Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. pp. 294-303, 26-30 September 2005, Istanbul – Turkey

PM2.5 COMPOSITION IN MILAN (ITALY)

G. Lonati, M. Giugliano and S. Ozgen

Department of Environmental, Hydraulic, Infrastructures and Surveying Engineering
Politecnico of Milan, 20133, Milan, Italy

ABSTRACT

In sampling campaigns -carried out by means of a high-volume gravimetric sampler-performed between August 2002 and December 2003, 24-h PM2.5 samples have been collected at an urban background site in downtown Milan and analysed for elemental and organic carbon, ionic species (i.e., chloride, nitrates, sulphates and ammonium) and some elemental species. Chemical speciation data are evaluated also in terms of primary and secondary components of fine particulate matter, and in particular SOA and the primary contribution from traffic are estimated.

Key words: PM2.5, SOA, OC/EC, crustal matter

1. INTRODUCTION

In Lombardy, Italy's most industrialized region, air quality standards for PM10 are frequently exceeded, especially in Milan, the main city of the region, and in its metropolitan area, where about three millions inhabitants live. The first Daughter Directive (1999/30/EC) to the Air Quality Framework Directive (96/62/EC) that lays down limit values for PM10 does not establish a limit value for PM2.5 but prescribes the installation and the operation of measuring stations to supply data on PM2.5 concentrations. CAFE (Clean Air For Europe) Working Group on particulate matter reconsidered in the II Position Paper on Particulate Matter the existing limit values for PM10 set by the First Daughter Directive. The Working Group recommended the use of PM2.5 rather than PM10 as the principal metric for assessing exposure to particulate matter in the light of World Health Organisation's (WHO) statement that "fine particles (commonly measured as PM2.5) are strongly associated with mortality and other endpoints such as hospitalization for cardiopulmonary disease". The Working Group suggested an annual average PM2.5 limit value in the range of 12-20 µg m^{-3} and a 24-h average limit value around 35 µg m^{-3} not to be exceeded more than 10% of the days of the year. As at the present moment in Milan information on the fine fraction of PM10 is scarce, the goal of this study is to define the composition and the contributions of various species to PM2.5 bulk mass in Milan.

2. PM2.5 SAMPLING

The monitoring site was Via Messina downtown Milan (UB site) which can be considered an urban background site not directly exposed to traffic emission. Sampling campaigns were performed from August 2002 through December 2003: 118 24-h samples have been collected and analyzed for elemental and organic carbon, ionic species (i.e., chloride, nitrates, sulfates and ammonium) and elemental species (sulfur, potassium, iron, copper, zinc, lead, titanium, vanadium).

The sampling of PM2.5 has been carried out by means of a high-volume (30 m^3 h^{-1} flow rate) gravimetric sampler DIGITEL DA-80H, equipped with PM2.5 cut-off inlet and 150 mm quartz filters (www.digitel-ag.com). Specific experiences with high-volume samplers support the hypothesis, assumed in this work, that negative and positive artifacts coexist with no significant variation in 24-h mass concentration (Tsai and Perng, 1998).

The PM2.5-loaded filters have been punched in three portions for separate analytical determination of ionic, carbon and elemental species. The carbon species, elemental carbon (EC) and organic carbon (OC), have been determined by Thermal-Optical Transmission (TOT) method (Birch and Cary, 1996; Schauer et al., 2003) at the Sunset Laboratory (www.sunset.com). The ionic components (Cl^-, NO_3^-, SO_4^{2-}, NH_4^+) have been ultrasonically extracted from the filter sample with 20 ml of deionized water for 30 minutes and then determined by means of high pressure liquid chromatography technique (HPLC). Elemental composition was determined by Energy Dispersive X-Ray Fluorescence (XRF) spectrometer SPECTRO X-LAB 2000 (www.spectro.com). Different targets (Mo, Al_2O_3, Highly Pyrolytical Orientated Graphite - HOPG) were used as polarizer or secondary target.

3. RESULTS AND DISCUSSION

At the UB site 24-h concentration levels of PM2.5 are in the 7.8-133.4 µg m^{-3} range, with an annual average of 40.0 µg m^{-3}. The analysis of seasonal data points out relevant differences in concentration levels between cold and warm seasons (October to March and April to September, respectively); the highest concentrations are usually observed in the cold season, while the lowest concentrations tend to occur in the warm one.

The seasonal distributions differ significantly (Table 1): during the warmer months 59% of the PM2.5 concentration data are within the range of 20 to 40 µg m^{-3}, almost all the data are lower than 60 µg m^{-3} (98th percentile = 46 µg m^{-3}) and none exceeds 80 µg m^{-3}. Conversely, 72% of the colder months’ observations are higher than 40 µg m^{-3} (39 samples out of 54) and 10% exceeds 100 µg m^{-3}.

Table 1 Percentiles of 24-h average PM2.5 concentrations (µg m^{-3} @ 20°C and 101.3 kPa)

	Annual	Warm	Cold
Minimum	7.8	7.8	12.2
25th percentile	22	19	37
50th percentile	30	23	56
75th percentile	54	28	69
90th percentile	72	37	100
98th percentile	111	46	129
Maximum	133.4	66.6	133.4

The distribution of PM2.5 24-h concentrations is well fitted by a lognormal model (Figure 1), characterized by a geometric mean of 33.2 µg m^{-3} and by a geometric standard deviation of 1.83. On seasonal basis, lognormal fitting results in a geometric mean of 22.8 µg m^{-3} and in a geometric standard deviation of 1.47 for the warm season; corresponding figures for the cold season data set are 51.8 µg m^{-3} and 1.66.

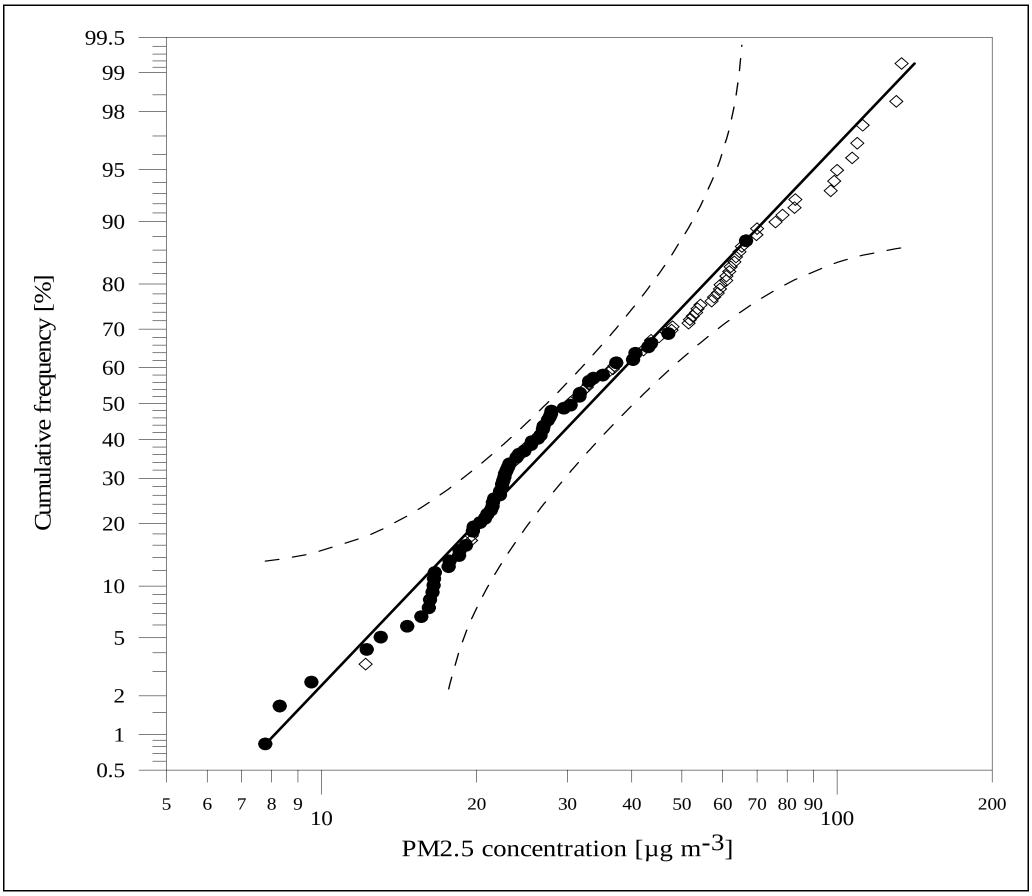

Figure 1 Distribution of PM2.5 24-h concentration data (Warm season data: white diamonds; Cold season data: black dots; Lognormal distribution model: solid line; 95 % confidence region for the cunulative distribution function of the PM2.5: dashed lines).

From the analysis of major chemical species (Table 3) it is seen that on the annual basis a substantial fraction (65.8%) of the fine particle mass is constitued by particulate organic matter (POM) (12.9 µg m^{-3}), nitrate (8.7 µg m^{-3}) and sulfate (4.7 µg m^{-3}). In addition to carbon, POM includes other atomic constituents that make up organic molecules, mainly hydrogen, oxygen, and nitrogen: to account for the presence of these latter in the organic compounds, OC concentrations were multiplied by a factor of 1.4 to estimate the organic mass (US EPA, 2004). POM levels are more than twice (19.7 µg m^{-3}) in the cold season than in the warm season (7.2 µg m^{-3}).

Table 3 Average mass composition (mass ± std. dev.; µg m^{-3}) of PM2.5 samples and relative contributions (%) to PM2.5 mass

	Year		**Warm season**		**Cold season**	
Samples	**118**		**64**		**54**	
Parameter	Concentration	Relative contribution	Concentration	Relative contribution	Concentration	Relative contribution
Elemental Carbon	**1.4 ± 0.7**	3.5	**1.2 ± 0.5**	5.0	**1.6 ± 0.8**	2.8
POM	**12.9 ± 10.1**	32.3	**7.2 ± 3.9**	29.4	**19.7 ± 11.0**	33.7
Chloride	**0.3 ± 0.6**	0.9	**0.1 ± 0.1**	0.2	**0.7 ± 0.7**	1.2
Nitrates	**8.7 ± 11.2**	21.7	**3.2 ± 3.6**	13.0	**15.2 ± 13.5**	26.1
Sulfates	**4.7 ± 2.9**	11.8	**4.2 ± 2.1**	17.2	**5.3 ± 3.6**	9.1
Ammonium	**3.0 ± 2.8**	7.5	**1.7 ± 1.3**	6.8	**4.5 ± 3.2**	7.8
Crustal Elements	**1.5 ± 1.1**	3.8	**1.6 ± 0.9**	6.6	**1.3 ± 1.3**	2.3
Metallic Oxides	**0.3 ± 0.2**	0.8	**0.1 ± 0.1**	0.5	**0.3 ± 0.2**	0.6
Reconstructed Mass	**32.9 ± 24.3**	82.2	**19.3 ± 9.1**	78.7	**48.7 ± 26.8**	83.5
Unidentified Mass	**7.1 ± 7.2**	17.8	**5.2 ± 4.3**	21.3	**9.6 ± 9.2**	16.5
Total Measured Mass	**40.0 ± 26.4**	-	**24.5 ± 9.9**	-	**58.3 ± 28.0**	-

Sulfate average concentration (4.2 µg m^{-3}) is greater than nitrate concentration (3.2 µg m^{-3}) in the warm season, nevertheless, nitrate concentrations in cold season (an average about 15.2 µg m^{-3}) are much higher than those of sulfate (around 5.3 µg m^{-3} on average). This may be due to the fact that ammonium nitrate formation is favoured under conditions of high relative humidity and low temperature, frequently occurring in the winter period (US EPA, 2004), and that the instable atmospheric conditions occuring in summer period facilitate the aqueous phase formation of sulfate in the interstitial spaces of clouds and fog droplets. On some days with high PM2.5 concentrations nitrate concentrations overtake POM concentrations (i.e., on 13 days out of 33 when PM2.5 concentrations were greater than 50 µg m^{-3}). Ammonium average concentration is greater in the warm season (1.7 µg m^{-3}) than in the cold season (4.5 µg m^{-3}), with an annual average around 3.0 µg m^{-3}. Elemental carbon levels do not change very much throughout the year (1.2 µg m^{-3} and 1.6 µg

m^{-3} in warm and cold season, respectively) with an average concentration of 1.4 µg m^{-3} on the annual basis. The generic "crustal matter" component of PM2.5 samples has been estimated based on Al, Si, Ca, Fe, K and Ti oxides by the following formulation (Marcazzan et al., 2001):

$$\text{Crustal matter} = 1.89\text{Al}+2.14\text{Si}+1.4\text{Ca}+1.36\text{Fe}+1.2\text{K}+1.67\text{Ti} \tag{1}$$

where only a fraction of iron and potassium concentration of natural origin is considered. These fractions have been estimated based on crustal enrichment factors (Mason, 1966): iron of natural origin is about 50% and 30% of the total iron, respectively in warm and cold season; corresponding figures for potassium are 100% and 60%. The total concentration of oxides of metallic elements is composed of heavy metal oxides (CuO, ZnO, PbO_2, V_2O_5) and of the anthropogenic component of iron oxide (Fe_2O_3). The total amount of crustal matter and metal oxides average concentrations does not exceed 2 µg m^{-3} neither on seasonal nor on annual basis. Unidentified mass determined from mass closure analysis is constituted mainly by oxides of unaccounted elements and water.

Concerning carbon species, organic carbon is largely dominating and accounts for about 81% and 90% of the total carbon (OC+EC), in warm and cold season, respectively. Poor correlation is observed between organic carbon and elemental carbon suggesting lack of a single dominant source in the cold season and the secondary nature of a great part of organic carbon in the warm season. The OC/EC ratio ($[OC/EC]_{cold} = 8.6$; $[OC/EC]_{warm} = 4.2$), which is usually employed to estimate the extent of secondary organic aerosol formation, turns out to be larger than those registered for other UB sites around the world ($[OC/EC]_{cold} = 2.4\text{-}3.5$; $[OC/EC]_{warm} = 1.3\text{-}3.9$), and comparable to those noted for rural sites ($[OC/EC]_{rural} = 4.6\text{-}8.1$). Inspection of elemental and organic carbon concentrations shows that the high ratios observed in this study can be attributed more to low elemental carbon levels than to elevated OC concentrations. The amount of secondary organic aerosol is estimated using elemental carbon as a tracer of primary organic carbon (EC tracer method):

$$OC_{PRIMARY} = OC_{NC} + \left[EC \cdot \left(\frac{OC}{EC} \right)_{PRIMARY} \right] \tag{2}$$

$$OC_{SECONDARY} = OC - OC_{PRIMARY} \tag{3}$$

$$SOA = OC_{SECONDARY} \cdot 1.4 \tag{4}$$

where OC_{NC} represents the non-combustion POM (e.g., OC derivating from biogenic source), $(OC/EC)_{PRIMARY}$ is the ratio for the local primary source affecting the measured concentrations (Turpin and Hunzicker, 1995; Cabada and Pandis, 2002). The primary contribution from traffic is determined using the OC/EC ratio ($[OC/EC]_{PRIMARY\text{-}trf} = 0.67$) observed at a kerbside position in a road tunnel site in Milan. This latter value can be assumed as a suitable estimate of the OC/EC ratio characteristic of the real traffic source as the monitoring site is not affected by other emissions active in the area and is directly exposed to the traffic emissions. This ratio is in good agreement with the findings of Gillies et al. (2001) who found a ratio of 0.76 and with the primary OC/EC ratio that can be estimated based on OC and EC emission factors of the circulating vehicles (Cabada and Pandis, 2002; Kleeman et al., 2000).

As there was no pollution source other than traffic to generate organic carbon, the amount of secondary organic aerosol in the warm season (6.1 µg m^{-3}) is obtained by subtracting the primary particulate organic matter due to traffic from the total particulate organic matter mass. In the warm season the secondary organic aerosol constitutes about 83.9% of the particulate organic matter mass and 24.7% of the PM2.5 bulk mass (Figure 2). Due to the impossibility of discriminating between condensed semivolatile organic matter and primary particulate organics collected on filter samples, the ratio, obtained from the ambient measurements of carbon species at the UB site, can not be employed to estimate a primary OC/EC ratio representative of the area inclusive of all sources. The presence of pollution sources other than traffic, for example domestic heating, makes impossible the prediction of the amount of primary organic carbon directly from the elemental carbon concentrations, and therefore, the estimation of secondary organic aerosol in the cold season. However, it is possible to confirm that in the cold season secondary formation of organic carbon by photooxidation is expected to be negligible given the scarce insolation, low temperature and ozone levels.

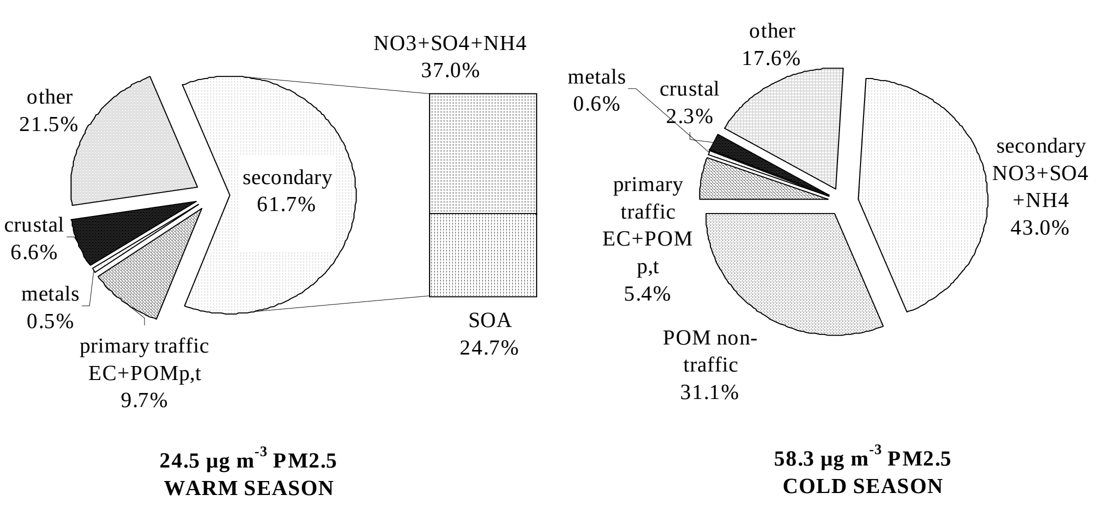

Figure 2 Primary and secondary contributions to PM2.5 bulk mass in warm and cold season.

With regard to elements, there is a strong enrichment of S and some metals (Cd, Pb, Zn and Cu) in the PM2.5 mass, whereas the enrichment factor of the other elements are next to unity (Table 2).

Table 2 Crustal enrichment factors for various elements

	S	K	Fe	Cu	Zn	Pb	V
Warm season	1283	1	2	17	94	757	2
Cold season	2647	2	6	175	872	5228	4
Year	1607	1	2	43	260	1964	2

According to a suggested classification criteria for crustal enrichment factor (Biegalski et al., 1998), an enrichment factor value lower than 3 is expected for an element of crustal origin, while one greater than 50 for an element of anthropogenic origin. Thus K, Fe and V appear to have a crustal origin, whilst the remaining elements are of anthropogenic origin. In particular, enrichment factors of S, Pb, Cu and Zn are much above 50; copper's enrichment factor results to be less than 50 in the warm season, but in any case above the stated limit for crustal origin.

Ionic composition of PM2.5 has been also evaluated with regard to the balance between the major anions (NO_3^-, SO_4^{2-}, Cl^-) and ammonium (NH_4^+). Although there is some scatter, data points generally fall above the 1:1 line, indicating that the ammonium is entirely taken up in neutralizing the anions and it is generally not enough to balance the negative charges of nitrate, sulfate and chloride; only very few samples are characterized by an excess of positive ammonium charges. (Figure 3)

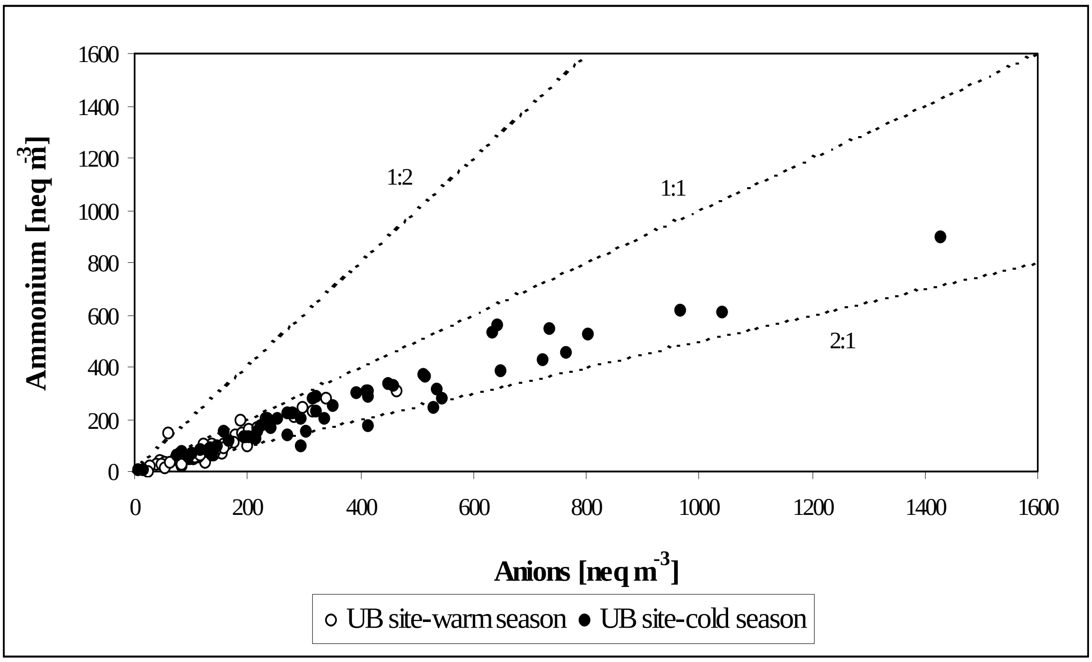

Figure 3 Ionic balance for PM2.5 24-h samples.

Linear correlation analysis between PM2.5 bulk mass and the analyzed species points out that:

- EC, V and crustal species such as Ti, Al, Ca, Si, show no relationship with the PM2.5 bulk mass on seasonal or annual basis;
- POM and secondary inorganic species such as nitrate and ammonium, are well correlated with PM2.5 bulk mass on both seasonal and annual bases;
- Sulfate, a secondary inorganic species, shows less correlation with PM2.5 mass in the cold season than in the warm season, while elemental sulfur shows more correlation in the cold season than in the warm season;

while the linear correlation analysis between the major species points out that:

- Secondary inorganic species (i.e., nitrate and sulfate) have strong relationship with ammonium, especially in the cold season;
- Concentrations of elements of crustal origin, such as Ti and K, have a high correlation;
- POM has a good relationship with all metals (except V) in the cold season;
- EC and OC concentrations show no correlation.

Comparing the the annual average PM2.5 concentration found in this study with levels for other countries in Europe given in literature (Querol, 2004), it is seen that PM2.5 levels in Milan (40 µg m^{-3}) are far greater than those observed at urban background stations in Northern and Southern Europe (8-15 µg m^{-3} and 19-25 µg m^{-3}, respectively), and slightly greater than those observed in Central Europe (16-30 µg m^{-3}). On the other hand it is noted that the PM2.5 levels in Milan are comparable to those of the traffic exposed sites in Central and Southern Europe (22-39 µg m^{-3} and 28-35 µg m^{-3}, respectively).

Particulate carbon levels (14.3 µg m^{-3}), expressed as the sum of POM and EC concentrations, are also comparable to those of the traffic exposed sites in Central and Southern Europe (8-16 µg m^{-3} and 8-12 µg m^{-3}, respectively).

Sulfate, nitrate and ammonium ion concentrations (16.4 µg m^{-3}) are much higher with respect to the concentration levels recorded in other countries either at urban background or roadside stations, which do not exceed 11 µg m^{-3}.

In terms of relative contributions to PM2.5 mass the findings of this study (35.8% and 41%, for carbonaceous matter and secondary inorganic aerosol respectively) are consistent with the figures reported in literature (Querol, 2004).

4. CONCLUSIONS

Based on 118 mass samples collected at the urban background site in Milan from August 2002 through December 2003, it is found that the PM2.5 mass concentration which varies between a warm-season minimum of 7.8 µg m^{-3} and a cold-season maximum of 133.4 µg m^{-3}, has an average value of 40 µg m^{-3}, and does not meet the limit values proposed for long-term and short-term in the II Position Paper. The threshold of 35 µg m^{-3} is exceeded 47 times in the 2003 and the annual average is two times greater than the upper limit value (20 µg m^{-3}). The average value observed in this study is far greater than the annual average PM2.5 levels in the majority of European urban background sites and comparable to those of the traffic exposed sites. The analysis of seasonal data points out relevant differences in concentration levels between cold and warm seasons; the highest concentrations (an average about 58.3 µg m^{-3}) are usually observed in the cold season, while the lowest concentrations (around 24.5 µg m^{-3}) tend to occur in the warm one. The presence of many emission sources and the meteorological conditions unfavorable for dispersion of the pollutants are responsible for the high levels observed in winter time.

Analyzing in terms of primary and secondary components it is seen that the primary component of fine particulate matter is mainly composed of elemental carbon, crustal matter, metal oxides and the primary fraction of particulate organic matter, on the other hand the secondary component is constituted by some ionic species (i.e., nitrate, sulfate, ammonium) and secondary organic aerosol. High PM2.5 episodes are principally due to secondary species, in particular due to increasing nitrate concentrations in winter time, and increasing particulate organic matter, which is mostly secondary in nature, in summer time. Secondary species account for 61.7% of the bulk mass in the warm season. In the cold season secondary inorganic species constitute the 43.0% of the bulk mass. The primary contribution from traffic is about 9.7% and 5.4% of the total PM2.5 mass in warm and cold season, respectively. The contribution of crustal elements and metal oxides is 7.1% in cold season, and 2.9% in warm season. The unidentified mass constitutes 21.5% and 17.6% of the bulk mass, in warm and cold season, respectively.

The temporal pattern comparisons of PM2.5 mass concentrations and ambient levels of nitrogen oxides, sulfur dioxide, ozone shows that these gases play a significant role in the particulate matter formation. Thus, intervention strategies other than on primary PM emissions, must also control the emissions of precursors gases, namely nitrogen and sulphur oxides and ammonia. However, the relationships between PM2.5 mass and individual species of precursor gases are not linear: thus a decrease in emissions does not necessarily brings an equal decrease in PM2.5 concentrations levels. Therefore, an exhaustive study on the secondary formation mechanisms of both inorganic and organic aerosol must be done when deciding short-term measures as well as elaborating long-term policies to control the ambient fine particulate matter levels.

A critical point is the exigency of a categorisation of volatile organic compound emissions as primary particles or as gases, which would make possible the determination of the real magnitude of the secondary organic aerosol also in winter time. Moreover, the present legislation estabilishes limit values for benzene alone (the Second Daughter Directive [2000/69/EC]), so this lack of information on volatile organic compounds' ambient air levels hinders the realization of air quality models.

REFERENCES

Biegalski, S.R., Landsberger, S., Hoff, R.M., 1998. Source-receptor modeling using trace metals in aerosols collected at three rural Canadian Great lakes Sampling Stations. Journal of the Air & Waste Management Association, 48, 227-237.

Birch, M.E., Cary, R.A., 1996. Elemental carbon-based method for monitoring occupational exposure to particulate diesel exhaust. Aerosol Science and Technology, 25, 221-241.

Cabada, J.C., Pandis, S.N., 2002. Sources of atmospheric carbonaceus particulate matter in Pittsburgh, Pennsylvania. Journal of the Air and Waste Management Association, 52, 732-741.

Gillies, J.A., Gertler, A.W., Sagebiel, J.C., Dippel, W. A., 2001. On-road particulate matter (PM2.5 and PM10) emissions in the Sepulveda tunnel, Los Angeles, California. Environmental Science and Technology, 35, 1054-1063.

Kleeman, M. J., Schauer, J. J., Cass, G. R., 2000. Size and composition distribution of fine particulate matter emitted from motor vehicles. Environmental Science and Technology, 34, 1132–1142.

Marcazzan, G.M., Vaccaro, S., Valli, G., Vecchi, R., 2001. Characterisation of PM10 and PM2.5 particulate matter in the ambient air of Milan, Italy. Atmospheric Environment, 35, 4639-4650.

Mason, B., 1966. Principles of geochemistry. Wiley & Sons, New York.

Querol, X., Alastuey, A., Ruiz, C. R., Artinano, B., Hansson, H. C., Harrison, R. M., Buringh, E., ten Brink, H. M., Lutz, M., Bruckmann, P., Straehl, P., Schneider, J., 2004. Speciation and origin of PM10 and PM2.5 in selected European cities. Atmospheric Environment, 38, 6547-6555.

Schauer, J. J., 2003. ACE-Asia intercomparison of a thermal-optical method for the determination of particle-phase organic and elemental carbon. Environmental Science and Technology, 37, 993-1001.

Tsai, C., Perng, S., 1998. Artifacts of ionic species for hi-volume PM10 and PM10 dichotomous samplers. Atmospheric Environment, 32, 9, 1605-1613.

Turpin, B.J., Huntzicker, J.J., 1995. Identification of secondary organic aerosol episodes and quantitation of primary and secondary organic aerosol concentrations during SCAQS. Atmospheric Environment 29, 3527-3544.

US EPA (Environmental Protection Agency), 2004. Air quality criteria for particulate matter. Vol. 1.