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Atmospheric Research 81 (2006) 17–35

ATMOSPHERIC RESEARCH

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Assessment of trace element concentrations and their estimated dry deposition fluxes in an urban atmosphere

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Received 20 April 2005; received in revised form 25 October 2005; accepted 25 October 2005

Abstract

Thirty-three ambient air samples were collected during spring and summer (2003) in the metropolitan area of Bursa, Turkey. All airborne samples were analyzed for crustal (Mg, Ca, Mn, Fe) and anthropogenic (Cr, Co, Ni, Cu, Zn, Cd, Pb) trace metals. A TSP sampler was employed using glass and quartz fiber filters to collect air samples. Average individual trace element concentrations fluctuated between 4896.3 ± 3754.3 ng/m^3 (Ca) and 0.7 ± 0.9 ng/m^3 (Cd). The measured concentrations of the trace elements were within the ranges of previously reported values obtained from different places including Turkey, Argentina, Spain, Korea, and Brasil. The concentrations were arranged according to day and night, weekend and weekdays, spring and summer samples. Concentrations were also evaluated based on the filter types used, glass fiber and quartz filters. Enrichment factors (EFs) were calculated to identify anthropogenic versus natural emission sources of trace elements. The prevailing winds from various sectors were examined to determine the transport of metal particles from different districts. Principal component analysis (PCA) was employed to define the possible origins of trace elements in airborne particulate matter. The result suggested that industrial activities along with traffic emissions and suspension of street dusts have important effects on ambient air concentrations of trace metals. Dry deposition fluxes were estimated using documented dry deposition velocities in the literature and concentrations measured in this study.

Keywords: Trace elements; Airborne particles; Enrichment factor; Air pollution; Bursa; Dry deposition

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doi:10.1016/j.atmosres.2005.10.003

1. Introduction

Recently atmospheric particle matter (PM) have been of considerable environmental interest due to their impacts on visibility, human health, plants, aquatic life and materials (Yatin et al., 2000; Gullu et al., 2000; Brewer and Belzer, 2001; Ho et al., 2003; Banerjee, 2003; Azimi et al., 2003). They may be emitted directly or be formed in the atmosphere (Seinfeld and Pandis, 1999; Samura, 2001; Kemp, 2002). Main sources of natural atmospheric particles are volcanic activities and dust storms. Industrial activities, energy production, construction, urban waste treatment and vehicle exhausts constitute anthropogenic sources (Sabbak, 1995; Bilos et al., 2001). Because of their wide range of sources and their effects on human and ecosystems, elemental constituents of atmospheric particles have been widely studied in different parts of the world (Kim et al., 2002; Miranda et al., 2002; Odabasi et al., 2002).

Trace elements are one of the important constituents of atmospheric PM. The chemical composition and levels of trace elements may vary according to the sources of the particles. For example, resuspension has a major influence on the presence of many metals in air close to highways (Harrison et al., 2003). Industries would be another important trace element source for inhabitants and concentrations are often well above natural background levels (Quiterio et al., 2004). Moreover, traffic should be considered as an important source for the city atmosphere (Colombo et al., 1999; Querol et al., 2001; Weckwerth, 2001; Sternbeck et al., 2002). Emissions of metals arise from different parts of motor vehicles including exhausts, wheels and brakes (Weckwerth, 2001). Cu, Zn, Cd, Sb, Ba, Pb, Cr, Ni, Sn and Mo are considered to be emitted from road traffic (Kemp, 2002; Sternbeck et al., 2002; Harrison et al., 2003; Bem et al., 2003).

Meteorological conditions and local sources have an important role on trace element concentrations. Therefore, temporal fluctuations have been examined in many studies (Hrsak et al., 2001; Kim et al., 2002; Morawska et al., 2002). For example, Kim et al. (2002) reported that some metals tended to exhibit seasonal peaks and good correlation concentrations are seen with PM in winter months. In another study, Morawska et al. (2002) observed particle number on weekdays and weekends and they reported a statistically significant difference between weekdays and weekends. It is likely there are observable differences between day and night samples depending on sources including traffic and industry (Colombo et al., 1999).

Airborne particles are important carriers of metals. Trace metals are therefore sampled with TSP collectors. Different types of aerosol samplers have been employed to collect trace elements such as: different models of high volume air samplers (HVASs) (Colombo et al., 1999; Moreno-Grau et al., 2000; Kim et al., 2002; Espinosa et al., 2002; Bem et al., 2003), Kleinfiltergerat impactor (Sternbeck et al., 2002), different types of cascade impactors (Brewer et al., 2001; Espinosa et al., 2002), dichotomous (Weckwerth, 2001), MOUDI (Harrison et al., 2003), cyclone (Celis et al., 2004), filterback sampler (Kemp, 2002). These collection devices were equipped with different types of filters including glass, quartz, cellulose, polycarbonate, borosilicate glass microfiber, Teflon membrane filters (Bilos et al., 2001; Brewer and Belzer, 2001; Hrsak et al., 2001; Kemp, 2002; Sternbeck et al., 2002; Kim et al., 2002; Bem et al., 2003).

In the scope of this research, ambient particulate matter samples were analyzed in spring and summer seasons at a point experiencing air pollution problem due to traffic. The differences in ambient trace element concentrations between glass fiber and quartz filters, day and night, weekend and weekdays, spring and summer seasons were studied.

2. Materials and methods

Sampling and meteorological information including sampling period, sampling duration, filter type, wind speed and direction, temperature and relative humidity are summarized in Table 1.

2.1. Site description

Ambient air samples were collected in Bursa 28° 10′– 30° 00′ N, and 39° 35′ –40° 40′ E, one of the metropolitans of Turkey (Fig. 1). It has a total population of about 1.2 million. It is an inland city but it is close to the sea and it is at an altitude of 155 m above sea level. The city is surrounded by several high mountain ranges (Uludag Mountain—2543 m) and this aspect has effects on dispersion levels.

The city has important industrial facilities that contribute significantly to the atmospheric pollutant load and they are mainly collected within 3 organized industrial districts. Textile

Table 1
Summary of meteorological data and sampling periods for each sample

Sample no	Sampling date	Duration (minute)	Dominant wind direction	Average wind speed (m/s)	Average air temp. (°C)	Average humidity (%)	Filter type
1	20.03.2003	510	WSW	2.7	7.5	59.0	QFF
2	23.03.2003	480	NE	3.8	1.2	57.7	GFF
3	25.03.2003	540	NE	4.2	7.6	53.3	QFF
4	26.03.2003	570	NNE	2.8	11.2	56.3	QFF
5	27.03.2003	580	NE	3.5	12.5	53.0	GFF
6	28.03.2003	530	NW	2.3	9.9	57.7	QFF
7	29.03.2003	565	NW	2.0	9.7	65.0	GFF
8	30.03.2003	585	NW	2.0	10.2	55.3	QFF
9	01.04.2003	570	N	3.5	12.6	74.0	QFF
10	04.04.2003	585	NNE	2.6	15.7	68.0	GFF
11	09.04.2003	580	NNW	1.7	8.1	59.7	GFF
12	10.04.2003	625	NW	1.4	12.7	57.0	QFF
13	12.04.2003	570	NW	1.6	19.4	63.3	QFF
14	17.04.2003	525	NW	3.6	11.1	74.0	GFF
15	21.04.2003	550	E	2.5	13.2	52.0	GFF
16	22.04.2003	570	NW	2.1	14.9	58.0	GFF
17	10.06.2003	510	NNE	4.0	27.8	59.7	QFF
18	10–11.06.2003	810	ENE	1.6	20.1	59.7	QFF
19	11.06.2003	610	NNE	3.7	26.7	49.7	QFF
20	11–12.06.2003	810	NE	1.4	20.9	49.7	QFF
21	12.06.2003	620	N	3.5	28.7	52.7	GFF
22	13.06.2003	400	NNE	3.1	30.9	55.7	GFF
23	13–14.06.2003	825	ENE	1.2	21.6	55.7	GFF
24	14.06.203	640	NNE	2.4	29.1	46.7	GFF
25	14–15.06.2003	810	ESE	1.0	20.8	46.7	GFF
26	15.06.2003	640	NNE	2.5	30.9	47.7	GFF
27	15–16.06.2003	820	WNW	1.1	23.2	47.7	QFF
28	16.06.2003	540	NNW	2.9	30.5	51.3	QFF
29	16–17.06.2003	870	WSW	2.1	24.0	51.3	QFF
30	17.06.2003	500	NNE	3.6	28.1	66.3	QFF
31	17–18.06.2003	940	E	2.2	21.0	66.3	QFF
32	18.06.2003	525	NNE	3.0	26.1	48.0	QFF
33	18–19.06.2003	900	NE	1.3	19.2	48.0	QFF

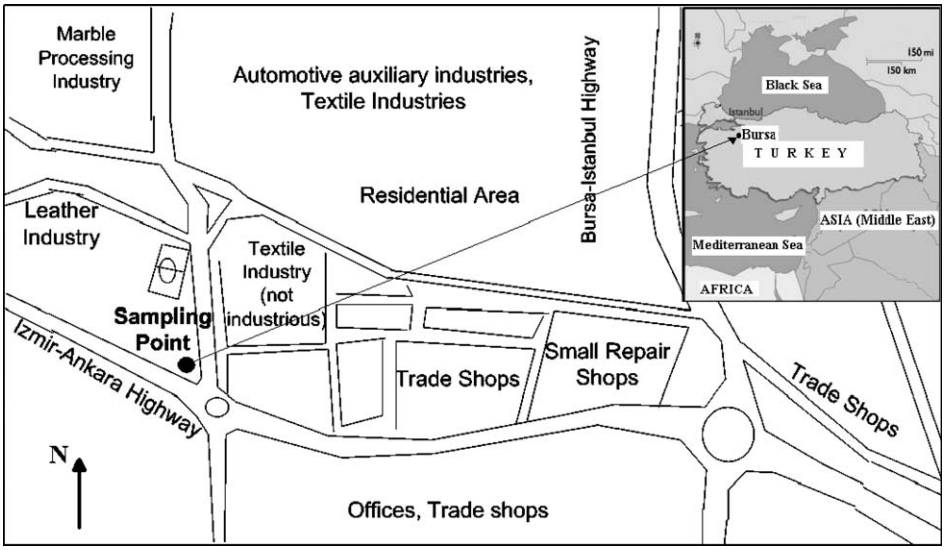

Fig. 1. The location of the sampling site, Bursa, Turkey.

production and painting, automotive production plants, metal manufacturing, cement production, food production, energy production, leather production and fabrication are the main industrial activities in these districts. Bursa has a heavy traffic problem due to its own traffic but also because it is located on the route to other important cities in Turkey such as Istanbul, Izmir and Ankara. Traffic and industrial activities are the main sources of traditional air pollutants in summer but in winter residential heating is the main air pollution source for PM and sulfur dioxide (Tasdemir et al., 2005).

The climate of Bursa is temperate and partly influenced by sea breeze. The major air movements over the city are observed mainly from northerly directions probably due to mountain–valley structure of the city. However, some strong southerly winds clean away air masses sinking over the city especially during the winter months.

The sample collection point was located in a urban /traffic area, beside one of the crowded roadways of the city. The average vehicle amount at this location was >12000 vehicles/hour (Bursa Metropolitan Municipality). The sampler was placed on the platform of an air quality monitoring station, which is located at ~2 m above ground level and about 3 m beside the closest road. Dispersion was limited because the site was situated at a geographically low relative to the city.

2.2. Sample collection

Thirty-three TSP (Total Suspended Particles) samples to analyze 11 trace elements including Mg, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb were collected in the period of March 2003–June 2003 using a High Volume Air Sampler (Andersen) equipped with filter holders. Trace elements in air were collected on 20.3 ± 25.4 cm^2 glass fiber filter (GFF) and quartz fiber filters (QFF). The sampler was placed at a height of 2 m above ground level on a platform. Samples were collected both during day and night times when there was no rain. Average sampling time was about 10 h and average sampling volume was around 1100 m^3 air. Care was taken in handling filters in order to avoid any contamination.

2.3. Sample preparation and analysis

Prior to air sample collection, preparatory cleaning procedures were applied to filters. Similar methods were also used by Fang (1992), Paode et al. (1998), Yi et al. (2001), Odabasi et al. (2002). Briefly, glass fiber and quartz filters were rinsed with 0.25N nitric acid and de-ionized (DI) water, wrapped loosely with aluminum foil, and dried in an oven at 105 °C for several hours. They were allowed to cool to room temperature in a desiccator. Cleaned filters were taken to the sampling site in a container without exposure to ambient air. After completing sample collection, filters were put back into their container and they were stored in a refrigerator (dark and cool place) until analyses were performed.

Filters were placed into flasks and filled with 125 mL 65% nitric acid (trace metal grade) solution (Odabasi et al., 2002). Then, flasks were placed onto a hot plate equipped with condenser column for 4 h (Fang, 1992). After extraction from the filter, dissolved metals in the extract were transferred to a beaker and the process was repeated with 125 mL of 65% nitric acid. This second extraction step was two hours. The extract taken from the last extraction was added to the same beaker. The acid solution in the beaker was evaporated to 20 mL volume with a hot plate at a temperature of >120 °C (Odabasi et al., 2002). Then, the digested solution was transferred to a vial by filtration through a precleaned glass fiber filter. After the filtration process, filter was rinsed with 5 mL of nitric acid into filtrate to prevent any trace metal loss. All the extracts were brought to a final volume of 35 mL with trace metal grade nitric acid solution. The filtrates were kept in the dark until analysis. Blank samples were extracted and concentrated with the same method described above.

Trace metal analysis was performed with inductively coupled plasma atomic emission spectroscopy (ICP-AES, Model: Optima 3100 XL). The instrument operating conditions were set according to the optimum recommended case for the device. Certified standards were used for determination of trace element concentrations in the samples. Due to sensitivity of ICP, all samples and blanks were treated by microwave digestion for 30 min at 160 °C with addition of 5 mL 30% HCl.

2.4. Quality control

Throughout the sampling, extraction and analysis steps, plastic apparatus and wares were preferred to prevent any metal contamination. Filters for high volume sampler and all other laboratory materials were rinsed with dilute laboratory grade nitric acid and DI water prior to use (Kural, 2004).

Possible sample artifacts were determined by employing operational blanks that were processed simultaneously with field samples (Fang, 1992). Blanks ($n=8$) were cleaned and prepared with the same procedures applied to the actual samples. Blanks were transported to the field in their containers without allowing ambient air exposure. All reported values in this paper were blank corrected. The sample concentrations were up to 83 orders of magnitude higher than blanks. Paode et al. (1998) reported similar values. In another study, the sample-to-blank ratios varied between 2.8 and 92 for the same elements (Yatin et al., 2000).

The limit of detection (LOD, mass) was determined from the mean noise, in mass units, plus 3 standard deviations (3 σ) (Cotham and Bidleman, 1995; Odabasi et al., 2002; Tasdemir et al., 2004). Blank samples were used to calculate mean mass (ng) and σ. Detection limits for individual trace metals ranged from 0.215 to 10,128 μg for Cr and Ca, respectively. In general, trace metal amounts in the samples were much higher than LODs. The LOD values obtained

from this study are in good agreement with other studies (Odabasi et al., 2002; Yun et al., 2002). Trace metal quantities exceeding the LOD in the sample were quantified and blank corrected. In order to determine analytical recovery efficiencies, unused filters were spiked with a known amount of trace elements before extraction. Average recovery efficiencies of the analyzed 11 elements varied between 86% and 104%. Similar results were reported by Yun et al. (2002) and Odabasi et al. (2002). No recovery correction was employed for samples due to high recovery efficiencies.

3. Results and discussion

3.1. Average concentrations

In this study, some of the crustal and anthropogenic trace elements (Mg, Ca, Mn, Fe, Co, Cr, Ni, Cu, Cd, Zn and Pb) were collected to determine their levels in the atmosphere of Bursa city, Turkey. These elements were commonly reported in some publications (Yi et al., 2001; Bilos et al., 2001; Sternbeck et al., 2002; Odabasi et al., 2002; Espinosa et al., 2002; Miranda et al., 2002; Kim et al., 2002).

The mean concentrations for trace elements ranged from 0.7 ng/m^3 for Cd (anthropogenic) and 4896.3 ng/m^3 for Ca (crustal). Average concentrations of trace elements measured in this study are given in Table 2. Bursa air contained both crustal and anthropogenic trace elements but the crustal metals (Mg, Ca, Mn and Fe) showed higher values in proportion to anthropogenic metals (Co, Cr, Ni, Cu, Cd, Zn and Pb). The maximum concentration was obtained for Ca (4896.3 ± 3754.3 ng/m^3) followed by Fe (2165.4 ± 1717.4 ng/m^3) and Mg (1204.0 ± 1101.3 ng/m^3). Higher crustal trace element concentrations indicated that re-suspension of soil-derived dust due to a heavy traffic had strong effect on the chemical composition of atmospheric aerosols. Cu (396.7 ± 391.7 ng/m^3) was the most abundant anthropogenic metal followed by Zn (250.5 ± 178.5 ng/m^3). Co (1.1 ± 0.7 ng/m^3) and Cd (0.7 ± 0.9 ng/m^3) were the trace metals with the lowest ambient concentrations. The elevated concentrations of Cu, Zn, Ni and Pb can be attributed to the heavy traffic near the sampling site (Qin et al., 1997; Sternbeck et al., 2002; Harrison et al., 2003). Motor vehicles have also been considered one of the major sources of Pb in Turkey due to the fact that many old cars, using mainly leaded gasoline, were in use while the sampling program was taking place (Yenisoy-Karakas and Tuncel, 2004). Ni, used as an additive in fuels, is related to combustion (Qin et al., 1997).

Fluctuations in crustal and anthropogenic trace element concentrations depending on the wind directions are plotted in Fig. 2. Because of the locations of textile and automotive industries, the trace element concentrations were in general high when dominant winds came from ENE-WNW directions. Lower concentrations were obtained when winds were low, especially for crustal elements. Similar concentration patterns for Mn, Fe, Ca and Mg could be attributed to the re-suspension of soil-derived dust. Mn may also be emitted from steel production but the steel production plant is about 50 km away from the sampling point and correlation with other crustal elements would be lower if significant inputs from this source were present (Table 3). In general, higher concentrations were observed for anthropogenic elements when winds brought emissions from industrial districts, which were located to the WNW-NNW and N-NNE of the sampling point. For example, the location of the leather industry caused an increase particularly on Cr levels when winds came from the WNW.

Table 2
Measured average concentrations and other reported values of trace elements

Trace elements	This study March–June, 2003		La Plata, Argentina, 1993[a]	Izmir, Turkey 2000–2001[b]	Gothenburg, Sweden, April 2000[c]	Seville, Spain, Spring 1996[d]	Sao Paulo, Brazil 1998[e]	Chicago, USA 1993–1995[f]	South Haven, USA 1993–1995[g]	Taejon, Korea, 1997–1999[h]
	Average	Std. dev.								
Mg	1204.0	1101.3	1472	3890	3700	173.1	–	285.9	84.9	–
Ca	4896.3	3754.3	5343	40202	8710	954	519	–	–	–
Cr	10.7	6.7	4.3	11	55	–	4.2	4.2	0.4	25.1
Mn	51.1	32.6	25.5	135	261	7.4	15.2	31.3	8.7	50.3
Fe	2165.4	1717.4	1183	3438	20690	260.8	674	–	–	1633
Co	1.1	0.7	–	–	–	0.3	–	–	–	1.5
Ni	5.1	4.1	3.2	39	–	1.4	5.1	–	–	37.9
Cu	396.6	391.7	29.5	154	404	9.57	10.2	18.7	7.3	41.1
Zn	250.5	178.5	273	733	759	–	94	135.8	37.3	240
Cd	0.7	0.9	0.4	8	0.8	0.2	–	–	–	3.2
Pb	77.2	78.7	64.5	111	113	43.7	16	48.4	10.1	243

[a] Bilos et al., 2001.
[b] Odabasi et al., 2002.
[c] Sternbeck et al., 2002.
[d] Espinosa et al., 2002.
[e] Castanho and Artaxo, 2001.
[f] Yi et al., 2001.
[g] Yi et al., 2001.
[h] Kim et al., 2002.

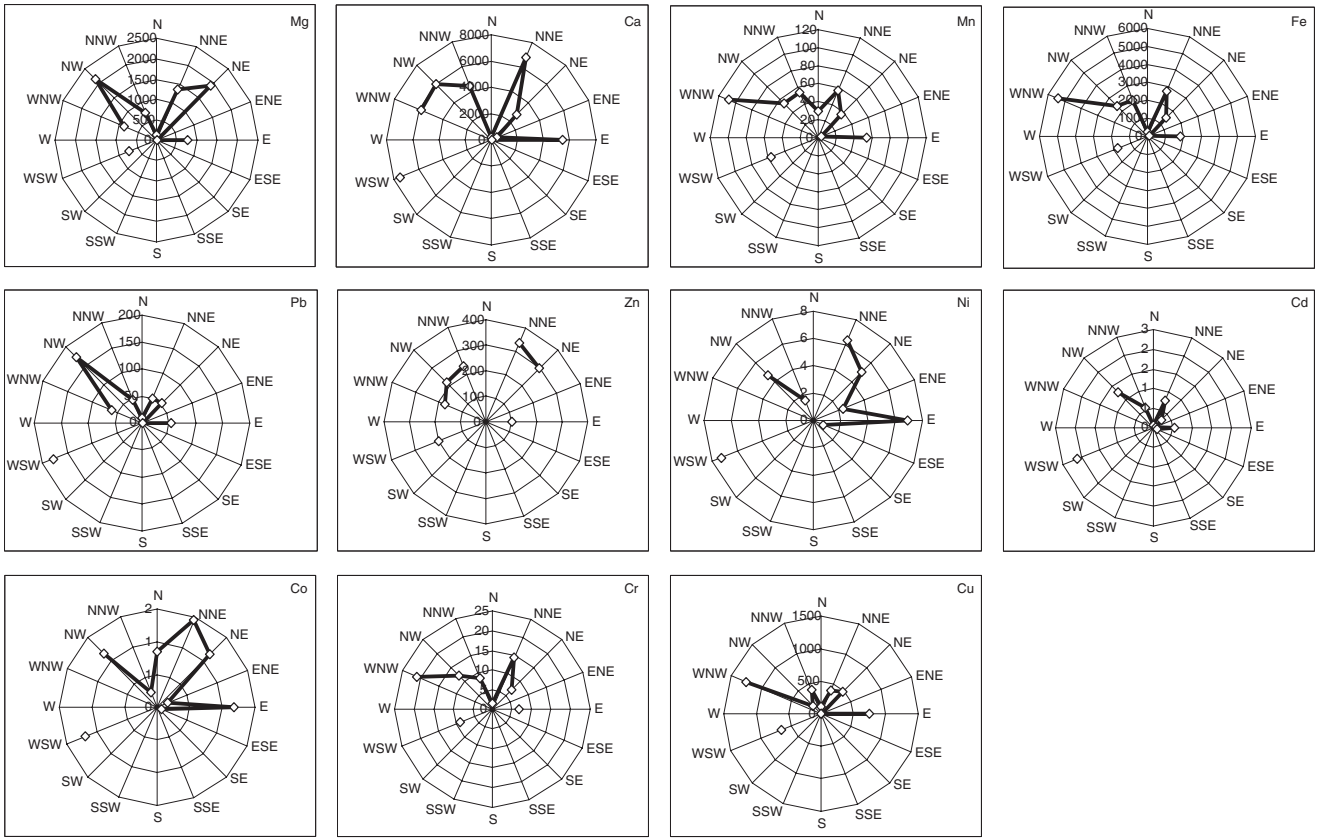

Fig. 2. Trace element concentration variations depending on wind directions.

Table 3
Matrix of correlation coefficients among trace elements and meteorological data

	Ca	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	Wind speed	Air temp.	Relative humidity
Mg	**0.776**	0.348	**0.469**	**0.608**	0.446	0.174	0.004	0.296	0.465	0.284	0.046	−0.024	−0.237
Ca	–	**0.674**	**0.816**	**0.756**	**0.841**	0.480	0.449	0.006	**0.560**	0.443	0.312	0.258	−0.158
Cr		–	**0.848**	**0.680**	**0.958**	0.499	0.338	0.542	0.300	0.076	0.200	0.459	−0.261
Mn			–	**0.920**	**0.906**	**0.723**	**0.637**	0.079	**0.581**	0.401	0.168	0.267	−0.118
Fe				–	**0.839**	0.530	**0.577**	−0.084	0.396	0.043	−0.067	0.382	**−0.475**
Co					–	**0.676**	0.393	**0.976**	0.472	0.318	**0.556**	0.188	0.176
Ni						–	**0.677**	**0.673**	**0.711**	0.395	0.039	0.286	0.188
Cu							–	−0.106	0.441	0.047	−0.180	**0.492**	−0.367
Zn								–	0.273	0.014	0.381	0.322	0.004
Cd									–	**0.797**	−0.219	−0.013	0.060
Pb										–	−0.274	−0.338	0.146

The values in bold indicate a significant correlation between those two parameters ($\alpha = 0.05$).

The measured average metal concentrations were summarized and compared with other reported values in Table 2. Ambient air concentrations varied depending on local sources and meteorological conditions; resulting in, high standard deviations were determined. Generally, crustal element concentration levels are higher than other places except Gotenburgh, Sweden and Izmir, Turkey. The high crustal element concentrations were probably due to re-suspension of street dusts because our sampling point was located to next to a road junction. Anthropogenic trace elements mainly originated from industrial activities and motor vehicles. However, during spring months, including March and April, residential heating was also partially considered as a source due to usage of fossil-fuels especially coal (Yatin et al., 2000). The anthropogenic trace elements measured in this study were generally higher than the ones measured in non-urban areas. For example, South Haven, USA can be considered as a non-urban area and in this place, Yi et al. (2001) reported concentrations that were about 15 to 120 times smaller than the ones measured in this study. In general, the anthropogenic trace element levels reported in this study were in an agreement with urban values (Qin et al., 1997; Yatin et al., 2000; Yi et al., 2001; Sternbeck et al., 2002; Kim et al., 2002).

3.2. Comparison of concentrations measured in this study

Differences between day and nighttime average concentrations of trace elements are presented in Fig. 3. Samples taken during the day showed elevated concentrations for Mg, Ca, Cr, Mn, Fe, Zn and Co. No significant diversity is apparent for the remaining trace metals. No statistical significant difference was observed between the data for the two periods for each trace metal (two-tailed, t-test, $\alpha = 0.05$). These results may be attributed to motor vehicle sources because roadway emissions and re-suspension of trace elements occur all day in a heavily trafficked area. Moreover, industrial activities may mask the statistical difference between day and night concentration levels because Bursa is an industrial city and industrial activities continue for day–night and weekdays–weekend for some industries.

The degree to which trace elements in the aerosols are enriched, or depleted, relative to a specific source can be assessed using EF (Chester et al., 1999). In general, an internationally accepted average crustal composition is used to calculate trace element EFs for ambient aerosols (Odabasi et al., 2002). Crustal EF values probably overestimate the anthropogenic imprint and therefore, actual local soil composition should be used for EF calculations (Yay

and Tuncel, 2001). Iron was used to determine the EFs in this study (Bilos et al., 2001; Kim et al., 2002).

$$\mathrm{EF} = \frac{C_{Xp}/C_{\mathrm{Fep}}}{C_{\mathrm{Xc}}/C_{\mathrm{Fec}}} \tag{1}$$

where,

C_{Xp} Trace metal X concentration in the aerosol
C_{Fep} Fe concentration in the aerosol

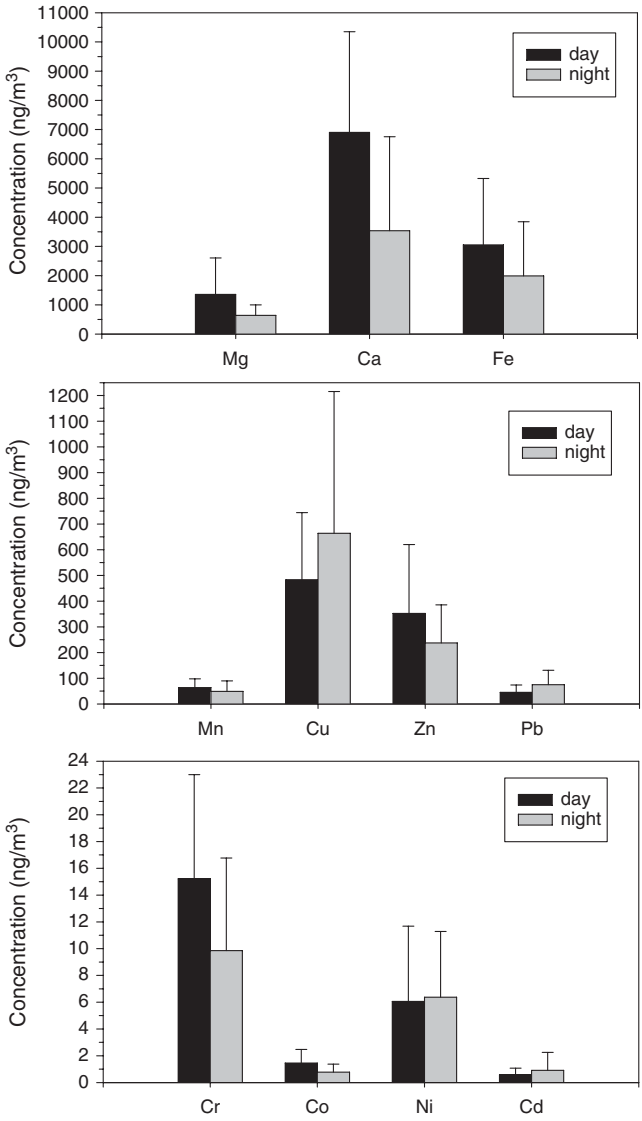

Fig. 3. Comparison of trace element concentrations between day and night.

C_{Xc} Trace metal X concentration in average crustal material
C_{Fec} Fe concentration in average crustal material

If the EF is less than 10, trace metal in aerosol has a significant crustal source but if EF is higher than 10, a significant proportion of an element has a non-crustal source. Results of the EF computation are plotted in Fig. 4 for day and nighttime periods. During the daytime, the EFs for the metals of Cu (42 ± 28), Zn (11 ± 10) and Pb (13 ± 19) were higher than 10 indicating that these elements had significant anthropogenic sources. Similar results were also reported by Odabasi et al. (2002) for the samples taken in Izmir. In addition to these trace elements, Cd (11.21 ± 0.45) passed the limit of 10 of EF in nighttime samples. These metals are known as they can be emitted mostly from vehicular transportation but industrial activities may have also a significant effect on their levels in our sampling site(Sternbeck et al., 2002; Harrison et al., 2003). In general, elements indicated by relatively low EFs suggest the local soil was polluted and contributed significantly to ambient trace element concentrations by re-suspension of dusts. The sequence for daytime EFs were Cu>Pb>Zn>Cd>Ni>Ca>Mg>Cr>Co>Mn. Meteorological conditions could affect the order of enrichment and concentrations of trace metals by transformation of particle size distribution (Hesketh, 1996). However, the correlations between trace metal concentrations and meteorological parameters pointed out that this was not the case for this study due to insignificant correlation coefficients (Odabasi et al., 2002).

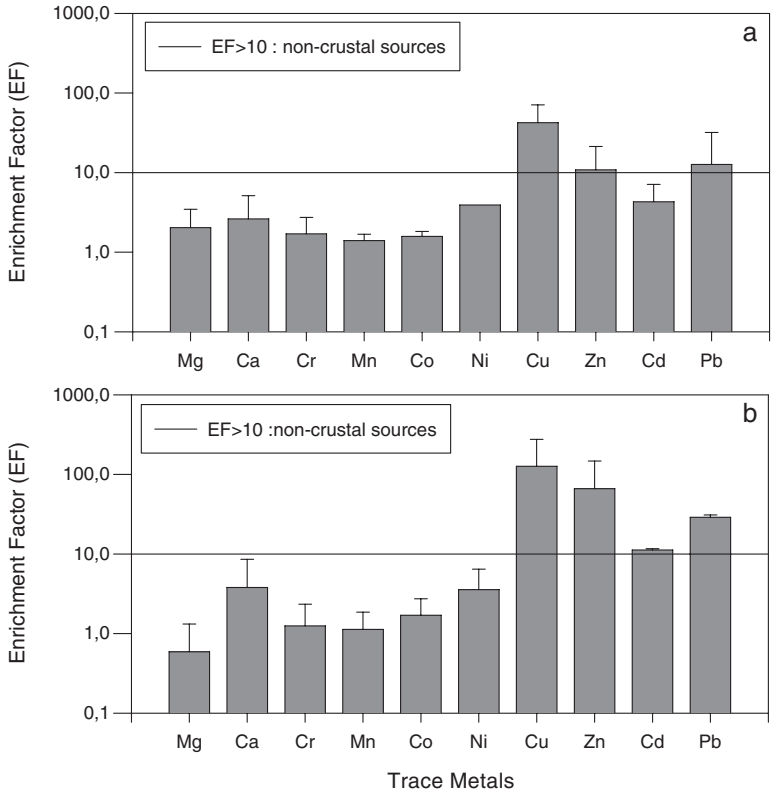

Fig. 4. Enrichment factors for day (a) and night (b) concentrations.

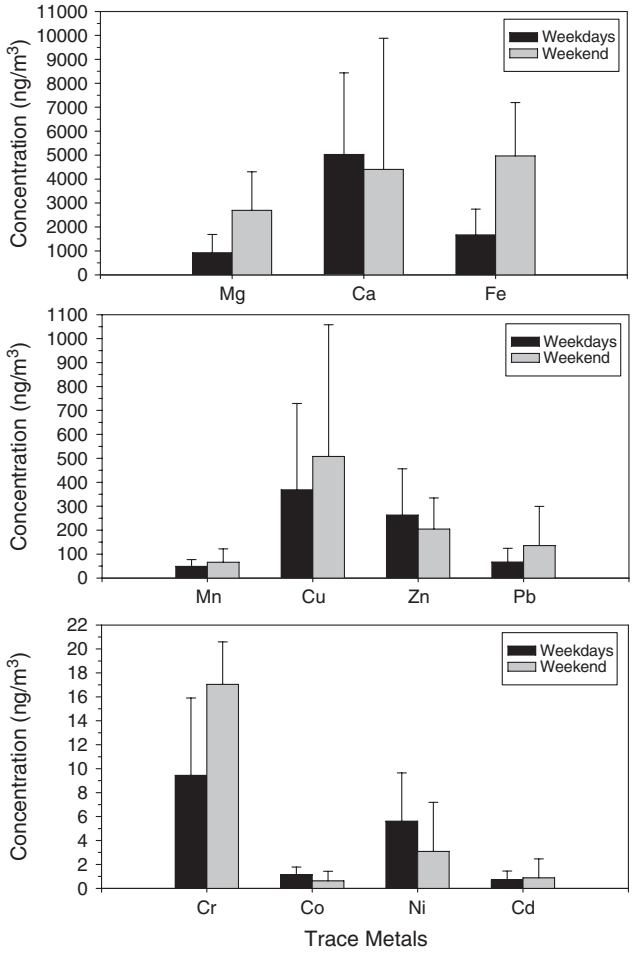

Fig. 5. Comparison of trace element concentrations between weekend and weekdays.

The average weekend and weekdays concentrations were calculated from the data collected within the same period for each trace element. The results are illustrated in Fig. 5. The p-values (two-tailed, t-test, $\alpha = 0.05$) did not support the existence of considerable diversity between weekday and weekend values except for Mg and Fe. There could be several reasons of the variation between concentrations such as higher emissions originated from some industries including marble, metal processing and textile during the weekends, some other fugitives and meteorological conditions.

Fluctuations of trace element concentrations can occur based on rain events. In this study, no samples were taken during rainy days. However, the day following a rain event was often sampled. Trace element concentrations were generally found to be under the LOD values. In another study, Qin et al. (1997) reported lowest trace element concentrations after rainy days. The decrease in concentration after rainy days was probably due to washout and obstruction of particle re-suspension.

The measured concentrations were arranged to evaluate the spring and summer concentrations of trace elements measured in this study (Fig. 6). Generally, average trace metal concentrations for

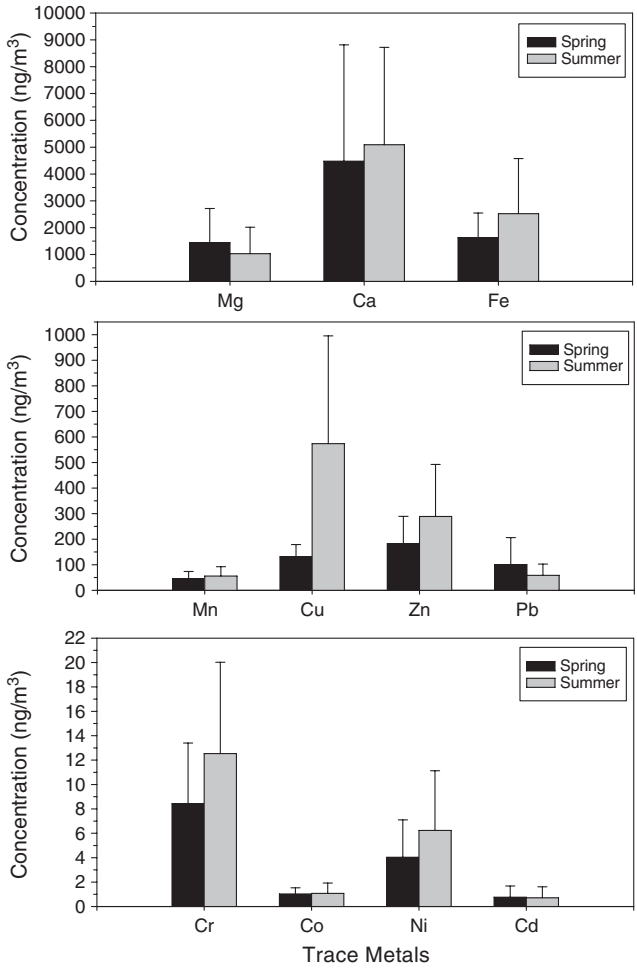

Fig. 6. Comparison of trace element concentrations between spring and summer seasons.

summer were higher than those of spring. Only the average concentrations of Mg, Cd and Pb showed higher values for spring season than summer season. Kim et al. (2002) reported similar elevated values for Cd and Pb. The difference between seasonal concentrations could be attributed to the precipitation levels. However, there was no statistically significant difference between average spring and summer metal concentrations ($\alpha = 0.05$) except for Cu. Statistically similar concentration levels were probably reasonable because the contaminant sources and turbulence originated from motor vehicles in the sampling point. It is known that Cu is emitted at a large proportion from the brake linings and is a major contributor to the element in coarse particles (Weckwerth, 2001; Harrison et al., 2003). The rainy days are frequent in spring, and this provides the removal of especially coarse particles containing Cu element. Moreover, there were several high concentrations for Cu indicating fugitive emissions during the summer season and they may cause the statistical difference.

Two types of filter were used in the study to collect ambient particulate samples for metal measurements. The concentration results obtained from quartz and glass fiber filters are

presented in Fig. 7 for all trace elements. Average concentrations obtained for both filter types showed generally similar levels. Despite the apparent difference for most metals such as Mg, Ca, Co, Ni, Cr, Pb and Zn metals, there is no statistically significant difference for the trace element concentrations collected with different filters, quartz and glass fiber filters ($\alpha = 0.05$). It is well documented that both filters were used for ambient particulate sampling. Odabasi et al. (2002), Bilos et al. (2001), Moreno-Grau et al. (2000), Kim et al. (2002) used glass fiber filters whereas Herut et al. (2001) and Ho et al. (2003) used quartz filters. Correlation analyses have been conducted and they are presented in Table 3. The values in bold indicate a significant correlation between those two parameters ($\alpha = 0.05$). The correlations indicate a potential common origin, especially for Co–Zn, Cr–Co, Mn–Fe, Mn–Co having correlation coefficient values higher than 0.9 and also noteworthy at $\alpha = 0.05$. A strong positive correlation between two elements indicates that the characteristics and origin of emission for both elements may be similar. Different correlation coefficients have been reported in the literature depending on the sources of trace elements and meteorological conditions (Eskikaya, 1993; Espinosa et al., 2002; Fang et al., 2004).

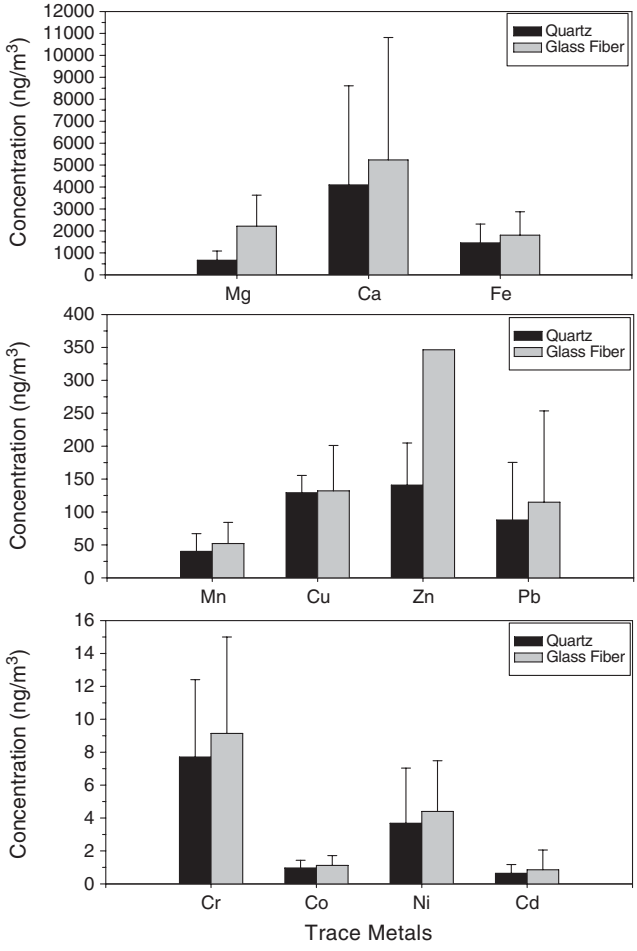

Fig. 7. Effect of filter type on trace element concentrations.

Some negative correlations between trace elements and wind speed values were observed. This could be a reasonable result because it indicated the dilution of elements. In general, correlation coefficients between trace elements and meteorological conditions including wind speed, temperature and relative humidity were relatively low.

3.3. Dry deposition estimation

Dry deposition of trace elements can be predicted from the ambient air concentrations and the deposition velocities (V_d) (Yi et al., 2001; Herut et al., 2001; Tasdemir et al., 2004).

$$F = V_d \times C \tag{2}$$

This model would not provide reasonable dry deposition flux results because it uses an average particle concentration and average deposition velocity. It is known that variations in deposition velocities with particle size are not linear and particle size distributions are highly variable, thus, usage of only one dry deposition velocity may lead overestimation or underestimation of predicted flux values. It is an important task to determine the complete size distributions in order to estimate dry deposition fluxes accurately. For this purpose, Eq. (2) is extended to include both fine and coarse particles separately.

$$F = C_f \times V_{d,f} + C_c \times V_{d,c} \tag{3}$$

where, C_f and C_c are the average concentrations of trace elements partitioned with the fine and coarse fractions, and $V_{d,f}$ and $V_{d,c}$ are the deposition velocities for fine and coarse particles. Dry deposition is closely related to the concentration associated with coarse particles. This is reasonable because $V_{d,c}$ is much higher than $V_{d,f}$ (Fang, 1992; Sweet et al., 1998).

Eq. (2) is used in our deposition flux predictions. The deposition velocities for coarse and fine particles were taken from Fang (1992) who collected ambient air samples from a highly

Table 4
Dry deposition velocities and estimated dry deposition fluxes of trace elements

Trace element	Dry deposition velocity (cm/s)		Total estimated flux (mg/m^2 day)
	Fine	Coarse	
Mg	0.234[a]	0.867[a]	0.682
	23.1[b]	4.6[b]	11.2
Ca	0.317[a]	1.839[a]	5.633
Cr	0.095[a]	2.298[a]	0.014
	0.3[b]	1.5[b]	0.01
Mn	0.149[a]	0.499[a]	0.017
	12.3[b]	1.1[b]	0.213
Fe	0.385[a]	1.405[a]	1.992
Cu	0.032[a]	2.316[a]	0.533
	2.8[b]	3.0[b]	1.005
Zn	0.037[a]	2.773[a]	0.403
	2.8[b]	3.0[b]	0.635
Cd	0.028[a]	3.143[a]	0.001
Pb	0.029[a]	2.433[a]	0.109
	2.3[b]	1.8[b]	0.131

[a] Fang, 1992.
[b] Yi et al., 2001.

urbanized site to analyze trace elements. The greased surface deposition plates (GSDPs), cascade impactor and noll rotary impactor (NRI) were employed in his study. Then, multiple regression was used to calculate the dry deposition velocities for coarse and fine particles and they are summarized in Table 4. In a recent study (Evren, 2005), ambient particulate samples were collected at our sampling site and it was determined that coarse particles were 2/3 of the total particulate concentration. Based on studies done by Fang (1992) and Evren (2005), dry depositions of trace elements were estimated (Table 4). The calculated dry deposition flux values agreed reasonably well with some other recent fluxes reported for trace elements (Morselli et al., 1999; Odabasi et al., 2002; Yun et al., 2002; Yi et al., 2001; Momani et al., 2000). However, it should be noted that Evren (2005) calculated an overall average dry deposition velocity of 6.9 ± 2.0 cm/s for particulate matter. This result, higher than the ones reported by Fang (1992), indicates that coarse particles are predominant in our sampling site and they lead to higher deposition fluxes than presented in Table 4. This is reasonable because our sampling point was located in a heavy trafficked location; thus, re-suspension and deposition of street dust due to mechanical turbulence was considerable.

3.4. Factor analysis

Factor analysis was performed using SPSS software in an attempt to analyze interrelationships among the trace metals and to explain them in terms of their common underlying factors (Yun et al., 2002). The appropriate number of factors for the analysis was determined by the means of principal component analysis (PCA). In this study, factors were selected based on the criteria of eigenvalues over 1.0. Varimax rotated factor analysis showed three possible factors, indicating three different contributing sources for the trace metals at the sampling site. The related results of PCA applied to the entire data set listed in Table 5. The three factors accounted for over 94% of the total data variance. The first factor, which explained 59.6% of the total variance, had its highest loading on Mg, Cr, Mn, Fe, Co, Ni, and Zn. The second factor explained 23.7% of the total variance and had high loading on Ca and Pb. 10.8% of the total variance was explained by the third factor, which was composed of Cu and Cd. These results indicate that both factor 1 and 2 represent contribution from industrial activities and

Table 5
Factor analysis on trace element concentration data set

Variable	Component			Communalities
	Factor 1	Factor 2	Factor 3	
Mg	0.930	−0.170	0.232	0.946
Ca	0.254	0.943	−0.188	0.989
Cr	0.779	0.560	0.150	0.944
Mn	0.908	0.130	0.374	0.981
Fe	0.872	−0.317	0.218	0.908
Co	0.962	0.099	0.108	0.948
Ni	0.644	−0.042	0.616	0.796
Cu	0.206	−0.335	0.898	0.961
Zn	0.818	0.294	0.466	0.972
Cd	0.360	0.509	0.748	0.947
Pb	−0.347	0.916	0.054	0.962
Eigen value	6.5	2.6	1.2	
Variance(%)	59.6	23.7	10.9	

local dust resuspension caused by traffic. Since Cu and Cd are typical markers of vehicular transportation the factor 3 represents sources from motor vehicles. However, it is difficult to ensure the exact sources without having any specific source results obtained in the vicinity of the study area.

4. Conclusions

Trace elements in the atmosphere of Bursa, Turkey were collected and analyzed for two main groups, anthropogenic (Cu, Zn, Pb, Cr, Ni, Co, Cd) and crustal (Ca, Mg, Fe, Mn) elements. The results showed that re-suspension of soil dust due to heavy traffic causes higher crustal trace element composition of atmospheric particulate matter samples. The order of airborne concentrations were Ca>Fe>Mg>Cu>Zn>Pb>Mn>Cr>Ni>Co>Cd at the sampling site. The fluctuations in the concentration levels are probably a direct function of particle size distribution, emission sources and the meteorological conditions (i.e., wind direction, wind speed, temperature, atmospheric stability). For example, Cr reached its maximum level when winds were from the WNW direction in which the leather industries were located. Higher crustal trace element concentrations indicated that re-suspension of soil dust due to traffic had strong effect on chemical composition of atmospheric aerosols. Much larger concentrations of crustal elements (i.e., 4896.3 ng/m^3) were detected compared to the anthropogenic elements (i.e., 0.7 ng/m^3). The elevated concentrations of Cu, Zn, Ni and Pb can be attributed to the industrial activities and heavy traffic near the sampling site while Co (1.056 ng/m^3) and Cd (0.736 ng/m^3) have the lowest values. Comparisons between weekend and weekdays, day and nighttime, spring and summer seasons, quartz and glass fiber filter types were statistically analyzed. The estimated dry deposition fluxes were in line with other reported values. However, the influence of coarse particulates was dominant on the flux calculations. Calculated EF values and PCA analysis revealed that the elevated trace element concentrations were caused generally by industrial emissions and re-suspension of dusts due to mechanical turbulence.

Acknowledgement

We would like to thank Dr. Gürdal Tuncel and Dr. Semra Tuncel (Middle East Technical University, Turkey) for lending us the air sampler used in this study.The constructive comments of two anonymous reviewers are greatly acknowledged.

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