Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. pp. 374-384, 26-30 September 2005, Istanbul – Turkey

ATMOSPHERIC PM_{10} AND $PM_{2.5}$ LEAD CONCENTRATIONS AND TEMPORAL VARIATIONS OVER A SUBURBAN SITE OF ISTANBUL (TURKEY)

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ABSTRACT

In this study, 92 daily aerosol samples of fine and coarse particles were collected near the Buyukcekmece Lake (41º2'35"N, 28º35'25"E). The samples were collected in random days during July 2002 to July 2003. Thse annual mean $PM_{2.5}$ and PM_{10} lead concentrations were found as 0.054 μg m^{-3} and 0.129 μg m^{-3}, respectively. Seasonal behavior of $PM_{2.5}$ and PM_{10} lead concentrations were investigated and their cyclic behaviors were defined, and the major sources of the lead emissions were investigated in study area. By comparing, the Pb levels measured in this study with those reported previously from various locations on Turkey and other parts of the world, the status of Pb pollution on a non-impacted suburban area of Istanbul metropolitan was evaluated. Emission sectors of lead in PM_{10} and $PM_{2.5}$ samples from different sources have been quantified.

Key Words: Air Quality, Meteorology, Fine and Course Aerosols, Modeling

1. INTRODUCTION

The objective of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales is to bring scientists working in education universities, research organizations, government and industry together, working on management of air quality problems. One of the most important air quality criteria pollutants is the inhalable particulate matter. Recently the $PM_{2.5}$ part of the aerosols gained a big attention and new standards has been established by USA-EPA. In EU countries there are limited studies on $PM_{2.5}$ whereas in Turkey there are few studies (Samura, 2003). In Istanbul city, this is the first reported study regarding Pb in segregated aerosol samples. The current interest in atmospheric fine particulate matter ($PM_{2.5}$) is mainly due to its effect on human health (Christoph H. et al., 2005) Preliminary data indicate that large regions in the United States have ambient $PM_{2.5}$ concentrations that exceed the new $PM_{2.5}$ NAAQS resulting in unhealthy conditions for a significant fraction of the population in North America (Tony H., et al., 2005).
The aim of this study was to determine the Pb concentrations in segregated parts of aerosol and to determine their possible sources.

Concentrations of some pollutants in urban air may differ because of human activities. For this reason, a continuous air quality monitoring is important to understand the relationship between meteorological parameters and human related emissions. Atmospheric particulates, especially anthropogenic fine particles, typically enriched by a number of toxic metals (e.g., Pb, Sb, and Zn), are found to potentially influence human health (Samura, 2002; Karaca, et al. 2005).
On a global basis, anthropogenic inputs of Pb predominate over natural sources. Among several anthropogenic inputs, vehicular and roadside emissions of particles were often found to be the most important sources (Waleed, 1990). It was recorded that some 25% of vehicular emissions of Pb is coarse grained and deposited close to the road, while the remaining 75% is fine and may remain airborne (Hana and Al-Bassam, 1983).
During the study period, lead containing gasoline usage in cars decreased steadily and it was completely prohibited by the end of the February-2004 by the Turkish government. Because of this reason, this study has a particular importance to explain the outcomes of these actions. The goals of this study are:
1) To check and identify seasonal variations of Pb concentrations
2) To assess the influence of meteorological factors on temporal variations
3) To define the sources of Pb concentrations in airborne particles collected over a non-impacted suburban area of Istanbul metropolitan area
4) To compare the effects of limitations of lead containing fuels in cars

2. METHODS AND SAMPLING

2.1. Monitoring Site

Monitoring has been performed between July 2002 and July 2003. In this work, 92 daily aerosol samples of fine (< 2.5 μm) and coarse (2.5-10 μm) particles were collected. Samples were collected on daily basis randomly. Accordingly, at least six samples were collected monthly. The sampling site was chosen at a suburban area of Istanbul, located approximately 5 km north from the town of Büyükçekmece (41º2'35"N, 28º35'25"E). The Istanbul Water and Wastewater Administration (ISKI) compound, near the Büyükçekmece Lake, was chosen as the sampling station location because of easy access, availability of electrical power, and provision of enough protection for the sampling instrument. The location of the sampling station is shown in Figure 1.

The sampling site is located 10 m above the sea level and within the first zone of the watershed area, and sufficiently far away from residential areas, so that there is no significant stationary or mobile emission source within 5 km around the sampling site. In view of this fact, this area is suitable to monitor the regional and long-range effects on the characteristics of particulate matter (Karaca et al. 2005-a).

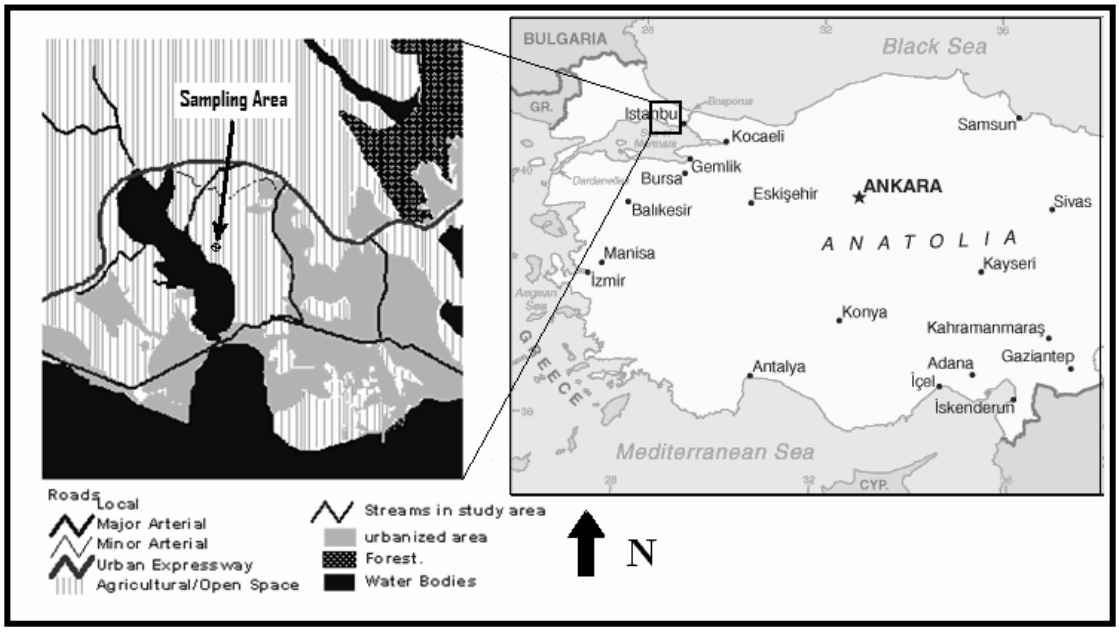

Figure 1. The location of the sampling site

2.2. Sampling Instrument

A size segregation dichotomous sampler (Anderson sampler) with automatic sample changer was used to collect aerosol samples. It has an aerosol inlet cut-off, which samples only particles smaller than 10 µm. In addition, the particles are being size-segregated by means of virtual impaction into fine particles smaller than 2.5 µm ($PM_{2.5}$) and coarse particles between 2.5 and 10 µm ($PM_{2.5-10}$). The particles were collected on 37 mm, 2 µm pore sized Teflon® membrane filters which are recommended for gravimetric and quantitative determination of trace metals (Karaca et al. 2005-a). The sampling flow rate was 1 m^3 $hour^{-1}$. The gravimetric determination technique is described by Karaca et al. (2005-a).

2.3. Chemical Analysis

The empty filters were pre-conditioned to stable weight at constant relative humidity (in silica gel desiccator) for at least 24 hours, and then the filters were transferred and weighted by means of a 4 digit sensitive balance. CEM MARS 5 microwave digestion system (CEM Corporation, Matthews, NC, USA) was used for the dissolution of all the collected aerosol samples.

The optimized digestion mixture was found as: 5 ml of concentrated HNO_3 (Ultrex, J.T. Baker, Phillipsburg, NJ 08865, USA), 4 ml H_2O_2 (30-32%, semiconductor grade, Aldrich Chemical Company, Inc., Milwaukee, WI, USA), 0.5 ml HF (47-51%, environmental grade plus, Alfa AESAR, Ward Hill, MA. 01835, USA), and 5 ml of saturated H_3BO_3 solution 5%, (puratronic, 99.9995%, Alfa AESAR,. Ward Hill, MA 01835, USA).

The digestion temperature was increased slowly to 210 °C by using maximum power (1200W) for 20 minutes digestion time. After cooling the digestion vessels, the

content was transferred to a 25 ml measuring flask and diluted to the mark with de-ionized pure water.
Graphite Furnace Atomic Absorption Spectrometer (GFAAS) technique was used to determine the Pb in aerosol samples, which is a suitable technique for the low concentrations found in aerosols matrix. Varian® (model) GFAAS instrument equipped with auto sampler and utilizing coated Varian® graphite tubes was used for Pb determination.
To obtain calibration curves aqueous standard solution method was used. The multi-standard solution (MERCK), which contains 23 different elements with concentration of 1000 mg/L, was used to prepare the calibration curve. R^2 value of the calibration curve was 0.99937 with curve-fit equation represented by the equation $y = 0.0038\ x$.
The accuracy of the instrument and method was tested using standard reference materials (SRM) IAEA-336 and IAEA Soil-5. The recovery of Pb from these SRM`s was 110.2% and 97.1%, respectively.

3. RESULTS AND DISCUSSION

The PM_{10} aerosol mass annual arithmetic mean value of 47.1 μg m^{-3} was found to be lower than the Turkish air quality standard of 60 μg m^{-3}. On the other hand, this value was found higher than the annual European Union air quality PM_{10} standard of 40 μg m^{-3}. Furthermore, the annual $PM_{2.5}$ mean concentration of 20.8 μg m^{-3} was found higher than the United States EPA standard of 15 μg m^{-3}. During wintertime, especially in November and December, there was a clear peak for both PM_{10} and $PM_{2.5}$. This could be related to seasonal meteorological conditions and extensive use of fossil fuel for domestic heating (Karaca et al., 2005).

The annual mean Pb concentration of $PM_{2.5}$ and PM_{10} was found as 0.054 μg m^{-3} and 0.129 μg m^{-3}, respectively. The temporal variations of Pb concentrations for PM_{10} and $PM_{2.5}$ fractions are given in Figure 2. The Pb concentration in both aerosol fractions followed nearly the same pattern with higher concentrations in the PM_{10} fraction. Furthermore, there is a clear peak during summer time, especially in PM_{10} fraction.

There is national neither standard nor international limits for Pb in fine and coarse aerosol fraction. Consequently, the best way to evaluate the air quality with respect to Pb levels is to compare our study with others. These measured aerosol Pb concentrations were compared with national and international studies and given in Table 1. As it can be seen from this comparison, the annual average Pb concentration over Buyukcekmece region is neither as high as polluted industrial areas in Milan-Italy (Vaccaro et al.., 2001) nor as low as in unpolluted remote areas. Result of this study could be classified among urban or sub-urban studies. This shows clearly the effect of urbanization and industry on suburban area, especially the one like Buyukcekmece watershed area.

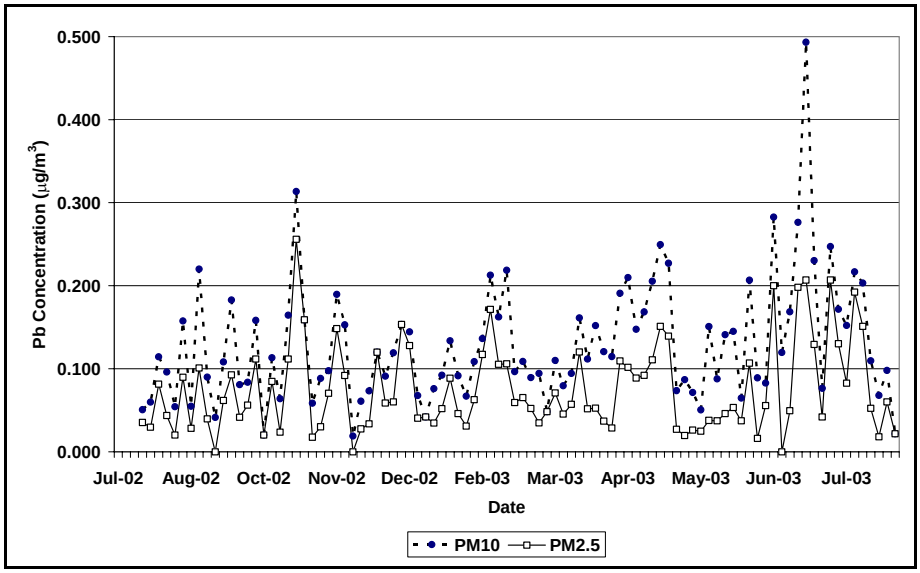

Figure 2. PM_{10} and $PM_{2.5}$ Pb concentrations during study period

Table 1. Some measured Pb concentrations in similar studies

Region	**Measured Concentration ($\mu g\ m^{-3}$)**		
	PM_{10}	$PM_{2.5}$	$PM_{2.5-10}$
Büyükçekmece (this study)	0.129±0.074	0.075±0.054	0.054±0.038
Geneva (Switzerland) (Chiaradia ve Cupelin, 2000)	0.045±0.016		
Milan (Italy) (Vaccaro et al.., 2001)	0.215±0.112	0.138±0.75	
Shanghai (China) (Zheng et al., 2004)	0.515		
Bursa (Türkiye) (Alusine et al., 2003)	0.151	0.120	0.031

3.1. Seasonal Characteristics

In order to evaluate seasonal characteristics of the data set, monthly average Pb concentrations are calculated and illustrated in Figure 3. In general, lead concentrations of fine particles are higher than the coarse fraction, except in August 2002 and May 2003. This difference is much more significant during wintertime periods. One of the reasons of this seasonal behavior is the effect of the increase of anthropogenic activities such as fossil fuel combustion, and industries during heating season. We can assume that traffic is stable during whole sampling period; on the other hand there is significant increase in fossil fuel combustion to facilitate heating. The heating season of the sampling period corresponds to 10/2002-4/2003 interval. Another reason of this difference could be the effects of meteorological conditions. Exceptionally summer period of this study, an arid season was observed. There are

several studies, which mention that it is possible to observe less coarse particle concentrations during wet seasons than dry seasons (Helda et al. 2005, Hueglin, 2005).
Conversely, general trend of the data set shows that the atmospheric lead concentration is stable. This indicates that, principally, the effecting sources of lead over Büyükçekmece area are not conditional to seasons; expect the coarse fraction during wintertime. This outcome brings a necessity to the statistical investigation of the relationships of meteorological conditions and concentrations. This relationship is evaluated in the following sections.

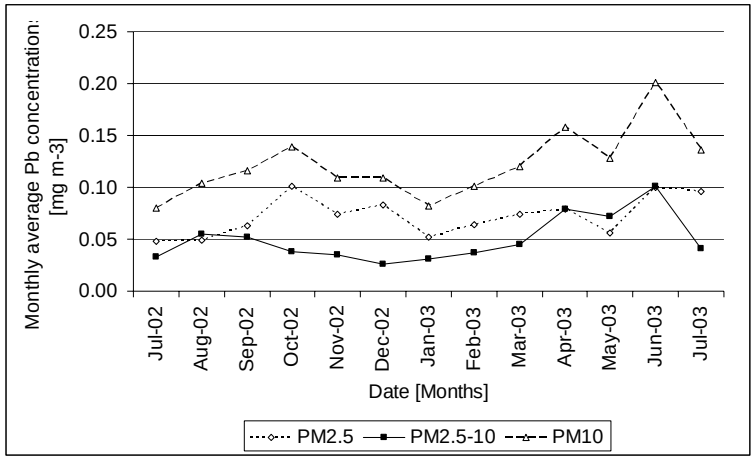

Figure 3. Monthly average atmospheric lead concentrations

The monthly average ratios of $PM_{2.5}/PM_{10}$ and $PM_{2.5–10}/PM_{10}$ could be a useful tool to figure the seasonal effects over lead containing particles (see Figure 4). As it seen from Figure 4, fine particles have more than 50% contributions to lead concentrations of inhalable particles during sampling period. This ratio changes only during two periods in August 2002 and May 2003. This result confirms the conclusions of previous assumptions.

Summer and winter time averages of lead concentrations of fine particles are calculated as 0.075 ± 0.056 μg m^{-3}, 0.076 ± 0.052 μg m^{-3} respectively. The summer and winter values are nearly equal, which confirm that the emission of fine fraction lead concentration is fairly constant during seasons. Moreover, summer and winter lead concentration standard deviations are almost the same which confirm that their seasonal fluctuations have the similar characteristics. It is possible to speculate that atmospheric fine lead containing particles over Büyükçekmece area are emitted dominantly by traffic and industrial sources which are stable during seasons. Heating could not be the main source of atmospheric lead because otherwise it could not stable during all sampling period. A high standard deviation values indicates the receptor point is effected mainly by mobile sources which could fluctuate and unstable during weekly period.

On the other hand, if the standard deviation is considerably smaller, it means that the receptor site mainly effected by point and stable sources. Standard deviations of both

seasons are about 70% of average values, which could be accepted as noticeably high value. Because of this conclusion, one can say that, atmospheric lead over Büyükçekmece area is emitted generally by automobile sources as fine particles.

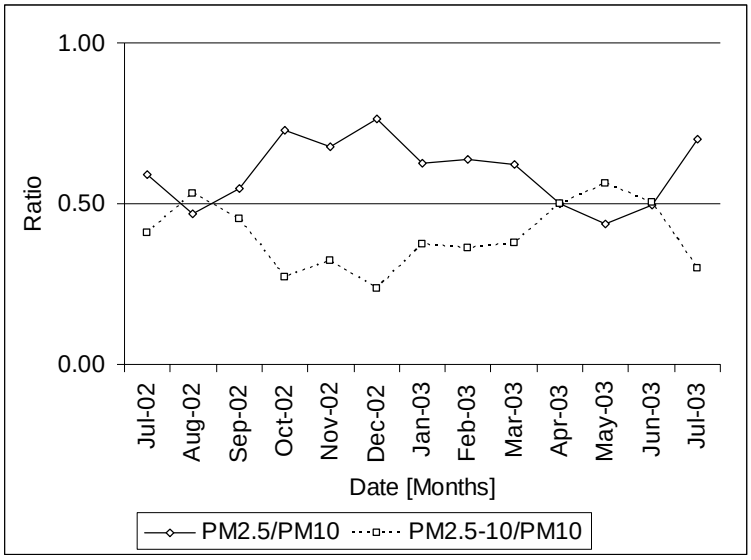

Figure 4. The monthly average ratios of $PM_{2.5}/PM_{10}$ and $PM_{2.5-10}/PM_{10}$

Summer and winter time averages of lead concentrations of coarse particles are calculated as 0.067 ± 0.043 μg m^{-3}, 0.036 ± 0.022 μg m^{-3} respectively. Summer time average value is 1.84 times higher than winter time. It seems interesting due to lower concentrations, which are observed during winter times, but this acceptable if one consider the effects of meteorological conditions on the generation of atmospheric coarse particles.

Processes, especially, precipitation, dryness, and atmospheric wet deposition processes are the factors which governs the concentration of atmospheric particles (Karaca et al, 2005). Some rain samples were collected and analyzed in Büyükçekmece area by Başak and Alagha (2004), and they observed that precipitation samples collected during winter time have higher lead concentrations than summer times. This confirms that atmospheric lead particles are washed out by precipitation and atmospheric lead concentrations of wet seasons could be less than dry seasons. Generally, coarse particles are generated by natural effects like wind blowing, sea sprays, soil erosion etc. It was found that these coarse particles decreases in wet seasons and increase in dry seasons. This could be another reason of the decreased wintertime concentrations.

3.2. Relationships between Aerosol Mass and Lead Concentrations

Some useful information could be obtained by comparing measured lead and mass concentrations. By this way, it could be possible to figure that the cyclic behavior of enriched lead containing particles reaching the sampling site and the frequency of the episodes can be defined more properly. The time series of the ratios

$PM_{2.5}Pb/PM_{2.5}Mass$ [mg/g] and $PM_{2.5\text{-}10}Pb/PM_{2.5\text{-}10}Mass$ [mg/g] are given in Figure 5 and Figure 6 respectively. It is clear that the most observed particles peaks (episodes) are observed during summer times.

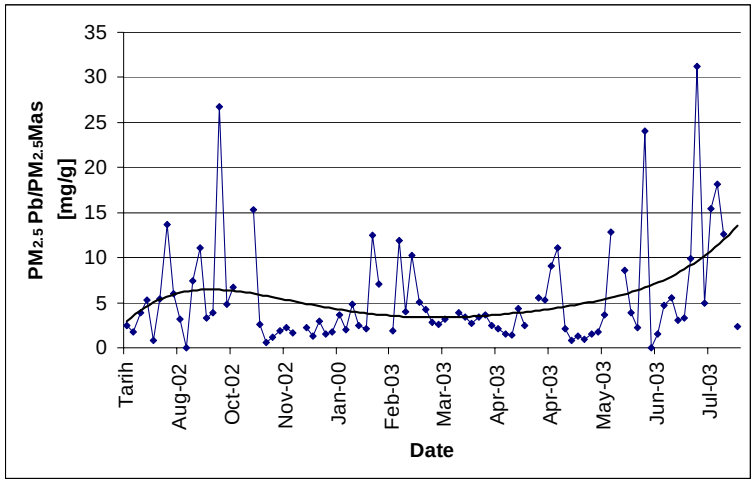

Figure 5. Seasonal behavior of $PM_{2.5}Pb/PM_{2.5}Mass$ [mg/g] ratio

According to these figures, the seasonal behaviors of both ratios are similar to each other. They have some sharp fluctuations during summer times, but more steady during winter times. We believe that this kind of unsteady behaviors can be explained by the effects of meteorological factors. Because of the similar trends in the cyclic behaviors of both ratios, one can think that the origins of fine and coarse lead containing particles are same.

Correlation coefficients (R^2) between particulate matter mass and lead concentrations for fine and coarse particles are calculated as 0.35 and 0.33, respectively. It shows that there is not any significant correlation between mass and lead concentrations. This means that the lead containing particles are not a constant share of particles and may not be emitted directly from any local sources but several regional sources. This figure is completely different for heating season concentrations. The correlation coefficients between mass and lead concentrations of fine and coarse particles are 0.62 ($P<0.01$) and -0.03 during heating season, respectively. The significant correlation (0.62) indicates that there is a valid relationship between mass and lead concentrations of fine fraction.

On the other hand no correlation (-0.03) is found for coarse particles. This result indicates that lead concentrations of fine particles are mostly generated by local and steady sources which are related by heating activities like some lead containing fossil fuels.

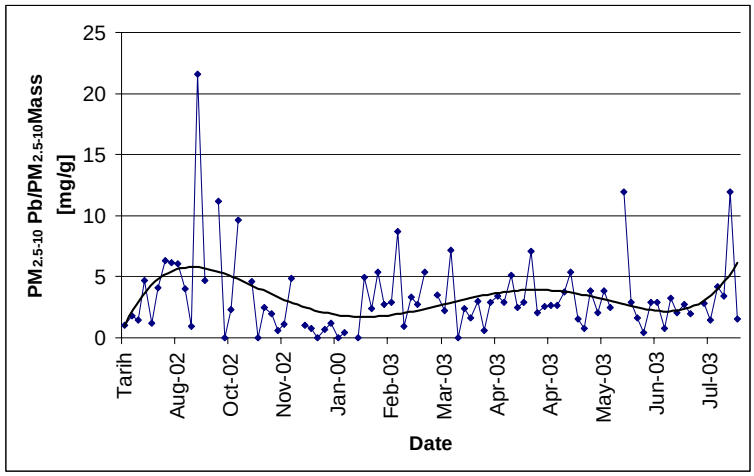

Figure 6. Seasonal behavior of $PM_{2.5-10}Pb/PM_{2.5-10}Mass$ [mg/g] ratio

Last of all, the relationships between lead concentrations of fine and coarse particles are calculated and found as 0.35. Contrary to the previous conclusion assumption, it can be speculated that lead concentrations of fine and coarse particles may be not generated by common sources or similar processes. Fine and coarse particles containing lead are generated mainly by traffic during summer time from several regional sources. However, maybe fine particles containing lead are mainly generated by seasonal heating during wintertime from local sources.

3.3. Definition of Possible Sectors of Episodes

Lead bearing episodes are of particular concern. Episode values are more critical than regular trends; possibly, they are enriched over a particular area or affected by some point sources. The highest 30% lead level samples of the total data set were defined as episodes. In addition to that, the region of the study is divided into geographically 16 sectors and these sectors are given in Table 2. Occurrences of the observed wind directions according to these sectors are counted and the repetition numbers are calculated. This is very useful method to define the sectors, which are the responsible of episodes. After that, it could be possible to focus on particular sectors to search possible sources of episodes within these sectors. These sectors could be collected into four main sectors: North-East (NE), South-East (SE), South-West (SW), and North-West (NW).

According to this sectoring, the major part of the episodes, about 54%, is generated from the North-East sector. South-West sector is found as the second major sector with the value of 23% (see Figure 7). Two main residential areas, Hadımköy and Büyükçekmece are located in the northeastern and southwestern parts of study area, respectively. During sampling period, natural gas distribution system was not connected to these residential areas. Coal and fuel oil had been used extensively for residential heating. The episode values seem related with residential activities, like city inside traffic, residential heating.

Secondly, in the northeastern part of the study area, industrial activities are standing out. It is clear that industrial activities of this sector are the one of the responsible

sources of atmospheric lead over Buyukcekmece lake basin. In addition to that, there is a cement factory located on the southwestern part of sampling area. However, in the literature, generating of atmospheric lead from cement factories is not clear, one should note that, as a conclusion of our personal observations; they possibly use several materials (car tires, coal, etc) as fuel.

Table 2. Wind directions and episodes occurrence

Wind Direction	Repetition	Wind Direction	Repetition
E	2	S	0
ENE	3	SE	1
N	4	SSE	0
NE	4	SSE	1
NNE	5	SW	2
NNW	2	SWS	2
NW	2	W	2
NWW	0	WSW	0

Finally, TEM and E-5 motorways can be pointed as atmospheric lead sources. E-5 and TEM are located in South-East, South-West and North-East, North-West locations, respectively. Probably they have significant contributions to atmospheric lead episodes.

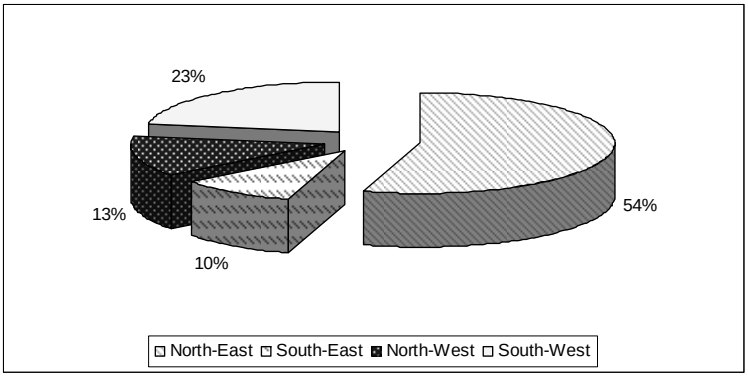

Figure 7. Sectors of atmospheric lead episodes

4. CONCLUSION

In this study, the annual mean Pb concentration of $PM_{2.5}$ and PM_{10} was found as 0.054 μg m^{-3} and 0.129 μg m^{-3}, respectively. These values are moderate according to literature values of remote and urban sites. Generally, fine particles lead levels are higher in summer that in wintertime, which is related to traffic and industrial activity. There was no significant correlation between particulate matter mass and lead concentrations for fine and coarse particle. This may be explained by the fact that, the lead containing particles are not a constant share of particles and may not be

emitted directly from any local sources but several regional sources. On the other hand, a significant correlation (0.62) between mass and lead concentrations of fine and coarse particles indicates that there is a valid relationship between mass and lead concentrations of fine fraction. Episodic sectoring resulted in a conclusion that the major part of the episodes, about 54%, is generated from the NE sector while SW sector is found as the second major sector with the value of 23% for the observed episode values.

5. ACKNOWLEDGEMENTS

We would like to thank to Nuclear Research and Education Centre, Department of Chemistry and its personnel for their valuable helps and supports. This project is supported by Fatih University, Institute of Sciences. Project #: P50080102.

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