 µg/m$^3$ in restaurants and photocopy centers; respectively. Lim et al. (2012) investigated $PM_{2.5}$ concentrations in restaurants performing cooking with charcoal and they determined average $PM_{2.5}$ concentration as 388.1 ± 378.8 µg/m$^3$. In another study (Baek et. al., 1997), average indoor $PM_{2.5}$ concentration in restaurants was found as 171 ± 101 µg/m$^3$.

Lee and Hsu (2007), investigated the levels of particulate matter smaller than 2.5 µm at 12 photocopy centers and the average background-corrected eight-hour $PM_{2.5}$ in the 12 photocopy centers was found as 40 µg/m$^3$.

Table 1. Descriptive statistics of particulate matter (µg/m$^3$)

| *Size Fraction* | *N* | *Minimum* | *Maximum* | *Mean Concentration±SD* |
|---|---|---|---|---|
| **Restaurants:** | | | | |
| A | 14 | 5.19 | 121.0 | 42.5 ± 31.7 |
| B | 14 | 4.81 | 41.78 | 18.6 ± 9.9 |
| C | 14 | 3.21 | 39.69 | 16.3 ± 9.5 |
| D | 14 | 9.63 | 165.0 | 69.9 ± 50.7 |
| F | 14 | 35.3 | 313.4 | 130.1 ± 102 |
| $PM_{2.5}$ | 14 | 52.9 | 559.9 | 235.0 ± 158 |
| **Photocopy Centers:** | | | | |

| | | | | |
|---|---|---|---|---|
| A | 9 | 10.10 | 40.67 | 25.9 ± 11.7 |
| B | 9 | 2.12 | 33.64 | 17.5 ± 9.1 |
| C | 9 | 4.70 | 28.03 | 13.0 ± 7.1 |
| D | 9 | 10.10 | 40.05 | 17.1 ± 9.2 |
| F | 9 | 13.73 | 120.16 | 41.4 ± 34.8 |
| $PM_{2.5}$ | 9 | 38.18 | 198.36 | 89.1 ± 48.6 |

As a result of samplings performed in restaurans, the average concentrations of particulate matter were found 42.5 ± 31.7, 18.6 ± 9.9, 16.3 ± 9.5, 69.9 ± 50.7, 130.1 ± 102 µg/m$^3$ for the five different size fractions, respectively. In photocopy centers, these values were measured as 25.9 ± 11.7, 17.5 ± 9.1, 13.0 ± 7.1, 17.1 ± 9.2, 41.4 ± 34.8 µg/m$^3$, for the five different size fractions, respectively.

When percent particle concentrations are taken into account; it was observed that particles smaller than 2.5 µm constituted 77% of total particles in photocopy centers. For restaurants, this value was 84%. Particles smaller than 0.25 µm constituted 46% and 55% of $PM_{2.5}$ particles in photocopy centers and restaurants, respectively.

The particles collected on 5 different size fraction was presented in Fig. 1 and the differences between particle concentrations in restaurants and photocopy centers were investigated. The particles collected on stage-D (0.5 – 0.25 µm) and stage-F (<0.25 µm) were found as high concentrations in selected restaurants; while the particles collected on stage-F (<0.25 µm) was found as high concentrations in photocopy centers.

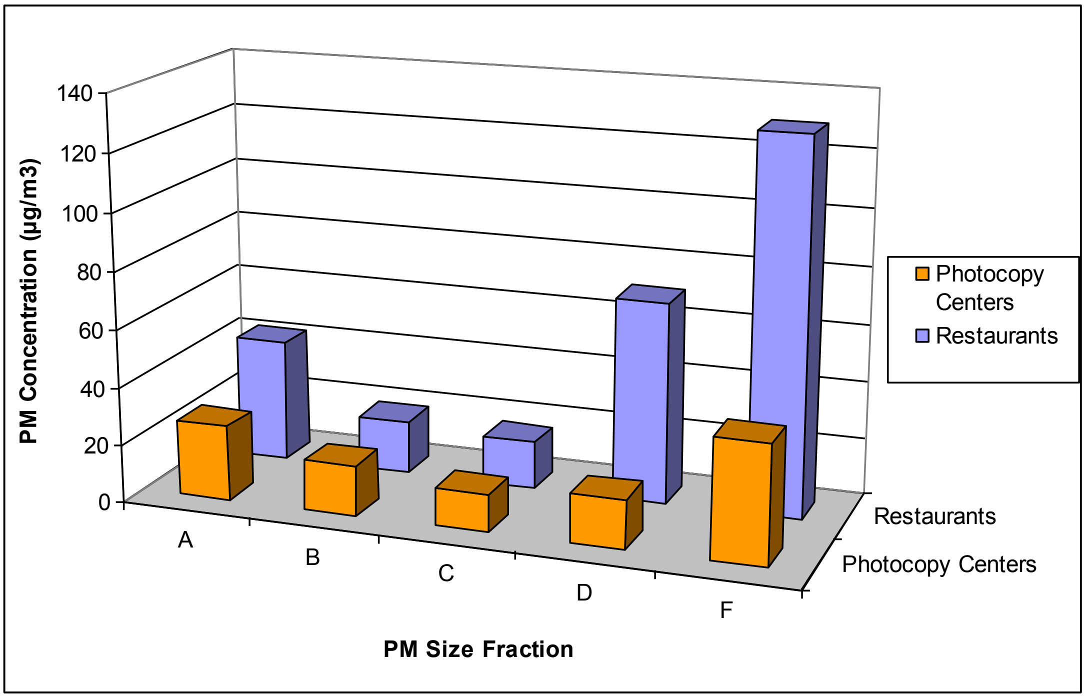

Figure 1. PM concentrations in 5 different particle size fraction

To determine the statistical significance of difference in $PM_{2.5}$ concentrations between photocopy centers and restaurants, the independent sample T-test was performed and the results were presented in Table 2.

Table 2. Independent sample T-Test

| | | **t-test for Equality of Means** | | | | |
|---|---|---|---|---|---|---|
| | | **t** | **df** | **Sig. (2-tailed)** | **Mean Difference** | **Std. Error Difference** |
| **PM$_{2.5}$** | **Equal variances assumed** | 2.676 | 21 | 0.014 | 145.96556 | 54.53684 |
| | **Equal variances not assumed** | 3.233 | 16.542 | 0.005 | 145.96556 | 45.15334 |

Because the Sig (2-tailed) value was found as 0.014 (which is below 0.05), the difference in PM$_{2.5}$ concentrations between photocopy centers and restaurants is statistically significant.

## 4. CONCLUSIONS

This study outlines the mass concentrations of particles generated from different indoor activities including cooking (with charcoal) and photocopy. Although fine particles (PM$_{2.5}$) are higher than coarse particles (PM$_{>2.5}$) in all sampling points, PM$_{2.5}$ concentration in restaurants was found higher than photocopy centers. According to the independent sample T-test, this differences was found as statistically significant ($p<0.05$, 95% confidence interval). The results suggest that concentrations of fine particles are higher than coarse particles in microenvironments where open fire occurs.

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# ILL-EFFECTS OF INDOOR AIR POLLUTION ON HEALTH OF LUCKNOW POPULATION

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## ABSTRACT

Indoor air quality is a major health concern. Humans spend most of their lives indoors, therefore, any evaluation of human health risks caused by exposure to air pollution requires a detailed understanding of the concentration of pollutants present indoors. In addition, an estimation of the contribution of outdoor pollutants to indoor pollution should be made. Increased concern over the adverse health effects of air pollution has highlighted the need for measurement of concentration of various air pollutants in urban areas, where many sources of production of air pollutants are normally monitored outdoors as part of the obligations under the National Air Quality Strategies but very little is known about air pollutants present indoors. In fact, the maximum exposure to indoor pollution causing ill-health probably occurs in the developing world as compared to the households, schools, and offices of developed countries where maximum research work and control efforts are being focussed upon. As a result, most of the ill-health effects from indoor air pollution worldwide seem to occur among the poor and most vulnerable population of developing countries. Keeping this in mind, 250 patients from ENT and pulmonary department of Sanjay Gandhi Post Graduate Insitute of Medical Sciences (SGPGIMS), Lucknow, India were asked to complete a proforma/questionnaire providing information related to their house characteristics, number of family members, different methods of collecting and storing wastes, cooking, cleaning etc. The questionnaire was aimed to obtain a real picture of patient's internal environment in general and also to get some knowledge about the problems which may have be encountered while monitoring the levels of different air pollutants . On the basis of the results obtained from the survey, 5 different monitoring sites were established in Lucknow. Concentrations of $PM_{10}$ and $PM_{2.5}$ were monitored simultaneously and the data was collected from August 2011 to December 2011. On comparison, by WHO and NAAQS standards, levels of $PM_{10}$ are found to exceed by 3 and 2 times and 2 times for $PM_{2.5}$ by WHO standards at busy roadside and urban residences respectively. Few house occupants/patients also reported irritation of eyes, lungs, throat and sinuses along with increased severity of existing lung diseases such as asthma, emphysema, pneumonia, bronchitis and risk of heart-attacks. Long term exposure to such kind of indoor pollution may lead to chronic obstructive lung disease, chronic bronchitis, increased risks of cancer and cardiovascular diseases. In absence of complete data, we cannot make any definitive conclusions but the preliminary observations suggest a higher level of $PM_{10}$ and $PM_{2.5}$ at indoors. Long term database of pollutant levels will be useful for sate and federal regulatory agencies, researchers, consultants, and the general public and thus will help decision makers to formulate and implement policies to manage and control environmental as well as indoor air pollution.

**Keywords:** Indoor air pollution; Particulate matter; Health effects

# VERTICAL AND TEMPORAL VARIATION OF THE INDOOR AIR QUALITY OF THE WORKING OFFICIES IN METU IN TERMS OF VOLATILE ORGANIC COMPOUNDS

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## ABSTRACT

Indoor concentrations of 35 volatile organic compounds (VOC) were measured at 32 sampling locations in classes, offices and corridors of the Environmental Engineering Department (ENVE) in Middle East Technical University (METU). Outdoor samples were also collected around the department, during sampling campaigns. The VOC samples were collected using passive samplers and analyzed using a GC equipped with a flame ionization detector. Two sampling campaigns, one in summer and the other one in winter were performed. Summer samples were collected between 24 and 28 May 2010, and the winter campaign was performed between 21 and 25 February 2011. Average indoor concentrations were higher than outdoor concentrations for most of the VOCs, indicating a significant contribution of indoor sources, not only solvents used in laboratories, but also emissions from paints, varnishes, insecticides, floor polishes etc., on measured VOC concentrations. Average indoor/outdoor concentration ratio (I/O) was 10.9 in winter and 3.7 in summer. Lower I/O in summer is partly due increased in ventilation. Winter indoor concentrations of VOCs were higher than their summer concentrations, except for Methylcyclopentane+2,4-Dimethylpentane, 1,2,4-Trichlorobenzene and 1-undecene. Higher winter concentrations are expected due to more effective ventilation of the building during summer months. However the group of VOCs with higher concentrations in summer samples was the ones that are strongly affected from solvent evaporation in laboratories. Vertical variation of VOCs from ground lever was also determined by placing passive VOC samplers at different floors in the Central Engineering Building (MM building), which is a 10 storey administration building, highest in the campus. Passive VOC samplers were located at 2 m (ground floor), 5 m (first floor), 8 m (second floor), 14 m (fourth floor), 17 m (fifth floor), 24 m (seventh floor) and 29 m (ninth floor) from the surface. Indoor concentrations of VOCs in MM building were significantly lower than those found in the ENVE building, due to lack of science laboratories in the MM building. Measured outdoor VOC concentrations do not show statistically significant ($p<0.05$) variation with the altitude, indicating a well-mixed atmosphere in the first 30 m and lack of strong sources at the bottom of the MM building. Unlike outdoors, concentrations of some VOCs within the building decreased with altitude ($p<0.05$). This is probably due to lack of sources within the building, except a food center at ground level and a photocopying center in the first floor. Indoor/outdoor concentration ratios of measured VOCs were >1.0 at all altitudes and for nearly all measured compounds. This also highlighted existence of indoor sources affecting organic air quality in the MM building.

**Key words:** VOCs, BTEX, T/B ratio, I/O ratio, Vertical variation

## 1. INTRODUCTION

Different definitions of VOCs are available because VOC family consists of many organic compounds which have very different properties. According to the EC Directive 1999/13/EC, VOC is defined as an organic compound whose vapor pressure is 0.01 kPa or higher at 20 $^{o}$C.

Volatile organic compounds (VOCs) are a group of air pollutants, that attracted increasing interest in last years, owing to their mutagenic effects on humans (Khoder, 2007; Parra et. al, 2006). In addition to their adverse effects on humans they also participate in the formation of ozone and other secondary pollutants in polluted atmosphere (Hoshi et al., 2008; Khoder, 2007; Parra et al., 2006). Therefore control of VOC concentrations is essential to decrease tropospheric ozone concentrations and frequency of photochemical smog formation (Yang et al., 2005).

The most important VOC sources in atmosphere are gasoline and diesel powered vehicles. However, VOCs are also emitted from other anthropogenic sources, such as, landfills, agriculture (Figueroa et al., 2009), solvents, LPG leaks and even from power plants (Barletta et al., 2005).

As people passed most of their times in indoor, human exposure will be more efefctive than the outdoor exposure. Moreover due to enforcemen of the limit values of some organic compounds in the ambient atmosphere, the concentrtaion of these compounds decreased nearly 10 fold over 15 years (Fuselli et al., 2010).

In the present study, indoor concentrations of 35 VOCs were measured at 32 sampling locations in classes, offices and corridors of the Environmental Engineering Department (ENVE) in METU. Outdoor samples were also collected around the department, during sampling campaigns. In this purpose, two sampling campaigns were performed. Summer samples were collected between 24 and 28 May 2010, and the winter campaign was performed between 21 and 25 February 2011. Moreover to examine the effect of vertical variation on VOC concentrations different stores of a 10 storey administration building was used as sampling environment.

## 2. MATERIALS AND METHODS

Volatile organic compounds were collected onto Tenax adsorbent packed stainless steel tubes and passive sampling campaign was followed for both of sampling camapings. During the sampling campaigns, passive sampling tubes were kept in the department and MM for the 5 consecutive working days (monday-friday). Collected samples were stored in the refrigiretor until the analysis.

VOCs collected on adsorbent tubes were analyzed using an Agilent 6990 Gas Chromatography (GC)-Flame Ionization Detector equipped with a Deans Switch device is used to obtain better resolution of the peaks with two different types of column that was coupled with Unity Thermal Desorption System. In the system, samples were desorbed in the thermal Desorber at 250$^{\circ}$C.

The instrument was calibrated by a standard gas mixture obtained from Environment Technology Center, Environment Canada (Ottawa, Canada). The mixture contained 148 VOCs between $C_2 – C_{12}$. Although there were large numbers of VOCs in the standard, 34 of these were regularly detected in samples. Five-point calibration curves were prepared for each organic compound and slopes of these curves were used in quantification. The stability of the calibration was checked at every analysis day by injecting one of the mid-point standards.

Precision of measurements was monitored by replicate measurements of low-level standards. Relative standard deviations for all VOCs measured in this study was <10%. In addition to precision tests and calibration checks, laboratory and field blanks and desorption efficiency of the samples were routinely measured as parts of the QA/QC program in the study.

The VOC masses measured on field blanks was <10% of average masses of VOCs collected on sample tubes. Desorption efficiency of the analysts ranged from 92% to 99% with an average of 96%.

## 3. RESULTS AND DISCUSSION

As the temporal variation of the I/O ratios of the organics were examined, winter I/O ratios of VOCs were found higher than their summer ratios, except for n-hexane, octane, styrene, isopropylbenzene and 1,3,5-Trimethylbenzene. Lower summer ratios are expected due to more effective ventilation of the building during summer months. Probably increase in the usage of the solvents and evaporation of these solvents from the laboratories into the building are the possible reasons of the higher I/O ratios for n-hexane, octane, styrene, isopropylbenzene and 1,3,5-Trimethylbenzene in summer than winter. Temporal variations of the I/O ratios of the measured organic compounds are given in Figure 1.

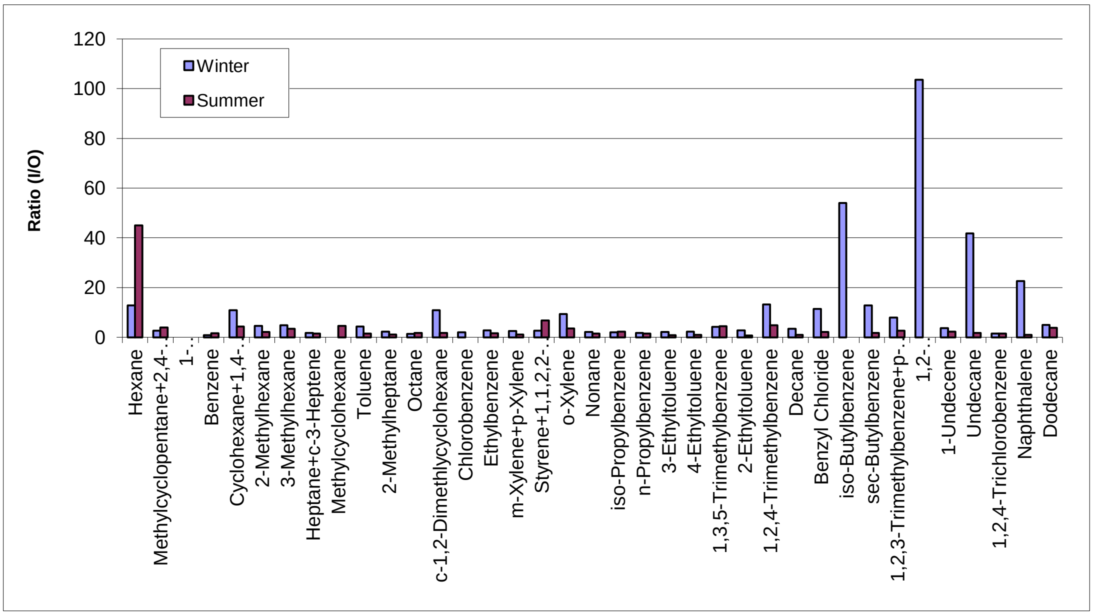

**Figure 1.** Temporal variation of the I/O ratios of the measured organic compounds in ENVE

Total concentrations of the typical organic compounds are given in Figure 2. As can bee seen from the figure, in winter total concentration of the aromatic group is nearly three times higher than the summer one. Same situation was also observed for the BTEX. However, for another groups namely, chlorinated compounds, alkanes and alkenes any significant variation could not be observed.

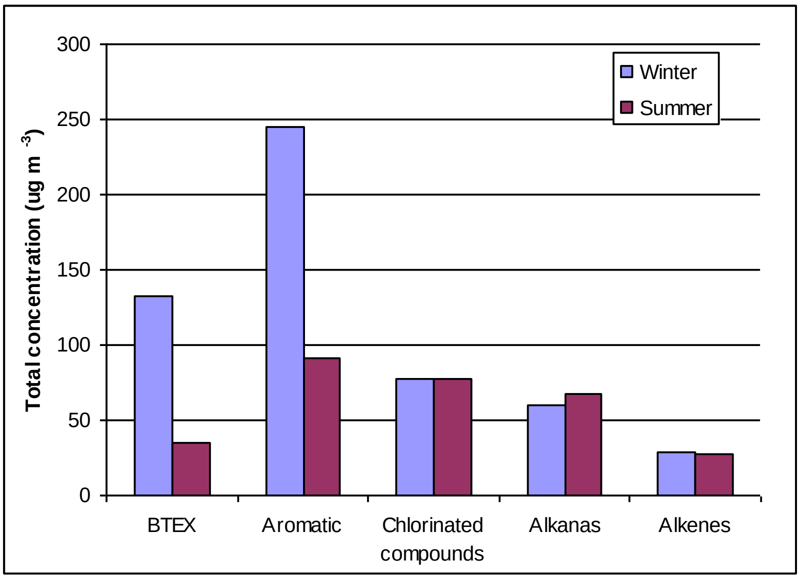

Figure 2. Temporal variation of the aromatic groups in ENVE

For the identification of the vertical variation of the organic compounds in the campus, a sampling campaign was also performed. Passive sampling tubes were also placed into different offices of the MM building at different stores. This campaign was performed between 28 February and 4 March 2011. Characteristics of the offices and sampling points are given in Table 1.

Table 1. Summary of the office characteristics for the MM Building

| **Floor Level** | **0th** | **1st** | **2nd** | **4th** | **5th** | **7th** | **9th** |
|---|---|---|---|---|---|---|---|
| **Height (m)** | 2 | 4,70 | 7,60 | 13,50 | 16,50 | 23,70 | 29,20 |
| **Floor Area ($m^2$)** | 64,23 | 37,14 | 27,53 | 24,63 | 51,05 | 35,23 | 26,98 |
| **Number of Personnels** | 3 | 2 | 1 | 1 | 3 | 1 | 1 |
| **Average Room Temperature** | 23 °C | 22 °C | 21 °C | 21,5 °C | 21 °C | 22 °C | 22 °C |
| **Average Humidity** | % 39 | % 28 | % 28,5 | % 36 | % 31 | % 30 | % 29 |
| **Floor Material** | Vinyl Floor Covering | Parquet | Parquet | Parquet | Parquet | Parquet | Parquet |
| **Ventilation** | Natural | Natural | Natural | Natural | Natural | Natural and AC | Natural |
| **Smoking** | No | No | No | No | No | No | No |
| **Exposure Times (min)** | 6010 | 6006 | 6000 | 6010 | 5992 | 5998 | 5985 |

The ratio of the indoor concentrations to outdoor concentrations of VOCs, reveals the relationship between outdoor and indoor sources. If Indoor/Outdoor value >1; there might be some indoor pollution sources, and if < 1 that means component is generated due to outdoor sources.

The alteration of the I/O ratio of the organics with altitude is also analyzed in this study. This relationship also might be an indicator of the source of a compound. If this ratio gets smaller with respect to altitude the reason can be either the reduction of indoor concentrations which means the origin of source is in lower floors; or the increase in outdoor concentrations which means the penetration of outdoor pollutants at the upper floors are higher.

According to the results, I/O values of Hexane, 3-Methylhexane, Toluene, Octane, c-1,2 Dimethlycyclohexane, Ethylbenzene, m-Xylene+p-Xylene, 1-Nonene, o-Xylene, n-Propylbenzene, 1,2,4-Trimethylbenzene, Decane, Benzyl Chloride, 1,2,3-Trimethylbenzene+p-Cymene, 1,2-Dichlorobenzene+Limonene, 1-Undecene, Undecane, Naphthalene > 1. For Methylcyclopentane+2,4-Dimethylpentane, Benzene, Nonane, 1,2,4-Trichlorobenzene and Hexachlorobutadiene, I/O <1. Consequently, for most of the organic compounds, indoor levels exceed those outdoors due to dominant sources of VOCs indoors .

Probably due to good mixing of the air within the 30 m, any statistically significant ($p<0.05$) variation could not be observed for all measured organics. Just for benzene a small decrease were observed up to second floor (Figure 3). However, after that point concentration stayed nearly same. Probably due to traffic exhaust and parking area which are very close to building very high concentrations were observed up to 8 m.

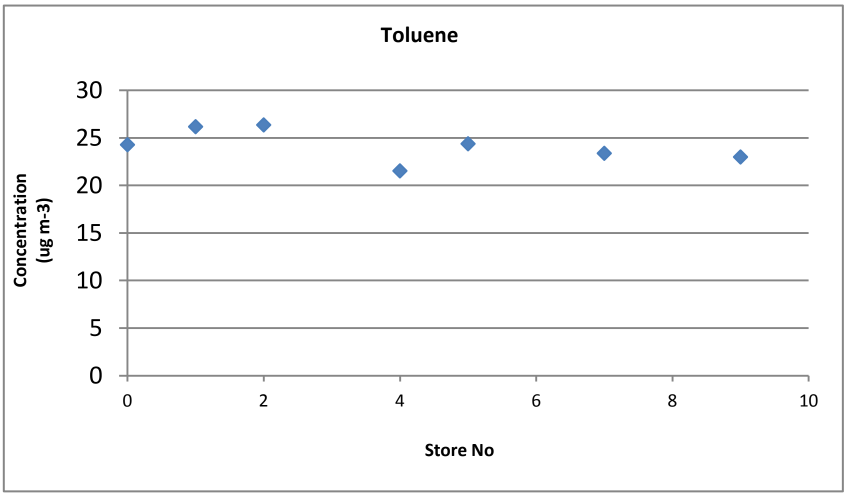

Figure 3. Variation of the outdoor VOC concentrations with altitude

However, the concentrations of the some of the compounds; toluene, octane, m,p-xylene and n-nonane decreased with altitude within the MM building ($p<0.05$). This is probably due to lack of sources within the building, except a food center at ground level and a photocopying center in the first floor.

## 4.CONCLUSION

The VOC level of the ENVE building was found than the MM building. Indoor concentrations of the nearly all measured compounds were found higher than the outdoor concentrations. In winter season higher I/0 ratios were observed as compared to summer season. Up to 30 m, any significant variation could not be observed for the measured VOC compounds in METU campus.

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# INDOOR/OUTDOOR CONCENTRATIONS OF POLYCYCLIC AROMATIC HYDROCARBONS AND PARTICULATE MATTER, SEASONAL VARIATION IN A SEMI ARID REGION OF RURAL INDIA

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## ABSTRACT

Twenty-three Polycyclic aromatic hydrocarbons (PAHs) and $PM_1$, $PM_{2.5}$ and $PM_{10}$ Particulate mass concentrations were measured in a semiarid region of rural India during winter, summer and rainy season (November 2008 - September 2009). The simultaneous indoor and outdoor PAHs were collected by using XAD-2 resin tubes (600 mg) for gaseous phase PAHs and PTFE filter paper (37 µm dia) for particulate PAHs. The individual PAHs were identified by using a gas chromatograph with mass spectrometry detector (GC/MS). For Particulate mass concentrations Grimm aerosol spectrometer was used. The mean concentration of $PM_1$, $PM_{2.5}$ and $PM_{10}$ in indoor air was 96.98, 136.55 and 229.51 $\mu g/m^3$, whereas in outdoor it was 110.32 $\mu g/m^3$ ($PM_1$), 148.51 $\mu g/m^3$ ($PM_{2.5}$) and 217.85 $\mu g/m^3$ ($PM_{10}$). The concentration of TPAHs in indoor was 1324.12 $ng/m^3$ with an average concentration of 77.88 $ng/m^3$ and in outdoor air it was 1627.04 $ng/m^3$ with an average of 73.95 $ng/m^3$. The total concentration of PAHs in winter season was 53.19%, 48.28% higher in indoor and outdoor from summer season. From rainy season it was 162.58% (indoor), 167.56% (outdoors) higher. Monthly and seasonal variations of coarse and fine particulate matter have also been studied. Significant seasonal variations of particulate pollutants were obtained using the daily average particulate concentrations. The two, three and four rings PAHs were predominantly in vapor phase while the five and six rings PAHs were primarily associated with the particulate phase. Among the 23 studied PAHs, naphthalene was the abundant PAH contributed 29-55% to the sum of the total PAHs concentration. The average B(a)P-equivalent exposure, calculated using Toxic equivalent factors (TEFs) was 16.24 $ng/m^3$ in indoor and 41.46 $ng/m^3$ in outdoor air. Factor analysis revealed that in indoor sources of PAHs were oil fumes, smoking and incense burning whereas in outdoor PAHs mainly generated from biomass burning, cooking activities and diesel exhaust.

**Keywords**: Rural India, Indoor/outdoor air, Particulate Matter, PAHs, Seasonal variation.

AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES
4th International Symposium and IUAPPA Regional Conference
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# WET DEPOSITION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN SEMI-URBAN ATMOSPHERE

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## ABSTRACT

In this study, the wet depositions of 18 PAHs were investigated for the term of February-June 2010 in Atatürk University. Manually controlled precipitation collection container was used for sampling. The highest PAH concentration was measured as 966,9 ngL$^{-1}$ for the CcdP, while the lowest concentration was 1,7 ngL$^{-1}$ for the Ant. It was observed that 48% of PAH compounds were in the non-dissolved phase, while 52% of them were in dissolved phase for all samples. Furthermore, that the values of wet deposition in winter season were higher than summer season pointed that the effective source of PAH in winter season was domestic heating.

**Keywords:** Air pollution, Wet deposition, Passive sampling, Polycycling aromatic hydrocarbons, Erzurum.

## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are one of the substantial air pollutants that studied intensively in recent years because of the toxic effects. The PAH is released into the atmosphere from natural and anthropogenic sources. Forest fires and volcanic eruptions can be shown as natural resources of the PAH, also anthropogenic sources is identified as motor vehicles, domestic heating, power generation plants and industrial processes. (Wu et al., 2012; Demircioglu et al., 2011; Moon et al., 2006).

Even the low concentrations of PAHs are carcinogenic, mutagenic and toxic indications effects (Nie et al., 2012). PAH's carcinogenic effects on humans have case high especially for benzo [a] anthracene, chrysene, benzo [b, k] fluoranthene, benz [a] pyrene types. The amount of the PAH compounds which is available in the form of gas phase in the atmosphere or adsorbed to particulate matter depends on vapor pressure compound, atmospheric temperature, PAH concentration, the nature and quantity of material (Esen et al., 2008). PAH compounds are usually found in the gas phase, but when molecular weight increase, concentration in the gas phase is decreasing. Also according to this raise, the concentration of adsorbed is increasing in the particulate matter as well (Wang et al., 2011).

The PAH compounds which is available in the form of gas phase in the atmosphere or adsorbed to particulate matter are accumulation to any surface with the oxidative and photolytic reactions (water, soil, etc.) by the way of atmospheric deposition that has natural cleansing mechanism (dry and wet deposition). Wet deposition, that one of the atmospheric deposition mechanisms is the removal process from the atmosphere by means of hydrometeors and collected using various collection methods to investigate the wet deposition of PAHs, samples were collected from rainfall (Bayraktar and Turalıoğlu, 2004). There are many different sampling techniques (manual and automatic devices) in the literature.

In this study, PAH's wet deposition investigated by using manual precipitation sampling in the city atmosphere of Erzurum during February to June of 2010. Manually controlled rainfall collection containers made of stainless steel was used as a wet deposition sampler. Collected samples were analyzed in the Gas Chromatography-Mass Spectrometry (GC-MS) instrument after passed through the appropriate stages of extraction and cleanup.

## 2. MATERIALS AND METHODS

Erzurum is located in the eastern part of Turkey and is one of the most important winter tourism centers in the country. It is surrounded by high mountains. The city center area is 52.8 $km^2$ with the population of 402570. At an altitude of 1950 m, Erzurum is one of the coldest cities of Turkey. As a consequence, home heating is required for at least 6 months during year. Because of limited industrial development, in the city the main sources of air pollutions are domestic heating and urban traffic.

Wet deposition samples were collected in the Atatürk University (Erzurum, Turkey) campus during February-June 2010 period. The location of the sampling point and sampler is depicted in Figure 2.1. The campus is in a suburban area, approximately 1 km from the city center. The sampler was located at the roof of the observatory at approximately 2,5 m from the surface.

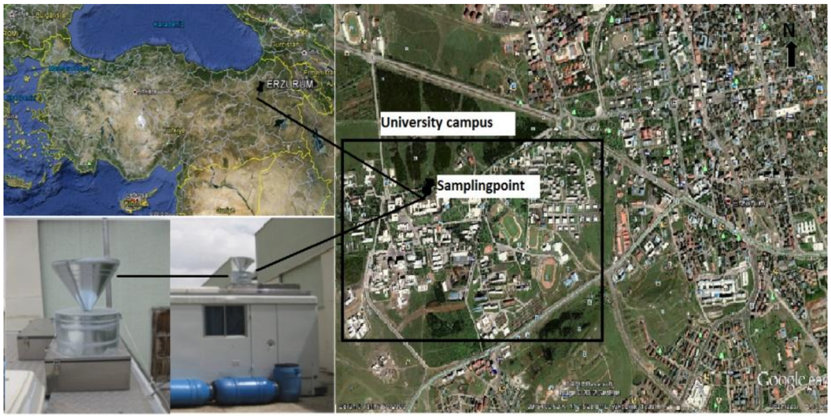

**Figure 2.1.** Sampling area

Manually controlled rainfall collection containers were used for the rain sampling. A rainfall collection container which is made of stainless steel does not disrupt the chemistry of precipitation and also container is composed of two apparatuses (see Figure 2.2). While the top cover which has funnel-shaped providing to collect an effective rainfall samples, the lower part that is in the form of a round cylinder allow to minimal evaporation of the collected rainfall sample.

**Figure 2.2.** Manually controlled precipitation collection container

Containers which are open to the atmosphere have been checked as a daily routine before the rain. The containers were cleared in each control with the hexane and distilled water to prevent from dry sedimentation and contamination that may occur from external factors. During the rain sampling period, daily meteorological data were obtainable from www.meteor.gov.tr. during sampling period. The meteorological data and physical properties of precipitation samples is given in the Table 2.1.

**Table 2.1.** The physical properties of precipitation samples and average meteorological data of sampling days.

| Date | Precip. (pH) | Precip. V (mL) | Temper. (°C) | Pressure (mb) | Wind direction | Wind speed (m/s) |
|---|---|---|---|---|---|---|
| 04.02.2010 | 6,47 | 3200 | -3,9 | 820,1 | W | 1,3 |
| 11.02.2010 | 7,18 | 100 | 6,6 | 826,3 | WSW | 2,3 |
| 15.03.2010 | 7,07 | 2250 | 7,6 | 812,6 | SW | 5,2 |
| 30.03.2010 | 6,54 | 2500 | 1,6 | 821,7 | E | 2,2 |
| 31.03.2010 | 6,62 | 600 | 1,2 | 822,6 | WSW | 3,5 |
| 07.04.2010 | 6,47 | 450 | 5,9 | 817,7 | E | 3,9 |
| 12.04.2010 | 6,61 | 750 | 6,6 | 815,1 | NE | 3 |
| 13.04.2010 | 6,64 | 800 | 1,6 | 819,6 | W | 3,2 |
| 19.04.2010 | 5,96 | 725 | 7,6 | 825,1 | SSE | 1,3 |
| 23.04.2010 | 6,16 | 1390 | 4,7 | 823,5 | ENE | 3,9 |
| 28.04.2010 | 6,17 | 620 | 6,6 | 822,2 | E | 6,2 |
| 29.04.2010 | 6,25 | 1300 | 6,1 | 820,2 | E | 2,7 |
| 03.05.2010 | 6,28 | 690 | 8 | 820 | W | 3,9 |
| 11.05.2010 | 6,36 | 1650 | 10 | 822 | NE | 1,8 |
| 12.05.2010 | 6,6 | 830 | 11 | 823 | E | 1,6 |
| 08.06.2010 | 6,44 | 210 | 19 | 819,8 | S | 1,3 |
| 15.06.2010 | 6,72 | 675 | 15 | 822,9 | S | 1 |
| 17.06.2010 | 6,62 | 395 | 13 | 823,5 | S | 2 |
| 18.06.2010 | 6,58 | 210 | 16 | 824,7 | WSW | 2,3 |

Before sampling, glass bottles were used to bring the collected precipitation samples to laboratory and also all bottles are exposed to four-stage washing operation. Washed glass bottles if sample collection dried in oven at 50 °C. Collected precipitation samples put that glass bottles and made pH and conductivity measurements. Precipitation samples stored in the refrigerator at -180 degrees until the extraction operation.

## 3. RESULTS

Precipitation samples (snow, rain) were collected from Erzurum Ataturk University campus near the city center between February-June 2010. Precipitation sample quantities ranged between 0.1 L and 1.30 L. 18 PAH component were analyzed by using CS-MS in the 19 precipitation samples collected. Volume correction is done for the precipitation samples during the sampling period and their descriptive statistic properties are given in Table 3.2, According to the results shown in the Table 3.2, the highest concentration of PAH were measured CcdP compound as 966.9 ngL$^{-1}$, the lowest concentration was measured for Ant as 1,7 ngL$^{-1}$.The same change was observed for each of the two compound`s maximum and minimum values ( max CcdP =6715,5 ngL$^{-1}$, min Ant =1 ngL$^{-1}$).

**Table 3.2.** Descriptive statistical properties of collected precipitation from the sampling point at Ataturk University campus, (ngL$^{-1}$)

| | Number data | Average | Standard deviation | Max. | Min. |
|---|---|---|---|---|---|
| Acy | 37 | 122,5 | 170,2 | 703,9 | 7,60 |
| Ace | 37 | 103,6 | 148,7 | 618,2 | 5,30 |
| Flu | 37 | 69,60 | 99,70 | 416,1 | 3,80 |
| Phe | - | - | - | - | - |
| Ant | 3 | 1,7 | 1,10 | 3,00 | 1,00 |
| Flt | - | - | - | - | - |
| Pyr | - | - | - | - | - |
| CcdP | 37 | 966,9 | 1726,3 | 6715,5 | 36,70 |
| BaA | 37 | 356,4 | 635,2 | 2470,0 | 13,50 |
| Chr | 37 | 217,6 | 385,5 | 1495,0 | 8,20 |
| BbF | 37 | 167,5 | 120,9 | 447,90 | 17,90 |
| BkF | 37 | 127,8 | 92,10 | 341,70 | 13,60 |
| BeP | 37 | 127,5 | 91,80 | 340,40 | 13,60 |
| BaP | 37 | 186,5 | 134,9 | 499,60 | 20,00 |
| Ind | 37 | 278,9 | 201,9 | 747,80 | 29,90 |
| DahA | 37 | 311,9 | 225,8 | 836,40 | 33,40 |
| BgP | 37 | 201,9 | 146,2 | 541,30 | 21,60 |
| Anth | 37 | 389,4 | 282,0 | 1044,2 | 41,70 |

On the other hand in the collected precipitation samples 48% of the total PAH compounds were observed as undissolved phase, remain 52 percent was in dissolved phase. Rates of dissolved and undissolved phrase for each compound of PAH are also shown in Figure 3.4.

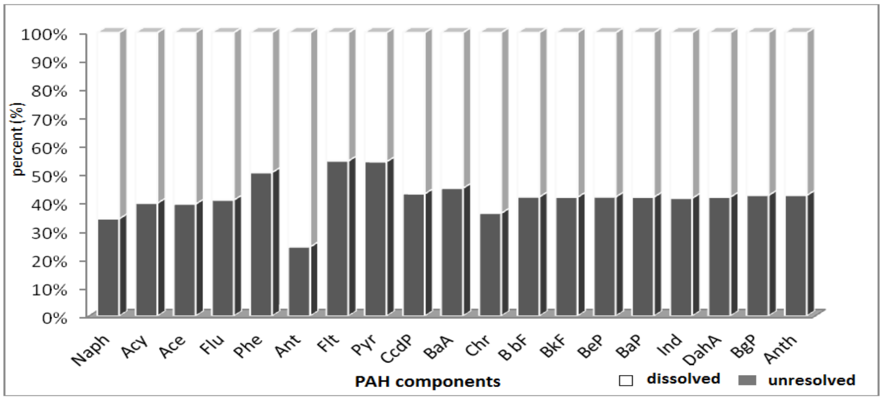

**Figure 3.4.** Rates of dissolved and undissolved phase of PAH components in the university precipitation samples

Monthly and seasonal variations of PAH components are very important in terms of air quality and pollution exposure. The temporal trend of total concentrations (soluble + insoluble PAH) of 3 PAH compound obtained (Ace, Baa, Anth) from the sampling point which is believed to represent semi-urban area are shown in the Figure 3.5.

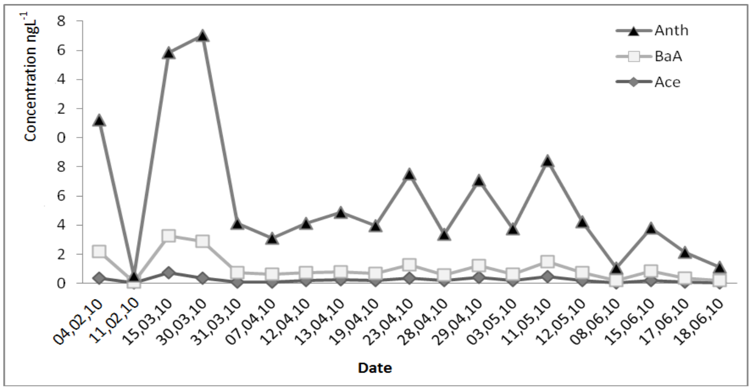

**Figure 3.5.** The temporal trend of three PAH compound for the observed precipitation in the sampling point.

As seen from Figure 3.5, PAH compounds are observed in the higher concentrations for the winter period (February - April 15), concentrations gradually decreasing in the summer period (15 April-June).On the other hand before the completion of atmospheric loading by air pollutants, a concentration decrease for each PAH component was observed in the collected precipitation samples taken between very short periods. This also shows the effect of atmospheric wet deposition to the cleaning the atmosphere in urban and rural areas.

Atmospheric PAH compounds can be sources of heating, traffic and industrial in urban areas. Methods that depending on various statistical bases (PMF, FA, CMB, Diagnostic ratios and so on.) are available for resource survey of PAH components. In this study, resource survey was made using the diagnostic ratios of collected precipitation that is specified in the literature and shown in Table 3.4.

**Table 3.4.** The diagnostic rates of PAH component for the sampling point of University

| **Emission Source** | **Flt/Flt+Pyr** | **BaP/BgP** | **BaA/BaA+Chr** | **BaA/Chr** | **Ind/BgP** | **Ind/Ind+BgP** |
|---|---|---|---|---|---|---|
| Traffic | - | 0,3-0,78[a,b] | - | 0,63[b] | - | - |
| Petrol | 0,44[h] | 0,3-0,4[d] | <0,5[h] | 0,28-1,2[c,d] | 0,4[e] | 0,09-0,22[h] |
| Coal | >0,5[h] | 0,9-6,6[a] | >0,5[h] | 1-1,2[c,f] | | 0,57[h] |
| Diesel | 0,39[h] | 0,46-0,8[f] | 0,38 | 0,17-0,36[d,g] | 1[e] | 0,35[h] |
| University winter (PM+Filtrate) | - | 0,92 | 0,62 | 1,64 | 1,38 | 0,58 |
| University Summer (PM+Filtrate) | - | 0,92 | 0,62 | 1,63 | 1,38 | 0,58 |

([a] Daisey et al., 1979; [b] Harrison and Smith, 1996; [c] Gschwend and Hites, 1981; [d] Rogge et al., 1993; [e] Caricchia et al., 1999; [f] Masclet et all., 1987; [g] Khalili et al., 1995; [h] Yunker et al., 2002)

As shown in diagnostic rates, Coal, diesel, and gasoline were mainly contributed as sources of PAH in the university campus. In this study shows that the reason of the observed coal was domestic heating in the city center of Erzurum. It was included that diesel engines passenger buses used in urban transportation and heavy vehicles used for carrying loads such as truck and van are important source of PAH. As the sampling site is located when the short distance to areas that high population density takes into consideration, coal and the natural gas combustion is expected as a first factor for keep PAH concentration. In addition, due to of Erzurum, the coal is used extensively for many years, but in recent years there are turn to meteorological contation to the natural gas in the city.

Mean of the PAH components obtained from the collected precipitation in the city center of Erzurum are taken and the results compared with the results of studies that conducted in rural areas. All findings are shown in Table 3.5.

**Table 3.5.** Comparison of average precipitation findings in the city center of Erzurum with the literature value.

| **PAH (ngL$^{-1}$)** | **This study** | **Taishan China (a)** | **Lake Balaton, Hungary (b)** | **Gdansk, Poland (c)** | **Gebze, Turkey (d)** |
|---|---|---|---|---|---|
| Acy | 704-8 | - | - | - | 1520-170 |
| Ace | 618-5 | - | - | - | 1380-150 |
| Flu | 416-4 | 65.36-1.65 | 150-9.1 | 354-15 | 1820-180 |
| Phe | - | 102.86-6.15 | 451-43 | 3396-5 | - |
| Ant | 3-1 | 15.53-0.91 | 45-0.4 | 310-5 | - |
| Flt | - | 46.39-1.47 | 210-29 | 8200-11 | 2230-180 |
| Pyr | - | 34.60-1.36 | 431-21 | 4000-7 | 1930-110 |
| CcdP | 6715-37 | - | - | - | - |
| BaA | 2470-14 | 31.55-0.30 | 89-1.8 | 10000-5 | 10620-1100 |
| Chr | 1495-8 | 20.83-0.51 | 83-1.2 | 8000-5 | 1440-90 |
| BbF | 448-18 | 16.06-0.43 | 143-3.8 | 12800-11 | 1620-120 |
| BkF | 342-14 | 30.54-0.34 | 111-0.4 | 2500-0,52 | 1060-110 |
| BeP | 340-14 | - | - | - | - |
| BaP | 269,4 | 31.26-0.47 | 147-2.2 | 573-0,34 | - |
| Ind | 748-30 | - | - | - | - |
| DahA | 836-33 | 10.80-0.95 | 15-2,5 | 814-0,4 | 4570-200 |
| BgP | 542-22 | - | - | - | - |
| Anth | 1044-42 | - | - | - | - |

((a) Wang et al., 2010; (b) Kiss et al., 2001; (c) Dunajska et al., 2006; (d) Burcu Binici, 2008).

As seen from Table 3.5, according to result of study in Erzurum university campus, CcdP compound is observed as the most dominant compound with the max 6715, min 37 NGL$^{-1}$ concentration value, also for the same region Ant compound has the minimum value with max 3, min 1 NGL$^{-1}$ values. When the atmospheric PAH composition for the Erzurum urban atmosphere are compared with the intensive industrial urban areas (the province of Poland and Turkey Gebze) the results shows that the rates are low in the Erzurum urban. But PAH concentrations in Erzurum city are higher than in some rural areas (i.e. Mount Taishan China).

## 4. DISCUSSIONS

18 PAH components have been analyzed in the 19 pieces of collected precipitation samples taken from the city center of Erzurum (semi-rural, Atatürk University Campus) between February-June 2010. In this study, CcdP compound was observed as the dominant component and the maximum and minimum concentration value was measured as 6715.5 and 36.7 NGL$^{-1}$ respectively. On the other hand, for this region, Ant compound has the lowest value and its max. and min. concentration values are observed as 3 and 1 ngL$^{-1}$.

When temporal variations of PAH concentrations in precipitation samples are investigated, there are a decreasing trend towards summer months from winter months for PAH concentrations. In this study, collected PAH values are observed lower than values given in the literature in urban areas, also higher than the values in the rural fields. Considering the precipitation composition, although usage of natural gas increased in recent years in the Erzurum, PAH values are higher than most literature values. Also when in view of the atmospheric PAH's, this study determine that motor vehicles can an important factor for the environmental risk related to toxic air pollution.

According to the study results, reducing of coal consumption, acceleration of transition to natural gas, encouraging to the public transport, increasing environmental awareness and transition to renewable energy are some important solution of reducing the PAH pollution.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# A STUDY ON THE SEASONAL VARIATION OF CARBON COMPONENT IN THE SUBWAY PARTICULATE MATTER(PM)

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## ABSTRACT

The subway is one of the major transportation systems South Korea being used by people. Lots of particles are generated during the subway operation. Authors need to understanding the composition of particles in order to reduce the particle. In this study, sampling and analyzing the carbon component of particles in the subway to find out the seasonal characteristics. The measurement was performed to collect particles at the “Mia-samgeori” subway station. Particles were collected outside, at the platform, and subway’s tunnel. The measurement was conducted in spring, summer, fall and winter for pre-schedule periods. Particles were collected by the Mini Volume Air Sampler at the platform and outside. Particles were collected by Particle Mass Samplers at the subway’s tunnel. Quartz filters were used for sampling. Particles were collected on the filter and analyzed for the carbon component using Thermal/Optical Carbon Analyzer. NIOSH 5040’s TOT (Thermal/Optical Transmittance) was applied to analysis method.

**Key Words:** subway, environment, carbon component, particle,

## 1. INTRODUCTION

The subway is a means of transportation used by many people. About more than 4.8 million people use it in Seoul (Seoulmetro, Smrt., 2012). But several problems are generated by active and frequent movement of passengers and trains. Among them, scattering of particles by train operation and particles didn’t go out the tunnel seem to have a great impact on the concentration of particles in the subway environment.

Carbon component is the major cause to impair visibility and transports harmful materials to long distance, causing health problems to human body (Bjorseth et al., 1979). Carbon component can be exposed to people in case that polluted air comes into the subway or pollutants exist. Because the subway relies upon ventilating system for air circulation.

Therefore, People has focused on the environmental issues of the tunnel and it is asked to prepare an effective management plan to reduce particles in the tunnel. In this respect, it is thought that analyzing the components of particles should be attempted for the reduction of the particles.

Accordingly, in this study, the authors try to investigate the seasonal characteristics of the carbon components of PM10 and PM2.5 at the Site-A(outside), Site-B(platform) and Site-C(tunnel).

## 2. MAIN TEXT

### 2.1. Periods and Sampling

This study was carried out to investigate the carbon component in PM 10 and PM 2.5. The sampling point is at the Miasamgeori station in Seoul Metro line 4. It also measured in each season and site to analyze the characteristics of particles in the subway station.

Table 1. shows the conditions for analyzing the characteristics of particles in subway station.

Table 1. The configuration of sampling sites and periods

| Area | Miasamgeori Station of Subway Line 4 in Seoul | |
|---|---|---|
| Site | Outside | Site-A |
| | Platform | Site-B |
| | Tunnel | Site-C |
| Periods | Spring | 2010.04.21 ~ 2010.04.28 |
| | Summer | 2010.07.13 ~ 2010.07.21 |
| | Fall | 2010.10.12 ~ 2010.10.19 |
| | Winter | 2011.01.11 ~ 2011.01.17 |
| Filter | Quartz filter (Whatman co.,) | |

Table 2 shows the sampler's name, sampling flow, sampling time of Site-A, Site-B and Site-C

Table 2. The summary of installed samplers at each sampling site

| Site | Installed Sampler | Flow rate (L/min) | Sample time (hour) | Remarks |
|---|---|---|---|---|
| Site-A (Outside) | Mini volume air samplers (Model 4.1, Airmetrics co., USA) 2ea | 5 | 24 | PM10, PM2.5 |
| Site-B (Platform) | Mini volume air samplers (Model 4.1, Airmetrics co., USA) 2ea | 5 | 24 | PM10, PM2.5 |
| Site-C (Tunnel) | Particle Mass Samplers (Model PMS-102, APM Eng, CO., Korea) 2ea | 16.7 | 24 | PM10, PM2.5 |

## 2.2. Analytical Method

For carbon analysis, the authors used the carbon analyzer, (Sunset Laboratory Inc). on the basis of TOT(Thermal/Optical Transmittance) method. This analyzer can increase and decrease temperature by step and quantify OC and EC in accordance with NIOSH 5040 protocol (NIOSH, 1996). Table 3 shows the heating conditions.

Table 3. The heating conditions of the carbon analyzer in NIOSH 5040 protocol

| NIOSH-OC (Helium) | NIOSH-EC (2% $O_2$ in Helium) |
|---|---|
| 250℃, 30sec | 650℃, 1min |
| 500℃, 30sec | 750℃, 1min |
| 650℃, 1min | 850℃, 1min |
| 850℃, 1.5min | 940℃, 2min |

The analysis method is as follow. The sample is cut to 1 x 1.5 ㎠ and placed into the oven. The oven is heated up by helium and oxygen to convert carbon into methane. And then FID detection after the analysis of the sample is done, a certain level of methane is injected to check the sensitivity and carry out modification.

## 2.3. Results and Discussions

Figure 1 and Table 4 show the result of the analysis on mass concentration of carbon in PM10 and PM 2.5 by season during sampling periods.

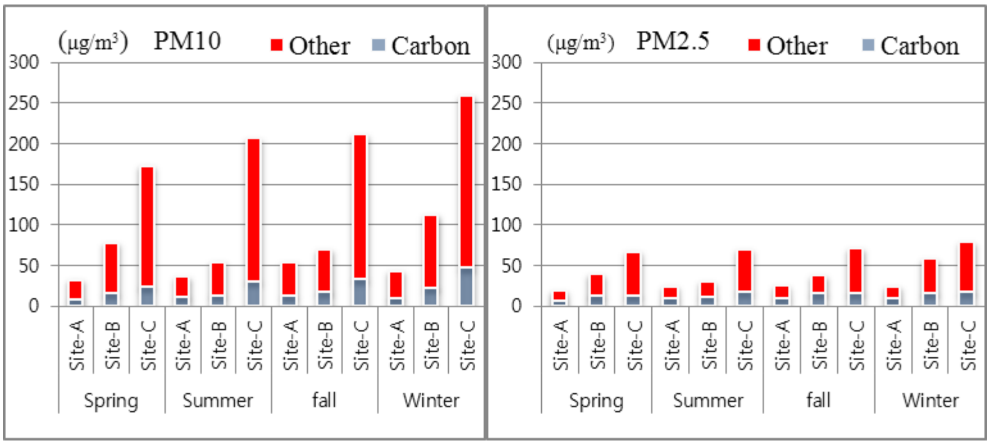

Figure 1. Carbon component of PM10 and PM2.5 (Based on the mass concentration)

Table 4. Carbon component and other of PM10 and PM2.5 (Based on the mass concentration)

| Season | Site | PM10 (μg/㎥) | | PM2.5 (μg/㎥) | |
|---|---|---|---|---|---|
| | | Carbon | Other | Carbon | Other |
| Spring | Site-A | 8.55 | 24.25 | 7.38 | 11.78 |
| | Site-B | 15.84 | 62.27 | 12.64 | 26.56 |
| | Site-C | 24.02 | 148.93 | 13.09 | 54.28 |
| Summer | Site-A | 11.51 | 24.65 | 9.58 | 15.07 |
| | Site-B | 13.54 | 41.05 | 12.05 | 18.07 |
| | Site-C | 31.12 | 175.34 | 17.52 | 52.37 |
| Fall | Site-A | 13.05 | 41.45 | 10.59 | 14.39 |
| | Site-B | 17.71 | 52.07 | 15.85 | 21.89 |
| | Site-C | 33.26 | 178.15 | 16.41 | 54.70 |
| Winter | Site-A | 10.24 | 33.3 | 9.24 | 15.01 |
| | Site-B | 22.67 | 90.13 | 16.51 | 41.56 |
| | Site-C | 47.42 | 211.98 | 17.68 | 61.17 |

The results show the concentration of particles at the Site-C is known higher than any other locations. The results show that the property of the location of Site-C, caused a lot of PM as well as the high carbon component.

Figure 2 shows the result of the mass ratio of the carbon in PM10 and PM 2.5 by season during sampling periods.

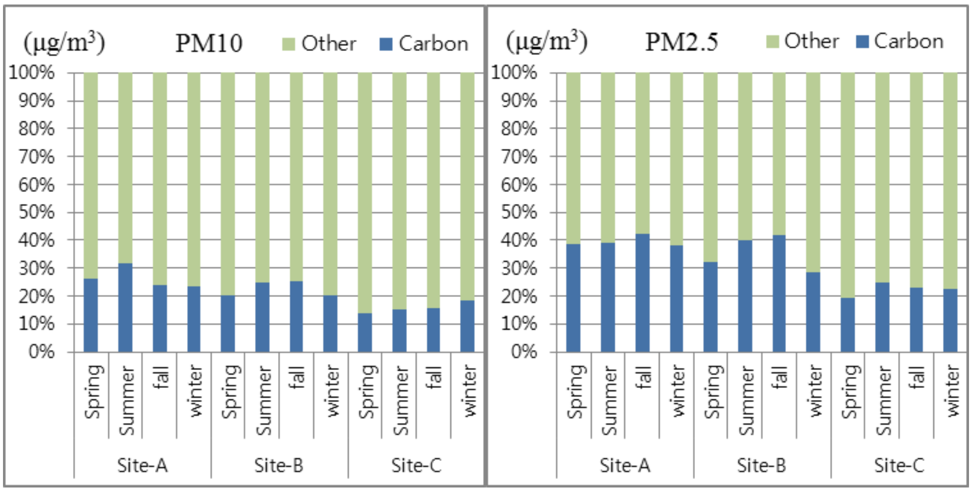

Figure 2. The ratio of carbon component and other component in PM10 and PM2.5

There was no big difference between a platform and outside about the ratio of carbon component, however it largely accounts for a low percentage in the tunnel. This means that the ratio of carbon component gets lower because of increased Fe by the wear of rail in the tunnel. The ratio of carbon component were not different both outside and platform. According to result, the platform is likely to be influenced by outside. There was not a much difference about ratio of carbon component by the location and each season. Also, ratio of carbon component was the lowest at Site-C.

## 3. CONCLUSION

The concentration of carbon component was the highest in the tunnel(based on the mass concentration). However, it is estimated the generated during scattering of particles by the subway operation, so the concentration of carbon increases in the subway. The ratio of carbon component of particles in the tunnel appeared to be low. Because Fe and other substances increased from the wear of rail and wheel, the carbon component was measured to be low relatively. It can be seen that high concentration of carbon component in PM2.5. There is a higher possibility to effect on people to be exposed, so there need to be the plan of carbon reduction. Therefore, the authors thought that the researches on the ratio of carbon component with time series the will be carried out.

## 4. ACKNOWLEDGMENTS

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# THE APPLICATION OF ISO 14064 IN TURKEY

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## ABSTRACT

International Standard Organization (ISO) 14064 is an offset protocol. It is independent, voluntary Green House Gases (GHG) project accounting standard, and is deliberately policy neutral. Targeted for release in 2006, the three-part ISO 14064 was developed as a practical tool to enable government and business to measure and manage GHG and reduction activities. ISO 14064 protocols quantifies the GHG reduction from a deployment that leads up to the trading of credits. This activity is aimed at motivating a potential user to deploy these solutions to assist in the preservation of the environment, though decreased emissions resulting from decreased fuel consumption. ISO is intended to be used conjunction with other regulations and standards. The first part (ISO 14064-1) specifies requirements for designing and developing organisation of entity-level GHG inventories. The second part (ISO 14064-2) details requirements for quantifying, monitoring and reporting emission reductions and removal enhancements from GHG projects. The third part (ISO 14064-3) provides requirements and guidance for the conducting of GHG information validation and verification. To learn more about ISO 14064 implementation a written survey was conducted with ISO 14064 certificated organizations. In April 2011, the number of organizations registered to the standard of ISO 14064 was four. The questionnaire was sent to four companies registered to the standard. Two of them replied questionnaire. The reasons for the organizations to implement ISO 14064 are numerous, such as: -motivation of workers; -the ISO 14064 certification enhances company image and share; -monitoring and management of quantity of GHG;-measuring and reporting of GHG; -increasing risk management of organizations; -allowing organizations take part in emission trading schemes.

**Keywords:** ISO 14064; Green House gas emissions, Emission trading, Turkey.

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# A STUDY ON THE COMPONENTS OF INORGANIC ELEMENTS IN THE SUBWAY PARTICULATE MATTERS

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## ABSTRACT

The subway is one of the most public transportation system used by many people in Seoul. Based on the awareness of the importance of IAQ(Indoor Air Quality) with PSDs(Platform Screen Doors) were installed in all stations in order to improve IAQ. Because of this, the air quality of platforms has been improved, but the tunnel is isolated from outside by installed PSDs. The air pollutants have accumulated in the tunnel and the air quality in the tunnel gets worse. In this study, analyzing the components of Inorganic elements of fine particle in the tunnel would be available to establish reasonable measures for the management of air quality. Measurements were performed to collect particles from the Mia-samgeori subway station. The measurement was conducted in spring, summer, fall and winter for pre-scheduled periods. Samples were collected by the Mini Volume Air Sampler by 5 L/min for 24 hours on the platform and outside. Particles were collected by Particle Mass Sampler by 16.7 L/min for 24 hours on the subway tunnel. Zeflour filters were used for sampling. Particles were collected on the filter analyzed fourteen species (Ag, Al, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Si, Ti, V, Zn) using ICP-AES(Inductively Coupled Plasma-Atomic Emission Spectrometry).

**Keywords:** inorganic elements, subway, tunnel, seasonal.

## 1. INTRODUCTION

The subway has been opened continuously since Subway line 1(Cheongnyangni – Seoul) was opened in 1974. Now it is being operated line 1 ~ 9 and is going to expand lines continuously. As more passengers used the subway, it has become to increase the number of people who are exposed to the subway environment, and it began to appear some problems that had not experienced from the train operation (Lee, K.B., 2009).

Among them, particulate matters(PM) can absorb easily heavy metal due to large surface area.

When particulate matter is inhaled in the human body by respiratory, penetration becomes to maximum into the lungs and it is known to cause lung cancer(Buell, P., 1967).

Also, the inorganic elements for this study were analyzed in the subway station.

The purpose of this study is to establish useful data, the through analyzing inorganic components of fine particle, for subway’s air quality management.

## 2. EXPERIMENTAL METHOD

This study was performed at Mia-samgeori subway station in line 4 subway. The sampling points are the outside, platform and tunnel. It was analyzed mass concentration and inorganic elements of PM10&PM2.5.

Based on these results, the status of air quality of this study area was figured out. In order to analyze the inorganic elements, the Author used for ICP-AES(Inductively Coupled Plasma-Atomic Emission Spectrometry, Leeman Labs Inc.).

It is also measured to analyze the characteristic of particulate matter in the subway station.
The location of sampling sites and periods are shown in Table 1.

Table 1. Measurement point & date

| Area | Subway line 4 in Seoul (Mia-samgeori) | |
|---|---|---|
| Sampling Site | Outside | Site-A |
| | Platform | Site-B |
| | Tunnel | Site-C |
| Period | Spring | 2010.04.21 ~ 2010.04.28 |
| | Summer | 2010.07.13 ~ 2010.07.21 |
| | Fall | 2010.10.12 ~ 2010.10.19 |
| | Winter | 2011.01.11 ~ 2011.01.17 |

### 2.1. Sampling method

Sampler at each site, flow rate, and sampling time are shown in Table 2.

Table 2. The summary of installed samplers at each sampling site

| Site | Installed of the Samplers | Flow rate (L/min) | Sampling time (hour) | note |
|---|---|---|---|---|
| Site-A (Outside) | Mini volume air sampler (Model 4.1, Airmetrics co., USA) 2ea | 5 | 24 | PM10, PM2.5 |
| Site-B (Platform) | Mini volume air sampler (Model 4.1, Airmetrics co., USA) 2ea | 5 | 24 | PM10, PM2.5 |
| Site-C (Tunnel) | Particle Mass Sampler (Model PMS-102, APM Eng, CO., Korea) 2ea | 16.7 | 24 | PM10, PM2.5 |

The author used Zeflour Filter (Diameter 47mm, Pore size 2μm, Pall corp., USA) in this study.

## 2.2. SAMPLING ANALYSIS

### 2.2.1. Pre-treatment of sample

Pre-treatment method for analyzing inorganic elements was applied microwave method of CWA(Clean Water Act) notified by U.S. EPA(1992. 10. 13)

Also, the pre-treatment methods were performed by the Questron(Questron corp., Model Q-15 MicroPrep, USA) nitric-hydrochloric acid

### 2.2.2. Analysis of inorganic elements

Inorganic elementals of PM10 and PM2.5 were analyzed fourteen species (Ag, Al, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Si, Ti, V, Zn) by ICP-AES in this study.

## 3. CONCLUSION

In case of PM10, Si, Fe, Zn, Al are higher concentration than the other elements at Site-A. Fe, Si, Zn, Al are higher concentration than the other elements at Site-B. Fe, Cu, Si, Mn are higher concentration than the other elements at Site-C.

In case of PM2.5, Si, Fe, Zn, Al are higher concentration than the other elements in Site-A. Fe, Si, Zn, Cu are higher concentration than the other elements at Site-B. Fe, Si, Cu, Al are higher concentration than the other elements at Site-C.

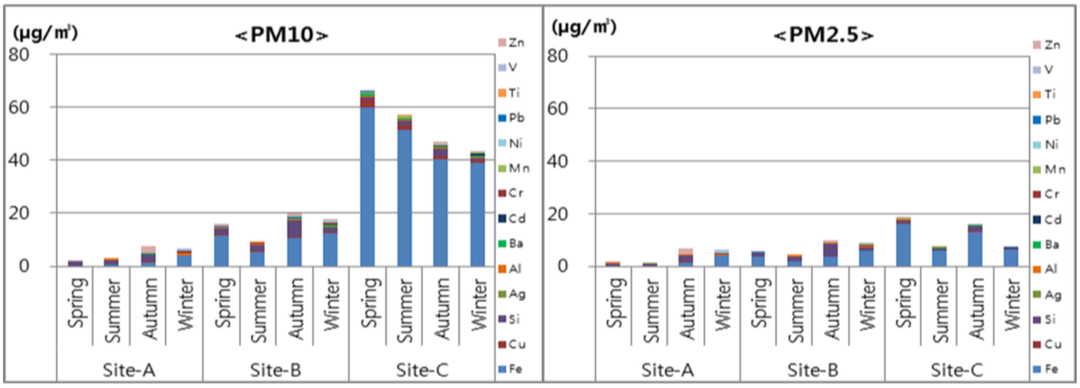

Figure 1. The inorganic components of PM10 and PM2.5

Looking at the concentration of inorganic elements at each point, the concentration of PM10 of numerical mean were analyzed in Site-A 4.793 ㎍/㎥, Site-B 15.444 ㎍/㎥, Site-C 55.116 ㎍/㎥. The concentration of PM2.5 of numerical mean were analyzed in Site-A 3.841 ㎍/㎥, Site-B 7.073 ㎍/㎥, Site-C 15.569 ㎍/㎥.

As the results, the concentration of Fe is the highest at Site-A in winter, because the boiler used heavy oil for heating in winter. It is included Fe in heavy oil, so the concentration of Fe is considered high. The majority pollutants in the tunnel are Fe and Cu. The concentration of Fe and Cu in the tunnel is higher than other sites. It may be due to wear of the rails or the wire when the subway is moved. In addition, Brake is included a metal powder in the filler of friction material. And it is estimated that metal fraction of particles is high by wear of brake.

Therefore, this study can expect that the adequate management for not only PM10 but also specifically PM2.5 within tunnel can be identified for each inorganic element.

## ACKNOWLEDGMENTS

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# A STUDY ON THE IONIC COMPONENTS IN THE SUBWAY'S PARTICULATE MATTER

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## ABSTRACT

The Subway is one of the major transportation systems used in Seoul. Thus, it is necessary to identify corresponding sources and to estimate pollutant sources in order to protect people's health and to keep cleaning subway environment. The purpose of this study, the subway air is analyzed the ionic components of fine particle in the tunnel and it is available to establish useful data for air quality management. The measurements were performed to collect samples at the Mia-samgeori subway station. The measurement was conducted in spring, summer, fall and winter for pre-scheduled periods. Samples were collected by the Mini Volume Air Sampler by 5 L/min for 24 hours at the platform and outside. The samples were collected by Particle Mass Sampler by 16.7 L/min for 24 hours at the subway tunnel. Zefluor filters were used for sampling, and Ion Chromatography was used for ion analysis. The Eight item were analyzed, $SO_4^{2-}$, $NO_3^-$, $Cl^-$, $NH_4^+$, $Na^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$.

**Key Words:** subway, ionic components, fine particle.

## 1. INTRODUCTION

The Subway is one of the major transportation systems used in Seoul. In recent years, PSDs (Platform Screen Doors) have been installed to all of stations in Seoul. Because of this, the passengers are protected from accidents, and the air quality of platforms is improved (Sohn, J.R. et al., 2009). However, polluted air of outside flows into the tunnel without ejection from the tunnel due to the installation of PSDs. So the air quality in the tunnel has been worse.

Fine particle of polluted air in the tunnel is the main cause to induce a reduction in visibility. Pollutants are broke into the human body through breathing and attached bronchial and lung ; this may have an effect on health. Therefore, there are many researches have been performed for the reduction of fine particle for subway air quality. To figure out the source of pollutants, the atmospheric concentration and their relationship, it is very important to know about the components of PM10 and PM2.5 (Karlsson, 2005).

The purpose of this study is to establish useful data, through analyzing ionic components of fine particle, for subway air quality management.

## 2. MAIN TEXT

### 2.1. Measurement Period and Sampling point

The ionic components of PM10 and PM2.5 were analyzed in the tunnel of subway.
The measurements were performed to that the samples at the Mia-samgeori subway station

Line 4.

The location of sampling sites and periods are shown in Table 1.

Table 1. The location of sampling sites and periods

| Area | Mia-samgeori Station of Subway Line 4 in Seoul | |
|---|---|---|
| Sampling Site | Outside | Site-A |
| | Platform | Site-B |
| | Tunnel | Site-C |
| Period | Spring | 2010.04.21 ~ 2010.04.28 |
| | Summer | 2010.07.13 ~ 2010.07.21 |
| | Fall | 2010.10.12 ~ 2010.10.19 |
| | Winter | 2011.01.11 ~ 2011.01.17 |

Zefluor filters (PALL Co.) were used for sampling. Samplers at each sampling site, flow rate, and sampling time are shown in Table 2.

Table 2. A summary of installed samplers at each sampling site

| Site | Installed samplers | Flow Rate (L/min) | Sampling Time (hour) | Remarks |
|---|---|---|---|---|
| Site-A (Outside) | Mini volume air sampler (Model 4.1, Airmetrics co., USA) 2ea | 5 | 24 | PM10, PM2.5 |
| Site-B (Platform) | Mini volume air sampler (Model 4.1, Airmetrics co., USA) 2ea | 5 | 24 | PM10, PM2.5 |
| Site-C (Tunnel) | Particle Mass sampler (Model PMS-102, APM Eng, co., Korea) 2ea | 16.7 | 24 | PM10, PM2.5 |

## 2.2. Analytical Method

Particle were collected on the filters were extracted by ultrasonic extractor for 20 minutes with distilled water for analysis of ionic components.

Samples were analyzed for major water-soluble ions using Dionex DX-400 Ion Chromatograph. Analytical conditions of ion chromatography are shown in Table 3.

Table 3. Analytical conditions of Ion Chromatograph

| | Anion | Cation |
|---|---|---|
| Ions | $Cl^-$, $NO_3^-$, $SO_4^{2-}$ | $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$ |
| Instrument | DX-400 (Dionex) | DX-400 (Dionex) |
| Standard Solution | Regecon Co. | Regecon Co.,<br>Mallinckrodt Co. |
| Column | IonPac As12A | IonPac Cs12 |
| Eluent | 2.7 mM $Na_2CO_3$<br>0.3 mM $NaHCO_3$ | 20.0 mM Methanesulfonic Acid |
| Flow Rate | 1.5 mL/min | 1.0 mL/min |
| Suppressor | Anion Micro Membrane Suppressor | Cation Micro Membrane Suppressor |
| Detector | Conductivity | Conductivity |

## 3. CONCLUSION

In this study, the subway air is analyzed the ionic components of PM10 and PM2.5 in the tunnel.

Of all sites, in case of tunnel, mass concentration of particulate matter was the highest all season excepted for the winter PM2.5.

PM10 and PM2.5 ionic composition and the ratio of other components are shown in table 4 and Figure 2.

Table 4. Ionic component and other of PM10 and PM2.5 (based on the mass concentraion)

| Season | Site | PM10 (μg/㎥) | | PM2.5 (μg/㎥) | |
|---|---|---|---|---|---|
| | | TI | Other | TI | Other |
| Spring | Site-A | 12.75 | 20.05 | 6.03 | 13.14 |
| | Site-B | 17.58 | 60.52 | 7.15 | 32.05 |
| | Site-C | 21.40 | 151.55 | 13.38 | 53.99 |
| Summer | Site-A | 10.10 | 26.07 | 7.71 | 16.94 |
| | Site-B | 13.69 | 40.89 | 8.20 | 21.93 |
| | Site-C | 31.22 | 175.24 | 14.87 | 55.01 |
| Fall | Site-A | 16.04 | 38.46 | 5.10 | 19.88 |

| | | | | | |
|---|---|---|---|---|---|
| | Site-B | 11.72 | 58.06 | 4.92 | 32.82 |
| | Site-C | 25.29 | 186.13 | 10.46 | 60.66 |
| Winter | Site-A | 14.33 | 29.22 | 6.36 | 17.90 |
| | Site-B | 22.93 | 89.87 | 12.94 | 45.13 |
| | Site-C | 27.77 | 231.64 | 11.34 | 67.50 |

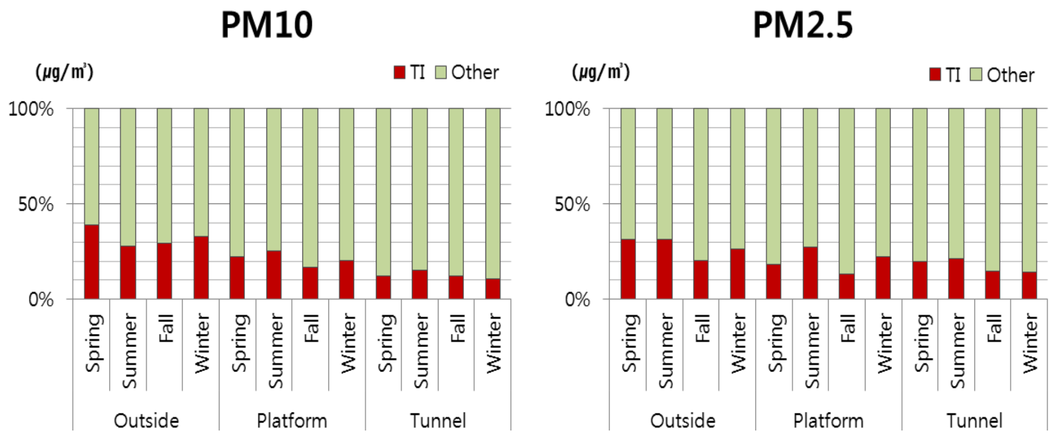

Figure 1. The ratio of Ionic components and other component in PM10 and PM2.5

The result of the analysis of ionic components, in case of the outside, concentration of $SO_4^{2-}$ and $NO_3^-$ was the highest.

In case of the platform, concentration of $NO_3^-$ was the highest in all seasons. In case of the tunnel, concentration of $SO_4^{2-}$ and $NO_3^-$ was the highest.

The analysis on ion composition is shown in Table 5.

Table 5. The average annual concentration of ionic components of each sampling site

| | Site | Average annual concentration (㎍/㎥) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $Cl^-$ | $NO_3^-$ | $SO_4^{2-}$ | $Na^+$ | $NH_4^+$ | $K^+$ | $Mg^{2+}$ | $Ca^{2+}$ |
| PM10 | Site-A (Outside) | 1.72 | 3.19 | 2.21 | 1.59 | 2.15 | 0.46 | 0.23 | 0.80 |
| | Site-B (Platform) | 1.89 | 3.70 | 2.39 | 1.76 | 2.37 | 1.33 | 1.20 | 2.16 |
| | Site-C (Tunnel) | 2.45 | 5.53 | 6.06 | 2.05 | 4.04 | 0.83 | 0.92 | 5.05 |
| PM2.5 | Site-A (Outside) | 1.51 | 2.07 | 0.62 | 1.03 | 0.41 | 0.35 | 0.13 | 0.46 |
| | Site-B (Platform) | 0.99 | 2.23 | 1.46 | 0.85 | 1.32 | 0.41 | 0.29 | 0.99 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Site-C (Tunnel) | 1.30 | 2.61 | 2.54 | 0.99 | 2.34 | 0.42 | 0.48 | 2.05 |

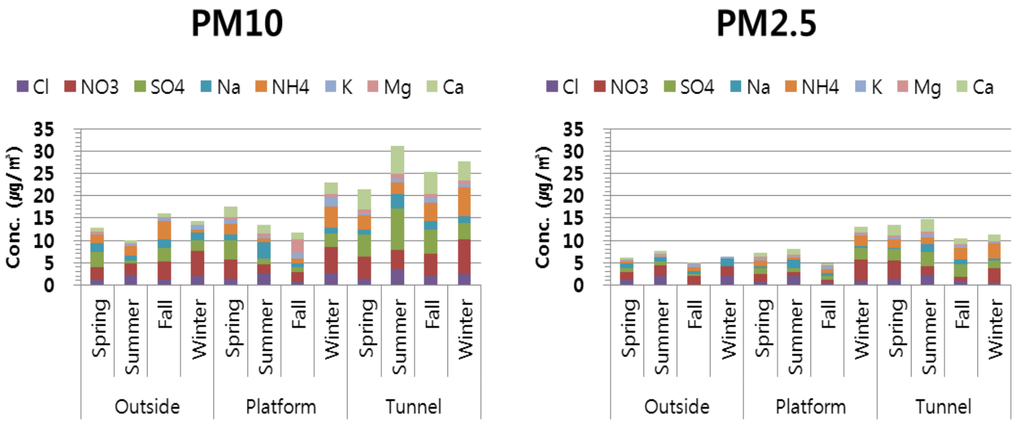

Figure 2. The concentration of Ionic Components according to seasons and sites

The result of the analysis on ionic components, the ratio of ionic components at the platform and the tunnel was similar to outside.

According to this, the platform and tunnel were likely to be influenced by outside.

The concentration of $SO_4^{2-}$ was the highest in all sites.

It is considered to be a high concentration of salt particle in nearby the street market.

Also, $NO_3^-$ was the highest in all sites. It is considered that the ammonia reacts with nitrogen oxides to produce $NO_3^-$ .

We expect that the result of this study is useful for adequate management about PM10 and PM2.5 in the tunnel.

## ACKNOWLEDGMENTS

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# REMOVAL OF PARTICULATE MATTER IN A WET SCRUBBER USING ELECTROSPRAY

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## ABSTRACT

As numerous strategies have been developed and introduced to air quality management the standards for the ambient air quality and emission source have been gradually intensified. This in turn enforced the industry to use clean energies or to install control devices with high efficiencies, to comply with such regulation. Among control devices, the particulate matters from industrial boilers or production process contain hazardous air pollutants such as heavy-metal and polycyclic aromatic hydrocarbons which contribute to high health risk. The fine particles also have light scattering and absorption characteristics which can lead to visibility impairment. Precipitator requires a high collection efficiency to remove fine particle. Wet scrubbers are a diverse set of control devices that can be used to collect both particles and gases, but usually are not at high efficiency simultaneously. This is because particulate scrubbers are designed to generate high inertial forces or electrostatic forces on particles to drive them into droplets or sheets of liquid. Gas absorbers are designed to have high liquid surface areas and relatively long residence times to maximize the absorption of contaminants into liquid droplets or sheets. Despite the fundamental operating differences, most particulate scrubbers have at least modest efficiencies for gaseous contaminant removal, and most gaseous absorbers have modest efficiencies for the removal of particulate larger than approximately 3 ㎛. This study focuses on the use of electrospray as a tool to increase the collection efficiency on sub-micron sized particles. In order to resolve the drawbacks of the preexisting wet scrubber technique, we developed a modified wet scrubber in which an electrospray system is installed. The modified wet scrubber was built in a clean wind tunnel. The test system consisted of a high-efficiency particulate air (HEPA) filter, a particle generator, and a wet scrubber. To provide clean air into the air supply system, the HEPA filter was installed. To test the efficiency of our improved wet scrubber, particles were generated artificially using TMDS (1, 1, 3, 3-tetramethyl disiloxane ($((CH_3)_2SiH)_2O$, Aldrich). Dust collection efficiency was also examined in relation to the power supply by changing its values from the highly negative voltage to the increased levels of -15 to -19kV and water flow rate of 80, 160, 240 mL. The size distribution and its mass concentration of particles were measured to assess the collection efficiency of the system by using an cascade impactor (Low Pressure Impactor, Dekati) with isokinetic sampling (EPA method 5). With this modification, we can acquire a relatively high collection efficiency of fine particles. The dust collection efficiency changes in relation to changes in the electrical field and the liquid-to-gas ratio inside the scrubber. The results confirm that the higher the electrical field strength, the higher the dust collection efficiency.

**Keywords:** wet scrubber, electrospray, electrical field strength, fine particle

## 1. INTRODUCTION

The dust of an industrial boiler or production process is emitted as fine particle of which its diameter is 1 ㎛ or smaller in diameter. The fine particle itself is very harmful and may negatively affect the human body or atmospheric environment if it contains harmful pollutants such as polycyclic aromatic hydrocarbons. Fine particles are rarely removed in the air and may cause serious respiratory diseases as it might flow deeply into the lungs through breathing (Englert, 2004; Samanta et al., 1998). In addition,a visible ray in the atmosphere. In addition, it may diffuse or absorb the visible rays in the atmosphere, causing the reduced visibility or unusual change in the weather as acting as condensation nucleus (Hoobs et al., 1993).

The restrictions on fine particles are strictly reinforced due to the arousal of people’s attention as the no. of damaging cases by fine particles increases. In Korea, the ambient airquality standard was reinforced from TSP (Total Suspended Particulate) to $PM_{10}$ (particulate matters than 10 ㎛ as an aerodynamic diameter) and recently, the standards on $PM_{2.5}$ (particulate matters than 2.5 ㎛ as an aerodynamic diameter) have been established. As the atmosphere environment standards have been reinforced, the effort to increase the efficiency of the existing dust collector or install a high efficient dust collector is necessary.

To process fine particles, the electrostatic precipitator, bag filter, wet Scrubber and other devices are used. Among them, a wet scrubber features processing particles and gases pollutants simultaneously by using a liquid. Although using a liquid may eliminate explosive materials but it is disadvantageous to treat the wastewater of the liquid (Kim, 1999).

In general, the types of wet scrubbers used for industrial applications contain the spray tower scrubber, packed-bed scrubber, venturi scrubber and etc. although they tend to have less collection efficiency (Cooper and Alley, 2002). To improve the low collection efficiency, many methods have been studied when recently, a method using electrospray has been examined.

Electrospray lets conductive liquid pass through a nozzle and if +/- high voltage are allowed, the ions contained in the liquid move to the surface of liquid by repulsion and attraction. If the voltage allowed for a nozzle is low, the electric power and the reactive power of cation are less than the surface tension, no liquid drops are generated. However, if the voltage is increased, the electric power and the reactive power of cation are larger than the liquid surface tension, starting liquid drop spraying (Michelson, 1990; Bailey, 1998).

The study is intended to improve the particle collection efficiency of the wet scrubber by using electrospray system. First of all, an induction charging type electrospray system was installed on the existing spray tower scrubber while the particle collection efficiency was measured by changing the applied voltage and the volume of liquid.

## 2. EXPERIMENTAL DEVICE AND METHOD

As in Figure 1 it's a lab size device and consists of HEPA filter, particle generating system and spray tower scrubber. The experiment measures the particle collection efficiency, so the concentration of particle is very important. Therefore, the device is maintained with clean air.

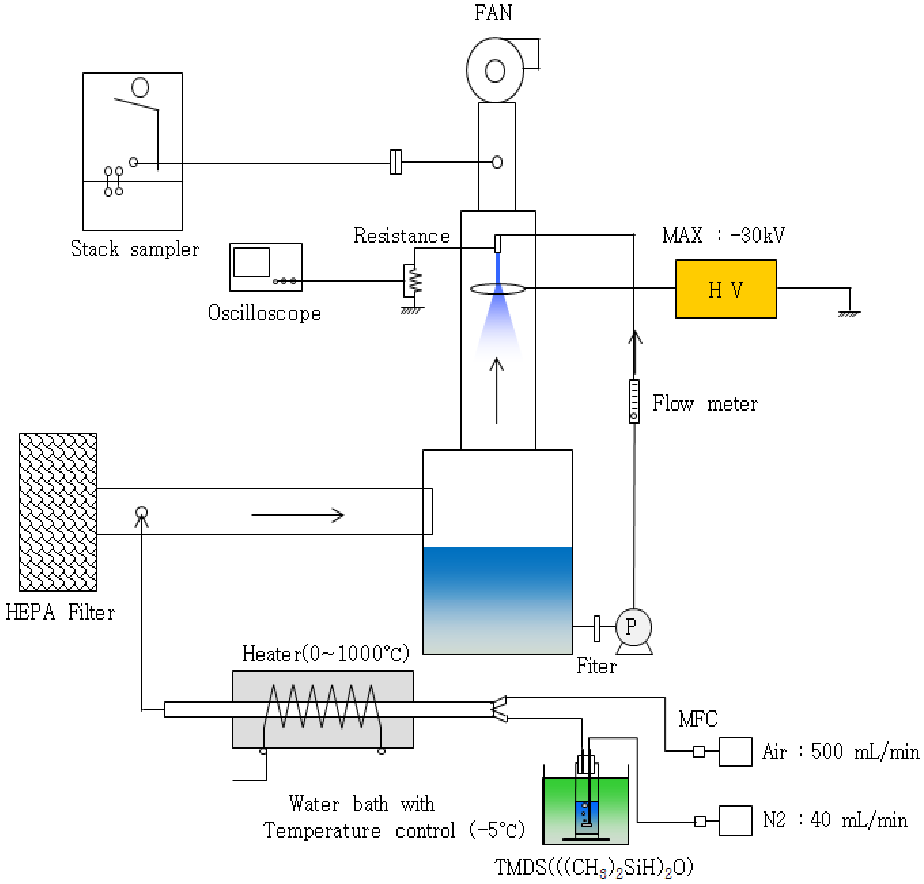

Figure 1. Experimental setup to measure the collection efficiency of a spray tower scrubber by installing HEPA filter

The fine particle used in the experiment was TMDS (1, 1, 3, 3-tetramethyl disiloxane $((CH_3)_2SiH)_2O$, Aldrich) as a precursor while bubbling the impinger containing TMDS by nitrogen gas, gasifying it. The particles of $SiO_2 \cdot SiO_4$ were generated by passing TMDS gas and air into a tube furnace (DTF-30300-PT). After passing the furnace in the state of gas, TMDS is grown up as a particle through the processes of nucleation, condensation and coagulation (Hwang, 2010; Lee et al., 2005).

In addition, to observe the removal efficiency of gases pollutant, hydrogen chloride gas was generated by bubbling 35 wt % HCl soln with nitrogen gas.

The scrubber device is 110 mm dia. and 600 mm long and its spraying length is about 550 mm. As seen in Figure 1 water was sprayed by installing a nozzle as countercurrent while the water used for spraying was circulated by using a pump. The nozzle's inner diameter was 3mm while a 95mm dia. ring was installed 50 mm away from the lower part of the nozzle. To supply the electricity, a power supply (KSH-N30/5CD) was used which allows negative (-) voltage up to 0 ~ -30kV. A fan was a turbo fan type of which its max. wind volume was 2.7 $m^3$/min and regulated by an invertor.

The voltage was measured by connecting a high voltage probe (Tektronix, P2220), connected to the power supplier, to a digital oscilloscope (Tektronix, TDS 2014B). The current was measured by using a 10 kΩ of resistor onto the ground.

To measure the particles, a cascade impactor (Low Pressure Impactor, Dekati) was used while the mass concentration was calculated by measuring the 3 times and averaging them (EPA method 5).

Gases pollutants were pumped to two 50 mL serial impingers containing 50 mL for 20 minutes and 1 LPM each, collecting 20 L, which was analyzed by absorption photometry.

The experiment method was to measure the changes of particle collection efficiency by changing the allowed voltage (-16, -17, -18 kV) and the volume of liquid (80, 160, 240 mL/min) of the electrospray system.

## 3. RESULT AND DISCUSSION

The particle generation condition was to supply nitrogen gas to an impinger containing TMDS by 40 mL/min while air was supplied to a tube furnace by 500 mL/min. The temperature of furnace was controlled at 700 ℃. The concentration of particle generated in the conditoin was approximately 90 ㎎/㎥. Considering the general concentration scope generated from industrial facilities (50~200 ㎎/㎥), it is considered appropriate (Kim et al., 1999; Kim et al., 1995).

Figure 2 shows the particle size distribution of the generated particles. The distribution ranges between 0.1 ~ 1 ㎛ while a band of 0.2 ㎛ showed the highest concentration. The distribution is the scope showing low particle collection efficiency in almost particle collectors as well as scrubbers. In addition, the size is considered appropriate to perform the study.

Geometric mean and geometric standard deviation were calculated by using an accumulated probability paper, in which the geometric mean was 0.2 ㎛ and the geometric standard deviation was 0.91, as presented in Figure 3.

The occurrence concentration is called monodisperse particle if the geometric standard deviation is 1.2 or lower, and called polydisperse if it is 1.2 or higher. The particle in the experiment was 0.91, which means it is monodisperse (Hinds, 1982).

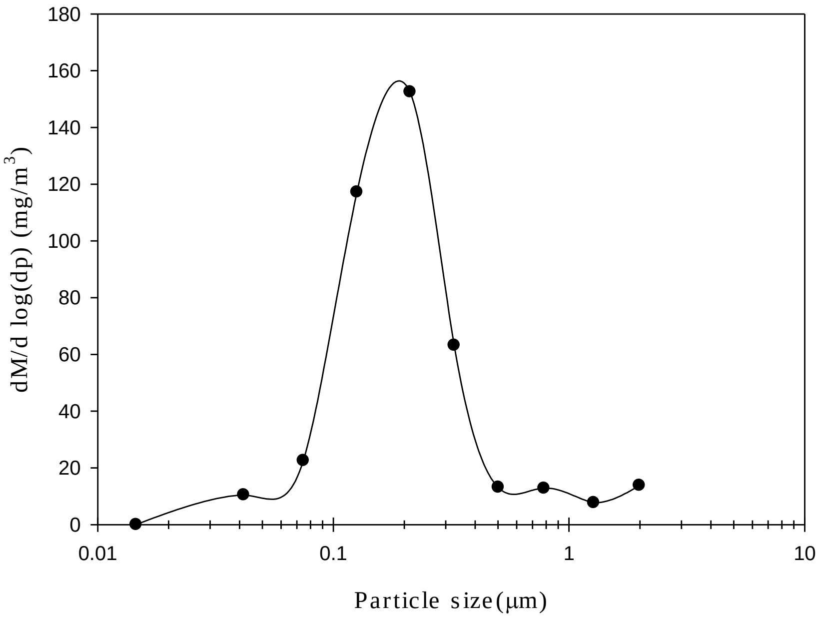

Figure 2. Size distribution of test particles

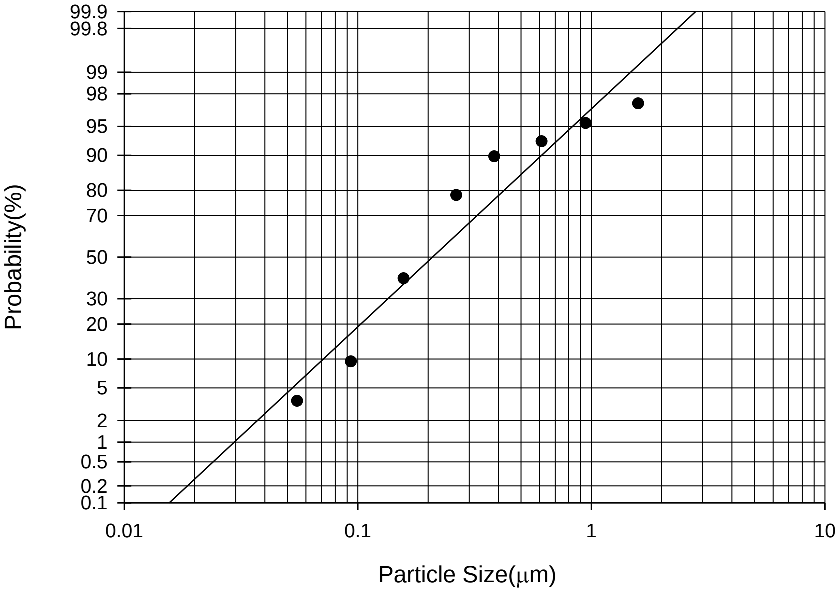

Figure 3. A log-probability graph in test particles

Figure 4 shows the results of voltage-current measurements. When the voltage became -15 kV by allowing high voltage, discharge started to occur and the currents were measured as 30.2, 34.4, 42.6, 50.4 and 59.2 μA respectively when charging the voltage to -15, -16, -17, -18 and -19 kV. Also, when the voltage was increased, the current increased rapidly and once discharge occured, it showed corona discharge in which the current rapidly increases (Jack R. McDonald 1977). In addition, the current also increased as the volume of liquid increased.

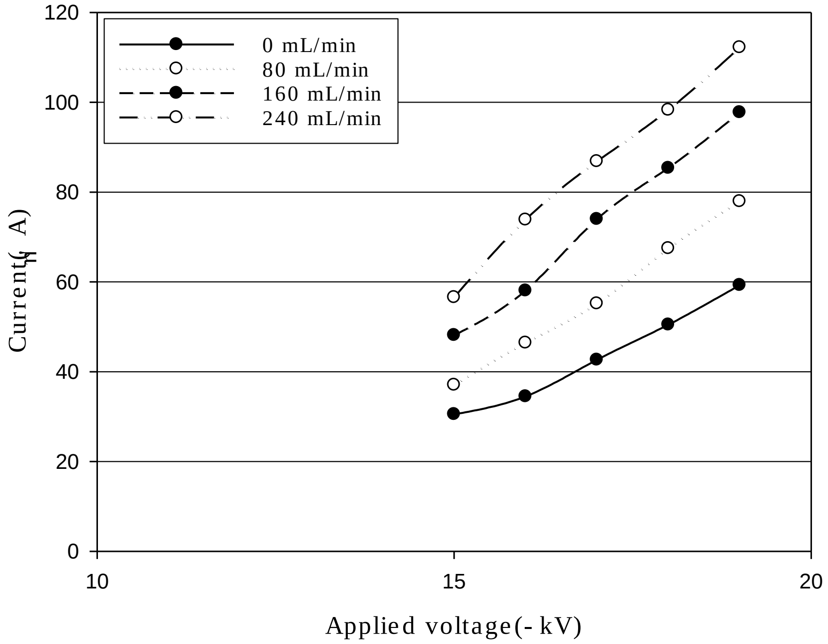

Figure 4. Voltage-current characteristics in electrospray nozzle

Figure 5 shows the results of the particle collection efficiency experiments. If representing the liquid-to-gas ratio comparing the sprayed water volume to the volume processed by a scrubber, the liquid-to-gas ratio were 0.18, 0.35 and 0.53 L/m$^3$ respectively when supplying 80, 160 and 240 mL. In the experiment at the applied voltage of −16, −17, and −18 kV, the electrical field strengths were calculated as −3.2, −3.4, and −3.6 kV/cm, respectively.

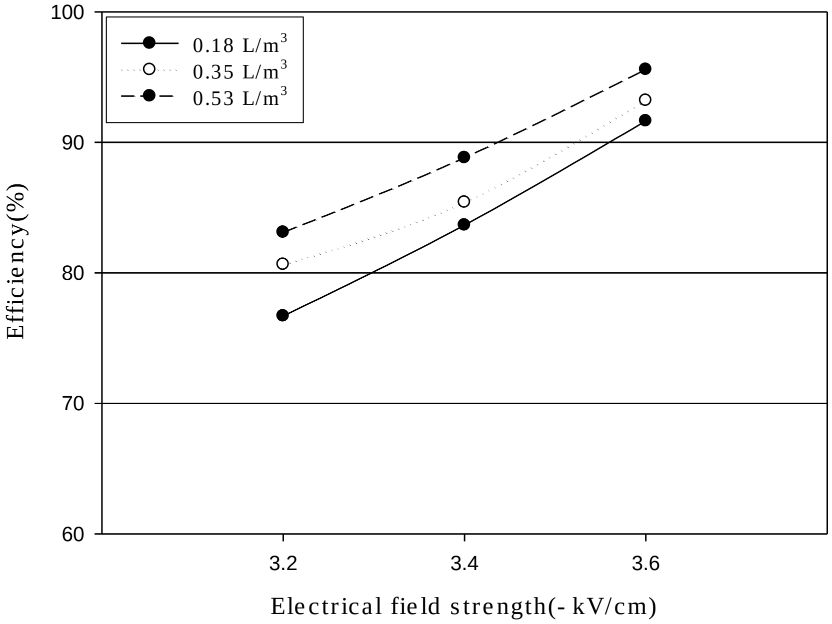

Figure 5. Particle collection efficiency in an electrospray nozzle scrubber

Table 1. Efficiency collection on the experimental conditions

| Electrical field strength (-kV/cm) | Liquid-to-gas ratio (L/m$^3$) | | |
|---|---|---|---|
| | 0.18 | 0.35 | 0.53 |
| 3.2 | 76.7 | 80.6 | 83.1 |
| 3.4 | 83.7 | 85.4 | 88.8 |
| 3.6 | 91.6 | 93.2 | 95.6 |

Table 1 shows the particle collection efficiency as the electrical field strength and liquid-to-gas ratio were changed. The electrical field strength, the particle collection efficiency was more improved. In addition, the higher the liquid-to-gas ratio, the efficiency was improved more.

Considering that the liquid-to-gas ratio of a general spray tower scrubber is between 0.5 and 1.5 L/m$^3$, the study showed that the electrospray nozzle srubber had a very high efficiency even with a very small liquid-to-gas ratio (Cooper and Alley, 2002).

A wet scrubber advantageously processes both particles and gases pollutants. The study measured the particle collection efficiency of fine particles and the removal efficiency of gases pollutant simultaneously.

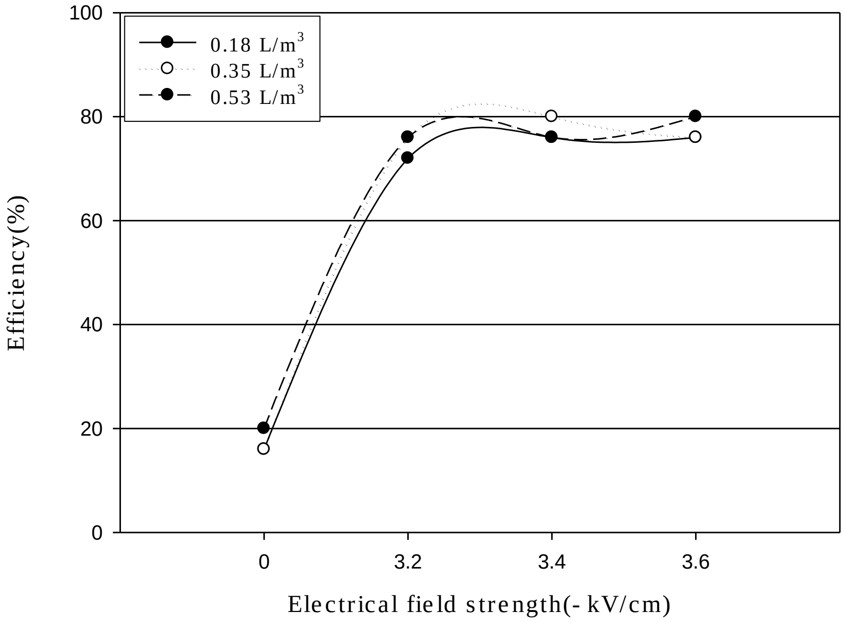

Figure 6. HCl removal efficiency in an electrospray nozzle scrubber

To see the removal efficiency of gases pollutants, the concentration of hydrogen chloride was measured in the same conditions of the particle collection experiment which is displayed in Figure 6. The concentration of hydrogen chloride generated was around 2.5 ppm.

When allowing -3.2, -3.4 and -3.6 kV/cm of electrical field strength to an electrospray system, the removal efficiency of hydrogen chloride did not change as the electrical field strength was changed and measured as about 70 % efficiency. In addition, the removal efficiency was not changed even when signficantly changing the volume of liquid.

The particle collection mechanism of a general scrubber was diffusion, interception, impact and electrostatic attraction between droplet and particles; the particles smaller than 0.05 ㎛ are worked by diffusion, the particles between 0.05~1 ㎛ are worked by all particle collection mechanisms such as diffusion, interception and impact, and the particles larger than 1 ㎛ are worked by inertia impact (Hinds, 1982). Regarding the size of the particles in the study, the particles between 0.08~0.5 ㎛ occupy about 90%, so nearly all of the particle collection mechanisms such as diffusion, interception and impact will work (Hwang et al., 2010).

The increased particle collection efficiency is considered when sprayed by high voltage, the droplet size is reduced (Kim and Bae, 2001) and the number of droplet increases.

The electric charge quantity of droplet increases when the droplet sprayed is getting smaller (Park et al., 2006). Also, the efficiency would be improved by the electrical coagulation between discharged liquid droplet and particles (Sachchida et al., 2002).

## ACKNOWLEDGMENTS

To improve the particle collection efficiency of spray tower scrubbers, the study intended to improve it by installing the electrospray system of inductive charging type, resulting in the conclusion.

The higher the electrical field strength allowed to the electrospray nozzle system, and the higher the liquid volume supplied, the particle collection efficiency was improved more, which was considered that the efficiency was improved as the liquid drop finely occurred and the volume also increased.

The removal efficiency of gases pollutant (HCl) increased as the electrospray occurred, but the efficiency was not increased as the voltage or liquid was changed.

Therefore, in conclusion, the particle collection efficiency can be improved by applying electrospray system to the existing spray tower scrubber while not affecting the removal efficiency of the gases pollutant.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# AN ENERGY USAGE ANALYSIS OF THE GHG EMISSION BY SOURCE INVENTORY DATA IN SEOUL

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## ABSTRACT

The Green-house Gas(GHG) emissions from electricity and gas consumption take parts in stationary sector. In Seoul, these emissions are the major components of the GHG and expected to have large reduction potential by energy saving and upgrading efficiency. To accomplish energy saving in Seoul, we need to understand the energy using the patterns and characteristics. In this study, we collected and used the energy consumption data from source database. To make space segmentations in Seoul, we divided target areas as the resolution 697 grids of 1km × 1km, and calculated the energy consumption data for each grid. We classified energy usage as lighting, appliances-operation, cooking & water-heating, cooling & heating energy. As the result, the total energy consumption in stationary source is 134,746 Tcal/year. The consumption for the lighting is 15.7%, the appliance-operation 35.4%, the cooking & water-heating 8.9%, the heating 32.4%, the cooling 7.6%.

When we make use of this result for construct source-inventory database, we can make an effective and detailed GHG reduction plan. Moreover, as the fuel consumption is closely related to the urban air pollution, the results of the energy usage data can be used as the actual input data for air pollution modeling.

**Keywords:** green-house gas, energy usage, bottom-up inventory

## 1. INTRODUCTION

South Korea, as a non-annex 1 country, made a voluntary and unilateral pledge that satisfies the highest demand recommended by international community. The government urged to reduce greenhouse-gas(GHG) of buildings that are biggest energy consumption sources arising from deciding national GHG reduction Goal ; 30%.

Seoul, as the largest local-government in Korea has a distinguished energy consumption pattern. Industrial energy is the largest amount of consumption among the total energy consumption in South Korea. On the other hand, in Seoul, energy consumption part of residential & commercial is the most (69.20%) and transportation part (22.66%) is second largest energy consumption part. This means the characteristic of Seoul that developed service part than manufacturing part. And most of petroleum energy used as transport part, electricity and city gas energy used as building energy.

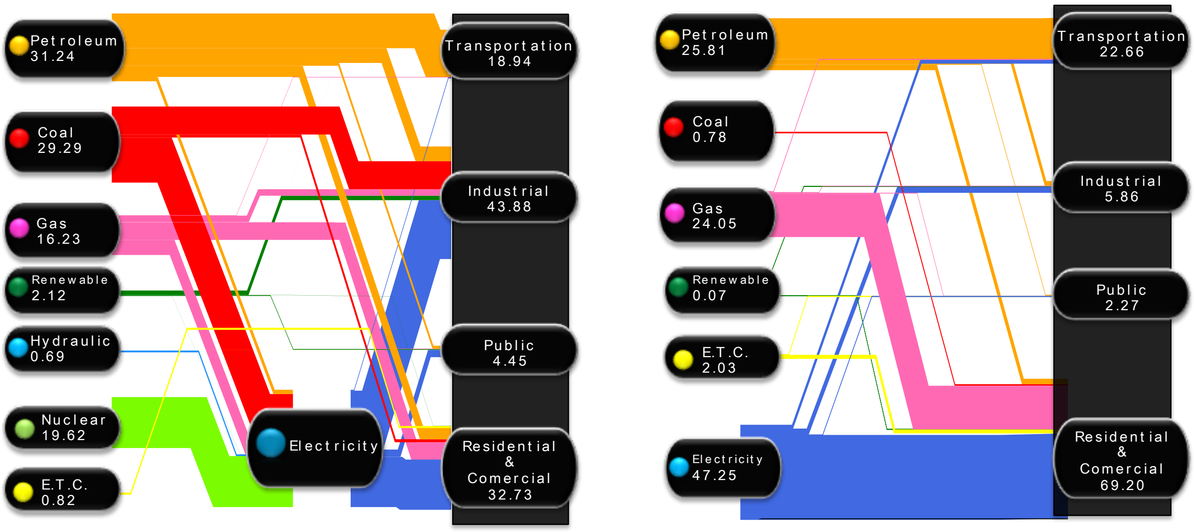

Figure 1. Energy Flow of South Korea(left) and Seoul(right)

There are two main sources as building energy : Electricity and City gas. We investigated electricity energy in building, there are 4 cases of usage : Lighting, Appliances-operating, Heating and Cooling. There are 3 cases of usage : Cooking & Water-heating, Heating and Cooling for the gas consumption sector.

To accomplish energy saving in urban area, we need to understand the energy using patterns of commercial and residential buildings which occupies the most of energy consumption. In this study, we studied on Seoul city and analyzed energy using patterns of each building

## 2. ANALYSIS METHOD

Generally, electricity and gas energy consumptions can be divided into three areas of energy usage: heating, cooling, lighting and appliances-operation (TV, refrigerator, computer etc.) for electricity consumption and heating, cooling, cooking and hot water for gas consumption. In this study, energy conservation potential was taken into account in the heating and cooling areas. To divide the total energy consumption by each area, we used the following method as Figure 2.

First, the energy consumption of each month was calculated to determine the month with the minimum energy use consumption in comparison with the monthly data of 2006. Second, the differences between each monthly energy use datum and the minimum monthly datum that were calculated in the first step were determined. When this difference value was zero, the monthly consumption was assumed to be the Base-Level-Consumption(BLC), and the energy consumptions that were equal to the minimum monthly energy use data were assumed to be lighting and appliances-operation for the electricity consumption sector and cooking and hot water for the gas consumption sector. When the monthly consumption was lower or higher than the BLC, the differences between each monthly energy use datum and the minimum monthly datum were termed heating energy and cooling energy, respectively.

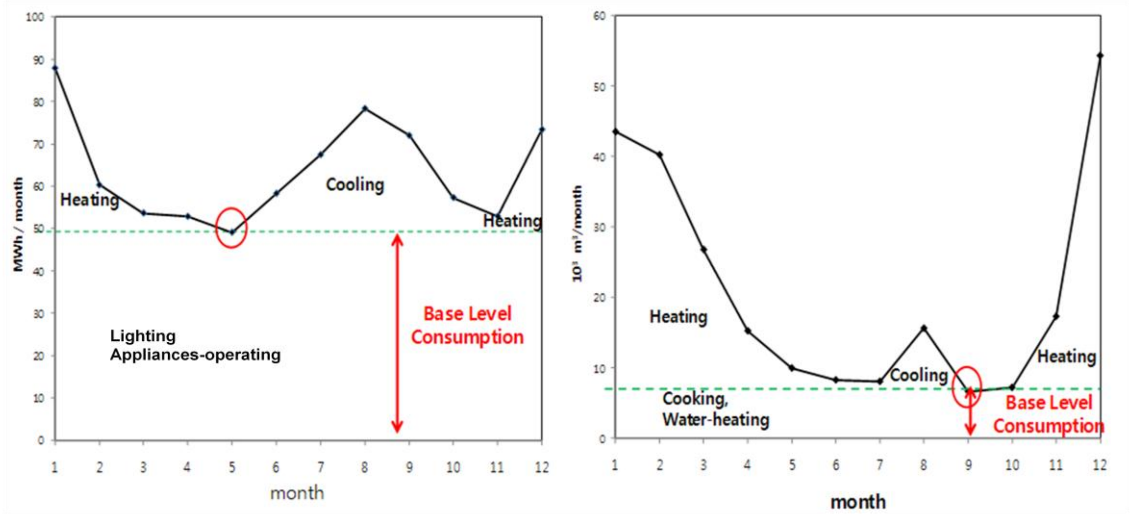

Figure 2. Samples of Energy Consumption Pattern ; Electricity(left), Gas(right)

There are approximately 0.63 millions of land number in Seoul : area 605 km$^2$. We devided Seoul into 697 grids as 1km by 1km and calculated the energy consumption by usage.

## 3. RESULT and DISCUSSION

Energy consumption pattern has wide variation. There are primary peak of energy consumption in winter season because of heating energy, and secondary peak in summer season because of cooling energy. From an energy source point of view, electricity 59.3%, gas 40.7%. Calculated the consumption of each usage of two energy sources. Lighting 14.7%, appliances-operating 33.2%, cooking & water-heating 9.9%, heating 32.9%, cooling 7.3%. Lighting, appliances-operating and cooking & water-heating parts are consumed constantly in year. We can calculate the amount of GHG emission from this energy consumption data. Its results are shown in the Figure 3.

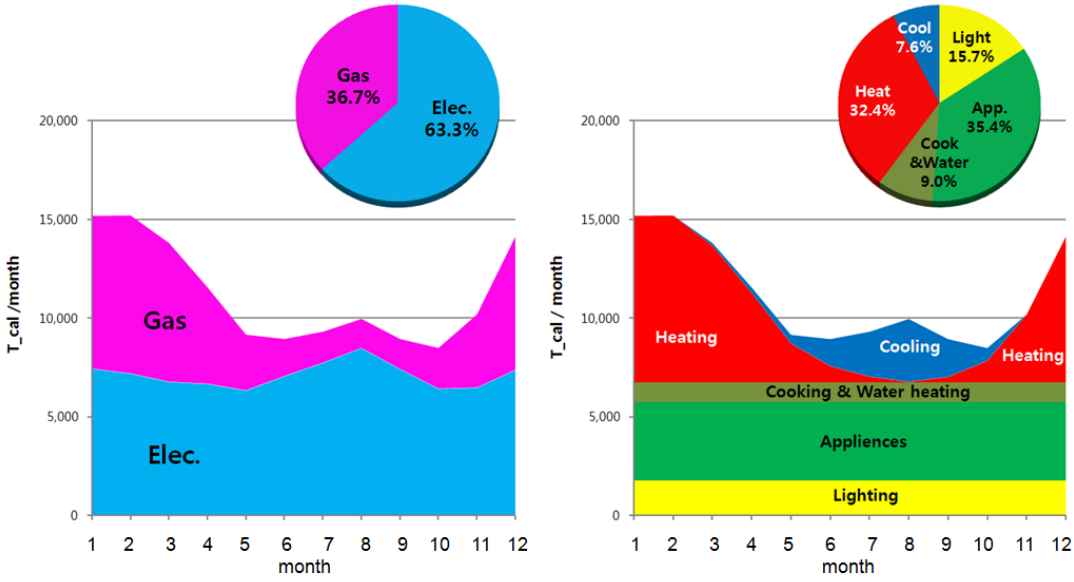

Figure 3. Energy Consumption Pattern of each Usage

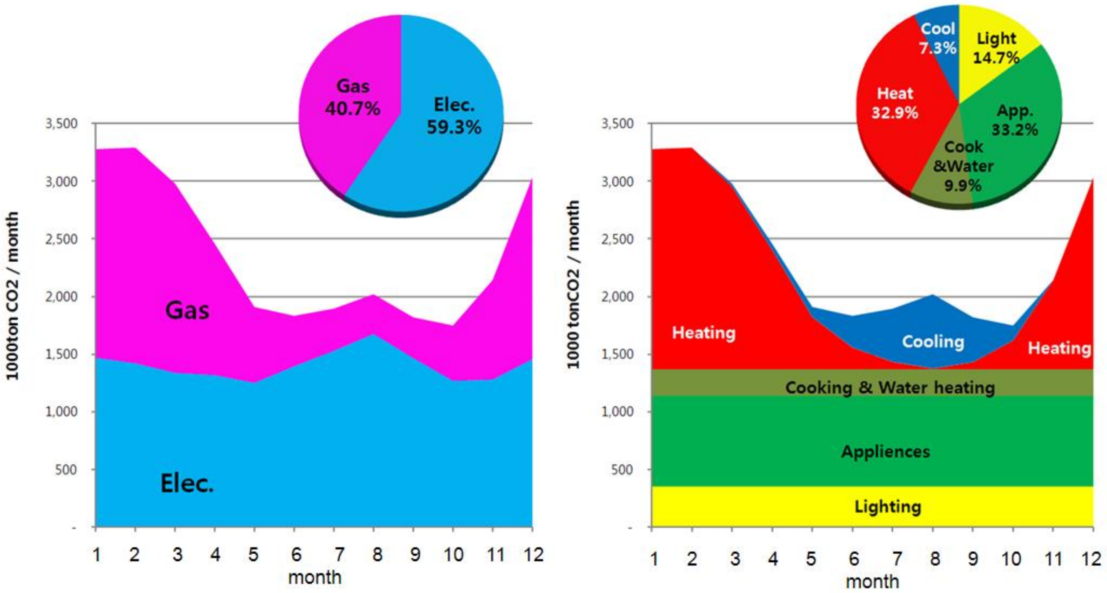

Figure 4. GHG Emission pattern of each Usage

There are spatial distribution of GHG emission from building in the Figure 5. The grids that are located in downtown of Seoul or Commercial zone such as Jongno-Gu and commercial zone of Gangnam-Gu are shown as high emission of GHG.

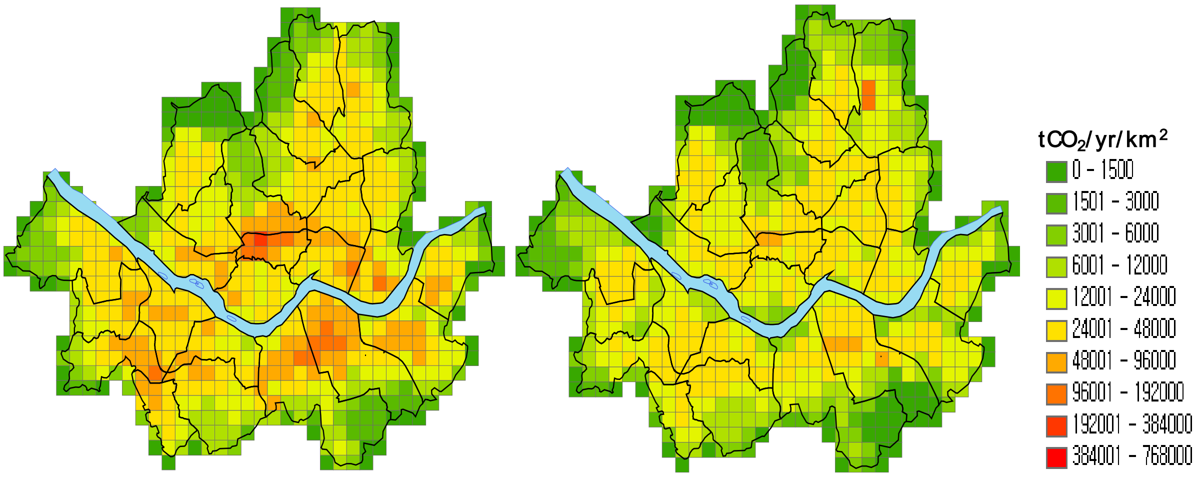

Figure 5. Spatial distribution of GHG emission from building ; Electricity(left), Gas(right)

The main object of this study is to divide GHG source by Usage. We could subdivide the electricity and gas by usage as lighting, appliances-operating, cooking & water-heating, heating and cooling energy. And we develop the monthly energy usage data of Seoul as 697 grids ; 1km by 1km.

When we make use of this result for constitute Source-Inventory database, we can make a effective and detailed GHG reduction plan. Moreover, because of the fuel consumption is basis of urban air pollution, the result about energy usage data to help actual input data for air pollution modeling.

## ACKNOWLEDGMENTS

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# A STUDY ON THE ESTIMATION OF THE NATURAL VENTILATION BY TRAIN-INDUCED WIND IN THE SUBWAY TUNNEL

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## ABSTRACT

As the volume of the road traffic increases, the underground transportation has been focused and developed recently. Especially, the subway is the main transportation system in Seoul as well as in other major cities for public. The environment of subway is not desirable due to its structural characteristics, and it is also exposed to citizens. The examination has been conducted for the air purification system for the management of the subway air quality and Platform Screen Doors(PSDs) installed to prevent pollution by train-induced wind. After installing PSDs, the platform air quality was improved, but the tunnel air quality got worse. Moreover, the aerodynamic effect became bigger when the train runs in the tunnel, but the accurate assessment and analysis are insufficient for the aerodynamic effect. The effect by train-induced wind of the ventilation in the tunnel is significant. So the reasonable and quantitative train-induced wind has to be evaluated and has to be applied to the design stage. This study was aimed to produce useful data for the IAQ(Indoor Air Quality) in subway; especially the train-induced wind has been investigated by means of field surveys and analyses. We carry out the field measurements to quantify the train-induced wind generated by train operation. We found out the quantitative train-induced wind and how the airflow forms by the train arrival and departure. We believe the results from this work will help engineers to understand the airflow in tunnels with PSDs. The recent updates including the quantified characteristics of the train-induced wind will be represented in this paper.

**Keywords:** train-induced wind, piston effect, subway, tunnel, ventilation shaft

## 1. INTRODUCTION

As the urban road traffic increases rapidly due to urbanization and industrialization, the subway, with superior punctuality and speed, has become the main transportation system in Korea as well as in other major countries. Recently, Platform screen doors (PSDs) have been introduced to prevent train-induced wind and dust, and to keep passengers from falling onto the track. The ventilation of a subway is crucial so that the passengers will have fresh and high quality air (Lowndes et al., 2004). The installation of PSDs have a significant impact on the air flow and smoke spread in case of a fire, and it will be necessary to optimize the design of the ventilation and smoke control systems in a subway equipped with PSDs. After installation of platform screen doors (PSDs) in subway stations, particulate matters (PMs), which are originally ventilated through the platform, are accumulated inside the tunnel of the subway system. It deteriorates an air quality in the tunnel. To ventilate the accumulated PMs in the tunnel, the ventilation shaft is used only. In addition, the installation of PSDs can affect to the changes in aerodynamic(aerodynamic variation) in the tunnel, since the PSD system was not considered factor when the tunnel ventilation system was designed. However, the researches for the tunnel ventilation system are not good enough. Therefore, this study is carried out for three objectives: 1) to measure the velocity of air current at the ventilation shaft by the train-induced wind, when the train passes through the tunnel, 2) to investigate the typical patterns of air current by quantitatively evaluating the characteristics of inflow/outflow of air current which passes through the natural ventilation system, and 3) to gather useful IAQ data from subway areas and to study the effect on IAQ caused by train-induced wind through field surveys and air quality analyses.

Earlier CFD simulations of tunnel ventilation system mainly focus on the emergency situation such as fire condition (Modic, 2003; Carvel et al., 2001). Many scientists and researchers (Gao et al., 2004) have done much work on this. Analysis of unsteady-state flow in the subway tunnel caused by subway operation should be developed as a basic design technology. Unsteady-state three-dimensional flow analysis in a subway tunnel with diverse variables such as train specifications, train speed, tunnel and station configurations can be effectively carried out with numerical methods. The objective of these efforts is to understand the flow field, including variation of aerodynamic forces and generation of compression waves during tunnel entry motion. The numerical method can model the moving boundary of the train in a subway equipped with PSDs, where the train has a simple shape. The moving grid method can effectively represent the complex solid shape and has been applied to studies on high-speed trains which have various flow features.

This study can suggest the basic standard to newly design the tunnel of the subway system as well as the ventilation system. We carried out field measurements to quantify the train-induced wind generated during train operation. The quantified characteristics of the train-induced wind will be represented in this paper.

## 2. EXPERIMENTAL METHOD

The experimental study was conducted at the ventilation shaft located at the subway tunnel in Seoul on May 27 in 2010. This section describes the facility (see Figure 1) and the experimental study was conducted to obtain field measurements for a station in operation. Figure 1 shows the schematic diagram of measurement. The upper image is the front view when the tunnel and the ventilation shaft are cut off vertical section and the lower image is the three dimensional view as the tunnel and ventilation shaft in figure 1. The gross-sectional area of the ventilation shaft is 13.52 ㎡. The measure point is 1.5m deep from the top of the ventilation shaft.

The purpose was to investigate the ventilation efficiency of piston effect for a draught relief shaft. The field measurement results for the station are presented in this paper. The push and pull of the piston effect will result in air movement in the draught relief shafts.

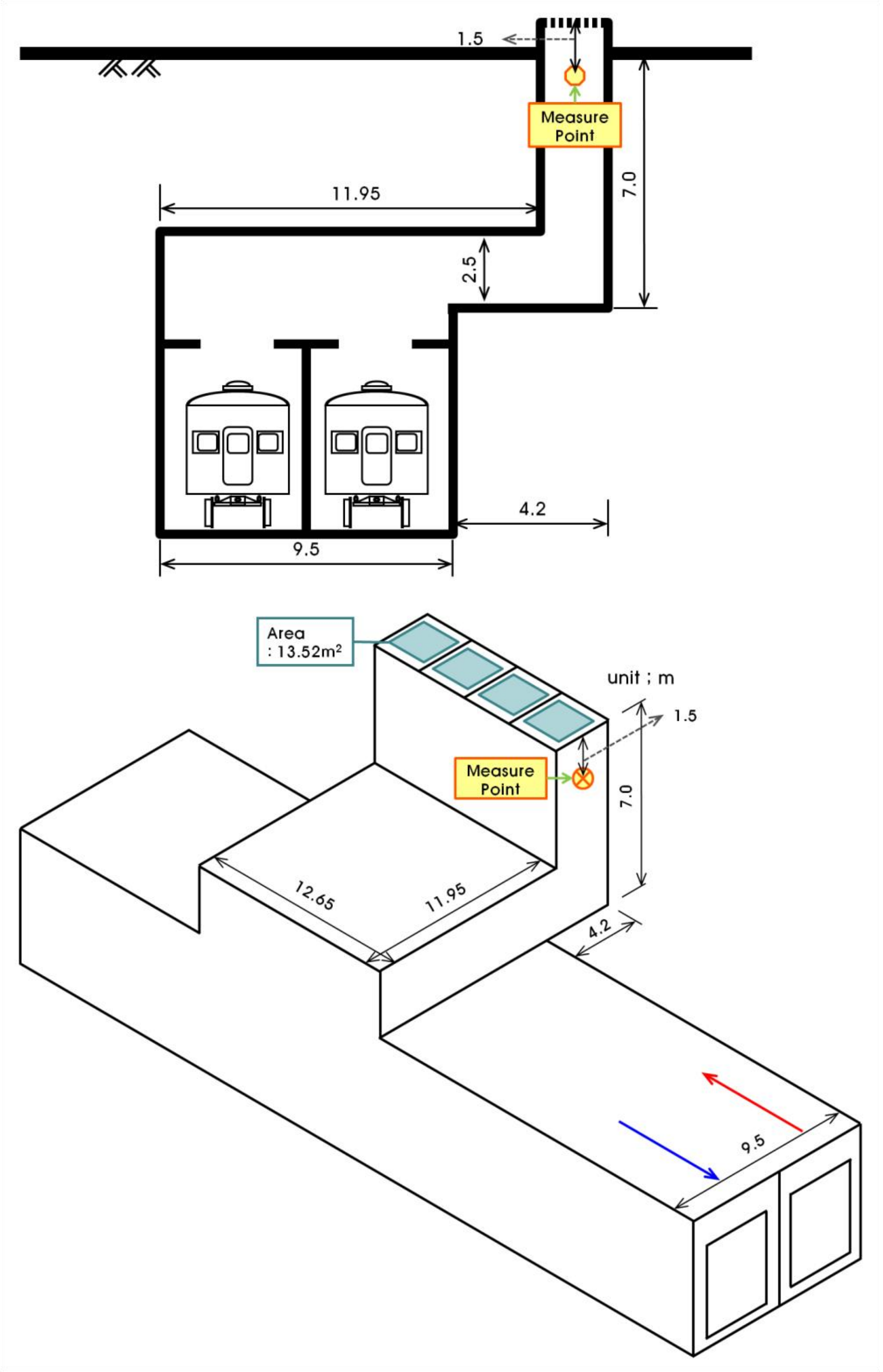

Figure 1. The schematic diagram of measurement (Front view and 3D)

The computational models were constructed and solved using STAR-CCM+ (5.02.009), general purpose commercial CFD software. The governing equations of implicit unsteady are mass conservation equation and Reynolds-averaged Navier–Stokes equations. The K-Epsilon turbulence model is used for turbulence closure: the model is based on the Boussinesq hypothesis with transport equations for turbulent kinetic energy and its dissipation rate.

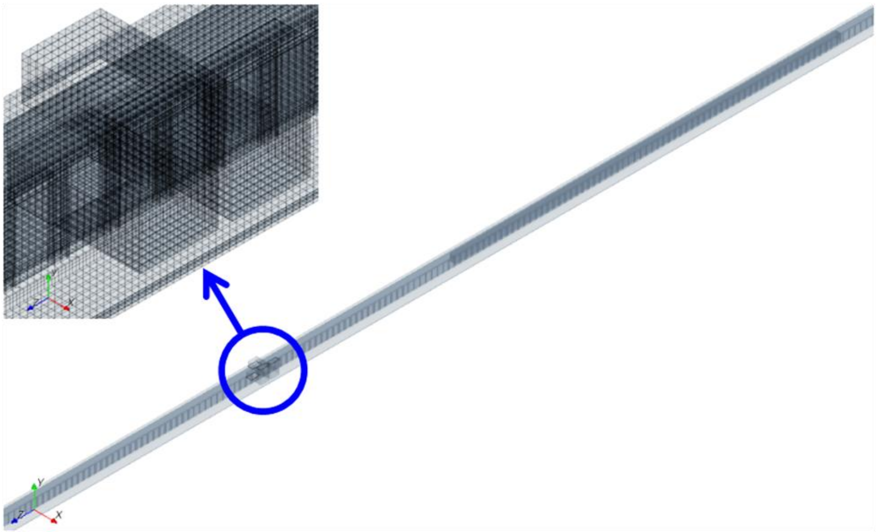

Figure 2. Geometry of the ventilation shaft (3D drawings)

Figure 2 shows the drawings of the tunnel and train and the solution domain and grid used is shown in Figure 3. The sharp interface method used in this study is numerical method for the moving boundary of an immersed solid. The entire solution domain of subway tunnel was divided into the moving area and station area by the boundary of sharp interface, and the area was set to be the solid three-dimensional boundary.

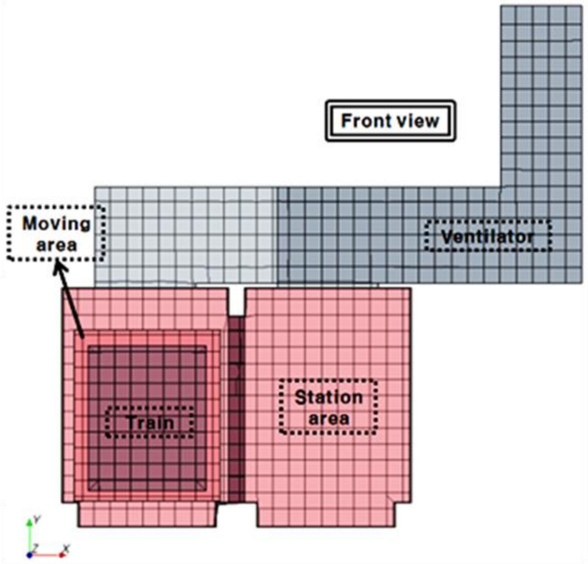

Figure 3. Computational domain of the tunnel, the train and the ventilation shaft 1

The numerical analysis was conducted for the case with the same geometric configurations and input velocity was the constant velocity (= 16 m/sec) as the experimental test to compare the results. The time step of unsteady analysis was set to be 0.1 s and the base surface size was set to be 0.4 m. The solution domain and grid used is shown in Figures 3~4 and the number of computational cells were total 1,348,330 cells.

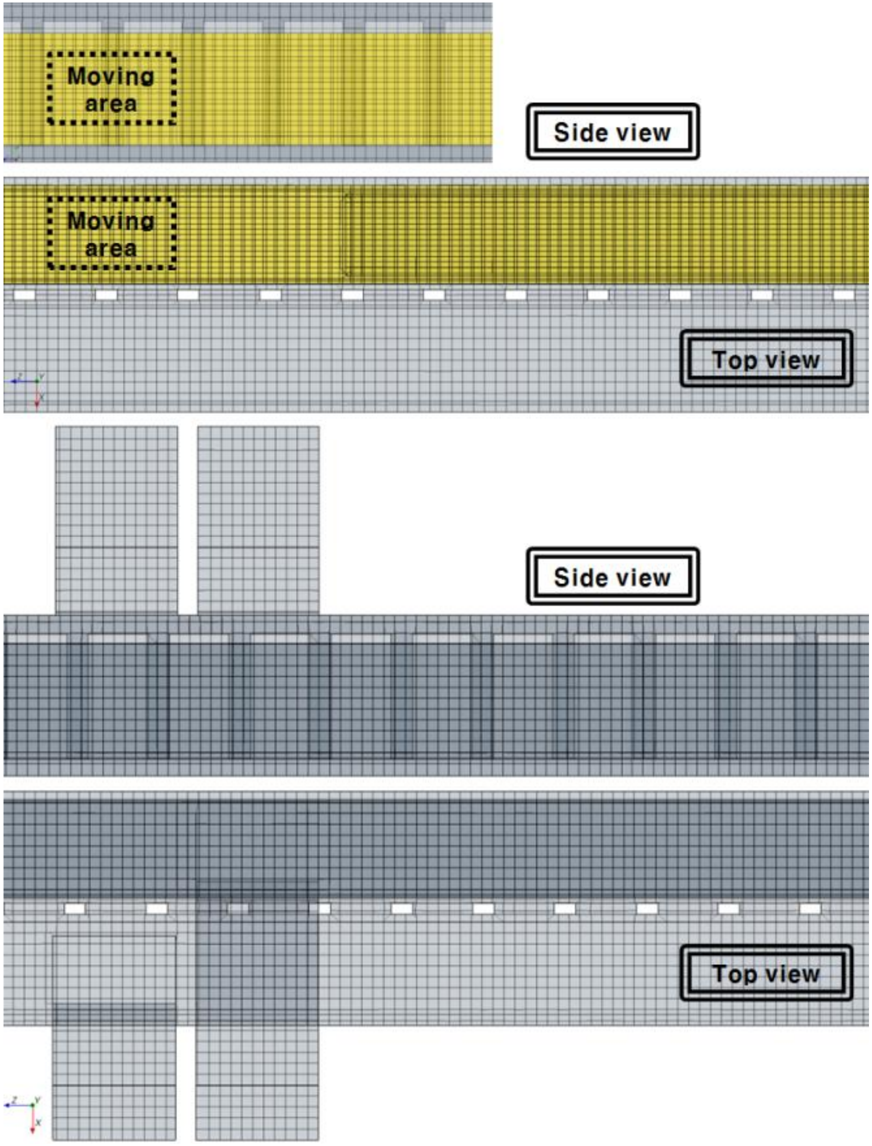

Figure 4. Computational domain of the tunnel, the train and the ventilation shaft 2

## 3. RESULT AND DISCUSSION

This study was focused on the characteristics of the air flow generated at the ventilation shaft when a train running the tunnel. We have conducted both experiments and numerical simulations with STAR-CCM+ (5.02.009) code which employed viscous coefficients to provide the required dissipation effect. We have described in detail the initial velocity rise and the velocity pattern once the train has left the confined area. We have confirmed the strong dependence of the pressure peaks on the train velocity and the nose shape, and detected their remarkable periodicity.

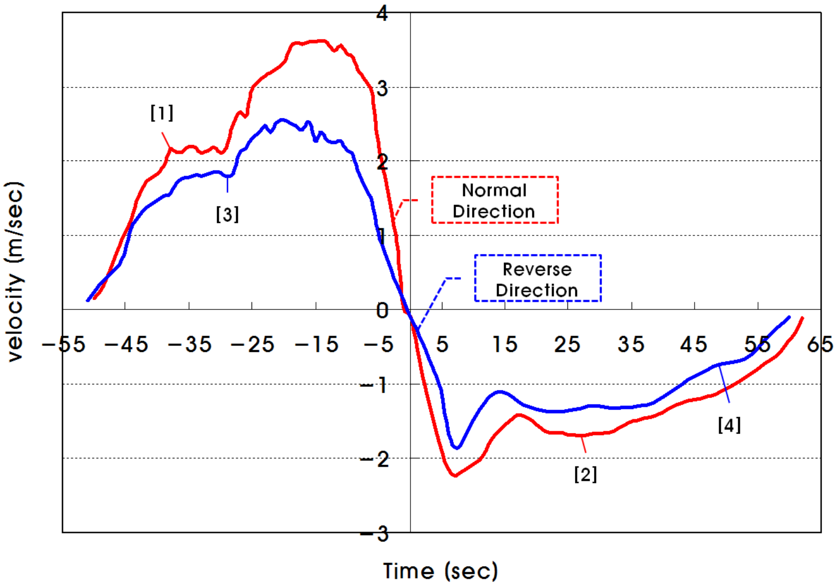

Figure 5. The result of the velocity at the ventilation shaft

Figure 5 shows the result of the velocity at the ventilation shaft when a train is running in the tunnel. The middle point of the horizontal axis (time = 0 sec) is when the train passes through the ventilation shaft. The push and pull of air due to train motion causes the air to flow back and forth in the shaft. The train operation is the prime factor for the piston effect. The train movement in the tunnel is a highly transient air moving problem. Piston effect was observed to be the main driving force for the shaft air flow. The left from the center express plus (+) and the right from the center express minus (-) in Figure 5. The direction of the wind expresses plus (+) when the wind comes out from the ventilation shaft and minus (-) when the wind comes into the ventilation shaft. The air is pushed out and pulled into the ventilation shaft about 50~60 sec. So the air flow data have positive and negative sign in Figure 5. The gross-sectional area of the ventilation shaft is 13.52m$^2$. So the volume flow rate data is shown in Table 1.

Table 1. The result of the quantification on the natural ventilation system

| | | Unit : m$^2$ |
|---|---|---|
| Normal Direction | Inflow | 1,567 |
| | Outflow | 1,149 |
| Reverse Direction | Inflow | 1,121 |
| | Outflow | 863 |

We have also compared the air flow trends generated by a train with the computational studies. The simulation results are shown in Figure 6. Vector contours at the ventilation shaft as a vertical section are presented. The direction of the subway operation (the front of the train) shows outflow velocity (about 1.8 m/sec) at the ventilator and the back of the train shows inflow velocity (about 1.3 m/sec) at the ventilator. The wind field formed by train operation is consistent with the experimental data.

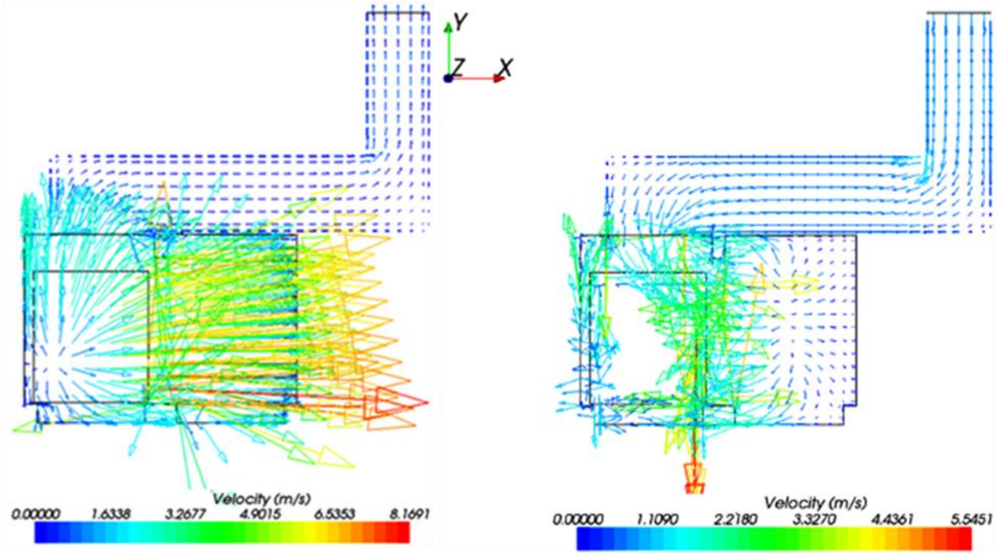

Figure 6. Vector contours in the vertical-section at the ventilation shaft

The main objective of this study was to investigate airflow in a subway tunnel at the ventilation shaft related with the running of the train. This study measured the periodic air flow due to piston effect of an operating underground subway in Seoul. A three-dimensional numerical analysis using the sharp interface method as a model for the moving boundary of an immersed solid was carried out to examine a train-induced, unsteady flow in a subway tunnel.

As the train passes by the tunnel, the flow rate increases suddenly. The train-induced wind is maximized immediately. Subsequently, as the train completely passes by the tunnel and starts to decelerate, the air flow continues increasing until the train enters in the tunnel at the ventilator. After the train goes out, the flow rate of air gradually decreases. The predicted numerical model results show good agreement with the experimental data.

## ACKNOWLEDGMENTS

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
**4th International Symposium and IUAPPA Regional Conference**
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# CHARACTERISTICS OF AIR POLLUTANTS EMISSION FROM BIOMASS BURNING IN KOREA : MAINLY COMMERCIAL CHARCOAL BURNER

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## ABSTRACT

Biomass burning is the burning of living and dead vegetation. It includes the human-initiated burning of vegetation for land clearing and land-use change as well as natural, lightning-induced fires. Scientists estimate that humans are responsible for about 90% of biomass burning with only a small percentage of natural fires contributing to the total amount of vegetation burned. Burning vegetation releases large amounts of particulates (solid carbon combustion particles) and gases (NOx, SOx, VOCs) including greenhouse gases that help warm the Earth. Greenhouse gases may lead to an increased warming of the Earth or human-initiated global climate change. Studies suggest that biomass burning has increased on a global scale over the last 100 years, and computer calculations indicate that a hotter Earth resulting from global warming will lead to more frequent and larger fires. Biomass burning particulates impact climate and can also affect human health when they are inhaled, causing respiratory problems. Commercial charcoal burners have operated in Korea, it has installed air pollution prevention equipments. But air pollution prevention equipments have emitted from oak commercial charcoal burner, the recent updates including the emission characteristics will be presented.

**Keywords:** biomass burning, charcoal burner, air pollutants, emission, oak

## 1. INTRODUCTION

Commonly source of air pollutants is a by-product from combustion process of substance. We heat house and drive the vehicles with burning of fossil fuel(coal, oil, natural gas, etc). Also, the house is heated by burning of vegetable biomass and people satisfy their appetite by grilling of animal biomass. When this fossil fuel or biomass burns complete combustion, there are by-products, carbon dioxide($CO_2$) and vapor. From these by-products, carbon dioxide($CO_2$) influences Global Warming. But burning of substance with incomplete combustion causes various air pollutants(NOx, SOx, fine particles, VOCs, PAHs, etc).

Now, it is assuming that commercial charcoal burner is the largest source of biomass burning in Korea(Park et.al., 2012). Commercial charcoal burner producing mainly charcoal mostly emissions air pollutants into the air without any air pollution prevention equipment. Part of commercial charcoal burner has air pollution prevention equipment but it’s difficult to work properly. The reason why air pollution prevention equipment has been out of order is regardless of characteristics of commercial charcoal burner emission. Especially, much wood tar excreted in exhaust emissions from oak charcoal manufacturing process. For this reason, air pollution prevention equipments can't work normally.

In this study, focusing commercial charcoal burner in biomass burning sector, we will provide preliminary data for effective processor and so on thereby understanding emission characteristics of air pollutants from oak charcoal manufacturing process.

## 2. METHOD

In this study, an object of study is commercial charcoal burner producing oak charcoal for understanding emission characteristics of air pollutants. Measure object is as following <Table 1>, it produces white charcoal mostly.

<Table 1> The sampling site and measuring period as time passed of exhaust gas from commercial oak charcoal burner .

| sampling site | charcoal burner number | charcoal type | charcoal making days | measuring period as time passed |
|---|---|---|---|---|
| Gapyeong #1 | 7 | fine charcoal | 7 | 2day, 4day, 6day |
| Yangpyeong #1 | 9 | | 6 | 2day, 4day |
| Yeoju #1 | 9 | | 6 | 1day, 2day, 3day |
| Hoengseong #1 | 33 | | 5 | 1day, 2day, 3day, 4day |

Air pollutants measuring in commercial oak charcoal burner can divide particulate matters($PM_{10}$, $PM_{2.5}$) and gaseous contaminants(CO, $SO_2$, NOx, offensive odor substance). Charcoal samples were collected from stack, the latter part of charcoal kiln. We took $PM_{10}$, $PM_{2.5}$ samples by isokinetic sampling using the stack sampler with cyclone kit(KNJ Engineering, EPA Method-5) and Whatman filter(47mm). It was taken for 30minutes. In addition, we used stack gas analyzer(Enerac, Model-500) for sampling CO, $CO_2$, NOx, $SO_2$, $O_2$. Offensive odor substance was sampled by gas sampler(KNJ Engineering) and tedler bag. GC/PFPD was used for analysis of offensive odor substance. Experimental facility list used measurement and analysis is as following <Table 2>.

<Table 2> The sampling items and measuring method of exhaust gas from commercial oak charcoal burner .

| Items | Sampling items | Measuring and analyzing method |
|---|---|---|
| Particulat | $PM_{10}$ | stack sampler with $PM_{10}$ Cyclone kit |

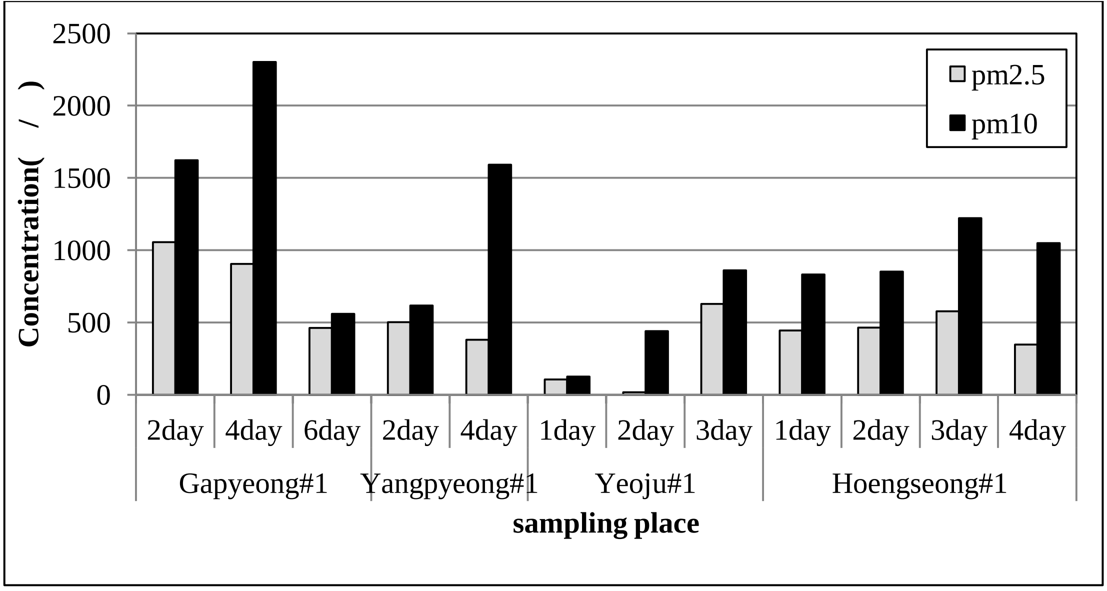
| | | | |
|---|---|---|---|
| matters | $PM_{2.5}$ | | stack sampler with $PM_{2.5}$ Cyclone kit |
| Gaseous | $CO$, $CO_2$, $NOx$, $SO_2$, $O_2$ | | Gas analyzer(Model 500) |
| Odor | Sulfide compound | Hydrogen sulfide<br>Methyl mercaptan<br>Dimethyl sulfide<br>Dimethyl sidulfide | GC/PFPD |
| | aldehyde | acetaldehyde<br>propionaldehyde<br>Butyraldehyde<br>Isovaleraldehyde<br>Valeraldehyde | HPLC - DNPH cartridge |
| | VOC | Toluene<br>Xylene<br>Styrene<br>Methyl ethyl Ketone<br>Methyl isobutyl ketone<br>Butyl acetate<br>Isobutyl alcohol | GC/MS |

<Figure 1> The sampling site of exhaust gas from commercial oak charcoal burner.

## 3. RESULTS

### 3.1 Particulate Matters

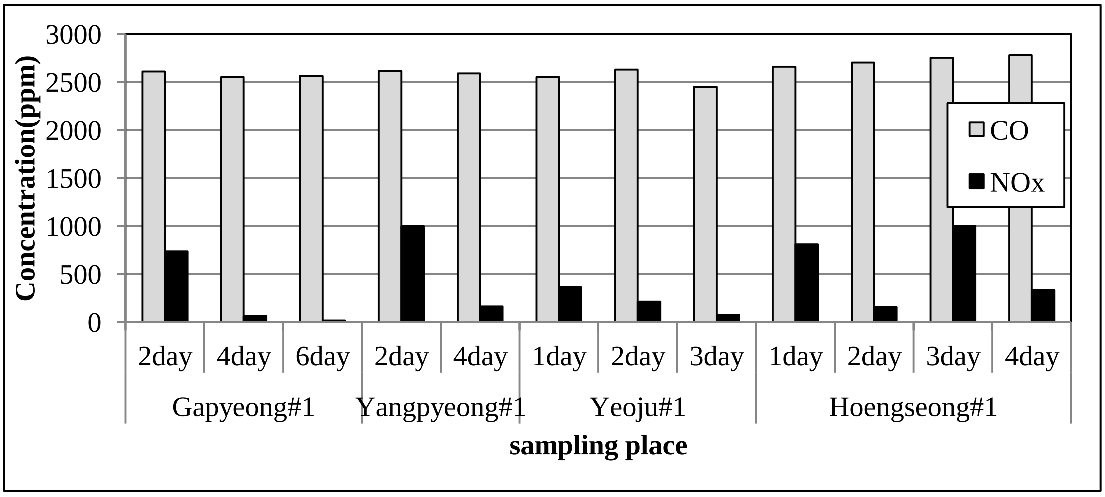
Concentration of $PM_{10}$ and $PM_{2.5}$ was measured by spot for measuring concentration of dust from each oak charcoal manufacturing process. The result of measurement is <Figure 2>. Average concentration of $PM_{10}$ was 1,005.93㎎/㎥, in case of $PM_{2.5}$ was 490.48㎎/㎥. These values were over the 100㎎/㎥ in TSP, this value was effluent quality standard of Clean Air Conservation Act. Generally, as time passed, concentration of $PM_{10}$ from oak charcoal manufacturing process increased from beginning to end, decreased in the end. Also moisture range in exhaust gas was about 30~60%, this moisture was condensed/collected and it used of pyroligneous liquor.



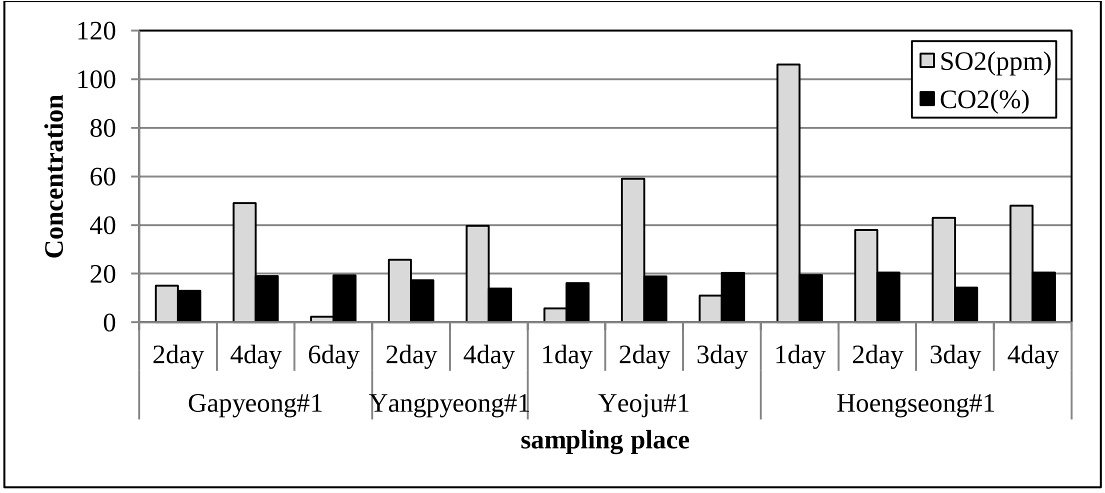
<Figure 2> The results of $PM_{10}$, $PM_{2.5}$ concentration from commercial oak charcoal burner.(Standard of TSP from stack of charcoal burner in Korea : 100㎎/㎥)

### 3.2 Gases

<Figure 3>~<Figure 4> is the concentration level of gaseous contaminants from oak charcoal burner vent. The result of gaseous air pollutants is as follows. Concentration of $O_2$ was the minimum 0.1%, it's quite low value. Concentration of $CO_2$ was the maximum 20.4%. It was considered the characteristic of pyrolysis process in oak charcoal manufacture. Average concentration of NOx was 410ppm. This value was over the 200ppm, that was effluent quality standard of Clean Air Conservation Act. Also average concentration of $SO_2$ was 37ppm, in case of CO was 2,621ppm.



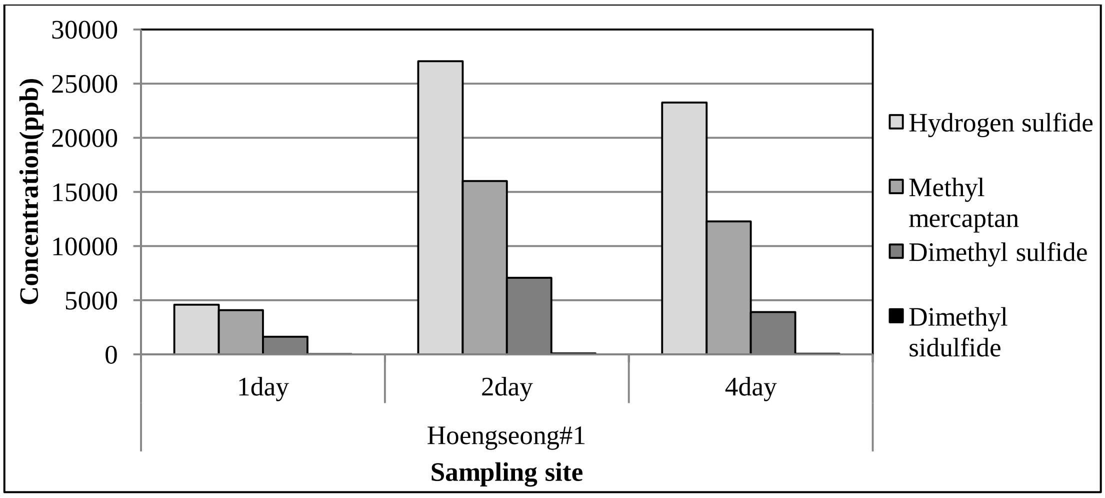
<Figure 3> The results of NOx, CO concentration from commercial oak charcoal burner.(Standard of NOx from stack of charcoal burner in Korea : 200ppm)



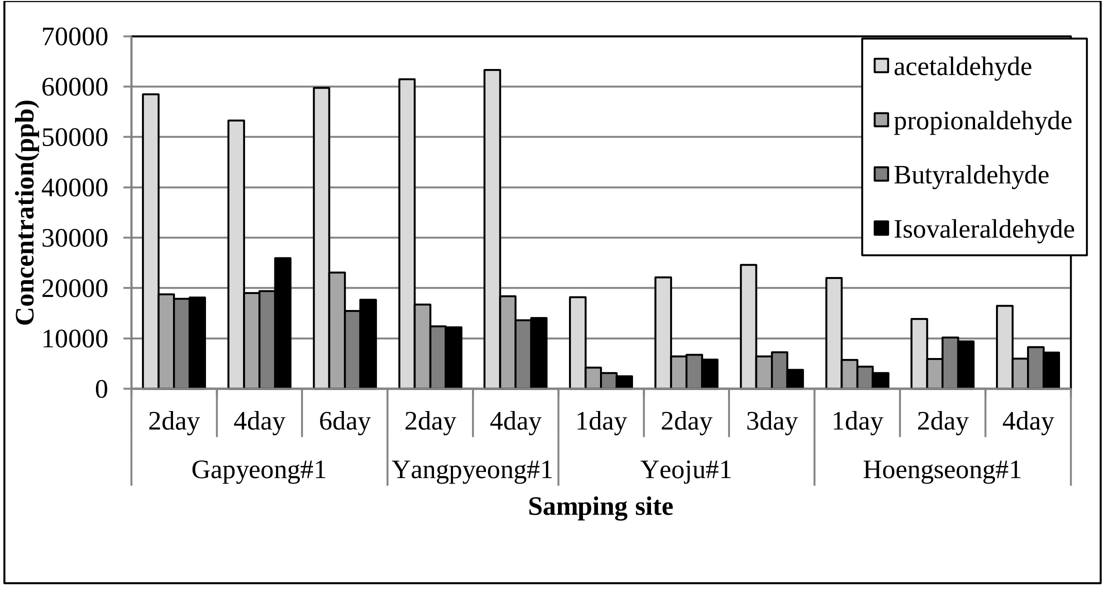
<Figure 4> The results of $SO_2$, $CO_2$ concentration from commercial oak charcoal burner.

### 3.3 Odor

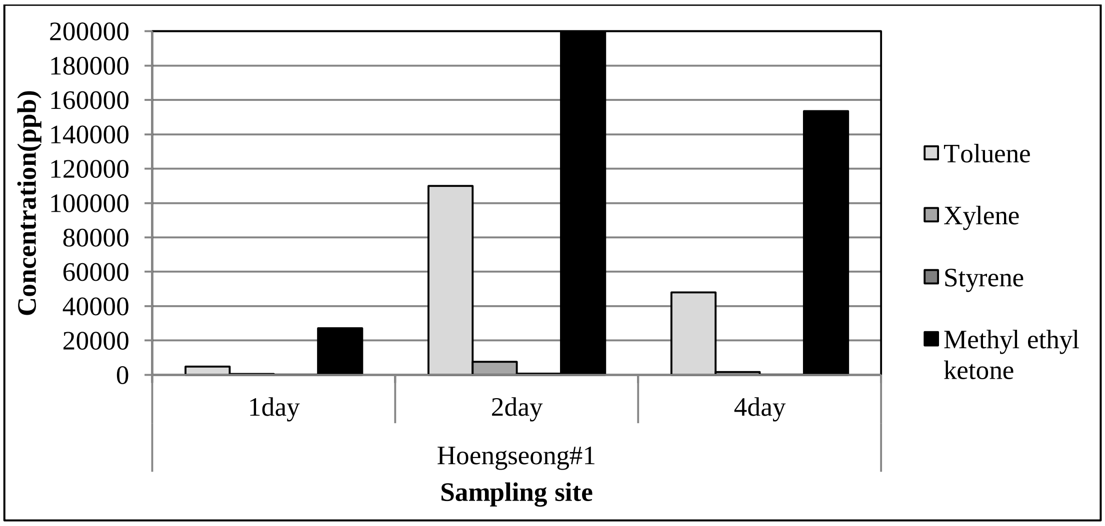
Offensive odor substance’s concentration level from oak charcoal manufacture process was shown very high. Concentration of sulfur compounds was exceeds compared with Korea odor effluent quality standard. It was appeared more than the maximum 1,000 times. Also, concentration of aldehyde type was over the standards except valeraldehyde. In case of VOCs, toluene was maximum 109,872ppb, xylan is maximum 13,282ppb. Concentration of VOCs from oak charcoal manufacturing process was mostly over the Korea odor effluent quality standard.



<Figure 5> The results of sulfide compounds concentration from commercial oak charcoal burner at Hoengseong#1.



<Figure 6> The results of aldehides concentration from commercial oak charcoal burner.



<Figure 7> The results of VOCs concentration from commercial oak charcoal burner at Hoengseong#1.

## 4. CONCLUSION

Results of air pollutants emission characteristics from commercial oak charcoal burner in biomass burning sector is as follows.

In each oak charcoal manufacturing process, average concentration of $PM_{10}$ was 1005.93㎎/㎥, in case of $PM_{2.5}$ was 490.48㎎/㎥. Generally, as time passed, concentration of $PM_{10}$ from oak charcoal manufacturing process was increased from beginning to end, was decreased in the end. Also moisture range in flue gas was about 30~60%. It was shown that average concentration of NOx was 410ppm, $SO_2$ was 37ppm, and CO was 2,621ppm.

Offensive odor substance's concentration level from oak charcoal manufacture process showed that very high concentration of aldehyde type was over the standards except valeraldehyde. In case of VOCs, toluene was maximum 109,872ppb, xylan was maximum 13,282ppb.

The result of field study, part of commercial charcoal burner had air pollution prevention equipment but it's difficult to work properly. Much wood tar excreted in exhaust emissions from oak charcoal manufacturing process. This wood tar causes many troubles sticking in the air pollutant prevention equipment. For handling particulate matters and gaseous air pollutants from oak charcoal manufacturing process in biomass burning, air pollutant prevention equipment design and management needs preprocessor for removal wood tar.

## ACKNOWLEDGEMENTS

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# Impact of biomass burning associated with anhydrosugars and carboxylic acids in ambient aerosol on Chiang Mai (Thailand) air quality

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## Abstract

Atmospheric particulate matter (PM) is a complicated mixture, mainly composed of inorganic substances and organic matter resulting from the marine pathway, biomass burning, agriculture burning, automotive exhaust emissions and anthropogenic emissions. These emissions impact on regional air quality and visibility, ecosystems and human health, and climate change. Chiang Mai sits in a basin and, with approximately 1 million inhabitants, is the largest city in northern Thailand. $PM_{10}$ aerosol was collected between February and April 2010 at an urban site (CMU) and an industrial site (TOT) in Chiang Mai and characteristics and provenance of water-soluble inorganic species, carboxylic acids, anhydrosugars and sugar alcohols were investigated with particular reference to air quality, framed as episodic or non-episodic pollution. Sulfate, a product of secondary photochemical reactions, was the major inorganic salt in $PM_{10}$. Acetic acid was the most abundant monocarboxylic acid, followed by formic acid. Oxalic acid was the dominant dicarboxylic acid. A high acetic acid/formic acid mass ratio indicated that primary traffic-related and biomass-burning emissions contributed to Chiang Mai aerosols during episodic and non-episodic pollution. During episodic pollution carboxylic acid peaks indicated sourcing from photochemical reactions and/or directly from traffic-related and biomass burning processes and concentrations of specific biomarkers of biomass burning including water-soluble potassium, glutaric acid, oxalic acid and levoglucosan dramatically increased. Levoglucosan, the dominant anhydrosugar, was highly associated with potassium ($r$=0.75~0.79) and accounted for 93.4% and 93.7% of anhydrosugars at CMU and TOT, respectively, during episodic pollution. Moreover, levoglucosan during episodic pollution was 14.2-21.8 times non-episodic lows, showing clearly that emissions from biomass burning are the major cause of $PM_{10}$ episodic pollution in Chiang Mai. Additionally, the average levoglucosan/mannosan mass ratio during episodic pollution was 14.1~14.9, higher than the 5.73~7.69 during non-episodic pollution, indicating that there was more hardwood burning during episodic pollution. Higher concentrations of glycerol and erythritol during episodic pollution further indicate that biomass burning activities released soil biota from forest and farmland soils.

**Keywords:** Aerosol; Biomass burning; Biomarkers; Anhydrosugars; Carboxylic acids; Levoglucosan; Sugar alcohols

# Bioaerosol microbial activity in indoor environments using ATP bioluminescence

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## Abstract

Adenosine-5'-triphosphate (ATP) exists in all living cells as a source of energy that can be easily stored and used when needed for cellular functions. The measured ATP reflects microbial activity and indirectly indicates the quantity of microorganisms present. Microbial biomass can be quantified by measuring ATP via bioluminescence, and because of this ATP bioluminescence technology has been widely applied in many fields in which microbial load/activity is important. An ATP bioluminescence method was developed for detecting microbial activity in indoor air. This method was compared with the traditional method of collection, culture and count of CFUs. The comparison showed that ATP bioluminescence, expressed as RLUs, was moderately correlated with the entire set of CFU counts ($r$=0.607), and that correlation improved to $r$=0.963 ($p$ value< 0.001) when outlying CFU counts were removed from the calculation. The ATP bioluminescence method was applied at four different sites; a hospital Chinese medicine diagnostic room, a library, a government office, and a railway station lobby. Results showed that microbial activity was far higher in the railway station lobby than at the other three sites and this was seen as a result of the higher volume and density of people in this space. At all four sites, higher microbial activity was linked to indoor plants, garbage cans, shoe racks, and furnished waiting areas. PCA of the data showed that microbial activity in the Chinese medicine diagnostic room was closely related to room temperature and humidity and hence lowering the room humidity can reduce the microbial activity potential here. At all four sites, no correlation was identified between microbial activity and airborne pollutants. The ATP bioluminescence method was applied for the rapid evaluation of room disinfection using chloride dioxide and results showed that twenty minutes after spraying with 100 ppm $ClO_2$, microbial activity was reduced to 38.7% of its original level. The results obtained in this research confirm that the proposed ATP bioluminescence technique is capable of instantaneously detecting microbial activity in an indoor environment. Moreover, the results can be implemented for on-line evaluation of room disinfection efficiency.

**Keywords:** ATP bioluminescence; Bioaerosol; Microbial activity; Relative light unit; Principal component analysis; Indoor air quality

# A MULTI-SITE STUDY OF RAINWATER CHEMISTRY WITHIN TURKEY

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## ABSTRACT

Turkish State of Meteorological Service has been operating stations at different parts of Turkey in an attempt to elucidate acidity of rainwater and to find the impact of local and remote sources influencing the chemical composition of the samples collected at the sites. In this manuscript, rainwater chemistry corresponding to four of these monitoring sites in nearby urban and rural areas has been evaluated in terms of major ions. Modified automated Andersen rainwater sampler was deployed to collect rainwater samples at Çatalca (2005-2011), Amasra (2004-2011), Balıkesir (2004-2011), and Antalya (2005-2011). The species concentrations ($SO_4^{2-}$, $NO_3^-$, $Cl^-$, $NH_4^+$, $Na^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$) were measured by Ion Chromatograph (Dionex DX120). The pH of the samples was measured by means of pH (Selectra 2001) meter. It has been found out that acidity of precipitation across Turkey has a decreasing gradient from west to east. Calcium and $Mg^{2+}$ are the dominant alkaline species taking part in the neutralization process.

**Keywords:** Rainwater Chemistry, Acidity, Major Ions, Neutralization

## 1. INTRODUCTION

The precipitation is an efficient scavenging way for pollutants present in the atmosphere as a result of biogenic and anthropogenic emissions. When pollutants associated with the particles scavenged with rain, they reach to terrestrial and aquatic environments, where they affect all biogeochemical processes (Santos et al., 2011).

The study of rainwater chemistry is important since it gives information about the sources of pollutants in addition to local and regional dispersion mechanisms affecting the precipitation chemistry. Although vast majority of the studies on the precipitation chemistry have been conducted over the Western Europe (e.g., Puxbaum et al., 2002; Avila and Roda, 2002; Celle-Jeanton et al., 2009; Ladouche et al., 2009), the studies on the Eastern counterpart including Turkey are very rare.

The main pollutants that generate the acidity are sulfur and nitrogen species are of particular concern in terms of precipitation chemistry. Figure 1 shows the sulfate trend in terms of sulfur over the Europe between 1993 and 2006. The data were compiled from the European Monitoring and Evaluation Program (EMEP) network. The only EMEP station that is located in Turkey is Çubuk station, which is in the capital city of Turkey, Ankara. The data for the Antalya station was generated between 1993 and 2001 (Öztürk et al., 2012).

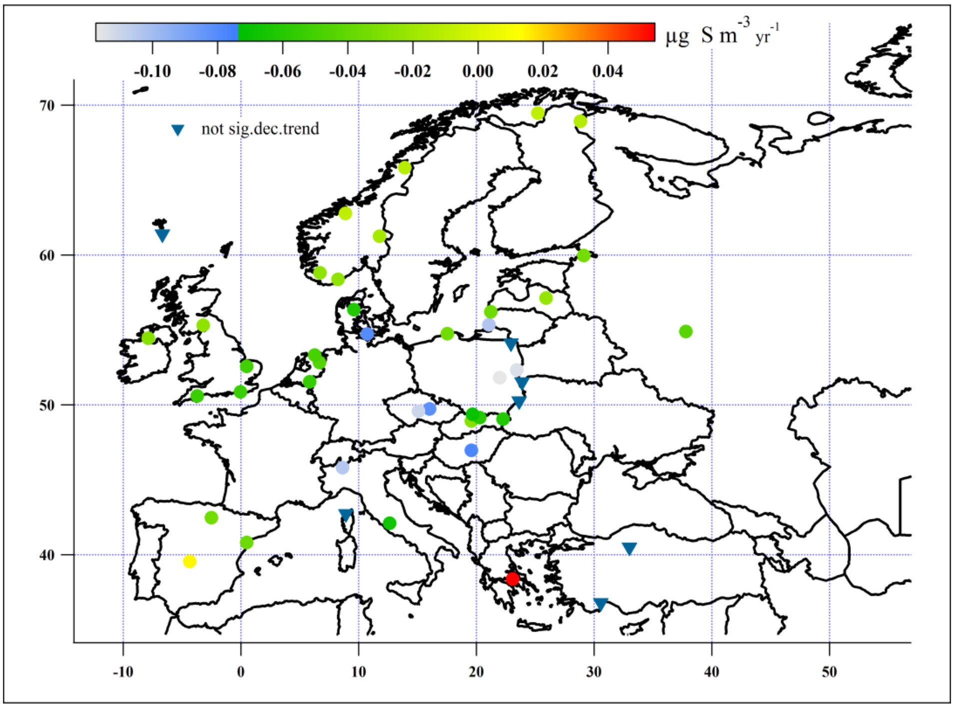

**Figure 1:** The temporal variation of particle bounded sulfate in Eastern and Western Europe between 1993 and 2006

It is clear from Figure 1 that significant decreasing trend ($p<0.05$) in sulfate concentration was recorded over almost whole Europe between 1993 and 2006. The decreasing trend for the two stations (Antalya and Çubuk) was also observed in terms of this acidifying pollutant but this is not statistically significant. Consequently, one might expect to see the contribution of sulfate as well as other pollutants to the acidity of rainwater samples collected across the country over the years.

State Meteorological Institute of Turkey has started a local network across Turkey in attempt to monitor the rainwater chemistry. The main objective of the network is to distinguish the local and remote sources influencing the chemical characteristics of precipitation samples collected currently at five different stations (Amasra, Trabzon, Çatalca, Balıkesir and Antalya).

The objectives of this manuscript are to compare the precipitation chemistry recorded at these five stations in terms of pH and major ions. The dominant neutralizing parameters and contribution of pollutants to the acidity of the precipitation will be discussed.

## 2. METHODS

Daily precipitation samples were collected by automated Andersen rain sampler at Amasra (32.38°E, 41.75°N, 2004-2011), Çatalca (28.36°E, 41.34°N, 2004-2011), Trabzon (39.63°E, 40.74°N, 2009-2011), Balıkesir (27.62°E, 39.74°N, 2004-2011) and Antalya (30.43°E, 36.97°N, 2005-2011) stations. The collected precipitation samples were analyzed by a combination of analytical techniques in terms of major ions and pH. The major ions ($SO_4^{2-}$, $NO_3^-$, $Cl^-$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, and $Na^+$) were determined by the Dionex DX120 Ion Chromatography (IC). Selectra 2001 model pH meter was used to measure the of the samples.

## 3. RESULTS and DISCUSSION

### a. Comparison of pH and Ionic Content of the Precipitation Data

The following two reactions occur in the pristine environment determine the acidity of the precipitation:

$$H_2O(l) + CO_2(g) \leftrightarrow H_2CO_3(aq) \qquad (Equation\ 1)$$

$$H_2O(l) + H_2CO_3(aq) \leftrightarrow HCO_3^-(aq) + H_3O^+(aq) \qquad (Equation\ 2)$$

According to the first reaction, carbon dioxide reacts with water and form carbonic acid, which then deliberates proton. The ability of carbonic acid to deliver proton makes this compound acid (Charlson and Rodhe, 1982). The second reaction set the pH of the rainwater to 5.6. In general, the rainwater having a pH value less than 5.6 is considered as acidic. The volume weighted mean pH values of precipitation samples collected at the aforementioned stations were calculated and results were depicted in Figure 2 below. The "NR" in Figure 2 stands for natural rainwater.

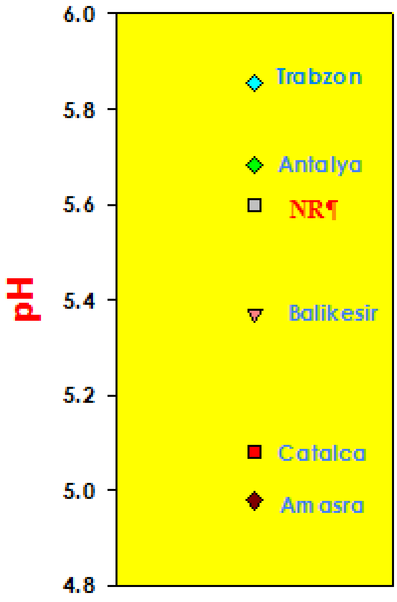

**Figure 2:** The volume weighted mean pH of rainwater samples collected at stations (**NR**: Natural rainwater)

It can be revealed from Figure 2 that Amasra, Çatalca and Balıkesir stations have pH values less than 5.6 indicating that acidic deposition is an issue for these stations. In contrast to these stations, Trabzon and Antalya stations receiving more basic rains since the mean pH value of the precipitation samples collected at these stations is greater than 5.6. The percentage of acidic and basic rains was also calculated and results were depicted in Figure 3. It is clearly shown in the Fig.3 that Amasra is receiving acidic rains almost 40 % of time while this value is just 6 % for Antalya station. The observed spatial trend in the pH of the precipitation can be explained by the density of the industry. The most of the heavy industry is located at the western part of the Turkey, particularly, around the Marmara region. The released pollutants contribute to the acidity of the precipitation around this region.

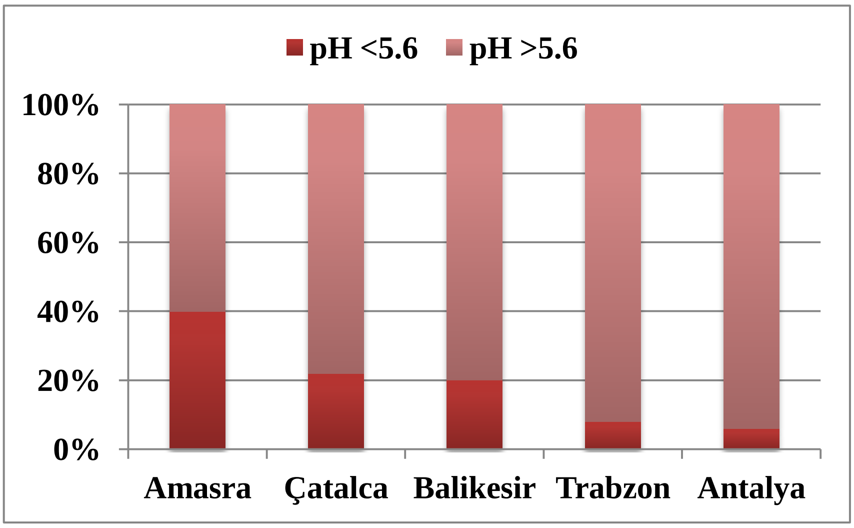

**Figure 3:** Percent of acidic and basic rains observed at the stations

Figure 4 shows the ionic composition of the rainwater samples collected at the station. With the exception of $Ca^{2+}$, all of the measured parameters showed maxima at Çatalca station. The highest (around 140 µeq L-1) $Ca^{2+}$ concentration was recorded at Antalya station. As it is expected from the discussion on the rainwater acidity, relatively higher concentrations of acidic compounds ($NO_3^-$ and $SO_4^{2-}$) were recorded at Çatalca, Amasra and Balıkesir stations.

## a. Neutralization of Acidity

The pH of the rainwater alone provides very limited information on the acidity of the collected samples. On the other hand, the chemical composition and hence acidity of the precipitation is determined by the basic and acidic species. The ions of $K^+$, $Na^+$, $Ca^{2+}$, $Mg^{2+}$ and $Cl^-$, are all common, mostly naturally emitted to the atmosphere, and their presence in the precipitation is minor environmental significance. On the other hand, $SO_4^{2-}$ and $NO_3^-$ are mostly released from the anthropogenic activities and they are converted to the $HNO_3$ and $H_2SO_4$ in the atmosphere and contribute to the acidity significantly. When speaking about the acidity of the precipitation, acidity caused by two major anions and neutralization by the existing alkaline species should be taken into account.

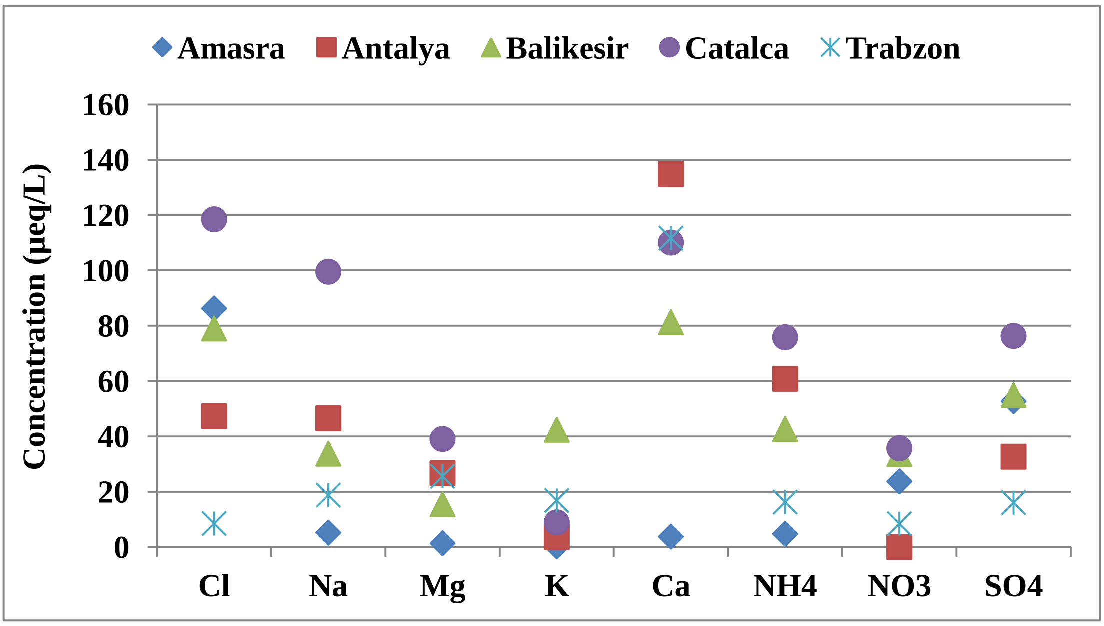

**Figure 4:** The ionic content of the precipitation samples collected at five stations

The equivalent molar ratio of $H^+$ to the sum of $SO_4^{2-}$ and $NO_3^-$ gives information on the neutralization capacity of the precipitation. The calculated ratios were depicted in Figure 5. The error bars show the ± one standard deviation. The calculated ratio for Amasra station is 20 % implying that 80 % of the acidity is neutralized by the basic species present in the precipitation samples at this station. The lowest ratio, around 5%, was calculated for Antalya station indicating that almost 95 % of the acidity is neutralized by the alkaline parameters at Antalya.

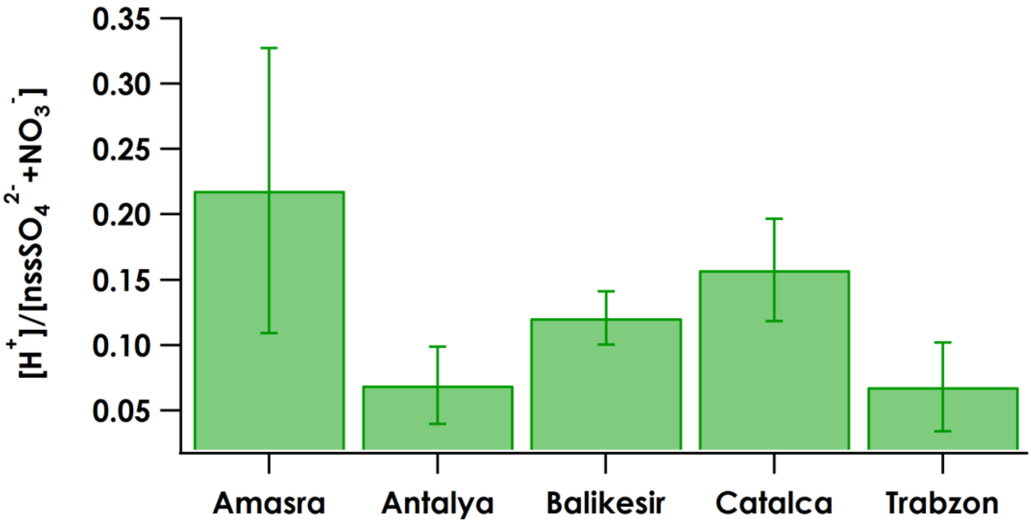

**Figure 5:** Fractional acidity at five stations

In order to make judgment on the relative contribution of two acidic compounds on the measured acidity, the equivalent ratio of $NO_3^-$ to the sum of $NO_3^-$ and $SO_4^{2-}$ was calculated for each station and results were depicted in Figure 6. The error bars stand for one calculated standard deviation.

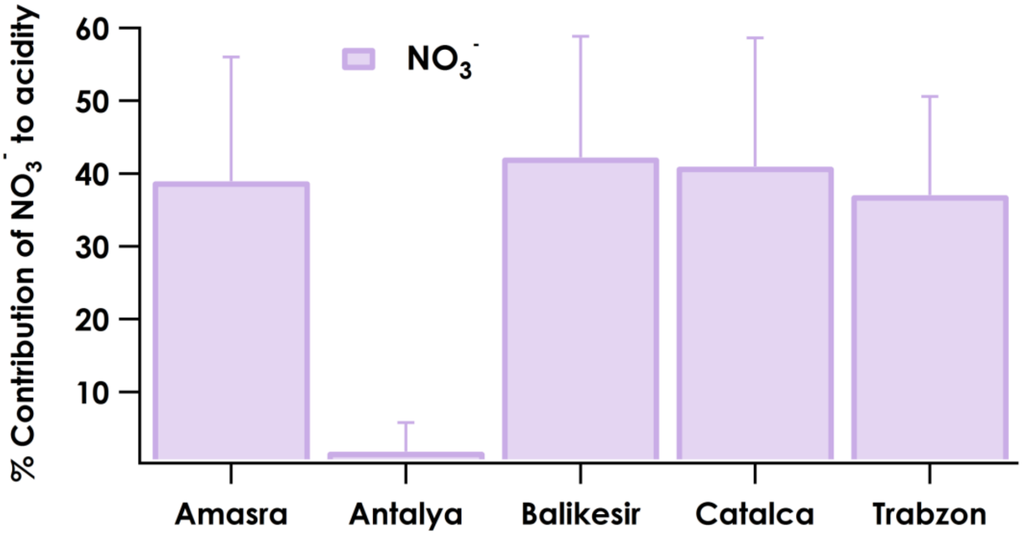

**Figure 6:** The contribution of $NO_3^-$ to the total acidity at five stations

It is clearly shown in the Figure 6 that the contribution of $NO_3^-$ to the acidity is about 40 % for all of the stations with the exception of Antalya, for which the contribution is only 2 %. The conclusion can be drawn from this result is that $SO_4^{2-}$ is the dominant acidic compound determining the acidity of the precipitation samples collected across the country.

Parashar et al. (1996) suggested the following formulae for the calculation of neutralization factor (NF) for different alkaline constituents ($NH_4^+$, $Ca^{2+}$, $Mg^{2+}$ and $K^+$) in rainwater:

$$NF(Ca^{2+}) = \frac{nssCa}{NO_3 + nssSO_4} \qquad (Equation\ 3)$$

Sodium and $Cl^-$ are emitted to the atmosphere through bubble bursting process in the form of sea salt and hence their contribution to the neutralization is negligible. Equation 3 was used to calculate the NF of other alkaline species. The NF value for each species and each station was calculated and results were depicted in Figure 7.

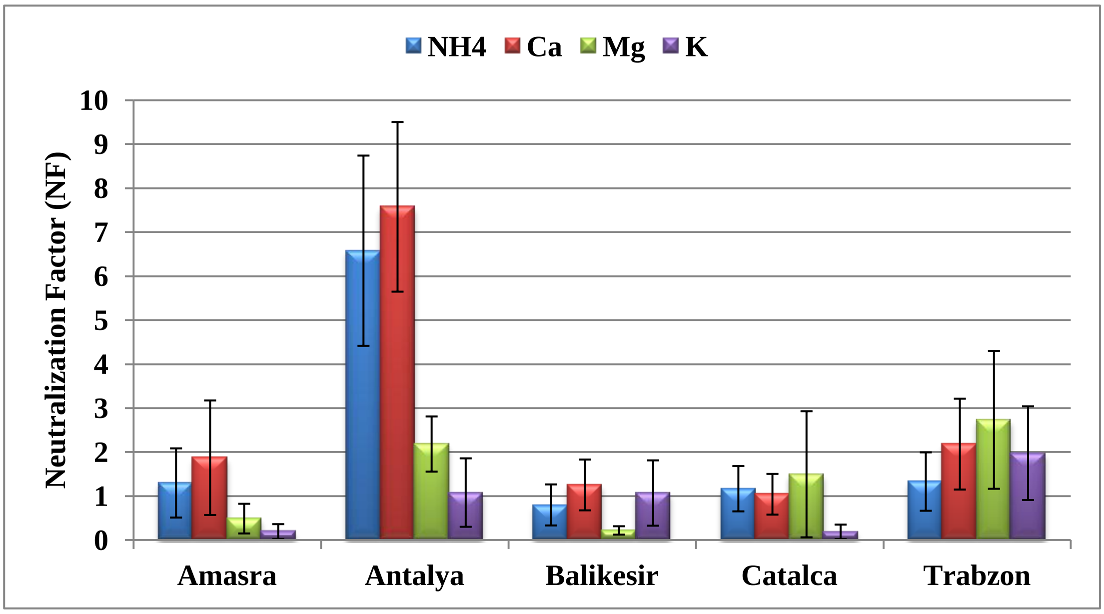

**Figure 7:** The neutralization factor calculated for different alkaline constituents for five stations

It can be revealed from Figure 7 that $Ca^{2+}$ is the main neutralizing agent in Amasra, Antalya and Balıkesir stations while $Mg^{2+}$ is the dominant alkaline specie in the neutralization of acidity in Trabzon and Çatalca stations.

## 4. CONCLUSION

Volume weigted mean pH values for precipitation samples were ranged from 4.98 to 5.68. Lowest mean $SO_4^{2-}$ level was recorded for Antalya (32.7 µeq/L) while Çatalca has the highest $SO_4^{2-}$ concentration (76.4 µeq/L) throughout the sampling period. Similar pattern was observed for $NO_3^-$ suggesting that contribution of sources on the air quality profile of western part of the Turkey is much more pronounced as compared to that of southern part of the country. Fractional acidity (equivalent ratio of $H^+$ to the sum of $nssSO_4^{2-}$ and $NO_3^-$) was calculated for stations and it has been found out that 80 % of the acidity was neutralized by alkaline species in Amasra station while this value was higher than 90 % for rest of the stations. Calculated neutralization factor values indicated that $Ca^{2+}$ served as major neutralizing component for Amasra, Antalya and Balıkesir stations while $Mg^{2+}$ is main neutralizing ion for Çatalca and Trabzon stations.

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AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES
4th International Symposium and IUAPPA Regional Conference
10-13 September 2012 Istanbul -Turkey

# A COMPARATIVE STUDY OF AIR QUALITY PARAMETERS MONITORED AT SIX DIFFERENT STATIONS IN TURKEY

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## ABSTRACT

$PM_{10}$ and gaseous pollutants (NO, $NO_2$, $O_3$, CO and $SO_2$) have been monitoring by Turkish Ministry of Environment and Urban Planning since 2006 both by ground base and mobile stations in most part of the Turkey. In this manuscript, data generated for six of these stations between 2006 and 2010 were evaluated. Three of these stations were located in Ankara, capital city of Turkey. In addition to pollutants listed above, $PM_{2.5}$ samples and meteorological parameters were also monitored in Ankara stations. Two of these stations were placed in İstanbul, which accommodates 15 million people as the largest city of Turkey. The last station was present in Kocaeli, which is about 110 km far away from the İstanbul and known as the one of the cities with poor air quality due to heavy industry. In this manuscript, the differences and similarities between the stations were investigated by means of cluster analysis. Used K-means clustering revealed that the similarity between stations located in Kocaeli and İstanbul is higher as compared to ones in Ankara, which can be linked to higher pollution in Marmara region, where Kocaeli and İstanbul present.

**Keywords:** $PM_{10}$, $PM_{2.5}$, Gaseous Pollutants, Meteorology, Cluster Analysis

## 1. INTRODUCTION

Jacobson (2002) defined the air pollution as “when gases or aerosol particles emitted anthropogenically, build up in concentrations sufficiently high to cause direct or indirect damage to plant, animals, other life forms, ecosystems, structures, or works of art”.

The condition of air pollution is generally expressed as air quality. Air quality is determined by number of factors including emission strengths, topography and meteorology. Concentrations, size and number distributions of particulate matter (PM) and concentrations of gaseous pollutants ($NO_x$, $SO_2$ and $O_3$) are the main metrics in deciding the quality of air.

Both PM and gaseous pollutants are released to the atmosphere from anthropogenic and biogenic sources. For instance, $PM_{10}$ and $PM_{2.5}$ (PM with aerodynamic size less than 10 and 2.5 µm, respectively) are directly emitted from sources such as biomass burning, incomplete combustion of fossil fuels, volcanic eruptions, wind-blown dust, sea-salt and plant debris. In addition to direct emissions, these particles are produced in the atmosphere either from gas to particle conversion and/or condensation of gases on pre-existing particles (Monks et al., 2009). The oxides of nitrogen, NO and $NO_2$, are among the most important species in atmospheric chemistry and sources range from fossil fuels combustion to soil (Seinfeld and Pandis, 2006). Ozone is a photochemical pollutant generated in the troposphere by the reactions between $NO_x$, CO, methane and non-methane volatile organic compounds (NMVOCs) in the presence of sunlight and high temperatures (Sillman, 2003; Jacob and Winner, 2009).

The objective of this study is to explore the diurnal and seasonal variations of air quality parameters ($NO_x$, $O_3$, $SO_2$, CO, $PM_{10}$, and $PM_{2.5}$) in six different stations in Turkey. In addition, the similarities and differences between the stations will be discussed.

## 2. DATA

Air Quality Network of Turkey is operated by the Ministry of Environment and Urban Affairs provides information on several pollutants such as $PM_{10}$, $NO_x$, $SO_2$, $O_3$ and CO in addition to $PM_{2.5}$ and meteorological information in some of the stations. The data is evaluated in this manuscript was obtained from this network for six stations (Alibeyköy, Kadıköy, Dilovası, Cebeci, Keçiören and Sincan) between 2006 and 2010. Cebeci, Keçiören and Sincan stations were located in Ankara, the capital city of Turkey. Alibeyköy and Kadıköy stations are in Istanbul, which is the city with the highest population density in Turkey. Dilovası present in Kocaeli, which includes many industrial establishments.

## 3. RESULTS and DISCUSSION

As it was stated previously, air quality data corresponding to the six different stations were obtained in this manuscript. However, since the diurnal and seasonal pattern of the pollutants show very similar pattern in all stations, the detail interpretation for only one station, Cebeci, was performed herein.

### a) Diurnal Variations

The annual average diurnal variation for $NO_x$, $O_3$ and CO was depicted in Figure 1 below.

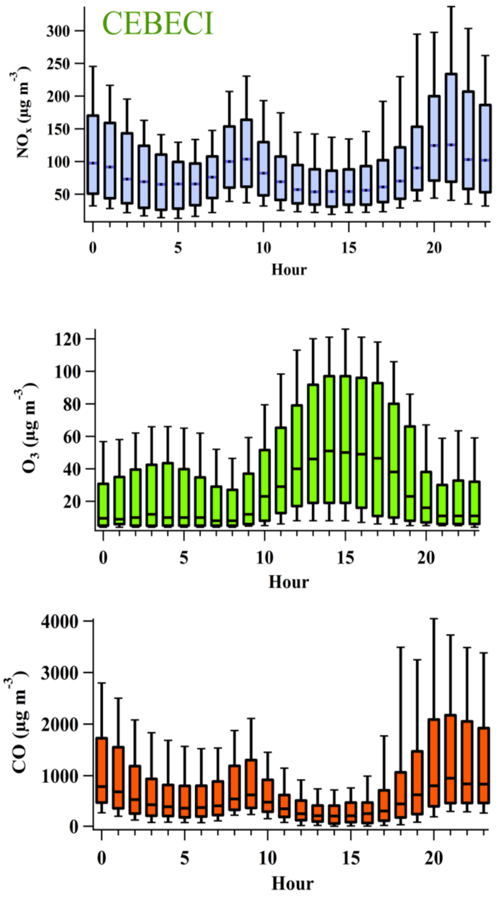

**Figure 1:** The annual average diurnal variation of $NO_x$, $O_3$ and CO

The daily cycles of these pollutants in urban atmosphere is determined by the traffic emissions, photochemical activity and mixing height. The pattern observed in this station was also recorded for other stations in Europe (e.g., Kourtidis, 2002; Vandaele et al., 2002).

The highest mean concentration for the secondary pollutant $NO_x$ was recorded in 8:00 and 9:00 local time (LT) in the morning (see Figure 1). Since traffic intensity and human activities peaked in the early morning at these hours, $NO_x$ emissions increases. The second peak of $NO_x$ in the evening hours (20:00-21:00 LT) is also consistent with the traffic density in the city. However, the concentration corresponding to the second peak is relatively higher than the morning hours, which can be attributed particularly to the increased $NO_2$ concentrations with time. The trend for CO is quite same with the one observed for $NO_x$. Carbon monoxide peaked at 9:00 LT and 21:00 LT in the morning and evening rush hours, respectively. Ozone concentration increases significantly starting from around midday and peaked at 14:00-15:00 LT due to increased photochemical activity. The concentration of $O_3$ decreased gradually after 16:00 LT.

In order to understand the impact of meteorological factors and emissions on the recorded $O_3$ concentration factor analysis was conducted on the data set and results were shown in Figure 2. Factor analysis identified three factors affecting $O_3$ levels.

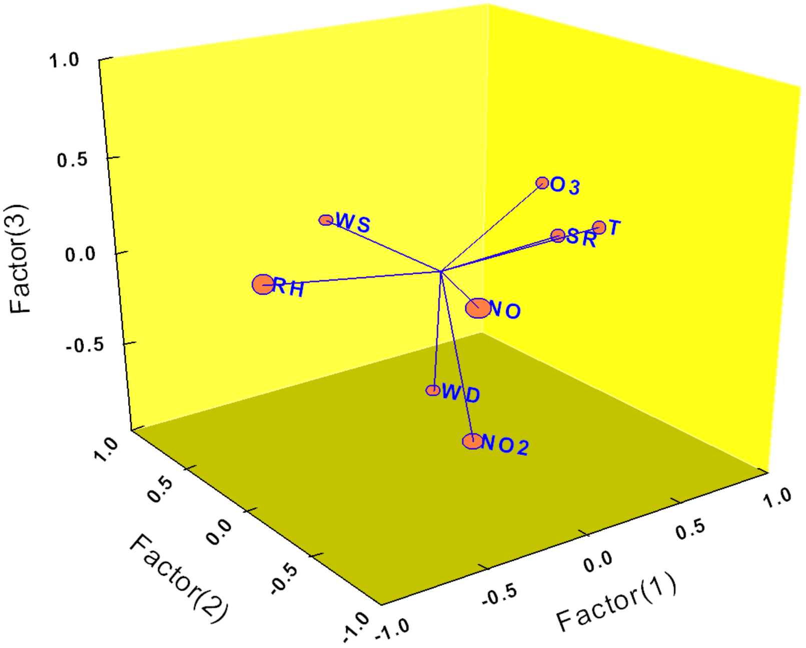

**Figure 2:** Factor analysis results for Cebeci station

Factor 1, which comprises $O_3$, temperature (T) and solar radiation (SR), Factor 2, comprising wind speed (WS) and relative humidity (RH) and Factor 3, which comprises wind direction (WD), NO and $NO_2$. Ozone is well correlated with SR and T, which is attributed to the photochemical production of ozone under high temperature and radiation. On the other hand, the rest of the parameters are inversely correlated with $O_3$ generation.

### b) Seasonal Variations

The seasonal evolution of measured pollutants in Cebeci station was illustrated in Figure 3. The observed patterns are quite similar for the pollutants with the exception of $O_3$ as is expected.

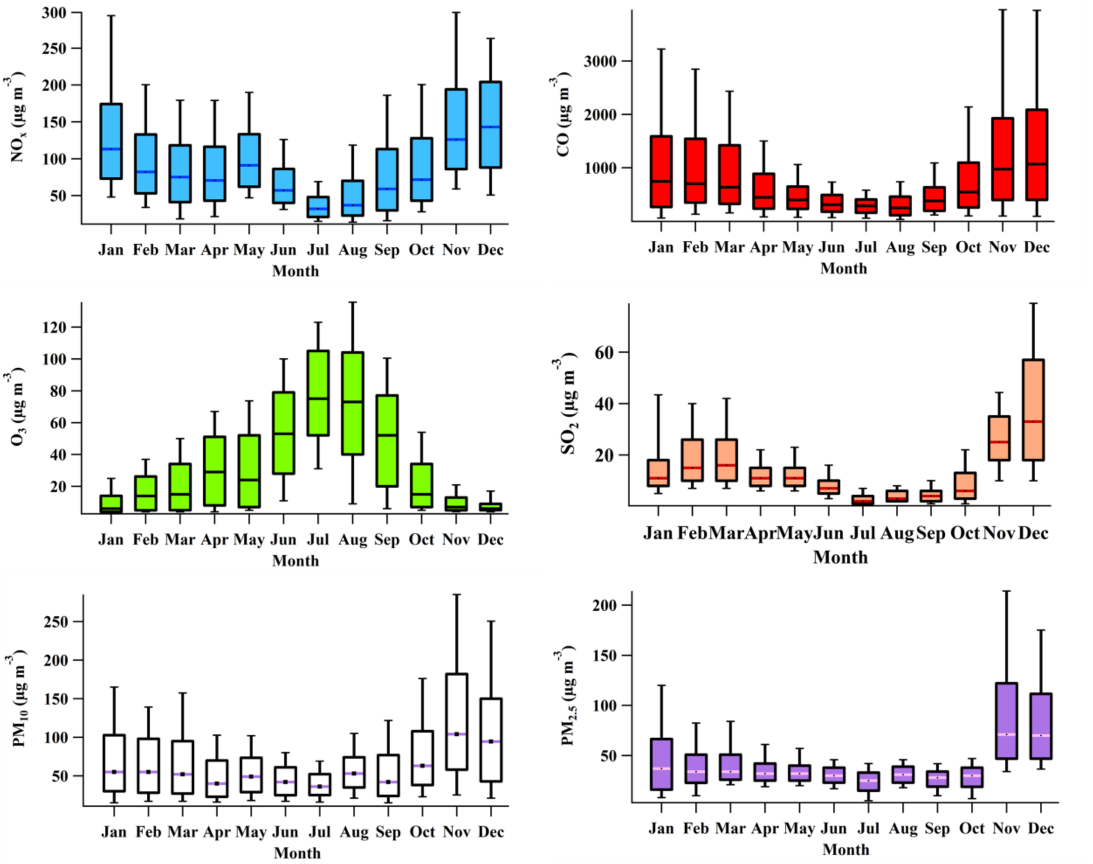

**Figure 3:** Seasonal variations of recorded pollutants in Cebeci station

Ozone levels increased in summer season (June-August) and peaked on July due to enhanced photochemistry. For the rest of the parameters, significantly higher concentrations of pollutants were recorded in winter and spring season (October-March), which can be attributed to the fossil fuel combustion for heating in residences and work places. The lower planetary layer in winter and spring season also results in the accumulation of pollutants within the city and hence its contribution to the observed levels should not be ignored.

### c) Cluster Analysis

Cluster analysis (CA) is a statistical technique used to classify the parameters into sub-groups based on the similarity and differences between the parameters. The CA approach is applied to air pollution data to apportion the sources (Marquardt et al., 1991), to the upper layer meteorological variables to find the dominant directions of air masses influencing a certain location (Brankov et al., 1998) and to classify the stations over a large area (Yu and Chang, 2001; Unal et al., 2011).

K-means clustering was applied to the PM$_{10}$, SO$_2$ and O$_3$ data corresponding to six stations to sub-group the stations. Euclidian distance was used as the clustering metric. If the distance approaches to zero, the parameters under consideration are similar in terms of temporal variation and magnitude within stations used in the analysis.

CA results were depicted in Figure 4. When the results were evaluated in terms O$_3$, it is obvious from Figure 4 that Cebeci and Sincan stations resemble to each other and hence they were classified under the same group. Alibeyköy, Dilovası and Kadiköy stations form the same group indicating that these groups have O$_3$ concentrations different than other stations used in the comparison. On the other hand, Keçiören station has completely different $O_3$ concentration both in terms of temporal variation and magnitude.

Cebeci, Keçiören and Sincan stations have similar $PM_{10}$ trend and level while Alibeyköy and Kadiköy are grouped together. Dilovası station is quite similar to Alibeyköy and Kadiköy but differs than the rest in terms of $PM_{10}$.

The stations located in Ankara are similar but different than Dilovası, Alibeyköy and Kadiköy in terms of $SO_2$.

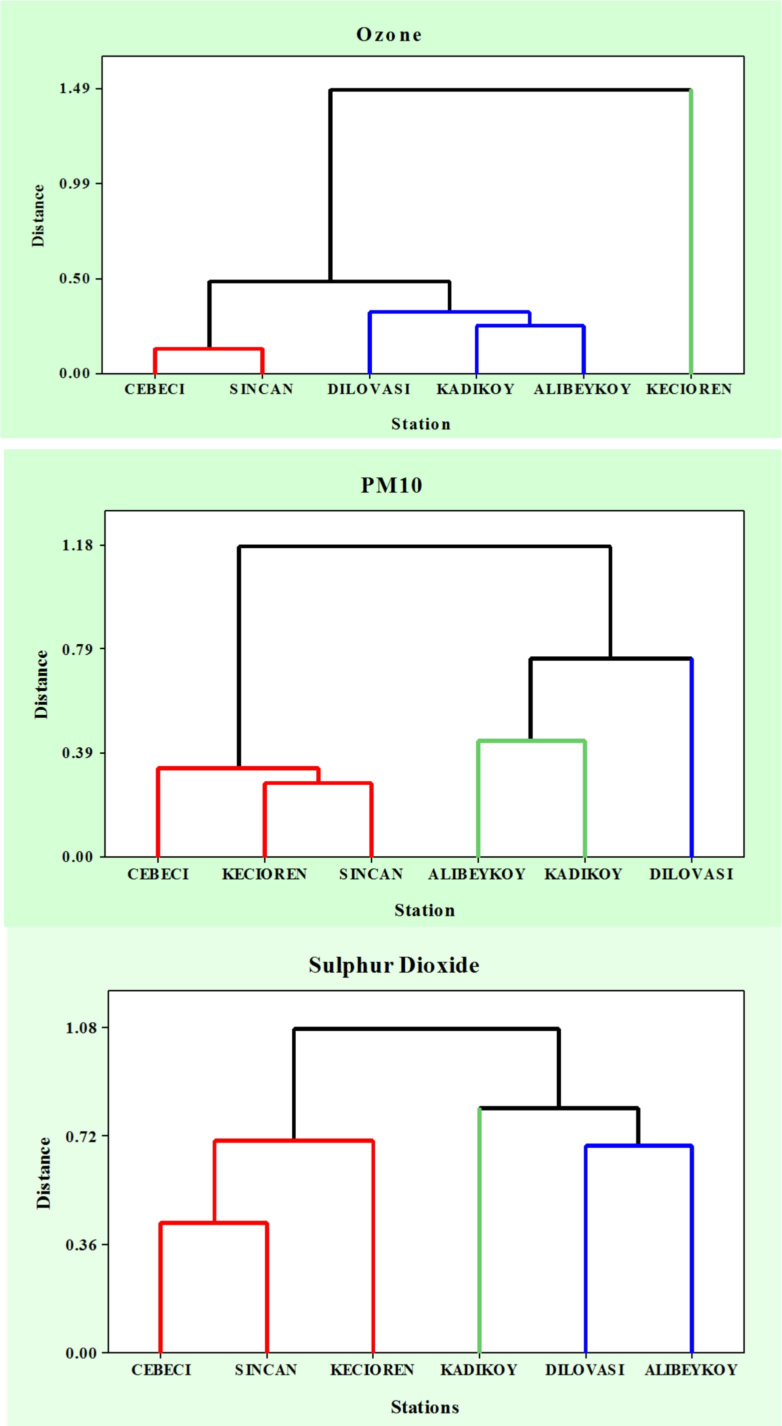

**Figure 4:** The results of K-means clustering

## 4. CONCLUSION

Air quality data corresponding to six different monitoring stations in Turkey were evaluated in this manuscript in terms of temporal variations and their similarities and differences. It has been found out that the generation of $O_3$ is photochemistry driven. Temperature and solar radiation are two important meteorological parameters influencing the concentration of $O_3$. All of the parameters evaluated showed well defined diurnal and seasonal cycles. The similarities and differences between the stations were discussed and with the exception of $O_3$, the stations located in Ankara are different from the other stations in terms of $SO_2$ and $PM_{10}$.

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# CHARACTERIZATION OF WET DEPOSITION IN DENIZLI, TURKEY

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## ABSTRACT

The urban atmosphere is subjected to large inputs of anthropogenic contaminants arising from both stationary and mobile sources. According to their physical and chemical properties, these pollutants are transported to the Earth’s surface through dry and wet deposition. Wet deposition plays important roles in carrying chemical species from the atmosphere to the surface and thus can bring potential adverse effects to the terrestrial and marine aquatic ecosystems. This study presents the chemical composition of the snow samples in Denizli, Turkey during the period of January 2012-February 2012. The snow samples were collected manually by using a plastic container of 25 cm diameter. At the end of the sampling, the samples were waited at the room temperature for melting. Then the volumes of samples were measured. pH, temperature and electrical conductivity of the samples were measured immediately. The samples were filtered and stored in tightly covered plastic bottles in the refrigerator at 4 $^0$C prior for ion analysis. The filtered samples were acidified to pH 2 by nitric acid and kept refrigerated until the heavy metals were analyzed. Heavy metal concentrations were measured using a Perkin Elmer OPTIMA 2100 model inductively coupled plasma-optical emission spectroscopy. Ion concentrations were measured using a Dionex ICS-1000 model ion chromatography.

**Keywords:** Wet Deposition, Precipitation, Snow, Heavy Metals, Ions

# USE OF PHAST, CIRRUS AND SHELL FRED SOFTWARES IN $H_2S$ AND $SO_2$ GAS PREDICTION FOR OIL & GAS INDUSTRIES EMISSIONS

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## ABSTRACT

Iran is considered as one of the biggest oil and gas resources in the world. There are many constructed and under construction refineries and petrochemical complex plants. Hydrogen sulphur is one of the emitted gases from these factories that come from the process lines and it is highly required to be controlled. As these Hydrogen sulphur gases can cause health and environmental problems, should be controlled before releasing to the atmosphere and must be kept in standard conditions. In this research, some famous software including PHAST, Cirrus and Shell Fred were introduced. PHAST can be used to calculate concentration of some material like as $H_2S$ and trace it. This material are exist in the input data. It means that we cannot calculate the concentration of materials which are not in the data. CIRRUS software is used to calculate the concentration of materials. In some industries sulphur is base of materials and after processing we will have emissions like as $SO_2$ or $H_2S$. In comparing with other software it seems that CIRRUS is appropriate software for gas dispersion modelling however, it is not complete and needs to be improved. SHELL FRED is employed for dispersion modelling. This software is similar to PHAST and it can be traced only the materials that insert as input data. However, there are not similar results as compared to the others. In this study, the result will be compared to produce new program to do gas dispersion modelling with the best result.

**Keyword:** $H_2S$, $SO_2$, PHAST, Cirrus, Shell Fred.

# HEAVY METAL CHARACTERIZATION OF ROAD DUST AND POSSIBLE CONTRIBUTION TO PM

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In this study, heavy metal concentrations in road dust samples were determined by x-ray fluorescence technique. Since the road dust contribute to particulate matter concentrations in ambient air environment of cities, it is important to know its elemental composition to consider possible health effects. Road dust samples were collected from two locations nearby to each other. The first sampling point was located on the Fahrettin Kerim Gökay Street with very heavy traffic and the second one on the Feneryolu Street with more modest traffic, both in Göztepe district of Kadıköy Province. Samples were collected from March 2010 to May 2010. Results showed that some traffic related heavy metals such as zinc, barium, and copper, likely to originate from mechanical abrasion of brake pads and tires of motor vehicles, had higher concentrations in the first sampling location indicating their correlation with the number of vehicles in traffic. In addition, the elements iron, chromium, cobalt, manganese, vanadium, and titanium, known to be associated with mechanical parts of motor vehicles and released as a result of mechanical friction, are also more concentrated in the first sampling location with heavier traffic density. According to the Enrichment Factor (EF) results with respect to soil, some elements such as arsenic, zinc, lead, and antimony have been enriched in road dust samples as a result of traffic activity. Some ambient air PM measurements performed earlier in the same area also indicated high EF values for these elements in PM samples. Therefore, at least some fraction of road dust is a clear source of PM in areas close to heavy traffic activity.

**Keywords:** Road dust, heavy metal, PM, traffic

# EFFECTS OF A COLD FRONT ON CONCENTRATIONS OF $O_4$ IN SAN SALVADOR

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## ABSTRACT

In this work we report on levels of $O_4$ in San Salvador (El Salvador) measured by Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS). We measured the $O_4$ differential Slant Column Density (dSCD in $mol^2.cm^{-5}$ of $O_4$ in the ultraviolet region of the electromagnetic spectrum using a fitting window from 340 *nm* to 370 *nm*. The measurements were taken during a campaign which included the days of November 26th, 27th and 30th in 2011 at different elevation angles, namely, 30, 100, 30 and 900. Diurnal average values of $O_4$ dSCD which ranges between $5.10^{42}$ $mol^2.cm^{-5}$ and $6.10^{43}$ $mol^2.cm^{-5}$ are observed. On November 26th lower values of $O_4$ dSCD were obtained in comparison to the other two days. Since the atmospheric $O_4$ profile is well know and nearly constant [T. Wagner *et al.*, 2004] this could be considered a surprisingly result. However, the meteorological conditions in San Salvador influenced by the presence of a cold front which affected in different ways the three days, allow, to some extent, a plausible explanation of these results by considering the role of the aerosol distribution and its impact in the atmospheric photon paths leading to an apparent decreasing of the $O_4$ levels. The role of the presence of aerosols in the atmosphere of San Salvador and its influence in the obtained $O_4$ dSCD results and its diurnal behavior will be extensively discussed in this paper.

**Keywords:** MAX-DOAS, tetraoxygen, cold front

# VARIATION OF $SO_4^{2-}$ SOURCE REGIONS AFFECTING $SO_4^{2-}$ CONCENTRATIONS IN THE EASTERN MEDITERRANEAN USING REGIONS OF INFLUENCE APPROACH

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## ABSTRACT

Mediterranean atmosphere, particularly the Eastern Mediterranean, is one the most complex air bodies around the world. Complexity of the atmosphere in this region stems from strong polarity of sources affecting chemical composition of the Mediterranean atmosphere. The region is under strong influence of natural sources located at North Africa and Middle East, and under the strong influence of anthropogenic sources located at the north of the basin. Sulphate anomaly is one of the peculiarities of the Eastern Mediterranean atmosphere. Concentrations of $SO_4^{2-}$ ion in aerosol and rain water is among the highest recorded in the Europe and North America. Although very high $SO_4^{2-}$ concentrations in the Eastern Mediterranean is well documented in literature, the reason for such high levels is not clear. In this study variation of $SO_4^{2-}$ source regions affecting $SO_4^{2-}$ concentrations in the Eastern Mediterranean atmosphere between 1990 and 2006 will be investigated using a source oriented trajectory statistics approach. Backtrajectories will be calculated for every day between 1990 and 2006 at Antalya and Çubuk. A different method which bases on distribution of $SO_2$ emission in Europe and transport of pollutants as called Regions of Influence (RoI) approach will be used. The advantage of this approach is that it can be applied at locations where measurement results are not available. The regions of influence approach will allow us to extend period of study both Antalya and Çubuk to early 1980 where measurements are not available. Weighting of regions of influence results with precipitation amount and trajectory segment will also be attempted to increase the accuracy of this approach.

**Keywords:** Backtrajectory, Regions of Influence, Eastern Mediterranean, $SO_4^{2-}$ concentration

# ENVIRONMENTAL ASBESTOS AEROSOL IN SPECIFIC AREAS OF PARANÁ STATE – BRAZIL

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## ABSTRACT

Asbestos is worldwide recognized as a public health problem due to its carcinogenic potential and for this reason; many countries have banned their industrial processing and usage. Nevertheless, many localized communities worldwide are continuously exposed to Naturally Occurring Asbestos (NOA), in areas for which the potential health hazard is still unknown. In developing countries, rocks containing asbestos minerals in their composition are many times inadvertently used as road paving. In this way, asbestos fibers, are exposed to the wind and can be blown into the air as aerosols, exposing the users of such roads and the local inhabitants to this invisible pathogen. The aim of this research is to assess the aerosol composition and characteristics in some specific areas of Paraná State -southern Brazil- where a large amount of asbestos-containing rocks are still being unknowingly used as road paving in rural areas for many decades now. This air quality assessment is the first NOA study of such in the region. Aerosol samples were collected during two weeks for fine and coarse particles and bulk; they were analyzed by electron- probe microanalysis, including facilities for low- Z element determination (low-Z EPMA) and by energy-dispersive X-ray fluorescence (EDXRF), in order to investigate the elemental composition of individual particles and bulk samples, respectively. Table 1 shows the relative abundance of Chrysotile (MgSiOx) measured in the atmosphere of Pien. Results are interpreted separately and as a whole with the specific aim of identifying compounds that could impact public health

**Table 1. Abundance of particle types obtained in Pien-Brazil**

| Size fraction | | Dust | Biogenic | MgSIOx | Soot | Organic | Fe-rich | Cu-rich | Total of particles |
|---|---|---|---|---|---|---|---|---|---|
| PM 0.5 - 4.0 | | 256 | 184 | 207 | 72 | 4 | 723 | 100 | 1546 |
| | Cluster % | 16,7 | 11,9 | 13,4 | 4,6 | 0,3 | 46,7 | 6,4 | |
| PM 0.5 - 2.5 | | 241 | 177 | 200 | 69 | 3 | 690 | 0 | 1380 |
| | Cluster % | 17,4 | 12,8 | 14,5 | 5,0 | 0,2 | 50,0 | 0,0 | |
| PM 2.5 - 4.0 | | 15 | 7 | 7 | 3 | 1 | 33 | 0 | 66 |
| | Cluster % | 22,7 | 10,6 | 10,6 | 4,5 | 1,5 | 50,0 | 0,0 | |

**Keywords:** Aerosol, asbestos, health
Acknowledgment: Fundação Araucária, CNPq, Capes

# POLLUTANT CHARACTERIZATION IN SOME BUS STATIONS AT CURITIBA, PARANÁ, BRAZIL

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## ABSTRACT

Air pollution monitoring has been increasingly explored, particularly with respect to the human health risks. The incomplete combustion of fuel used in public transportation releases a variety of pollutants into the atmosphere that can are related to development of diseases. The city of Curitiba has developed its own public transportation system which has been used as model for many cities around the globe. This was the first BRT system (Bus Rapid Transit) implemented in the world and has special stops named “tube stations”, because of its tubular shape. Concerned with the workers inside these stations, who are responsible for the ticket payment and are exposed to vehicles discharge at least 8 hours a day, this study has collected aerosol samples to characterize the air inside and outside of some stations, identifying compounds that could affect human health. Electron probe micro-analysis (with low-Z element determination) and x-ray fluorescence were run to determine the elemental composition of individual particles and bulk samples, an optical transmissometer was used to obtain black carbon concentrations. So far, a possible tendency of pollution accumulation on the inside environment was verified, with inside/outside ratio concentration bigger than 1 unit for most of the stations analyzed. High concentrations of black carbon were detected as well as a great contribution of fine particulate matter ($PM_{2.5}$), which has the capacity of deposition in the respiratory tract. Elements related to industrial and vehicles emissions had higher enrichment factors.

**Keywords:** Particle Matter, Gases, Petrochemical pollution

Acknowledgment: Fundação Araucária, CNPq, Capes

**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
**4th International Symposium and IUAPPA Regional Conference**
**10-13 September 2012 Istanbul -Turkey**

# DETERMINING THE IMPACT OF TRAFFIC ON AEROSOL COMPOSITION IN ISTANBUL

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## ABSTRACT

Recent researches on aerosol composition have considerably shifted to the situations in coastal cities. Coastal aerosol characterization and the effect of marine traffic on the aerosol composition were investigated on aerosol samples collected during April-October 2011 period, in Silivri and Kabataş regions of Istanbul which have distinctive geographical characteristics. Aerosol samples were analyzed for various ions and trace elements (anthropogenic or crustal originated) via Ion chromatography and ICP-OES techniques. Distinctive species in terms of source characterization were evaluated for the effect of natural or anthropogenic source apportionment. Results show that the highest concentrations were observed at Kabataş especially for $Na^+$ and $Cl^-$ species which are mainly marine based ions. This result indicates that the considerably dense marine-traffic has apparently affected the aerosol composition at Kabataş station when compared to Silivri station.

**Keywords**: Coastal city, aerosol composition, marine aerosol, marine-traffic, Istanbul

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# MOLECULAR DIVERSITY OF POTENTIALLY ALLERGENIC AIRBORNE *PENICILLIUM* SPP. ASSESSED BY DNA SEQUENCE AND BIOINFORMATIC ANALYSIS.

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## ABSTRACT

Airborne filamentous fungi have a key role in the risk of developing human respiratory allergies. In the present study, a phylogenetic approach based on DNA sequence data from multiple loci was carried out for the molecular characterization of microfungal taxa belonging to the genus *Penicillium* (Ascomycota) collected from bioaerosol in workplaces (Central Italy). As molecular markers, we used nuclear ribosomal RNA and protein coding gene sequences. The *Penicillium* strains were related or belonged to *P. chrysogenum*, *P. coprophilum*, *P. freii*, *P. notatum, P. paneum, P. raistrickii*, *P. simile* and *P. viridicatum*. Moreover, in the recently described *P. simile* and in its relative species *P. raistrickii*, we investigated the genes encoding the extracellular alkaline serine proteases (group 13), which were identified as major allergens in a few other *Penicillium* species examined to date. The octapeptide SHSDFGGR in the serine proteases of *P. simile* and *P. raistrickii* corresponds to known *Penicillium* IgE epitopes and 3D-models show this peptide region is exposed on the protein surface, as expected for IgE binding sites. Furthermore, high sequence similarity and phylogenetic comparison indicate that the deduced serine proteases of *P. simile* and *P. raistrickii* have high potential to be *Penicillium* allergens.

**Key words***:* aeroallergens, alkaline serine protease, bioaerosol, *Penicillium*, molecular phylogeny

## 1. INTRODUCTION

Previous works have shown that in various workplaces (including industrial environments) the microfungi are a relevant component of bioaerosol, which might be associated with human respiratory health effects. Indeed, certain species of these eukaryotic microorganisms have a critical role in allergic responses within the human respiratory tract with varying degree of severity. For example, airborne *Penicillium* species (most of these ascomycete moulds are detectable in air as viable conidia, mycelial fragments, secreted enzymes, cell wall components, cytoplasmic proteins, etc.) are frequently found in indoor workplaces where these filamentous ascomycetes have a key role (although it remains only partially understood) in the risk of developing adverse respiratory symptoms such as allergic airway diseases (Kurup et al., 2002).

Despite the pivotal importance for molecular allergy not only for research but also for diagnostics and clinical treatments, there is limited knowledge on the molecular diversity of airborne microfungi, particularly at the DNA sequence level. For many studies, a molecular diversity of microfungi assessed by DNA sequence analysis can allow to evaluate if the topologies obtained from phenotype analysis are congruent with molecular data (Davolos et al., 2012a,b). Additionally, a DNA sequence-based analysis can establish whether immunoglobulin E (IgE) data accord to the molecular phylogeny of the microfungi (allergen sources) and the respective allergen proteins.

Therefore, we are aimed to analyse microfungal DNA extracted both from samples typically including spores, mycelia and hyphal fragments collected especially from indoor air and from cultured (morphologically identified) mould species isolated from bioaerosol samples of the same locations. In the present study, for the phylogenetic ascription of new isolates to previously identified species or for the description of novel species, our analysis covers solely taxa in the genus *Penicillium*, an ideal model group that is present in the air of varied habitats. To infer evolutionary relationships of the *Penicillium* spp. we examined universally distributed nuclear genes, as detailed in Davolos et al., (2012a).

Additionally, we selected and analysed genes within *Penicillium* taxa that are greatly informative for allergy research of airborne moulds. In particular, we investigated the genes encoding the alkaline serine proteases (group 13), which are found in the *Penicillium* extracellular proteome (Jami et al., 2010) and are known to be major allergens of *P. chrysogenum* and a few other *Penicillium* species examined to date (Wang et al., 2005; Davolos and Pietrangeli, 2010b,c).

## 2. MATERIAL AND METHODS

Air samples were collected in various occupational environments, potentially with high levels of bioaerosol such as pig farms, agricultural settings and solid waste treatment plants, mostly located in Central Italy (further details will be provided on request). In addition, *P. simile* ATCC MYA–4591$^T$ was isolated from the bioaerosol in a cultural heritage restoration laboratory, Italy (Davolos et al., 2012a), while *P. raistrickii* G Smith strains A2a–8 and 3Ba–AP–1 were isolated from air samples in the Capuchin Crypt, Rome, Italy (see Davolos et al., 2012a).

Airborne microfungal samples (including the uncultivable fraction) were isolated by gelatine filter disposables with an Air Sampler (at standard air flow rates). The gelatine filters were dissolved after sampling to extract the total DNA from the membranes with different approaches (details of the methodologies used are available on request). In addition, the cultivable airborne microfungi were isolated with a surface Air Sampler (air flow rates will be provided on request) with plates containing Sabouraud Dextrose Agar plus chloramphenicol and then grown on selected media (CYA and MEA; see Davolos et al., 2012a). The differences in microfungal composition were evaluated by comparing the number of colonies in relation to the volume of air originally sampled, obtaining the quantity of colony-forming unit per cubic meter of air (CFU/m$^3$).

Genomic DNA was prepared from 3-day-old CYA cultures, according to the protocols detailed in Davolos et al., (2012a). The final DNA concentrations were 100-110 ng/μL as determined by optical density at 260 nm. Polymerase chain reaction (PCR)-protocols for DNA amplification and DNA sequencing of nuclear ribosomal RNA (ITS1-5.8SrDNA-ITS2, and 28S rDNA genes) and protein coding (beta tubulin (*benA*) and calmodulin (*cmd*)) genes are described in Davolos et al., (2012a,b). For the alkaline serine protease gene, the PCR mediated reaction and the DNA sequencing were performed by using new primers Penf, Penr, Penf3 and Penr4 (details will be provided on request) designed according to the alkaline serine protease gene sequences of *Penicillium* species available at GenBank (NCBI; http://www.ncbi.nlm.nih.gov). PCR-based methods applied to the genomic DNA extracted from the membranes were tentatively used to infer the number of cultivable and uncultivable microfungi (further details will be provided on request).

Phylogenetic analyses were conducted in MEGA 5 program (Tamura et al., 2011) as detailed in Davolos et al. (2012a,b). Standard multiple amino acid sequence alignments were carried out as reported in Davolos et al. (2012a,b), and BLASTP searches of the amino acid sequence from the alkaline serine protease of *P. simile* ATCC MYA–4591$^T$ and *P. raistrickii* strains A2a–8 and 3Ba–AP–1 were conducted at the NCBI.

Homology model for the deduced alkaline serine proteases of *P. simile* and *P. raistrickii*, based on the original (279 residues long) sequence of the Protein Data Bank (PDB) entry PDB id 3f7m, was constructed using 3F7M_A as a template and applying the SWISS-MODEL server and respective programs (Arnold et al., 2006). Prediction of allergenic proteins and mapping of IgE epitopes were performed by the program AlgPred (Saha and Raghava, 2006).

The annotated DNA sequences have been deposited at the GenBank (NCBI), partially reported in Davolos et al., (2012a). The sequences from the genes encoding the alkaline serine proteases have the following GenBank accession numbers: JQ177160 (*P. simile* ATCC MYA–4591$^T$), FJ617277 (*P. raistrickii* A2a–8), JQ177159 (*P. raistrickii* 3Ba–AP–1).

## 3. RESULTS AND DISCUSSION

As part of a research project to investigate potentially allergenic microfungi associated with workplaces in Central Italy (focusing on environments putatively with a high mould concentration in air; Davolos and Pietrangeli, 2007; 2011), this study continues the integrative analysis of molecular and classical taxonomy on taxa belonging to the genus *Penicillium* (Davolos and Pietrangeli, 2010a). The aim of our study is to improve understanding of molecular diversity at the DNA and deduced amino acid sequence especially on novel and cryptic *Penicillium* species, collected from bioaerosol in occupational environments.

The *Penicillium* strains examined in this work resulted evolutionary related to *P. chrysogenum*, *P. coprophilum*, *P. freii*, *P. notatum*, *P. paneum*, *P. raistrickii* and *P. viridicatum*. Importantly, among these species, generally considered taxonomically known, phylogenetic inferences based on the beta tubulin (*benA*) and calmodulin (*cmd*) coding genes indicate some *Penicillium* isolates to be new lineages, i.e. *P. simile* (Davolos et al., 2012a), as it is shown in Figure 1.

In general, some distinct taxa appeared locally abundant and other strains showed putative seasonal variation (mean values of the CFU/m$^3$) but currently there is insufficient data for conclusive and well supported comparison. However, our preliminary data on the molecular diversity of *Penicillium* spp. provides indication of extensive and more comprehensively sampling at different spatial scales. Moreover, considering that innovative culture-independent approaches, including next generation sequencing technologies, could be relevant for a more complete characterization of bioaerosol, we proposed such applications for a better way of examining the understudied non-cultivable microfungal (and other biogenic) components of indoor and outdoor aerosol (Davolos et al., 2011). Indeed, pyrosequencing approaches could greatly improve the accuracy in the determination (and monitoring over time) of microorganism biodiversity in air of different geographic locations (Nonnenmann et al., 2010; Davolos et al., 2011). Although there are ongoing discussions on the complex (intrinsic and extrinsic) factors that affect the severity and prevalence of human respiratory allergy, including the susceptibility genes in human populations for allergy, the various environmental components, and the relationship (or contribution) between certain microfungal species (and their concentrations) and the presence of respiratory diseases (indices related with the risk of exposure to airborne microbes still no defined), the above mentioned molecular applications could provide notable information on mould-induced respiratory diseases and generate an advanced characterization of (standardized) exposure to microorganisms in workplaces as well.

In addition, in this study we analysed the genes encoding the allergen alkaline serine proteases from cultured airborne *Penicillium* species (Davolos and Pietrangeli, 2010b,c). Specifically, we show that in the here investigated *Penicillium* species the introns have typical consensus 5' and 3' boundaries of GT and AG and belonged to phase 0, among others. As regards the deduced amino acid residues, our investigations showed a high degree of sequences similarity (from 84% to 92%) for most of the examined *Penicillium* isolates in relation to alkaline serine proteases from *Penicillium* species available at GenBank (NCBI). Of these, we recognized the residues characteristic of the catalytic site of the serine proteases which is formed by an amino acid triad consisting of histidine (H), aspartic acid (D) and serine (S) (see Chou et al., 2002; Wang et al., 2005). In general, our data solidify the role and the conservation of function of these secreted (ca. 33-kDa) serine proteases.

With a primary focus on *P. simile* ATCC MYA–4591$^T$, we show that its predicted amino acids of the alkaline serine protease, based on BLASTP searches limited to *Penicillium* species, were around 92% identical to those from Pen c 13 (previous name: Pen c 1) of *P. citrinum* strain 52-5 (Su et al., 1999; Chow et al., 2000) and Pen ch 13.0101 of *P. chrysogenum* CCRC 30568 (also known as *P. notatum*; Chow et al., 2000). Lower values (85-86%) emerged in comparison to Pc21g14160 of *P. chrysogenum* Wisconsin 54–1255 (van den Berg et al., 2008), to Pen ch 13 (GenBank acc. no.: AAM3382) of *P. chrysogenum* (Chou et al., 2002), and to the alkaline serine protease with GenBank acc. no.: AAT65816 of *P. nordicum* (Karolewiez and Geisen, 2005). The lowest value (84%) resulted in comparison to the alkaline serine protease (GenBank acc. no.: AAT09329) of *P. chrysogenum* FS010. As expected, for the alkaline serine protease from the phylogenetically related *P. raistrickii* strains A2a–8 and 3Ba–AP–1 (see Davolos et al., 2012a) the BLASTP searches showed similar results (data not shown). Indeed, the alkaline serine protease of *P. simile* displayed high sequence identity (97%) with the homologous protein of *P. raistrickii* in agreement with the close evolutionary history of these two penicilli (see Davolos et al., 2012a).

Lastly, phylogenetic trees and reasonable three-dimensional structural models of the deduced serine proteases were constructed to identify IgE-binding epitopes (data not shown). Notably, in the alkaline serine proteases of *P. simile* and *P. raistrickii* the octapeptide SHSDFGGR corresponds exactly to previously characterized IgE epitope of Pen ch 13.0101 from *P. chrysogenum* strain CCRC 30568 and of Pen c 13 from *P. citrinum* strain 52-5. Interestingly, modelling the structures of the two novel alkaline serine proteases reported in this paper (described elsewhere, manuscript in preparation), it has been possible to show that this octapeptide is exposed on the protein surface as expected for IgE binding sites. Therefore our findings support the idea that the alkaline serine proteases of *P. simile* and *P. raistrickii* have high potential to be orthologues to well known extracellular allergen proteins of other *Penicillium* species.

To sum up, the predicted alkaline serine proteases of *P. simile* and *P. raistrickii* appear novel isoallergens of known *Penicillium* allergenic proteins or at least capable of cross reactivity at some level of the immune response, as well as their putative allergen epitope SHSDFGGR is predicted to represent IgE binding sequence. Clearly, despite the compelling evidence reported in this paper, further studies are necessary for confirming allergenicity or ability to bind IgE of these newly extracellular proteolytic enzymes of *P. simile* and *P. raistrickii* as well as more research is required to identify their effects on human airway epithelial cells (Chiu et al., 2007). The elucidation of all the molecular aspects and the integration of emerging microfungal genomic data will likely have implication in terms of both mould exposure and more refined research for the complex nature of the respiratory allergies, as well as in providing relevant information in the clinical applications (see Edwards et al., 2012).

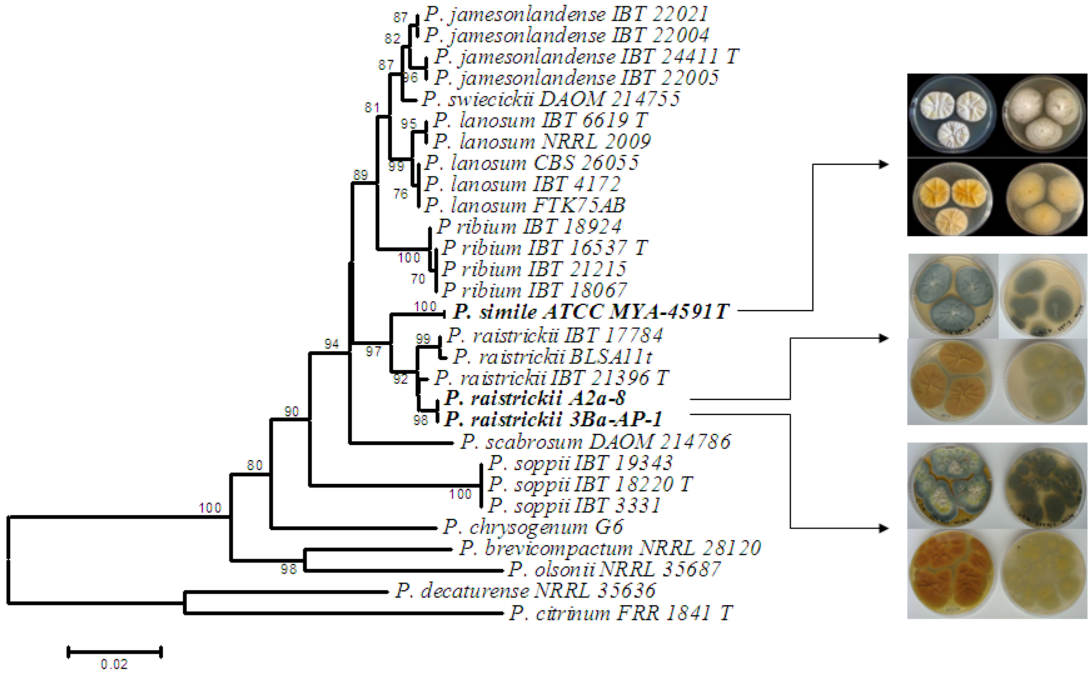

Figure 1. Neighbour–joining tree of *P. simile* D Davolos et al. ATCC MYA–4591$^T$ (highlighted in bold; see Davolos et al., 2012a), *P. raistrickii* G Smith strains A2a–8 and 3Ba–AP–1 (highlighted in bold; see Davolos et al., 2012a) and related *Penicillium* species based on pooled ITS region (including ITS1-5.8SrDNA-ITS2) and *benA* gene sequence data. Numbers near branches are bootstrap values (1000 pseudoreplicates); values less than 50% are not shown. Bar, 0.02 substitutions per nucleotide position. The colonies (the front and the reverse) of *P. simile* and *P. raistrickii* grown on culture media plate (CYA, left and MEA, right) are shown.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# RADIOACTIVITY IN THE AIR OF ZAGREB IN THE YEAR 2011

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## ABSTRACT

The monitoring of radioactivity in the air on a regular daily basis is being carried out at the Institute for Medical Research and Occupational Health, Zagreb (IMI). Monitoring includes absorbed dose rate measurement, determination of total beta activity in the air, gammaspectrometric determination of radioactivity in the air by large-volume air sampling on cellulose filters, determination of quantity of particulate matter with a defined aerodynamic diameter ($PM_{10}$) etc. Tragic events in Japan on March 2011 have resulted with a relatively large amount of radioactivity released into the atmosphere. Since then, from 11th March onward, no significant increase of the absorbed dose rate has been observed at the IMI location in Zagreb.

**Keywords:** absorbed dose rate, $PM_{10}$ particle fraction, total beta activity, $^{131}$I and $^{134}$Cs activity concentration

## INTRODUCTION

Survey and assessment of radioactivity in the air started in Croatia in 1961 and has been continued ever since, as part of an extended monitoring programme conducted by the Radiation Protection Unit of the Institute for Medical Research and Occupational Health in Zagreb (Franić et al.,1997). The total level of radioactive matter in the air is being determined by measuring ambient dose rate, total beta activity in the air and in fallout, radiochemical analyses of selected radionuclides as well as alpha, beta and gamma spectrometric analyses. Radioactive contaminants contained in the ambient air represent only a fraction of total air pollution and eventually possible human exposure. Whereas continuous monitoring of air pollution in Croatia started in the sixties, measurements of suspended particulate matter levels and heavy metals started in 1972, at first in Zagreb and later in other Croatian towns. According to the requirements of the HRN EN ISI/IEC 17025, HAA no. 1288 standard, the Institute has been approved to conduct *radioactivity measurement* (Radiation Protection Unit) and *determination of air quality and air pollutants* (Environmental Hygiene Unit).

Any increase of exposure dose rate and/or total beta activity in the air calls for additional specific measurements and analyses. Their principal purpose is to identify causes and to assess effective dose received by population, that is, possible effects of ionising radiation on health of the Croatian inhabitants. There is a significant correlation noticed between the total beta activity in the air and suspended particulate matter concentrations; the correlation is higher with smaller equivalent aerodynamic diameter of airborne particulate matter fractions (Marović et al., 2001, Marović et al., 2004). These facts were investigated and confirmed by the analyses of aerosol samples collected at the location with high traffic density at the air quality monitoring station Zagreb-1 (Marović et al., 2005).

On 11th March 2011, a catastrophic earthquake and subsequent tsunami set into motion a series of tragic events in Japan including the severe accident at Fukushima Daiichi nuclear power plant. Radioactivity released into the air became involved into atmospheric processes and the transport of matter in the biosphere, leading to the migration of particles over long distances and across international borders, causing global contamination.

## MATERIAL AND METHODS

Ambient dose rate measurement has been carried out at the location of the Institute for Medical Research and Occupational Health (IMI) (45°50' N, 15°59' E). Ambient dose rate was measured as absorbed dose rate by calibrated Geiger-Müller tube positioned 1 m above ground coupled to computer.

Continuous air monitoring involved collection of air samples in volume ranges from 100 to 200 $m^3$ daily, at a height of 1 m above the ground at the location of IMI. Air was pumped through the Schneider & Poelman filter paper (blue). The total beta activities were measured by beta counter for low-level activity measurements (RISØ beta GM multicounter system). In order to allow the decay of short-lived beta radionuclides the activity is measured 120 h after sample colection.

The samples of $PM_{10}$ particle fraction were collected in cooperation with the Ministry of Environmental Protection, Physical Planning and Construction, at the air quality monitoring station Zagreb-1 situated in close vicinity to a crossroad with high traffic density. Daily samples (noon to noon) of $PM_{10}$ particle fraction were collected from 720 $m^3$ of ambient air by means of DIGITEL Aerosol Sampler DHA-80 on quartz microfibre filters, diameter 150 mm. For total beta activity measurements, 32 mm diameter aliquot discs were used. The homogeneity of the aliquots of 2% was assessed as the relative standard deviation of total carbon determination in aliquots.

Also, a volume of air ranging from 10000 to 15000 $m^3$ daily was continuously sampled by pumping air through a cellulose filter (ASS-500 Aerosol Sampling Station). All air samples were gamma-spectrometrically analysed using GMX series gamma-X HPGe and/or Ge(Li) detector (resolution 2.24 keV on 1.33 MeV $^{60}$Co, relative efficiency 74.2%; resolution 1.78 keV on 1.33 MeV $^{60}$Co, relative efficiency 16.8%) with electronic units and software for analysis of gamma spectra on a personal computer. Measurement time was 80,000 sec or higher.

## RESULTS AND DISCUSION

The average value of ambient dose rate measured as absorbed dose rate for the period from 11th March to 30th June 2011 was 118 ± 11 nGy/h (Marović et al., 2012). Figure 1 shows ambient dose rate as absorbed dose rate measured daily over a three-month period following accident at Fukushima. Vertical green lines represent daily ranges of continuous data on one-minute basis, and yellow part of a vertical line indicates the difference between daily and cross-period average. The average value for year 2010 was 119 ± 12 nGy/h.

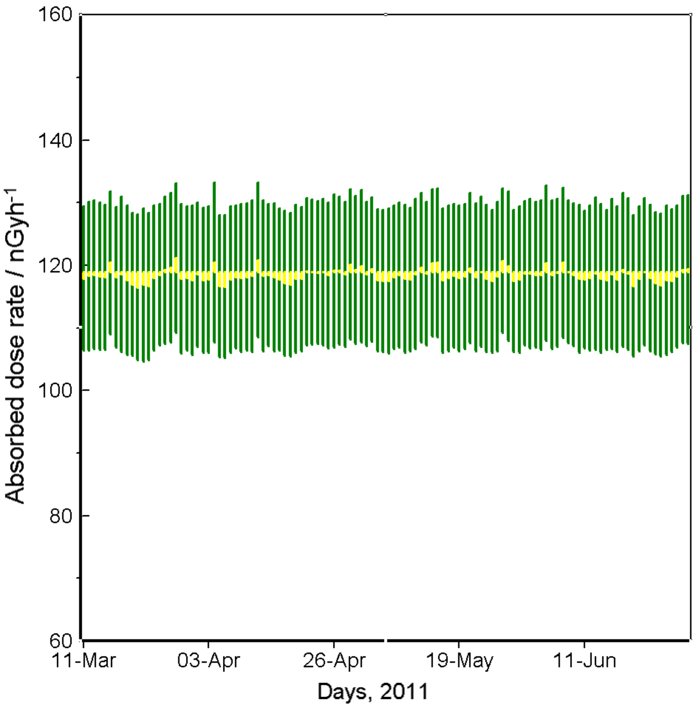

Figure 1. Ambient dose rate as absorbed dose rate (nGy/h) over the three months after 11th March

After the first information about the tragic events in Japan had been received, we started frequent air sampling. Ambient dose rate has not indicated any increase.

The total beta activity measured in the air at the IMI location ranged from 0.230 to 1.256 mBq/m$^3$, and at the air quality monitoring station Zagreb-1 the total beta activity of airborne particulate matter fraction PM$_{10}$ ranged from 0.113 to 1.577 mBq/m$^3$.

Total beta activity measured in the air at the IMI location and at air quality monitoring station Zagreb-1 also did not show any significant increase. Figure 2 gives values of total beta activity (Bqm$^{-3}$) in the period from 11th March to 30th June 2011. Total beta activity values of daily samples of PM$_{10}$ particle fraction at station Zagreb-1 were higher than those of samples measured at IMI. Station Zagreb-1 is situated near a crossroad with increased traffic exposure; measurement site at IMI is located at the residential part of Zagreb. Calculated specific total beta activity (amount of activity per unit mass of PM$_{10}$ particle fraction: Bqg$^{-1}$(PM$_{10}$)) and results presented in Figure 3 reveal an increasing trend of specific total beta activity in the period from 11th March to 30th June.

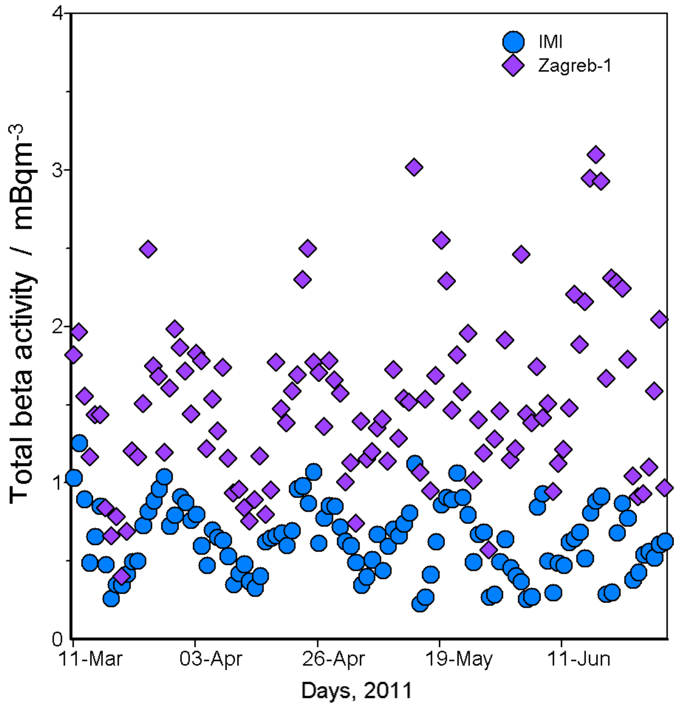

Figure 2. Total beta activity (Bqm$^{-3}$) in the period from 11th March to 30th June in Zagreb

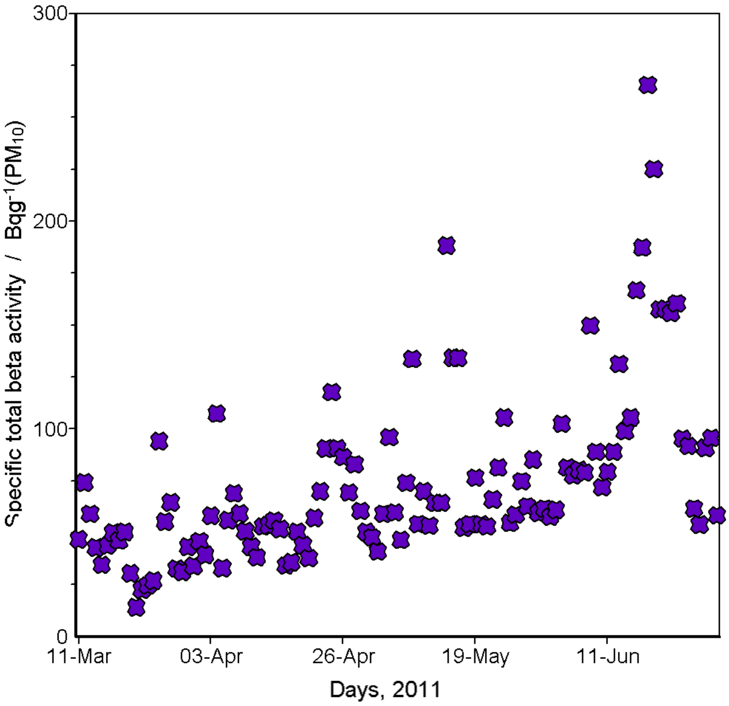

Figure 3. Specific total beta activity (Bqg$^{-1}$(PM$_{10}$) in the period from 11th March to 30th June in Zagreb at the station Zagreb-1

Determination of radioactivity by high resolution gammaspectrometry showed that radionuclides $^{131}$I and $^{134}$Cs are present again in the air of Zagreb. Maximum activity concentrations were measured in the period from 31st March to 7th April and they were as follows: for $^{131}$I: 383±1 µBqm$^{-3}$, for $^{134}$Cs: 24.1±0.2 µBqm$^{-3}$ and for $^{137}$Cs: 27.6±0.2 µBqm$^{-3}$.

The measured values were low and activity concentrations were too low to increase ambient dose rate, but measurements confirmed their presence (Figure 4).

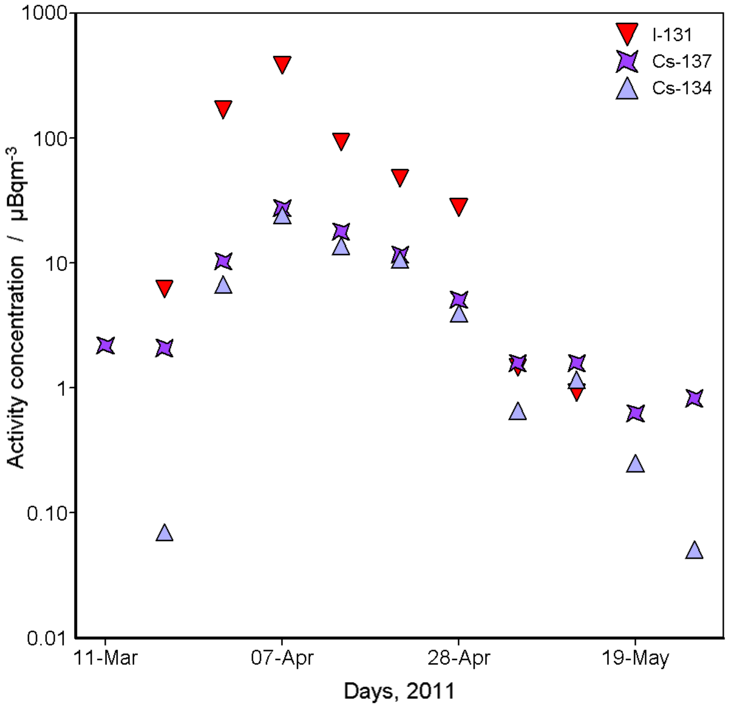

Figure 4. $^{131}$I, $^{134}$Cs and $^{137}$Cs activity concentrations (µBqm$^{-3}$) in the air of Zagreb from 11th March to 2nd June

Gammaspectrometrical measurements were also performed on the samples of $PM_{10}$ particle fraction collected at the air quality monitoring station Zagreb-1 from 11th March to 22nd April. Measurement was performed in December 2011 and the $^{131}$I activity concentration could not be determined ($T_{1/2}$, half-life of $^{131}$I is 8.04 days) (Table 1).

Table 1 $^{134}$Cs activity concentration (μBqm$^{-3}$) in the air of Zagreb

| **Sampling time** | **IMI** | **Station Zagreb-1** |
|---|---|---|
| 11th March – 22nd March | 0.10 ± 0.06 | 24.1 ±0.9 |
| 22nd March – 31st March | 6,75 ± 0.09 | |
| 31st March – 7th April | 24.1 ± 0.2 | |
| 7th April - 14th April | 13.7 ± 0.1 | |
| 14th April -21st April | 10.7 ± 0.1 | |

The effective dose incurred by inhalation of air contaminated by $^{131}$I, $^{134}$Cs and $^{137}$Cs was estimated for the period 11th March – 2nd June. Figure 5 presents data on estimated contribution of $^{131}$I, $^{134}$Cs and $^{137}$Cs activity concentrations to effective dose incurred by inhalation of air per an adult inhabitant in the period 11th March to 2nd June 2011.

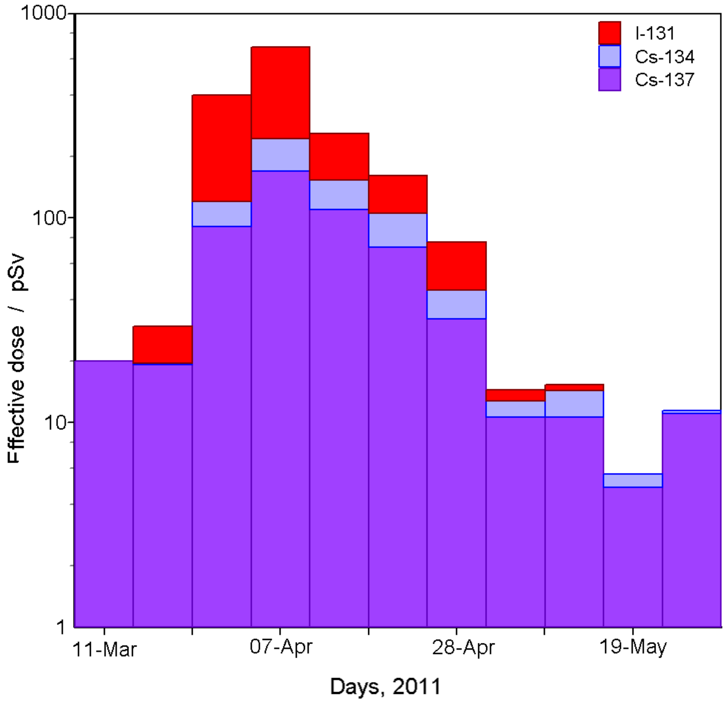

Figure 5. Estimated contribution $^{131}$I, $^{134}$Cs and $^{137}$Cs activity concentrations to effective dose incurred by inhalation per adult inhabitant of Zagreb from 11th March to 2nd June

According to our estimates, the additional effective dose for adult inhabitants of Zagreb due to inhalation of air contaminated with $^{131}$I and $^{134}$Cs was 1.5 nSv. For the sake of comparison, in the year 2010 the annual effective dose incurred by inhalation of air for an adult inhabitant was estimated to be 5.1 nSv. In the year 2011, the estimated effective dose incurred by inhalation of air for adult inhabitans of Zagreb was 9.6 nSv.

## CONCLUSION

The on-going and systematic measurements within the environmental monitoring programme of the Republic of Croatia, performed by the Institute for Medical Research and Occupational Health in Zagreb, provide continuous data indicating any event that might influence the quality of air and consequently affect both people and environment. The impact of the nuclear events in Japan was seen in the atmosphere throughout the world and it has also burdened the air of Croatia by additional radioactivity. However, our measurements confirmed that the consequences felt in Croatia were fortunately small. Although the detected activity concentrations for $^{131}$I and $^{134}$Cs were elevated again for the first time after the Chernobyl accident, the measured values have not significantly increased the total effective dose of ionising radiation received by adult inhabitants of Croatia.

## ACKNOWLEDGEMENT

This study was supported by the Ministry of Science, Education and Sport of the Republic of Croatia (Projects: 022-0222882-2335 i 022-0222882-2271).

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
**4th International Symposium and IUAPPA Regional Conference**
**10-13 September 2012 Istanbul -Turkey**

# TROPOSPHERIC OZONE BIOMONITORING WITH SNAP BEAN PLANTS IN RALEIGH, NORTH CAROLINA, USA

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## ABSTRACT

Ozone-sensitive (S156) and ozone-tolerant (R123) genotypes of snap bean (*Phaseolus vulgaris* L.) are being developed as a biomonitoring system for the evaluation of ambient ozone phytotoxicity potential. We utilized this system in order to: a) evaluate the ambient ozone phytotoxicity potential in Raleigh, North Carolina; and, b) validate its creditability. Eight plants per genotype were used according to the experimental procedure suggested by ICP-vegetation Programme. The experiment began (seeds sowing) on June 8, 2011 and lasted (up to harvest) about 11 weeks. Data of the following parameters were collected: visible leaf injury, yield, midday stomatal conductance (adaxial + abaxial) and hourly mixing ratios (in ppb) of ambient ozone. The AOT40 value over the 9 week growing period was 8 ppm h. S156 plants exhibited gradually increasing visible leaf injury. The percentages of leaves which exhibited injury between a) 5-25% and b) above 25%, at the end of the first week was 14% and 5% respectively while in the week before the harvest they were 7% and 59% respectively. Concerning R123, only a few symptoms were recorded on July 7 (5% and 7% respectively). These symptoms were attributed to the highest ozone levels monitored during the previous days (the highest daily AOT40 (415 ppb*h) was monitored on July 1st). Otherwise, foliar injury in R123 was less than 5%. Stomatal conductance during vegetative growth and anthesis in S156 and R123 averaged 940 and 1013 mmol $H_2O$ $m^{-2}$ $s^{-1}$, respectively. During pod-fill, conductance decreased to 340 mmol $H_2O$ $m^{-2}$ $s^{-1}$ in both genotypes, but diurnal measurements indicated that conductance was higher in S156 than in R123 by late July when S156 was severely injured. Results showed that ambient ozone levels in Raleigh, North Carolina was high egnough to cause extensive visible leaf injury in S156 but not in R123. Differences in sensitivity did not appear related to ozone uptake as midday stomatal conductances were similar between genotypes, except during late pod-fill in injured S156 leaves. Differential responses of these snap bean lines to ozone appears related to genetic differences in ozone sensitivity as evidenced by foliar injury. Differences in yield between genotypes may require longer experimental duration to become apparent.

**Keywords:** Ozone phytotoxicity, snap bean, S156, R123, stomatal conductance, AOT40

AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES
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# EVALUATING AIR TEMPERATURE CHANGES DUE TO İNCREASING $CO_2$ İN ISFAHAN PROVINCE IİLL 2050

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## ABSTRACT

Climate change is one of the most important challenges among scientists and researchers. This phenomenon has a complex dynamic and time depending and it needs to an integrated long time study. Scientific founding has shown that earth surface temperature has increased and it will increase during this century. The main reason is increasing Greenhouse gases especially $Co_2$. These changes can impact on terrestrial ecosystems. . The main goal of this study is determining air temperature change due to change in $Co_2$ concentration in Isfahan province till 2050 using different scenarios. Two scenarios including A2 and B1 with different $Co_2$ concentration and two General Circulation Models (GCMs) namely IPCM4, HADCM3 is used for this study. Linear regression was selected for statistical downscaling between predictant and predictors. Results indicated that maximum change of temperature will occur in the summer season, but its minimum change will appear in the autumn season. Also air temperature will increase till 2050 in the study area because of ascending $Co_2$ levels. Thus we must concentrate on suitable programming to manage this probable change.

**Keywords:** concentration, air temperature, scenario, downscaling.

**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# METEOROLOGICAL AND CLIMATOLOGICAL FOOTPRINTS IN OBSERVATIONS OF ATMOSPHERIC SURFACE OZONE AT THE CAPE POINT GLOBAL ATMOSPHERE WATCH (GAW) STATION

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## ABSTRACT

Surface ozone is among greenhouse gases which form a blanket that causes heat trapping effect and warms the atmosphere with related consequences including atmospheric temperature rise. The aim of this study was to investigate the temporal relationship between meteorological conditions and the surface ozone concentrations. In this study, surface ozone and meteorological measurements from Cape Point Global Atmospheric Global Watch station were investigated. Continuous surface ozone was measured by means of UV instruments type Dasibi (model 1008) analyser at 4 m and 30 m above the surface. The analysis was focused on 2007 hourly surface ozone concentration measurements and meteorological parameters. The seasons focused on summer (DJF), autumn (MAM), winter (JJA) and spring (SON). The seasonal cycle displayed the minimum of ozone concentration in summer and maximum in winter followed by autumn and spring. The diurnal cycle showed that lowest concentrations occur in the morning and evening, and peak concentration occurred during the afternoon hours. The seasonal cycle showed the minimum difference of ozone concentration between the two levels in spring and maximum in summer, followed by autumn and winter. The maximum surface ozone concentrations over Cape Point during the winter season are possibly influenced by northerly winds which transport local emissions from Cape Town. After sunrise, the ozone difference decreases slightly up to the afternoon and increase again to the late afternoon. These results suggest that enhanced mixing in the boundary layer may contribute to the small difference of ozone concentration in spring.

**Key Words**: Surface ozone, Boundary layer, Diurnal and seasonal cycle, Greenhouse gas

## 1. INTRODUCTION

Ozone in the troposphere is a key constituent from a number of atmospheric physical and chemical processes. These include the radiative forcing as ozone is an infrared absorber (green house gas). Tropospheric ozone is a trace gas with a large natural variability in space and time and the distribution is not homogeneous varying with latitudes. The continuing increase in the production of greenhouse gases, such as ozone ($O_3$) has given rise to worldwide concern that human activities are impacting negatively on climate with far reaching social economic implications. Greenhouse gases form a blanket which increases the heat trapping effect and hence atmospheric warming with associated consequences such as rise in atmospheric temperature and changes of pressure (Baumbach, 1996). In summary, monitoring of greenhouse gases and other trace gases such as ozone are crucial.

The high concentrations of ozone are found in the stratosphere between 15 and 50 km, peaking at height of 25 kilom. The concentration in the stratosphere is around 10 000 parts per billion by volume (ppbv) (NRC, 1991). Stratospheric ozone layer plays several environmentally important roles in addition to its influence on the climate system. It is vital to living organisms as it screens and absorbs the harmful part of the ultra-violet radiations and shields the earth from their harmful effects (NRC, 1991). The destruction of ozone in the stratosphere could lead to substantial increase in the incidence of skin cancer among human population. The urgent need to take measures to phase-out the use of ozone depleting substances (ODS) was confirmed by the 1980s' discovery of the ozone hole and severe levels of ozone depletion occurring in many regions of the world (UNDP, 2007). In 1987, Montreal Protocol adopted the first legally binding international agreement on substances that deplete ozone layer, formally recognized as the significant threat of ODS (UNDP, 2007). The Montreal Protocol and its subsequent amendments espoused a precautionary approach and provided a mechanism to reduce and phase-out the global production and consumption of ODS by setting out a strategy for immediate action, even before all the scientific ramifications were fully understood. The Montreal Protocol is structured around several groups of halogenated hydrocarbons that have been shown to play a role in ozone depletion. All of these ODS contain either chlorine or bromine (UNDP, 2007).

The ozone in the troposphere is within the depth of 6 km to 16 km, at the tropics and polar regions, respectively. The troposphere contribution of total column ozone is of the order of 10-15% (Fishman *et al*, 1990). Troposphere ozone is a trace gas with natural variability of space and time and the mixing ratio in the range of 10-100 parts per billion (ppv) (Zbinden *et al*, 2006). The origin of tropospheric ozone is either in-situ photochemical production from oxidation of hydrocarbons or carbon monoxide (CO) in the presence of oxides of nitrogen (NOx) or ozone transported downward from the stratosphere (UNEP, 1998). Tropospheric ozone is a secondary pollutant. Air pollutants are the products of natural activities especially fires and volcanic eruptions, and human industrial activities. NOx are substances which are produced by cars, trucks, industries, and combustion of diesel fuel, kerosene, oil, or natural gas.

For many years photochemical air pollution was considered as a problem mainly of local or regional significance, affecting clean air sites by the advection of polluted urban plumes that spread over the country side (Zbinden *et al*, 2006). Presently, it was revealed that smog-like reactions associated with the oxidation of methane and other hydrocarbons induced the photochemical production of ozone in the relatively unpolluted troposphere (Crutzen, 1973, 1974). The argument that occurred from the proponents of tropospheric ozone budget dominated by stratospheric downward transport (Fabian, 1974; Chartfield and Harrison, 1976) was anchored in the inability to clarify which, of stratospheric or photochemical production was responsible for the spring-summer lower tropospheric ozone maximum. The quantitative assessment of the cross tropopause mass fluxes of ozone and other chemical constituencies are of major importance for atmospheric chemistry and climate (Zbinden *et al*, 2006).

Human health, terrestrial ecosystems, and material degradation are impacted by poor air quality in troposphere (presence of ozone). Surface ozone is a pollutant and a high concentration of $O_3$ is hazardous to children, the elderly, and people with respiratory problems. It also damages rubber, nylon, plastics, dyes, paints and vegetation (EPA, 1999). Surface ozone, as a strong oxidant and, together with water vapor, as a precursor of the hydroxyl radical (OH), ozone has a strong influence on the oxidizing power of the atmosphere and hence on the rate at which many natural and anthropogenic compounds are eliminated from the atmosphere. While air quality concerns are focused near the surface, climatic and oxidizing impacts of troposphere ozone are significant through the entire depth of troposphere (Oltmans *et al*, 2006).

The global distribution and trends of surface ozone in the troposphere remain a major focus of interest. Comprehensive and continuous observations are crucial to assess surface ozone's role in climate change. The continuing increase in the production of pollutants, such as $NO_x$ which leads to the formation of surface $O_3$, has given rise to worldwide concern that human activities are impacting negatively on climate with far-reaching socioeconomic implications. Long-term observations of such surface ozone in background conditions make it possible to discover changes in the atmosphere.

Surface ozone measurements have been performed at the Cape Point laboratory since 1982 as part of a joint research program which in its present form is conducted by South African Weather Service (SAWS) (Brunke and Scheel, 1998). The Cape Point Global Atmosphere Watch (GAW) station is a coastal site of South Africa, at the southern tip of Africa ($34^0$S, $18^0$E and 210m a.m.s.l). The Cape Point laboratory is one of 24 World Meteorological Organisation GAW stations. The GAW research program involves comprehensive systematic monitoring of several trace gas species, such as carbon monoxide (CO), carbon dioxide ($CO_2$), ozone ($O_3$), methane ($CH_4$). In addition, the meteorological parameters are measured at Cape Point such as temperature, precipitation, wind speed and direction, solar radiation, so as to recognise the climatological condition of the area. The pristine location enables measurements to be made in air that has been transported over the vast clean southern ocean with minimum human influence (Brunke, *et al*, 2004). The total climatology of Cape Point GAW from 1960-1990 shows an average temperature of $15.7^0$C, annual rainfall of 353 mm, average pressure of 991 hpa, and average wind speed of 8.5 m/s and winds flow south easterly in summer and north westerly in winter (http://www.weathersa.co.za).

Surface ozone has been measured by means of UV instruments of the type of Dasibi (model 1008) analyser at Cape Point station since 1982. $O_3$ is sampled from 4 m and 30 m levels above the station. Automatic zero and span checks (approx. 50 ppb) are made once per day (Zellweger et al, 2006). The principle of this operation is based in the ultraviolet absorption (254 mm wave length) of the ozone molecule (Brunke and Allen, 1985). Two ozone analysers are currently used at the station for continuous parallel surface ozone measurements. Filtering of trace gas with respect to concentration is performed by automatic routines as well as by visual inspection of concentration level on a monthly and annually basis (Brunke, 1998). All instruments are calibrated against standard by an accredited agency and are fully compatible with EPA requirements (Turner, 1993). The data obtained from all continuous measurements at the site have been stored as hourly means in parts per billion by volume (ppbv).

The aim of this study was to explore the temporal relationship between the meteorological conditions and the surface ozone concentration measurements. The 2007 hourly surface ozone concentrations measurements at 4 metre and 30 metre levels were used in the analysis. The study focused on describing diurnal and seasonally statistical analyses for the two levels. The reason for studying the surface ozone concentration was to deliver the view of surface ozone and to explore the meteorological conditions at Cape Point influencing surface ozone concentrations, through the following objectives:

i) To describe the seasonal variations of ozone from both levels (4 m and 30 m) above ground level.

ii) To illustrate the diurnal cycles of the ozone concentrations.

iii) To describe the seasonal differences between the levels of ozone.

iv) To describe the concentrations of ozone changes with wind direction.

Finally, it was felt important to assess some of the meteorological conditions influencing the surface ozone concentrations measurements at Cape Point GAW Station.

## 2. DATA AND METHOD

The approach adopted in this study was to present the data in different data formats and emphasize the different aspects of these interactions so as to understand the origin and behaviour of surface ozone concentration.

To highlight the variations in diurnal, monthly, seasonally dependent trends, the 2007 hourly surface ozone concentrations measurements for both levels (at 4 m and 30 m) were analysed. The analysis was done to discriminate relationship between the seasonal or diurnal variations of ozone concentrations and meteorological parameters (e.g. wind and temperature) at Cape Point. The seasonal dependence of the trends was deduced by separately analysing calendar monthly averages of the data records and the average diurnal trends of the surface ozone records. The diurnal, monthly, seasonally dependence of ozone concentrations on meteorological parameters (e.g. wind speed and direction, temperature) at 4m and 30m levels respectively, were analysed. The monthly averages of the data dependence on the time varying characteristics of the episodes of surface ozone at both levels were illustrated.

## 3. RESULTS AND DISCUSSIONS

### *Diurnal temperature variations*

The temperature measurements in 2007 were averaged and presented seasonally. To show the diurnal mean temperatures variations, data were grouped into 10 metre level and 30 metre level. (Please note that lower level meteorological data are measured at 10 m, while Ozone concentrations are measured at 4 m). Hence meteorological data at 10 m were used to represent that at 4 m. The diurnal mean temperature graph (Figure 1), shows the typical diurnal temperature variations of a regular day-night cycle. The lowest temperature is recorded just before sunrise. Temperature rises with the onset of the day, peaking in the afternoon and falling in the late afternoon through night. Figure 1a, shows maximum temperatures of 21.5 $^0$C at 13:00 in summer, 19.2$^0$C at 14:00 in autumn and minimum of 17.2 $^0$C at 06:00 in summer 15.4$^0$C at 07:00 in autumn, observed at 10 m level. At 30 m level, maximum temperatures of 18.5 $^0$C at 14:00 in summer, 19.4$^0$C at 14:00 in autumn and minimum of 15.1 $^0$C at 06:00 in summer, 15.3$^0$C at 07:00 in autumn were observed. Figure 1b, the maximum temperatures was 15.1$^0$C at 13:00 in winter and 17.1$^0$C at 14:00 in spring and minimum of 12.5 $^0$C at 08:00 in winter and 13.3$^0$C at 06:00 in spring were observed at 10 m level. At 30 m level, maximum temperatures of 18.5 $^0$C at 13:00 in winter and 18.1$^0$C at 14:00 in spring and minimum of 15.1$^0$C at 07:00 in winter and 14.3$^0$C at 06:00 in spring were observed. Summer and winter showed maximum temperature differences between 10 m and 30 m levels. In autumn the temperature difference was minimum, followed by spring. The minimum temperature difference between 10 m and 30 m levels may influence the good mixing, especially in spring.

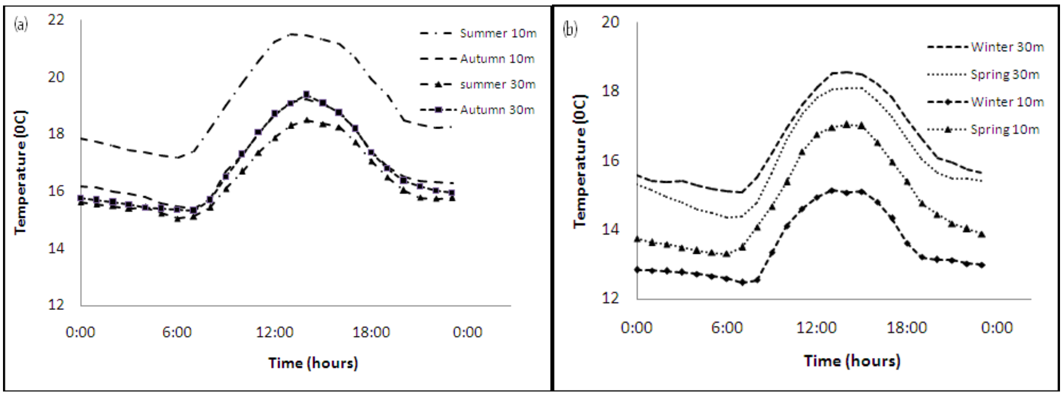

Figure 1. Diurnal cycle of temperature at 10 m and 30 m levels for the seasons of 2007, a) temperature variations in summer and autumn, b) temperature variations in winter and spring.

### *Surface ozone characteristics*

Hourly surface ozone concentrations measured at GAW Cape Point were collected in the year 2007. Considering the monthly mean of surface ozone concentrations over this period, the following general pattern demonstrated the annual variation of monthly mean of the ozone concentrations (Figure 2). The minimum monthly mean ozone concentrations in December-February were 15.3 ppb (at 4 m) and 15.3 ppb (at 30 m) respectively. The maximum of the monthly mean ozone concentrations was reached during June-August with almost 30.1 ppb and 31.8 ppb at 4 metre and 30 m levels respectively.

Seasonal variations of surface ozone showed the existence of annual variability with a maximum in winter and minimum in summer followed by autumn and spring. This indicates that surface ozone concentration over Cape Point during the winter season possibly is influenced by northerly winds which transport local emissions from Cape Town industrial areas (Brunke and Scheel, 1998).

In Europe the general seasonal variations have minimum in winter (December-February) and maximum in summer (July-August), while in Southern Africa the maximum occurred in winter (July-August) and minimum in summer (December-February). The seasonal development of the mean surface ozone concentration at Cape Point is similar to the patterns observed at Elandfontein and Verkykkop stations in Eastern Transvaal Highveld (ETH) South Africa, (Combrink *et all*, 1994).

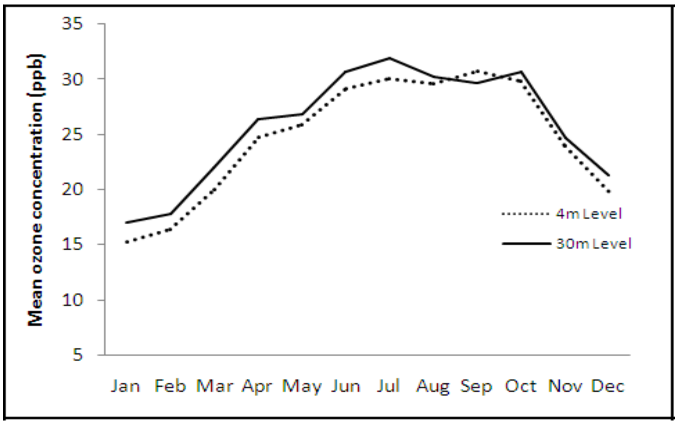

Figure 2: Mean monthly variations of surface ozone concntrations measured at Cape Point station for the year 2007.

The sun rises early in summer, followed by autumn, spring, and late in winter. This leads to the difference in peak hours of ozone concentrations at all seasons. In contrast, the summer (July-August) period was the most important for surface ozone production in Europe. The seasonal ozone concentration of the rural station of Aliartos and the Athens peripheral station of Liossia in Greece shows maximum ozone concentrations in summer (July-August) and minima in winter (December-January) (Kalabokas and Repapis, 2004).

The diurnal cycle of surface ozone at Cape Point is characterised by a minimum in mornings, evenings and maximum in afternoons. These diurnal patterns (Figure 3) indicate that the peaks of ozone concentrations occurred during daylight hours. The peak concentrations that occurred in afternoons were 21.1 ppb at 14:00 in summer, 28.1 ppb at 15:00 in autumn, 32.7 ppb at 17:30 in winter, and 29.6 ppb at 15:00 in spring, respectively.

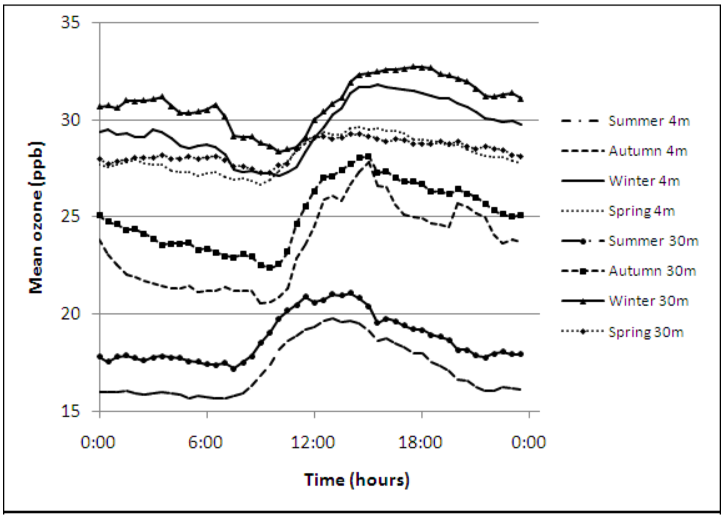

Figure 3: Mean seasonal diurnal variations of surface ozone concentrations measured at Cape Point station for the year 2007.

In late afternoons the concentrations declined slowly through night. The peaks possibly were influenced by the maximum solar radiation in afternoons. The minimum ozone concentrations were 17.2 ppb at 07:00 in summer, 20.6 ppb at 09:00 in autumn, 27.3 ppb at 10:00 in winter, and 26.7 ppb at 09:00 in spring respectively.

The differences of ozone concentrations between two levels (i.e. 4 m and 30 m) were observed (Figure 4). Seasonal variations of ozone differences were minimum in spring and maximum in summer, followed by winter and autumn. In spring the difference of ozone concentration between two levels was small. This was possibly influenced by good mixing in the boundary layer.

The diurnal cycle of ozone difference between two levels showed to be maximum in mornings and evenings and minimum in afternoon hours. Ozone difference increased from 00:30 to 05:00 in summer, from 00:00 to 02:00 in autumn, from 00:30 to 06:00 in winter and from 02:00 to 07:00 in spring. The variations of ozone difference steeply decrease to the afternoon from 07:30 to 14:00 in summer, from 09:30 to 15:00 in autumn, from 10:00 to 17:30 in winter, and from 03:00 to 15:30 in spring and increase again to late afternoon. After sunrise, the ozone difference decreases slightly up to the afternoon and increase again to the late afternoon. The highest concentration differences between the levels were 0.12 ppb at 05:00 in summer, 0.11 ppb at 02:00 in autumn, 0.08 ppb at 06:00 in winter, and 0.03 ppb at 07:00 in spring, respectively.

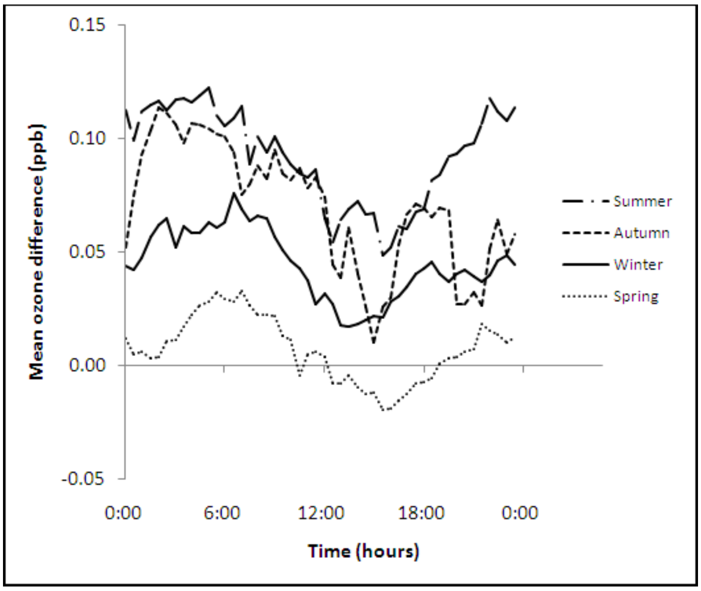

Figure 4: Difference in mean diurnal surface ozone between 4 m and 30 m levels for 2007 at GAW Cape Point station.

## 4. CONCLUSION

Diurnal and seasonal variations aspects of surface ozone measurements obtained at Cape Point GAW laboratory for 2007 period have been investigated. The study focused on the analysis of temperature and surface ozone concentrations at two levels above the ground at 4 m and 30 m. The analysis showed typical diurnal mean temperature variations of a regular day-night cycle. Temperature rises with the onset of the day, peaking in the afternoon and falling in the late afternoon through night. The diurnal cycle of surface ozone at Cape Point is characterized by a minimum in the morning and evening, and maximum in the afternoon. These diurnal patterns indicate that the peaks of ozone concentrations occurred during the daylight hours. The existence of seasonal cycles with a maximum in winter and minimum in summer followed by autumn and spring was observed. This indicates that the northerly winds in winter season at Cape point may be responsible for the transportation of local anthropogenic emissions from Cape Town. This agreed with the trend over Southern Africa the maximum occurred in winter (July-August) and minimum in summer (December-February) by Combrink *et all*, 1994. However, Central Europe has the general seasonal variations of minimum in winter (December-February) and maximum in summer (July-August), as reported by Kalabokas and Repapis, (2004).

The diurnal cycle of ozone difference between two levels shows a maximum in morning and evening, and minimum in the afternoon hours. Seasonal cycles of ozone differences were minimum in spring and maximum in summer, followed by winter and autumn. In spring the difference of ozone concentration between two levels is small, this possibly caused by the influence of good mixing in the boundary layer.

## ACKNOWLEDGEMENT

I am grateful to the Government of the United Republic of Tanzania for funding and the South African Weather Service (SAWS) for the provision of data used in this study. Special thanks are directed to P Gwaze for valuable comments. I finally thank all who devoted their time uncompromisingly during consultations and presentation of this work.

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# TELECONNECTION INDICES' EFFECT ON URBAN POLLUTANTS IN ISTANBUL

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Since the atmospheric circulation patterns that were effected by teleconnection indices influence the meteorological conditions throughout Europe, and the mega cities face serious air quality issues; it is important to research the antropogenic impacts on atmospheric composition in these cities. High concentrations of nitric oxides, sulfur dioxide, particulate matter, carbonmonoxide, ozone and hydrocarbons can be observed in the megacities due to anticyclonic weather conditions. As one of the ancient megacities in the world, Istanbul has a population of 13.5 million, roughly. Since the city is situated between the Black Sea from the North and the Sea of Marmara from the South and the Bosphorus channel divides the city to two continents; Asia and Europe on the direction of NNE/SSW, the weather conditions in Istanbul are mainly the result of interaction of large and local scale circulation systems with the environment and topography. In order to understand the relationship between atmospheric circulation patterns, as represented by teleconnection indices; Arctic Oscillation (AO), North Atlantic Oscillation (NAO), Multivariate El Niño-Southern Oscillation Index (MEI) and selected urban air pollutants; $PM_{10}$, $SO_2$, NO and $NO_2$ in Istanbul for the period of 2005-2012 were examined. Hourly concentrations of $PM_{10}$, $SO_2$, NO and $NO_2$ measured at ten locations for winter and summer with varying parameters like air pressure, temperature, wind speed and direction from the urban atmosphere of Istanbul were used in relation to teleconnections.
Correlations were run for levels of $PM_{10}$, $SO_2$, NO and $NO_2$; and AO, NAO and MEI . And as a result the trends for the teleconnection indices were examined and the potential of the effects on urban air pollution were assessed.

**Keywords:** Teleconnection indices, urban pollutants

**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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**10-13 September 2012 Istanbul -Turkey**

# IMPROVEMENT IN GASEOUS POLLUTANTS AND THE IMPACT OF NATURAL PHENOMENON ON $PM_{10}$ IN RURAL AREA - UNITED ARAB EMIRATES

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## ABSTRACT

Air pollution is a phenomenon by which particles (solid or liquid) and gases contaminate the environment. Such contamination can result in health effects on the population, which might be either chronic (arising from long-term exposure), or acute (due to accidents). During 2007-09, National Energy and Water Research Center (NEWRC), has conducted long term baseline study of air quality for nitrogen dioxide ($NO_2$), carbon monoxide (CO), sulfur dioxide ($SO_2$), ozone ($O_3$) and particulate matter (<10µm in diameter-$PM_{10}$) from the ambient air in the vicinity of Al Mirfa power plant in Abu Dhabi in the United Arab Emirates (UAE). The objective of this study was to establish baseline levels and behavior of airborne pollutants from natural as well as anthropogenic origins with temporal and spatial parameters. This study reveals that the average values for $NO_2$ (<150 µg/Nm$^3$), $SO_2$ (<150 µg/Nm$^3$), and (<CO 10 mg/Nm$^3$) were within the acceptable levels whereas the levels of $O_3$ (<120 µg/Nm$^3$) and $PM_{10}$ (>150 µg/Nm$^3$) occasionally exceeded the FEA permissible limits during 2007-09. Seasonal variation based on three years average reveals highest concentration of $NO_2$ and $SO_2$ during winter and CO and $O_3$ during summer months. Results indicates that the levels of $SO_2$ and CO were significantly controlled and improved while increased the fuel combustion of Al Mirfa power plant from 2007 to 2009. Dust has significantly impact on the air quality by elevated levels of $PM_{10}$ exceed in several instances associated with regional sandstorm during 2007-09.

**Keywords** Ambient air quality monitoring • Seasonal variations • Natural phenomenon

# AIR QUALITY APPLICATIONS IN PROCESS OF EU ADAPTATION

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## ABSTRACT

In process of EU adaptation, according to the Regulation on Air Quality Assessment and Management (AQAM) which was put into force in 2008, 13 numbers of pollutants have been determined in air quality terms. If limits of these pollutants exceed which are determined in the regulation, percentage of receiving data should be measured as %90 in permanent stations. These measures have been construed with source inventory and models of dispersion. Accordingly the said regulation, if there is no measurement for the territory, preassessment study will be made and it should be determine that permanent or representative measurement will be necessary. At the end of this study, numbers of permanent measurement stations will be determined using population information for that territory. In this context, it will be necessary that in addition to the current 122 stations which are fixed only one air quality monitoring center, 208 air quality monitoring stations should be established. Consequently, as mentioned above it will be difficult to manage all 330 stations from unique air quality monitoring center for whole country. Therefore, studies about establishing 8 air quality monitoring centers have been carrying out in order to measure and analyze more pollutant parameters determined within the context of AQAM.

**Key Words:** Air Quality, preassessment, zone and agloramation list,

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# EARLY STATISTICAL ANALYSIS OF SHIP EMISSIONS INVENTORIES IN THE ISTANBUL AREA

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## ABSTRACT

Ship emissions contribute substantially to air pollution. The Bosphorus, as one of the busiest straits in the world, has been influenced by the emissions of marine traffic. However, one of the main uncertainties in air quality assessments for coastal areas is ship emission inventories. In this study, the Ship Traffic Emission Assessment Model (STEAM) is applied to the Automatic Identification System (AIS) data from the Bosphorus Strait. In addition to AIS data, a ship database containing technical details of each and every vessel found in AIS data must be at hand. This database is a composite from many data sources, most significantly IHS Fairplay, ship owners and engine manufacturers. In case all the vessel details are not available for a specific ship, the model applies educated guesses to generate a reasonable estimate of emissions for that vessel. As a result, vessel specific emission inventories are generated; when the process is repeated for all vessels in an area, an emission inventory is obtained. However, vessels without the AIS equipment onboard will not be covered in the inventory. A snapshot of emissions from shipping is obtained in addition to detailed statistics of vessel traffic in the area. Pollutants which are currently covered consist of $NO_x$, $SO_x$, CO, $CO_2$ and PM, which is further divided to EC, OC, ash and hydrated $SO_4$. If dry PM mass is preferred then the water can be left out.

**Key Words:** Ship emissions, AIS, STEAM model, Bosphorus

## 1. INTRODUCTION

Emissions from ships have recently received more attention since they have become a significant concern for air quality in harbors and port cities (Schrooten et al. 2009). Sea transportation increases every day and causes air pollution, which has a negative impact on the environment and human populations. The issue of controlling air pollution form ships was discussed in the International Convention for the Prevention of Marine Pollution (MARPOL) in the 1973. However, it was decided not to include regulations concerning air pollution at the time. Long and short distance shipping plays important roles in facilitating international trade transportation over the world. Cargo transport by ships is about 70 percent of all trade between the European Union (EU) and the rest of the world (Harrison et al., 2004; Derwent et al., 2004; Jaffe et al., 2003; ENTEC 2005; Qinbin et al., 2002; Davies et al. 2000). Environmental and Engineering Consultancy (ENTEC) has studied ship emissions of SO2, NOx, CO2 and hydrocarbons in the North Sea, Irish Sea, English Channel, Baltic Sea, Black Sea and Mediterranean to determine these emissions for all vessels as well as separately for each vessel type and flag state (ENTEC, 2002). Ships are fast becoming the biggest source of air pollution in the EU. According to the Commission of the European Communities (CEC) unless more action is taken they are set to emit more $SO_x$ than all land sources combined by 2020 (CEC, 2005). The International Maritime Organization (IMO) notes in their study of greenhouse emissions from ships, there is an increasing awareness of the impacts of shipping emissions on onshore air quality. An estimated 85 percent of international shipping traffic occurs in the northern hemisphere, and 70 percent of that is within 400 km of land. Much of the shipping activity and associated emissions occur near major urban areas, many of which are already struggling with air quality problems (IMO, 2000; ENTEC, 2005; Acid News, 2006).

The ships passing from the Bosphorus contribute sea, air, noise pollution and other environmental risks like maritime accidents. The number of ships passing between İstanbul and Çanakkale has increased and these shipping activities contribute significantly to the air pollution in the Bosphorus. In this study, the STEAM emission model is applied to the Automatic Identification System from the Bosphorus Strait.The results of this study may help environmental scientists and policy makers, (Toros and Deniz, 2006).

## 2. DATA AND METHODOLGY

The Bosphorus is one of the most beautiful, historical and picturesque stretches of water in the world, which is a geological strait separating the European and the Asian parts of Istanbul and it lies between the Black Sea and the Sea of Marmara. Emissions from ships in transit through the Bosphorus have an impact on the air quality of densely populated areas. The Strait of Istanbul is approximately 31 kilometers long average depth 35 meters average width 1.5 km at the narrowest point is about 700 meters. The length of the strait of the Çanakkale is about 70 kilometers with a general width ranging 1-2 kilometers, (Toros and Deniz, 2006).The Strait of Istanbul through the Black, Marmara, Aegean and Mediterranean Sea, are unique in many respects in the world.

The Bosphorus is a significant and growing source of air pollution and one of the biggest problems in air quality studies is emission inventories. The use of Automatic Identification System (AIS) has given opportunity to a more accurate calculation of ship emission inventories. This system needs international and interdisciplinary collaboration between institutes and organizations. In this study, the ship emission inventories for the Bosphorus Strait will be produced using the AIS and Ship Traffic Emission Assessment Model (Jalkanen et al. 2009; 2012) as well as vessel specific emissions of NOx, SOx, CO, CO2 and PM.

The input data for STEAM consists of the activity data (AIS), ship technical specifications of every vessel (IHS Fairplay) and possible fuel requirements in the study area. The STEAM model structure is outlined in Fig 1. The effect of various emission abatement techniques are taken into account. The model determines the vessel resistance as a function of vessel speed. Engine power levels are estimated taking propeller, power transmission losses and vessel operational mode into account. For example, power requirements of onboard systems are very different in a case of an oil tanker than those of a large cruise vessel. Environmental effects, like waves and marine currents can be taken into account if specific datasets for these are available. Pollutants included in the model are NOx, SOx, CO, CO2 and PM, which is further subdivided into EC, OC, Ash and hydrated SO4 (Jalkanen et al. 2012).

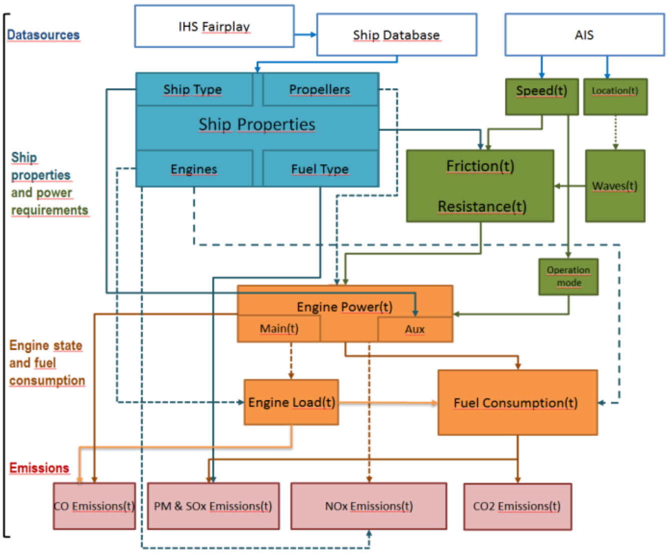

Fig 1. Schematic presentation of the STEAM model (Jalkanen et al., ACP 12, 2641-2659, 2012).

## 3. CONCLUSION

Preliminary runs indicate that there are areas of significant emissions north and south of the Bosphorus, where ships are waiting and loading/unloading. A summary of the results is given in Table 1. For this example, grid cell size of 100 by 100 meters was used. Air quality studies of the Bosphorus will determine the impact of ship emissions to the dense human population in the area. As seen Table 1, one month total emission of NOx, SOx, CO, CO2, PM is 860, 220, 250, 44.000 and 58 tons emitted in the Bosphorus sequentially. One of pollution result shown in Fig. 2 as a ship NOx emissions in the Bosphorus area during March 2012 based on AIS data and STEAM model.

Table 1. Ship emissions in the Bosphorus during March 2012 (in tons). The rightmost column shows the projected (assuming no seasonal variation) annual emissions based on one month of AIS data.

| **Pollutant** | **March 2012, tons** | **Projection, 12 months, tons** |
|---|---:|---:|
| **$NO_x$** | 860 | 10 300 |
| **$SO_x$** | 220 | 2 680 |
| **CO** | 250 | 3 000 |
| **$CO_2$** | 44 000 | 530 000 |
| **Total PM,** | 58 | 700 |
| *of which* | | |
| *EC* | 6 | 70 |
| *OC* | 16 | 189 |
| *Ash* | 4 | 51 |
| *Hydr. SO4* | 32 | 391 |
| **Fuel** | 14 500 | 174 000 |

Fig 2: Ship NOx emissions in the Bosphorus area during March 2012 based on AIS data and STEAM model. The scale indicates the total ship emissions in kilograms inside 100 by 100 meter cells.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# NUMERICAL MODELING OF AIR POLLUTION POTENTIAL HAZARD AT LAND USE PLANNING SCALE IN GOLESTAN PROVINCE, SOUTHEAST CASPIAN SEA, IRAN

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## ABSTRACT

In order to assess the potential hazard of air pollution at airshed and land use planning scalein Golestan Province, a weighted multicriteria numerical model was prepared and implemented in the framework of 198 equi-potential environmental units. This generic model contains three groups of parameters including decreasive (8, environment refinery capacity) increasive (31, pollution susceptibility) and bilateral parameters (8, critical limits or specific standards). Rate of parameter density class was determined on the range and allowable limit of ambient air standard in a 1 to 5 value, and weight of each parameter was determined according to its relative importance in air pollution potential and exceeding from ambient air standard in a -3 to +3 graded scale. Total number or hazard index of air pollution in each land use equi-potential unit was calculated by multiplying of weight to rate and sum of positive and negative values of all parameters, and finally divided to 5 classes. With implementation of model with different data sources, the potential hazard of air pollution in Golestan province evaluated and mapped as choropleth at 1:250000 scale. Results show that the province contains all of the 5 hazard classes of the model, and there are significant differences ($P<0.01$) between number and area of hazard class units. This numerical model has actually a necessary spatial and thematic resolution for planning of air quality management and control. So that , as a ground truth there are close spatial compatibility between high hazard classes and densely populated and urban-industry areas of the province. Therefore, it is possible to calibrate and validate this regional scale numerical model via systematic monitoring of index pollutants in different part of the province especially in the critical areas for land use allocation and sustainable development

**Keywords**: Numerical model; Air pollution; Potential hazard; Hazard map; Airshed;Golestan Province

**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# RISK EVALUATION OF EXPOSURE TO CO IN URBAN STREETS, TEHRAN, IRAN

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## ABSTRACT

Although using well-equipped fixed air toxics measuring stations and air quality modeling give us a total view of an urban air quality, but there are different routes of exposure during travelling by vehicles or walking and shopping in pavements associated with higher risk of exposure to toxic pollutants that cannot be monitored by fixed-site stations. Short-term human exposure to CO was investigated in and around a high traffic street and taxis cabins in Tehran downtown, Iran. 55 points at 5 sections of a bi-directional street and 336 taxis were selected for assessment. At each section, 11 s: one point at midline and 6 points at each side include: one at the near-side of the street where the people are waiting for catch up the taxis to go, one inside the pavement, and 3 in an alley at 10, 50, and 100 meters far from the edge of the pavement have been selected. CO concentration was measured for a full week during the daytime from 07:00 to 22:00, 3 times in a day at each season. Wind speed and its direction were also measured at each point. Co concentration in taxis cabins were measured while the operator used taxi for travelling among measuring sections. The arithmetic means and standard deviations values for CO concentration were 76.5(25.1), 58.4(20.2), 39.8(14.3), 36.4(12.6), 28.8(10.5), 13.7(6.3), 6.7(3.8), and 4.2(3.2) in Taxis cabin in traffic jam and moving modes, Street at midlines and near-sides, Alleys at 10, 50, and 100 meters distances from the edge of pavements. The absolute highest observed value for CO concentration during the study period could reach 117.6 ppm at a taxi cabin in traffic jam mode and the lowest one was 1 ppm which observed several times in alleys especially at weekends and strong windy conditions. All mean values except for alleys in distances more than 50 m from the edge of the pavements were higher than 8-hour recommended limit, 9 ppm, by WHO, EPA, and IDE. Comparing the individual measurements to 1-hour recommended value, 35 ppm, showed, almost more than 50% of the measurements in taxis cabins and streets locations were exceeded. The highest risk of exposure has been seen in the taxis cabins and hense all vehicle cabins in the traffic jam. It was clear that the taxis drivers, who reported 10 hours of work duration per day, were the most high risk group against CO intoxication in the city. Since at elevated concentrations, CO intoxication can causes problems in visual perception, manual dexterity, and mental ability, It can cause decreasing the drivers concentration significantly and may result in increasing accident rate.

**Keywords:** Air pollution, CO exposure, Taxi cabin, CO measurement

**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# ANALYTICAL STUDY OF CLIMATE CHANGE POLICIES IN THE ARAB WORLD

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The scientists agree that climate scientists will be rise the earth temperature, which is expected to rise in the Arab world and Central Asia by about two C0 in the period between 2030-2050 which will exacerbate the problems of soil erosion, and thus agricultural production will fall a lot, and to the extent of natural disasters. Some expectations to the radical changes will affect the weather patterns in our region, for example the storm surge destroyed and the spread of drought for long periods in many areas and the displacement of tens of millions, and the famine, water scarcity and pollution, and flooding would cause the spread of disease and a sharp rise in mortality Human groups cannot stop or slow down the primary cause of global warming, because of the large backlog of greenhouse gases produced by industry and transportation in the atmosphere, especially carbon, the phenomenon of global warming will worsen. With all that that implies changes in climate damaging during the past few decades Serious commitment should be rationalization of the consumption of fossil energy and reduce to a minimum of use, break the monopoly of scientific and technical knowledge of Western technology, green and put it fully accessible to poor people, search for crop varieties more resistant to drought and heat, the abolition of government subsidies for carbon-based fuels and to impose a price on pollution of the atmosphere through taxation, in turn, support the private sector to develop renewable energy technologies and effective, and governments to impose on their midst industrial systems work and the concrete steps reduce drastically the process of global warming, by increasing the efficiency of cars and trucks, power plants, and reduce electricity demand by 40% , through the use of efficient technologies in energy consumption, It is also expected until 2025 that the sea level rises 30 cm, what will lead to dumping about 200 km 2, of the land of Egypt, and as a result, it could displace more than half a million Egyptians. Deals with legislation dealing with the phenomenon of Arab climate change and puts forward a vision for the future development of environmental legislation Marginalized and poor countries most affected by climate change, as they have less capacity and opportunities to adapt to the impacts of climate change, women are most affected, they constitute 70% of the world's poorest people, are also affected by women from the conflicts that may arise from climate change differently, Most refugees are women and children

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# METHODOLOGY FOR ASSESSING POLLUTANT EMISSIONS FROM ROAD TRANSPORT IN THE FRAMEWORK OF SUSTAINABLE DEVELOPMENT(CASE OF MASCARA CITY IN NORTH WEST OF ALGERIA)

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## ABSTRACT

The atmospheric pollution is a very complex given the diversity of pollutants may be present in the atmosphere. The urbanization phenomenon accelerated mobility needs, which usually results in an increase in road networks. In Algeria, faced with various projects transport, we must first think about transportation issues in the context of sustainable development, which alone can take into account environmental issues seriously. However, an inventory of emissions of primary pollutants (CO, $CO_2$, $NO_x$) from utilities particular vehicles used extensively in Algeria for the car fleet in the city of Mascara was estimated by the software COPERT 4 (Calculation Of air Pollutant Emissions from Road Transport), which is based on the reference year 2005, and benefit from the experience gained in the implementation of measures emissions from vehicle traffic for the city of Blida by a levy system on board of a vehicle. The city of Mascara occupies a strategic central location of the territory of the North West region of Algeria. However, for each of the pollutants measured, the levels are compared with available references. These may be the limit values which must be respected, and the exceeding of which involves developing a reduction plan to reduce pollution. Consequently, the inventory also provides the essential elements to work arrangements consistent with the problem of air quality. Thus, understanding of these phenomena can finally, for each country having its own analysis of the issues, rather than reproduce without serious discussion of the issues identified elsewhere in very different conditions.

**Key Words:** Road Transport, Sustainable Development, Emission Inventories, Copert 4.

## 1. INTRODUCTION

The emissions from road origin, the exhaust of vehicles emit many products from the combustion of fuels (hydrocarbons) in air. These pollutants have different contributions in the stock of urban air pollution and global. The Pollution due to transport a long time been considered a proximity problem, mainly in the cities due to traffic density. Today we know that transportation, mainly road and especially automotive, are an important source of pollution. The main pollutants from vehicles are carbon monoxide (CO), a deadly toxic gas at a low dose, nitrogen oxides (NOx), irritating to the respiratory system, unburned hydrocarbons (HC), irritants and carcinogens and fine particulate matter ($PM_{10}$), which increase respiratory risks and are probably carcinogenic (Soylu, 2007). The cars also emit carbon dioxide ($CO_2$), greenhouse effect gas, the main cause of global warming (Soylu, 2007 ; Saija and Romano, 2002; Rudiment , 2005b ). Thus, transportation sources of pollution and are harmful to human health ( Fialaire, 2008).

However, the air quality is not only dependent on the amount of pollutants emitted by sources. It is also related to climatic conditions, meteorological, topological and morphological environment ( Lesieur, 1994 ). Once emitted by a source of pollutant, its evolution in the atmosphere depends on the wind, the stability of the atmosphere, solar radiation, topography and morphology of the environment. Other pollutants such as acid rain that manifest to at the regional level ( Lesieur, 1994 ). The unit emissions of vehicles are becoming an unavoidable datum for any given comparison of emission levels and calculations of inventory when looking for deposits of emission reduction becomes very important in the framework of the Kyoto Protocol ( EEA, 2000a ; EEA, 2000b ).

The sustainable development is a pattern of economic development seeking to reconcile economic, social progress and environmental protection, we consider it as a heritage for future generations. To reduce emissions of greenhouse gases produced from transportation, choose a transport "sustainable", which pollutes the least. For example, we must promote public transport that pollute much less compared to private vehicles. In addition we must optimize our movements ( Fialaire, 2008).

## 2. MATERIAL AND METHODS

### 2.1 Study area

The city of Mascara occupies a strategic central location and covers approximately 15% of the territory of the North West region of Algeria, which is considered to relay his location to the extent that it is crossed by the main roads (figure 1).

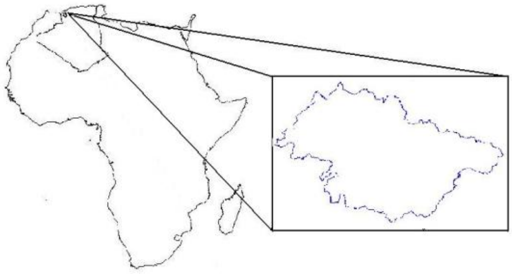


Figure 1. Location of the study zone situation

## 3. METHODOLOGY

The emissions calculated based on the basic equation:

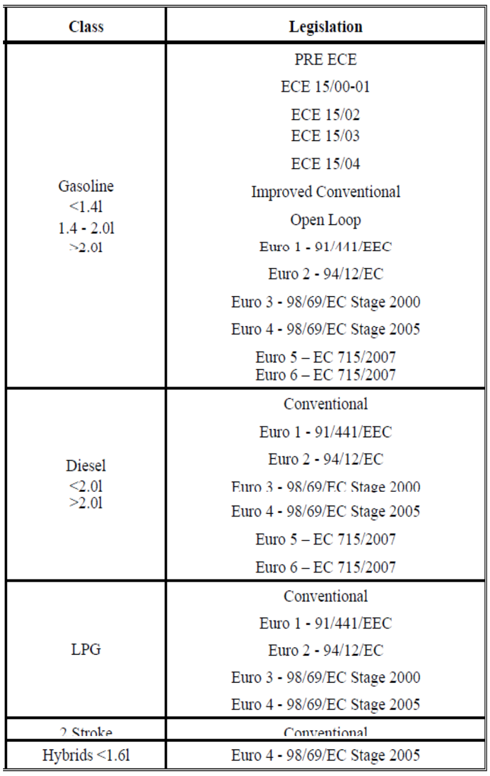
$$A = E \times EF \qquad (1)$$

Where E is the emission, usually expressed in mass, A the activity of the issuer (generally expressed in vehicles. Km) and EF an unit emission factor . This formula allows taking into account the variations in activity over time and space, which is essential for the study of emission scenarios. To illustrate this formula, for example, on-road emissions of certain substances can remain stable despite a decrease in the unit emission factor, if it is offset by an increase in activity, namely the number of vehicles. Km in the case of road emissions.

The model COPERT 4 (Calculation Of air Pollutant Emissions from Road Transport) ( Hickman et al, 1999 ; Soylu, 2007). is based on a database of road emission factors (EF of the equation (1)), factors that convert quantitative data of activity (by data on the characteristics of car traffic) in pollutant emissions. In the case of road traffic, the unit emission factor for a particular vehicle, in grams per kilometer, is the amount of pollutant emitted by the latter over a distance of one kilometer.

An emission factor (FE) is assigned to each pollutant and for each category of vehicle. It is determined by the type of vehicle (particular vehicle, utilities particular vehicles < 3.5 t, Truck, including buses and coaches), its mode of fuel (gaoline, diesel), the cylinder (or of its total weight authorized for the truck) and its date of circulation (to account for emission standards, including European standards (Table 1) and age). It is also based on the speed of the vehicle concerned, and more generally the use of the vehicle (load, ....) and traffic conditions.

Table 1: the different categories of utilities particular vehicles in COPERT



| Class | Legislation |
|---|---|
| Gasoline<br><1.4l<br>1.4 - 2.0l<br>>2.0l | PRE ECE<br>ECE 15/00-01<br>ECE 15/02<br>ECE 15/03<br>ECE 15/04<br>Improved Conventional<br>Open Loop<br>Euro 1 - 91/441/EEC<br>Euro 2 - 94/12/EC<br>Euro 3 - 98/69/EC Stage 2000<br>Euro 4 - 98/69/EC Stage 2005<br>Euro 5 – EC 715/2007<br>Euro 6 – EC 715/2007 |
| Diesel<br><2.0l<br>>2.0l | Conventional<br>Euro 1 - 91/441/EEC<br>Euro 2 - 94/12/EC<br>Euro 3 - 98/69/EC Stage 2000<br>Euro 4 - 98/69/EC Stage 2005<br>Euro 5 – EC 715/2007<br>Euro 6 – EC 715/2007 |
| LPG | Conventional<br>Euro 1 - 91/441/EEC<br>Euro 2 - 94/12/EC<br>Euro 3 - 98/69/EC Stage 2000<br>Euro 4 - 98/69/EC Stage 2005 |
| 2 Stroke | Conventional |
| Hybrids <1.6l | Euro 4 - 98/69/EC Stage 2005 |

The methodology of the latest model COPERT 4 8.1 is available with the associated tools on the site of the Laboratory of Applied Thermodynamics at the Aristotle University of Thessaloniki: http://www.emisia.com/copert/General.html. COPERT 4 is in Windows program used to the calculation of air pollutant emissions from road transport. The development of technical COPERT is funded by the European Environment Agency (EEA), in the activities of the European Centre on Air and Climate Change.

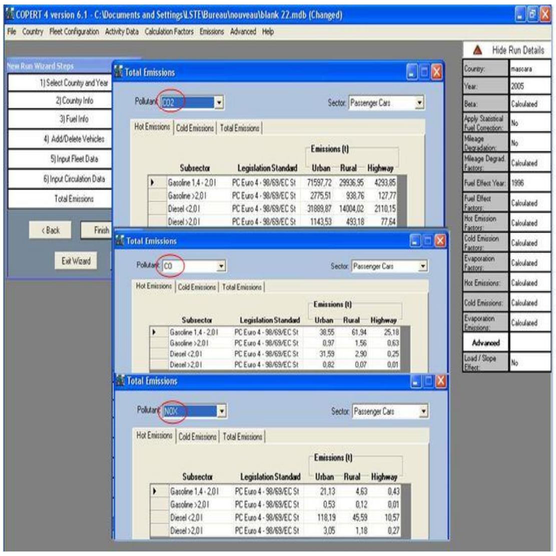
The emissions of vehicles in use are not only a problem of air quality in the cities of Algeria (Kerbachi et al., 2006a ; Boughedaoui et al, 2004 ) but also a constantly growing source of greenhouse gas emissions particularly in the developing countries. In Algeria, the utilities particular vehicles (UPV) are generally used with average annual mileage of 38,000 km for the class of vehicle age less than 5 years (Bulletin de ONS, 2005). This annual mileage decreases very slowly with time compared to European countries (Boughedaoui et al., 2004 ).

The development of COPERT ( Hickman and al, 1999 ) which is a European database containing data of European measuring emissions from different laboratories and process includes the majority of the brands and models existing in Algeria. These makes and models of vehicles traveling in Algeria are contained in COPERT ( Hickman et al., 1999 ). However, to meet standards and driving conditions different from those of European vehicles. This allows for comparison studies and analyzes on vehicles of the same origin to the different uses and environments.

Thus, the main objective of this work is to measure emission factors of utilities particular vehicles widely used in Algeria specific to the car fleet in the city of Mascara by COPERT ( Hickman et al., 1999 ) where UPV 21% of the national car fleet that totals more than 3 million vehicles for 2005. The car fleet of utilities particular vehicles rolling is 79% of European brand and only 17% of Asian origin (Bulletin de ONS, 2005). Thus, through the results obtained by Boughedaoui (Boughedaoui et al., 2004 ) by direct measurement of emissions from utilities particular vehicles (UPV) in circulation by a sampling system is embedded in the vehicle connected to the exhaust pipe.

The campaign of these measures took place from September to November 2005. The circuit is chosen to represent the arteries of the city of Blida busiest. A sample of ten vehicles (UPV) was selected from the Algerian car fleet with two gasoline and 8 diesel vehicles of equivalent power. Tests were conducted in total in urban areas and road and highway tests on circuit’s length from 10 to 15 km for each vehicle. Thus, the average emission factors for the entire of the sample of gasoline and diesel vehicles were measured. These emission factors are compared to the emissions equivalent vehicles rolling in the city of Mascara for the same year. One of the difficulties that emerged from this comparison is the absence of standards for vehicles Algerian where regulation of manufacture or import vehicle does not require a certification standard. However, these tests have the advantage of comparison to highlight the gap in part due to construction standards and the technology gap between vehicles rolling in Europe and Algeria for models and brands of identical vehicles.

The estimated emission factors vehicles has been the subject of various methodologies. We want to compare the emission factors obtained by the companion measure on the city of Blida by Boughedaoui (Boughedaoui et al., 2004 ) is based mainly on emissions of $CO_2$, CO and $NO_x$ that we will follow the methodology of COPERT 4 at the city of Mascara. Here we focus only on utilities particular vehicles. For each category, it is considered the cylinder, fuel type, weight, and the standard of remediation associated with the year of vehicle. COPERT 4 expresses emissions hot, cold and evaporation (Figure 2). In this methodology, emission factors are determined according to equations that are based primarily on the average speed at which vehicles are subject to urban areas, rural areas and highways.



Country: mascara
Year: 2005
Beta: Calculated
Apply Statistical Fuel Correction: No
Mileage Degradation: No
Mileage Degrad. Factors: Calculated
Fuel Effect Year: 1996
Fuel Effect Factors: Calculated
Hot Emission Factors: Calculated
Cold Emission Factors: Calculated
Evaporation Factors: Calculated
Hot Emissions: Calculated
Cold Emissions: Calculated
Evaporation Emissions: Calculated
Load / Slope Effect: No

Pollutant: CO2
Sector: Passenger Cars

| Subsector | Legislation Standard | Emissions (t) Urban | Rural | Highway |
|---|---|---|---|---|
| Gasoline 1,4 - 2,0 l | PC Euro 4 - 98/69/EC St | 71597,72 | 29936,95 | 4293,85 |
| Gasoline >2,0 l | PC Euro 4 - 98/69/EC St | 2775,51 | 938,76 | 127,77 |
| Diesel <2,0 l | PC Euro 4 - 98/69/EC St | 31889,87 | 14004,02 | 2110,15 |
| Diesel >2,0 l | PC Euro 4 - 98/69/EC St | 1143,53 | 493,18 | 77,64 |

Pollutant: CO
Sector: Passenger Cars

| Subsector | Legislation Standard | Emissions (t) Urban | Rural | Highway |
|---|---|---|---|---|
| Gasoline 1,4 - 2,0 l | PC Euro 4 - 98/69/EC St | 38,55 | 61,94 | 25,18 |
| Gasoline >2,0 l | PC Euro 4 - 98/69/EC St | 0,97 | 1,56 | 0,63 |
| Diesel <2,0 l | PC Euro 4 - 98/69/EC St | 31,59 | 2,90 | 0,25 |
| Diesel >2,0 l | PC Euro 4 - 98/69/EC St | 0,82 | 0,07 | 0,01 |

Pollutant: NOX
Sector: Passenger Cars

| Subsector | Legislation Standard | Emissions (t) Urban | Rural | Highway |
|---|---|---|---|---|
| Gasoline 1,4 - 2,0 l | PC Euro 4 - 98/69/EC St | 21,13 | 4,63 | 0,43 |
| Gasoline >2,0 l | PC Euro 4 - 98/69/EC St | 0,53 | 0,12 | 0,01 |
| Diesel <2,0 l | PC Euro 4 - 98/69/EC St | 118,19 | 45,59 | 10,57 |
| Diesel >2,0 l | PC Euro 4 - 98/69/EC St | 3,05 | 1,18 | 0,27 |

Figure 2. COPERT 4 version 6.1 interface

In order to facilitate inter-comparison exercise, the configurations shown in Figures 3, 4 and 5 were defined very precisely by giving up information. However, the specificity of each figure, leads to compare the emission factors for the two cities (Blida, Mascara) according to the type of fuel.

The $CO_2$ emissions are proportional to the distance traveled by vehicles, but they also depend on the type of vehicle. This difference is explained by the fact that $CO_2$ emissions are directly proportional to fuel consumption. It is clear from Figure 3, a very significant difference in favor of the city of Mascara in order of 75.52% of the emissions caused by gasoline vehicles and 64% for diesel vehicles.

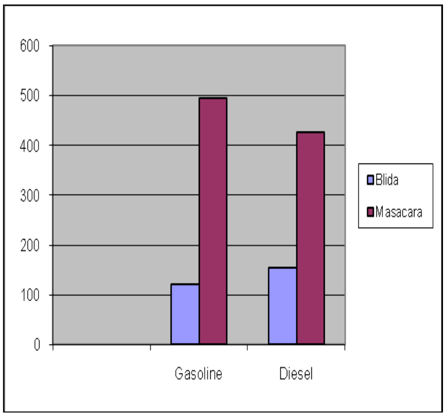


Figure 3: Comparison of emission factors for $CO_2$ (g / km) for utilities particular vehicles in the city of Mascara and Blida in 2005

Also, the natural conditions of the region are very unfavorable (steep slopes, hot weather, the load) are also involved to raise the level of pollution. However, $CO_2$ emissions largely responsible for global warming are increasing. The reasons are mainly due to buying patterns and car use. Also, the strong growths in traffic, passengers, and longer average travel distances have adverse effects on the environment.

The diesel vehicle is still cleaner than gasoline vehicles for CO (Figure 4). By cons is almost thirteen more $NO_x$ emitting species that vehicles for the city of Mascara (Figure 5)

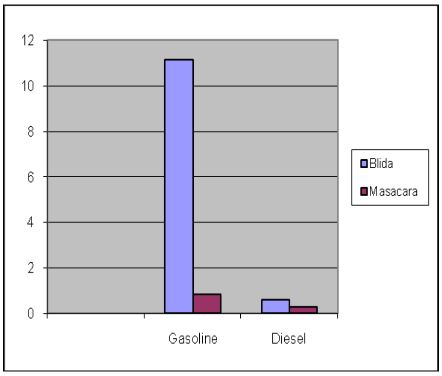


Figure 4: Comparison of emission factors for CO (g / km) for utilities particular vehicles in the city of Mascara and Blida in 2005

Also, we can see that for the diesel motorization, the emissions are more important on the hot cycle that the cold cycle unlike to the gasoline motorization. Thus, the total emission factors are higher on the gasoline engine that over the diesel engine.

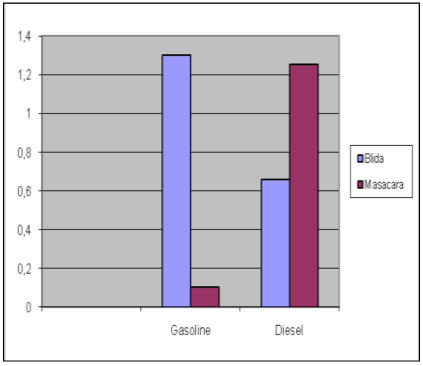


Figure 5: Comparison of emission factors for $NO_x$ (g / km) for utilities particular vehicles in the city of Mascara and Blida in 2005

The Highway emissions are significantly lower than in urban areas. In parallel, growth in demand of fuel depends from the increased distances, particularly for transit traffic. However, the comparison between results obtained from the COPERT method and experimental measurements demonstrates the difficulty of estimating emission factors for vehicles. However, these results were the basis for this projection of pollution, do not include other vehicle category whose number grows exponentially and significantly raising the level of pollution per resident.

## 4. CONCLUSIONS

It follows from the foregoing that the air quality deteriorates in terms of increased $CO_2$ in the Algerian cities. It thus contributes to the worsening of the greenhouse effect and the deterioration of the ozone layer. The high number of vehicles, age and type of motor vehicles, the quality and quantity of energy sources are the main factors of pollution, however, the bad condition of roads, congested urban mobility and natural conditions unfavorable (steep slopes, hot weather) are also involved to raise the level of pollution in cities.

This study assessed the impact of road transport vehicles in particular on the specific air quality in the city of mascara, and compared with the city of Blida. It retains that, to maintain quality, we must rethink and better organize road transport by acting on all elements of the system: traffic, vehicle condition, road condition, fuel quality. This is a measure of effective management of demand for the dual purpose of satisfying urban mobility while reducing the rate of pollution per resident. For proper management of the quality of ambient air in Algeria should therefore provide itself with the pollution standards, the technical control of vehicles is based on verification of the principal organs for a vehicle be safe, may also be interested in the engine with an incorrect setting causes the excessive production of exhaust pollutants. The knowledge of emissions and also the influence of various parameters on these issues is a tool for decision support as part of the evaluation of projects related to road transport. The emission is not an end in itself but a means of investigation designed to show areas where air pollution is excessive. Thus, it uses advanced techniques of physical-chemistry and is part of a multidisciplinary approach to our environment.

In addition, the concentrations of pollutants are punctuated by daily movements of travelers. In traffic site, working days, the highest levels are measured in the morning and evening, along with the traffic intensity. Overall, the traffic reduction is felt on the concentrations of weekends and holidays and there is a spreading of the highest levels later in the evening (Masclet, 2005).

However, the problem is to find a compromise or a balance between economic development and environmental protection. In Algeria, the LPG was the subject of a campaign. A grant to install the tank and an attractive sale price of fuel are factors that have influenced so strong to the decrease of air pollution ( Rahal, 2009 ).

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# METEOROLOGICAL MODELING OF THE PM10 EPISODE IN KAĞITHANE-ISTANBUL UNDER VERY STABLE CONDITIONS FOR NOVEMBER 6-9, 2010 EPISODE

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## ABSTRACT

This paper presents verification results of numerical simulations of meteorological conditions leading to an air pollution episode on 6-9 November 2010 in Istanbul. WRF-ARW ver 3.3 is run with GFS and ECMWF input. For verification, horizontal wind components and temperature data of nine meteorological stations are used for both simulations. Results indicate that the model is successful in simulating the meteorological conditions with both two different input data, especially with the GFS input, although ECMWF runs had a finer horizontal resolution of 1 km.

**Keywords:** PM10, episode, air quality, meteorological modelling, WRF.

# RADON IN ITU

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## ABSTRACT

Radon is a radioactive atomic gas, which may be found in rock formations beneath buildings or in certain building materials themselves. Radon is probably the most common serious hazard for indoor air. Radon is a heavy gas and thus will tend to accumulate at the floor level. The aim of this study is to collect some data on radon for use in cooperative research on radon exposure in various indoor environments in Istanbul Technical University Ayazaga Campus. For this purpose, the buildings in Ayazaga campus of Istanbul Technical University were classified into the categories according to their age and type of structural construction such as reinforced concrete or steel. There are total six buildings in the campus were considered; e.g. a reinforced concrete building Faculty of Science and Letters (FEB); Faculty of Civil Engineering (INB) and Energy Institute which were built in 1978; Faculty of Aeronautics and Astronautics (UUBF) which was built in 1990; Prof. Dr. Ali Ihsan Aldogan Dormitory Building which was constructed in 2010 and Molecular Biology Building which is a steel constructed building were chosen. In order to measure radon concentrations indoor environments at these buildings, we used passive CR-39 nuclear trace detectors for the two months period. The detectors were replaced on the basement of all buildings and additionally one more detector was replaced into the Chemistry laboratory on the fifth floor of the Faculty of Science and Letters (FEB) and one more detector was replaced into the library on the first floor in Faculty of Aeronautics and Astronautics (UUBF). The devices were provided by The Turkish Atomic Energy Authority (TAEK), Cekmece-Istanbul. The measurement period for 2 months has been started since 14th March 2012. The measured radon concentrations from the ongoing research will be assessed by the limit value, 4pCi/L of the tolerant value for World Health Organization. The measured concentrations of Radon will be evaluated for the health effect by the people who lives in these buildings.

**Keywords:** indoor air pollution, Radon, ITU

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# VOLATILE ORGANIC COMPONENT ANALYSIS IN KAĞITHANE

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## ABSTRACT

İstanbul is the biggest city of Turkey with population, industry and economy. There is a lot study about air pollution level of the city and most of them included only some basic air pollution parameters like PM10, SO2 and NO2. However, it has many risks to human health, relatively little is known about the levels of VOC in Istanbul. Air pollutant in the cities contains many components that originate from a wide range of industrial, heating, motor vehicle, and natural emissions sources. Turkish National Union of Geodesy and Geophysics (TUJJB) and Turkish Scientific and Technical Research Council Project (TÜBİTAK) are supporting air quality studies and one of them is Volatile Organic Component (VOC) Analysis in Kağıthane valley. In this study, ambient air quality measurements of 8 VOCs (Benzene, Toluene, m,p Xlene, Hexane, Heptane, Ethylbenzene, 1,3,5 Trimethyl benzene and 1,2,4 Trimethyl benzene) are analyzed and compared with literature values.

**Keywords:** Volatile Organic Compounds (VOC), air quality level, Kağıthane, İstanbul.

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**AIR QUALITY MANAGEMENT at URBAN, REGIONAL and GLOBAL SCALES**
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# THE VERTICAL DISTRIBUTON OF OZONE OVER ANKARA FOR 2007-2011 PERIOD ACCORDING TO BREWER SPECTROPHOTOMETER DATA

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## ABSTRACT

Vertical distribution of ozone is important parameter on the monitoring changes of the ozone layer. Today, to determine of the vertical distribution of ozone, the ground-based ozonesonde observations, Dobson or Brewer Spectrophotometer with a satellite-based instruments (such as TOMS-OMI) are widely used. In this study, the data set produced by Turkish State Meteorological Service (TSMS) in Ankara for periyot between 2007-2011 and Brewer Umkehr measurement data were analyzed to prepare the required ozone profile by using the TOMKEHR program developed by World Ozone Data Center (WODC) in 1992. On the vertical distribution of ozone over Ankara, Turkey, the maximum ozone concentration were found at the level of 22-24 km in stratosphere. The maximum average density of stratospheric ozone, respectively, 4.9 x $10^{12}$ molecules/$cm^3$ ozone in year 2007, 4,7 x $10^{12}$ molecules/$cm^3$ in the year 2008, 4,8 x $10^{12}$ molecules/$cm^3$ in the year 2009, 4,8 x $10^{12}$ molecules/$cm^3$ in the year 2010 and 4,7 x $10^{12}$ molecules/$cm^3$ the year 2011. Maximum average concentration of ozone considering months, usually were determined for the months of October, November and December in 24. km, for the months of January and September 22 and 24. km. and also between the months from February to August was in 22. km of the stratosphere. In the mid-latitudes of the northern hemisphere including Turkey, ozone are sensitive to dynamic effects. According to upper atmospheric researches, the distribution of total ozone shows changeable features with the weather patterns or the affecting dynamic systems.

**Key Words:** Vertical distribution of ozone, Brewer Spectrophotometer, Umkehr measurement, ozonesonde, stratospheric ozone.

## 1. INTRODUCTION

It is a known scientific reality since the 1970s that various chemical compounds occurred by human activities and released into the atmosphere have destroyed the ozone through the help of the control mechanisms established under the Montreal Protocol, many countries have a positive effort to resolve these current problems. Vertical Distribution of Ozone (Ozone Profile) is an important parameter into the ozone monitoring network in frame of the World Meteorological Organization (WMO) and the Global Atmospheric Monitoring Programme (GAW).

Total ozone data is an important indicator on measuring the amount of ground-level ozone, knowing concentration of ozone at any altitude, monitoring the vertical distribution of ozone, interaction with other gases, climate change and the regulation of atmospheric dynamics.

At the present time, ozone profile can be measured by using not only ground-based ozonesonde and the technique of Umkehr through devices of Brewer and Dobson Spectrophotometer but also satellites.

## 2. METHODOLOGY

Umkehr method is a technique used in the calculation of the vertical distribution of ozone. Algorithm of Umkehr measurements consists of precisely the vertical ozone distribution model and data analysis. Procedure of Umkehr algorithm in this study mostly uses Mateer and DeLuisi's inversion technique of the 1992 year. Umkehr algorithm include forward-looking estimates and inverse models (3).

Classical Umkehr curve, firstly, were seen in the studies of the seasonal and latitudinal variations of total ozone in the beginning of the 20. Century. In 1931, Götz discovered two wavelengths in ultraviolet radiation that were absorbed strongly and weakly by the ozone under conditions of the zenith sky (4). These wavelengths increase with increasing zenith angle of the sun, but when the zenith angle gets closer to 90 degrees, they decreases abruptly (4). This observation is called as Umkehr effect and gives information about vertical distribution of the stratospheric ozone.

### Ozone Profile Measurements

Profile measurements in order to obtain vertical distribution of ozone in Ankara have maintained by using ozonesonde since 1994 and Brewer Spectrophotometer since 2007. Both methods are ground-based and for the Brewer measurements, Umkehr inversion techniques are used. While data of layer from land to height of 50 km. about vertical distribution of ozone could be taken from Brewer ozone measurements, it is limited with ozonesonde and data can obtained only until 35-40 km (5).

### Ozonesonde

Ozonesonde method is a kind of ground-based method and releasing balloon with ozone transmitter from surface to deeper atmosphere. The balloon filled with the hydrogen gas (1200 g) and mounted the measuring device (ozonesonde transmitter) are used. This device goes up with balloon up to about 35-40 km level at which balloons generally blow up and it determines the vertical distribution of the stratospheric ozone by measuring the amount of ozone in air mass (5). Ozonesonde units designed by the NOAA Laboratories (Komhry, 1964, 1969; Komhry and Harris, 1971) make up the essence of this method and contain the electrochemical concentration cell (ECC) and are produced to determine the vertical distribution of ozone in the atmosphere as simple, lightweight and capable of using balloon (5).

**Figure 1.** Ozonesonde measurement.

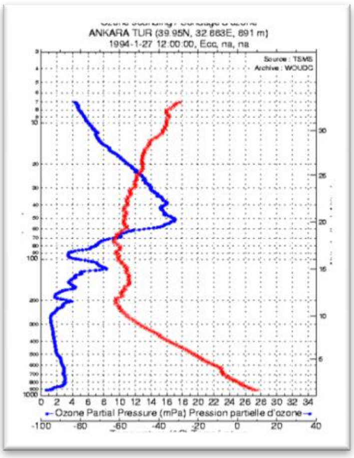

**Figure 2.** Vertical distribution of ozone in Ankara-WOUDC (27.01.1994).

## Brewer Spectrophotometer

The Brewer Spectrophotometer automatically follows the sun and measures total column thickness of ozone and sulfur dioxide ($SO_2$) in units of Dobson (Dobson Unit). The basis of measurements of total ozone and $SO_2$ are based on the measurement of the number of photons of sunlight at wavelengths selected. The density of ozone (vertical distribution of ozone) can be measured up to 50 km. by two km apart in the molecule/cm$^3$. It could have capable of measuring UV-B rays at the wavelength range between 290-325 nm and UV-A rays until 363 nm $_{(1)}$.

**Figure 3.** Brewer Spectrophotometer (188), Ankara.

## Brewer (188) Calibration Certificate

Brewer Spectrofotometer (188) was firstly calibrated by Mr. Ken Lamb from International Ozone Service in Ankara in 7-12 October 2008 by dint of financial supports of WMO. Turkish State Metetorological Service had second calibration Mr.Arjan Hoogendoorn (Kipp&Zonen) accomplish in Ankara 22-29 September 2010.

## 3. CONCLUSION

Ozone density at the vertical distribution of ozone was measured by using the Brewer Spectrophotometer in Ankara between 2007-2011 years. According to these conclusions, the maximum ground-level ozone concentration was found at 22. km of the atmosphere in mid-latitudes. Maximum of the average ozone density was found in 2007 as 4.9 x 10$^{12}$ molecules/cm$^3$, respectively, 4.7 x 10$^{12}$ molecules /cm$^3$ in 2008, 4.8 x 10$^{12}$ molecules/cm$^3$ in 2009, 4.8 x 10$^{12}$ molecules/cm$^3$ in 2010 and 4.7 x 10$^{12}$ molecules/cm$^3$ in 2011.

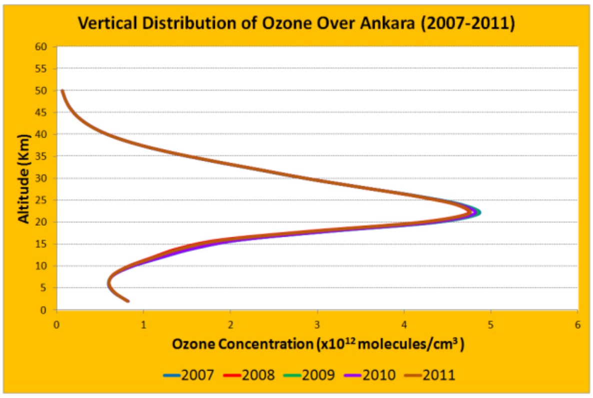

**Figure 4.** Vertical distribution of ozone over Ankara (2007-2011).

**Table 1.** The annual average of vertical distribution of ozone at Ankara (2007-2011).

| Altitude (Km) | Ozone Concentration $x10^{12}$ molecules/cm$^3$ | | | | |
|---|---|---|---|---|---|
| | Ozone Profile 2007 | Ozone Profile 2008 | Ozone Profile 2009 | Ozone Profile 2010 | Ozone Profile 2011 |
| 50 | 0,1 | 0,1 | 0,1 | 0,1 | 0,1 |
| 48 | 0,1 | 0,1 | 0,1 | 0,1 | 0,1 |
| 46 | 0,2 | 0,2 | 0,1 | 0,2 | 0,1 |
| 44 | 0,2 | 0,2 | 0,2 | 0,2 | 0,2 |
| 42 | 0,4 | 0,4 | 0,4 | 0,4 | 0,4 |
| 40 | 0,6 | 0,6 | 0,6 | 0,6 | 0,6 |
| 38 | 0,9 | 0,9 | 0,9 | 0,9 | 0,9 |
| 36 | 1,3 | 1,3 | 1,3 | 1,3 | 1,3 |
| 34 | 1,8 | 1,8 | 1,8 | 1,8 | 1,8 |
| 32 | 2,3 | 2,3 | 2,3 | 2,3 | 2,3 |
| 30 | 2,9 | 2,9 | 2,9 | 2,9 | 2,9 |
| 28 | 3,5 | 3,5 | 3,5 | 3,5 | 3,5 |
| 26 | 4,2 | 4,1 | 4,1 | 4,1 | 4,1 |
| 24 | 4,7 | 4,6 | 4,7 | 4,6 | 4,6 |
| 22 | 4,9 | 4,7 | 4,8 | 4,8 | 4,7 |
| 20 | 4,4 | 4,2 | 4,4 | 4,3 | 4,2 |
| 18 | 3,2 | 2,9 | 3,2 | 3,1 | 3,0 |
| 16 | 2,1 | 1,9 | 2,1 | 2,1 | 1,9 |
| 14 | 1,6 | 1,4 | 1,6 | 1,6 | 1,4 |
| 12 | 1,2 | 1,1 | 1,2 | 1,2 | 1,1 |
| 10 | 0,9 | 0,8 | 0,9 | 0,9 | 0,8 |
| 8 | 0,7 | 0,6 | 0,6 | 0,7 | 0,6 |
| 6 | 0,6 | 0,6 | 0,6 | 0,6 | 0,6 |
| 4 | 0,7 | 0,7 | 0,7 | 0,7 | 0,7 |
| 2 | 0,8 | 0,8 | 0,8 | 0,8 | 0,8 |

When the seasonal ozone profile data are evaluated, the highest value of ozone is in spring, the lowest value of ozone was found in autumn. The levels that these values are seen are determined as; about 20-22. km for the pring season, around 22-24. km in summer, around 24. km in autumn, and around 22-24. km in the winter.

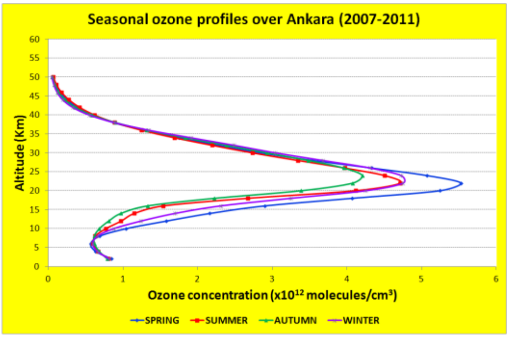

**Figure 5.** Seasonal ozone profiles over Ankara (2007-2011).

The maximum ozone densities were found at the 22. km between February and August in 2007. It is 24. km in January, October, November and December, at 22 and 24. km in September.

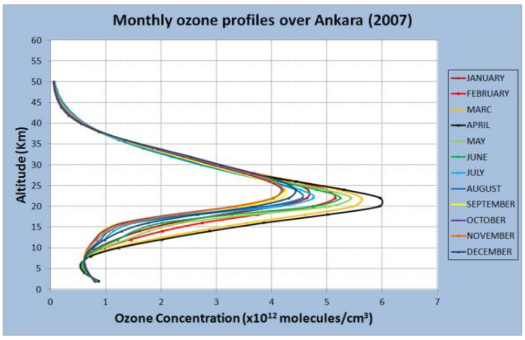

**Figure 6.** Monthly ozone profiles over Ankara (2007).

The maximum ozone concentration reaches at the 22. km between the months of February and August, at the 24. km in October, November and December, at the 22 and 24. km in January and September were found in 2008.

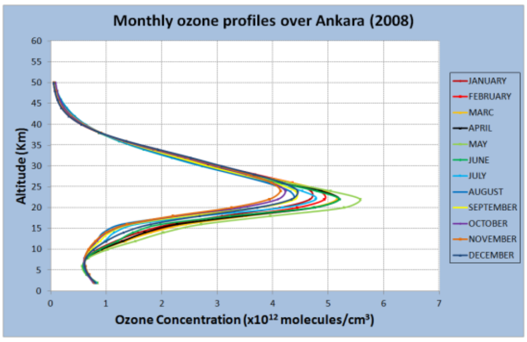

**Figure 7.** Monthly ozone profiles over Ankara (2008).

The maximum ozone density been encountered at 22. km between the months of February and August, 24. km in October and November, 22 and 24. km in January, September and December in 2009.

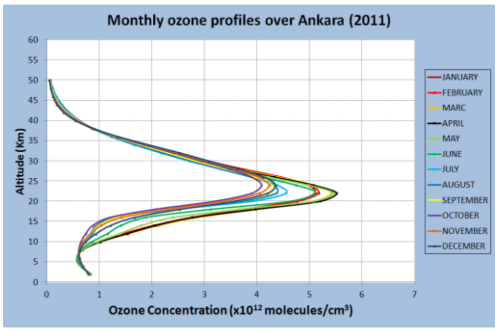

**Figure 8.** Monthly ozone profiles over Ankara (2009).

The maximum ozone densities were found at the 22. km between the months of February and July, in September, October, November and December at the 24. km and in January and August at the 22 and 24. km in 2010.

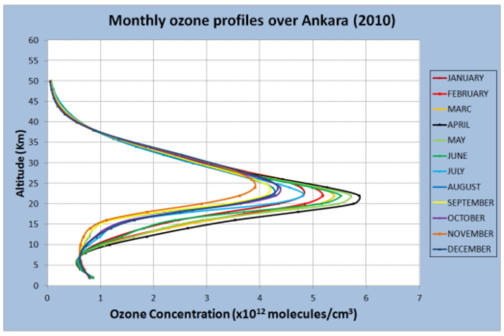

**Figure 9.** Monthly ozone profiles over Ankara (2010).

The maximum ozone concentrations were found between the months of January to August 22. km, in October, November and December 24. km and in September 22 and 24. km in 2011.

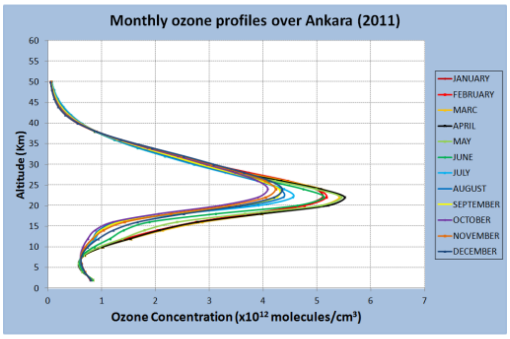

**Figure 10.** Monthly ozone profiles over Ankara (2011).

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# CHEMICAL COMPOSITION OF PRECIPITATION AT DIFFERENT PARTS OF TURKEY

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## ABSTRACT

Trace element and major ion composition of rainwater samples collected by the General Directorate of Meteorology at Antalya station are analyzed for approximately 50 trace elements using an inductively coupled plasma emission spectrometer equipped with a mass specific detector (ICPMS) and major ions by ion chromatography. Results are compared with trace element concentrations measured in the same region between 1992 and 2000. A decrease in $SO_4^{2-}$ concentrations between 1992 and 2011 is observed. Long term trends in concentrations of other elements are not as consistent as the trend observed in $SO_4^{2-}$ concentrations. Results demonstrated that most of the acidity in rainwater is neutralized by $CaCO_3$ in soil resuspended soil particles. The neutralization is not homogeneous throughout the year. Although more than 90% of the acidity in rain is neutralized in summer, fraction of acidity neutralized decrease in winter season. Approximately 30% of the rain events had pH less than 5.0 and most these events which can be considered acidic occurs in winter. Most of the measured trace elements and ions are wet deposited with few of the events, indicating that wet deposition is highly episodic in nature. Wet deposition fluxes of elements and ions are compared with their corresponding dry deposition fluxes calculated by assigning dry deposition velocities to their concentrations in aerosols. Results indicate that, wet and dry deposition fluxes of elements and ions are comparable at the Antalya region. This is attributed to relatively small rainfall in the region.

**Keywords:** Wet deposition, rain sampling stations, ICP-MS, seasonality, factor analysis, back trajectory.