DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

ELEMENTAL CONCENTRATIONS IN İZMİR ATMOSPHERE AND THEIR SOURCE APPORTIONMENT

by
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İZMİR

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Ph.D. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled "**ELEMENTAL CONCENTRATIONS IN İZMİR ATMOSPHERE AND THEIR SOURCE APPORTIONMENT"** completed by **Sinan YATKIN** under supervision of Assoc. Prof. Dr. Abdurrahman BAYRAM and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy

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ABSTRACT

The concentrations of particulate matter (PM) fractions ($PM_{2.5}$ and PM_{10}) were determined concurrently at suburban and urban sites in Izmir, Turkey. The sampling period was between June 2004 and May 2005. The PM concentrations showed significant temporal and spatial variations. The concentrations were higher in winter at urban site, whereas the summer concentrations of suburban site were higher. The elemental composition of PM were determined by measuring the concentrations of Al, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, V, and Zn using inductively coupled plasma-optical emission spectrometer. The elemental concentrations also showed temporal and spatial variations. The elemental compositions were dominated by terrestrial elements (i.e., Ca, Al, Fe and K) and Na. PM_{10} and $PM_{2.5}$ samples were also collected from the major PM emitters and they were characterized in terms of the same elemental composition. To determine the sources of PM and the contribution amount of the sources, some statistical methods and models (i.e., factor analysis, positive matrix factorization and chemical mass balance method) were used. The results indicated that the major sources that contributed to the PM concentrations were traffic, soil, mineral industries and fossil fuel burning. Although traffic was the major contributor to PM concentration at two sites, the contributions to trace elemental concentrations were limited. The major contributors to trace elemental concentrations were industry, fossil fuel burning and mineral industries.

Keywords: PM_{10}, $PM_{2.5}$, factor analysis, PMF, CMB, Izmir

İZMİR HAVASINDA ELEMENT KONSANTRASYONLARI VE KAYNAKLARININ BELİRLENMESİ

ÖZ

İzmir bölgesinde, dış havadaki partikül madde (PM) fraksiyonları ($PM_{2.5}$ ve PM_{10}), biri yarı kırsal diğeri şehir merkezindeki iki bölgede eş zamanlı olarak örneklenmiş ve konsantrasyonlar belirlenmiştir. Örnekleme periyodu Haziran 2004 ve Mayıs 2005 tarihleri arasıdır. PM konsantrasyonları önemli mevsimsel değişikler göstermiştir. Yarı kırsal bölgede yaz konsantrasyonları kış değerlerine göre daha yüksekken, şehir merkezinde kışın konsantrasyonlar daha yüksek ölçülmüştür. PM'in element içeriği (Al, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, V, ve Zn), indüktif eşleşmiş plazma-optik emisyon spetkrometresi ile belirlenmiştir. Element içeriği, büyük oranda, toprak elementleri (Ca, Al, Fe ve K) ve Na'dan oluşmuştur. Elementsel konsantrasyonların mevsimsel değişiminin de önemli boyutta olduğu belirlenmiştir. Önemli PM kaynaklarından PM_{10} ve $PM_{2.5}$ örnekleri toplanarak, aynı elementsel içerik belirlenmiştir. Dış havadaki PM konsantrasyonlarının kaynaklarının belirlenmesi ve katkı miktarlarının hesaplanması amacıyla istatiksel metot ve modeller (Faktör analizi, pozitif matris faktörizasyonu ve kimyasal kütle dengesi modeli) kullanılmıştır. Sonuçlar, dış havadaki PM konsantrasyonlarına en büyük katkıyı, her iki bölgede de, trafik, toprak, mineral endüstrisi ve fosil yakıt yakılmasının yaptığını göstermektedir. Her ne kadar PM konsantrasyonlarına en önemli katkıyı trafik yapmış olsa da, eser element konsantrasyonlarına yaptığı katkı oldukça sınırlı kalmıştır. Eser element konsantrasyonlarına en önemli katkılar, endüstri, fosil yakıt yakılması ve mineral endüstrisinden gelmiştir.

Anathar Kelimeler: PM_{10}, $PM_{2.5}$, Faktör analizi, PMF, CMB, İzmir

CHAPTER ONE
INTRODUCTION

Particulate matter (PM) is one of the most important air pollutants. The most important effect of PM is its capacity of altering the solar radiation balance and reducing visibility (Polissar, Hopke & Pairot, 2001). This reduction causes a drop in agricultural crop yield (He, et al., 2001). Enrichment due to air-water transfer in coastal ecosystems, and long-range transfer in open marine atmosphere (Gao, et al., 2002) is also a problem. Contribution to metal toxicity due to ecotoxic heavy metals associated with soluble fractions of PM is among important environmental effects of PM (Gao, et al., 2002). Presence of particulate matter in air causes several serious health effects such as aggravated asthma, increased respiratory symptoms like coughing and difficult or painful breathing, chronic bronchitis, decreased lung functions, premature death etc. (The United State Environmental Protection Agency, [USEPA], 1997). Increase in hospital admissions due to high PM concentrations is reported (He, et al., 2001). Due to recognition of importance of environmental impacts of PM, the number of studies regarding PM and its fractions have sharply increased recently. These studies were generally focused on determination of PM concentrations, elemental composition and source apportionment (Yatin et al, 2000; Polissar et al., 2001; He et al., 2001; Roosli et al., 2001; Gao et al., 2002)

Izmir is a large city with nearly 3 millions inhabitants and significant industrial activities, thus PM problem sometimes reaches critical levels, particularly near industrial areas and in the city center during winter periods. Most of industrial activities are located in the industrial zones of Bornova, Cigli, Gaziemir, Kemalpasa, Aliaga and Torbali. The first three are located in the city center. Two of the significant sources of PM, fossil fuels (coal and fuel oil), are used for residential heating throughout the city. PM_{10} (<10 µm) concentrations sometimes exceed 100 µg m^{-3} in the city center around a cement plant (Yatkin & Bayram, 2005). Evidently, health of the population must be protected, so to device an appropriate control strategy, concentration levels and source apportionment of PM and its fractions should be determined. Particularly, trace element content of particles is very important in terms of toxicity.

Several studies regarding PM and its fractions were conducted in different regions of Turkey. Ambient PM_{10} and $PM_{2.2}$ concentrations and elemental composition (40 elements and ions) were measured between February-June 1993 in Ankara (Yatin et al., 2000). Ambient concentrations and temporal variations were determined, but source characterization was not performed. Similar studies were conducted in Antalya (Gullu, Olmez & Tuncel, 2000) and in Bursa (Karakas & Tuncel, 1997) measuring ambient concentrations and temporal variations.

PM levels and trace element contents were studied previously by Odabasi, Muezzinoglu & Bozlaker (2002) and Yatkin et al. (2005) in Izmir. It was determined that PM_{10} (<10 µm) concentrations sometimes exceeded 100 µg m^{-3} in the city center around a cement plant (Yatkin et al., 2005). The concentrations and dry deposition fluxes of some elements were determined at a suburban site of Izmir (Odabasi et al., 2002). However, these studies did not perform source characterization and source apportionment for PM in Izmir.

The overall objective of this study was to determine the sources of PM and trace elements in Izmir by statistical tools and models. The specific objectives were:

1) To determine the ambient concentrations of PM_{10}, $PM_{2.5}$ and 16 elements (Al, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, V and Zn) at an urban and a suburban site.
2) To evaluate the influence of meteorological factors on PM and elemental concentrations.
3) To characterize the sources of PM.
4) To determine source apportionment of PM using statistical tools and models. These are factor analysis, Positive Matrix Factorization (PMF) and Chemical Mass Balance (CMB).

This study consists of five chapters. After the introduction, previous studies and concepts related to this study are summarized in Chapter 2. Materials and methods are described in Chapter 3. Results and discussion are presented in Chapter 4. Conclusions and suggestions for the future studies are stated in Chapter 5.

CHAPTER TWO
LITERATURE REVIEW

2.1 General Overview

Particulate matter (PM) is described as the total amount of particulates and droplets in the air and has a wide fractional spectrum. Particles are described by only one dimension, aerodynamic diameter that is described as ‘the diameter of a spherical particle having a density of 1 gm/cm^3 that has the same inertial properties (i.e. terminal settling velocity) in the gas as the particle of interest’ (USEPA, 2006a). Naturally, almost no particle has a perfect spherical shape; but the assumption of sphericity makes it easier to characterize the particles. The residence time of a particle in the atmosphere basically depends on it’s gravity and size. Small particles can stay in the atmosphere longer; thus can be transported over long distances by the wind.

PM_{10} and $PM_{2.5}$ (with aerodynamic diameter less than or equal to 10 µm and 2.5 µm, respectively) are the fractions of PM that are under separate treatment all around the world for many years. PM_{10} contains particles that can enter the inhalation system and reach to larynx. $PM_{2.5}$ can pass the removing mechanisms of upper inhalation system and penetrate into pulmonary alveoli. Physical and chemical characteristics of PM have also been investigated for many years. The elemental composition of PM has been determined to asses the possible toxic effects. Chemical profiles of PM are also the data of several tools and methods to determine the sources of PM.

2.2 Sources of PM and Trace Elements

PM in the atmosphere may be originated from natural and anthropogenic sources. The natural sources are splashed marine salt, wind blown dust, volcanoes, swamps, natural fires etc. (Roosli et al., 2001). The first two are the main natural contributors to PM. The natural sources can be more effective than anthropogenic sources

However, the dominant contributors to atmospheric PM are generally human activities that consist of fossil fuel burning, industrial activities, construction works, transportation on paved and unpaved roads etc. (Roosli et al., 2001).

PM can be of either primary or secondary origin. Primary particles are directly released into the atmosphere by natural and anthropogenic sources. Secondary ones are formed in the atmosphere by gas-to-particle conversion from gaseous species such as sulfur dioxide (SO_2), nitrogen dioxide (NO_2), ammonia (NH_3) and volatile organic compounds. Secondary particles are generally fine (<2.5 μm) particles (Roosli, et al., 2001).

Trace elements exist in all fractions of PM, particularly in fine fraction (Baumbach, 1996; Fang et al., 1999). Although natural sources may contribute to trace elements in PM, their major emitters are usually anthropogenic sources such as mining activities, metal industries, fossil fuel burning and transportation (Baumbach, 1996; Allen, Nemitz, Shi, Harrison & Greenwood, 2001).

2.3 Environmental Impacts of PM and Trace Elements

2.3.1 Health Effects

The health impacts of particles are generally based on the size and chemical structure of PM. Fine particles can penetrate deep into lungs and may cause more serious health problems. Several studies indicated that there is a significant relation between exposure to PM pollution and health problems (USEPA, 1997; Dingenen et al., 2004). The most important health effects are increased respiratory symptoms (i.e. irritation of the airways, coughing, or difficulty in breathing), decreased lung function, aggravated asthma, development of chronic bronchitis, irregular heartbeat, nonfatal heart attacks, and premature death in people with heart or lung disease (USEPA, 1997). Many epidemiological studies indicated that there is a significant relationship between PM concentration and mortality and morbidity (Hauck et al., 2004; Dingenen et al., 2004). Chemical characteristics of PM have significant impacts on human health (Hauck et al, 2004; Dingenen et al., 2004). Several chemical species associated with PM effects the health seriously. Particularly toxic elements and organic compounds have more serious effects and may increase cancer risk (USEPA, 1997; USEPA, 2006b). Although a large list of elements in the composition of PM was studied in this work, only the effects of trace elements (Cd, Cr, Cu, Ni, Pb and Zn) were discussed as below. The reason for choose of these elements is that more of them are toxic for human life and organisms.

Cadmium: Cadmium exposure by inhalation may cause a variety of neurotoxic, nephrotoxic and carcinogenic pathological effects (Raghunant et al., 1999; Ikeda et al., 1999; Agency for Toxic Substances and Disease Registry [ATSDR], 1999; Newhook, Hirtle, Byrne and Meek; 2003; Fortuol at al., 2005; Cui, et al., 2005). The most important effect of inhaled Cd occurs in kidneys (ATSDR, 1999). The effects may occur as increase in abnormality of renal function indicated by proteinuria and decrease in gromerular filtration rate (ATSDR, 1999). The frequency of kidney stone formation may increase due to exposure to Cd by inhalation (ATSDR, 1999). The relationship between occupational exposure to Cd and cancer particularly lung and prostate cancers has been determined (ATSDR, 1999). However, the role of Cd could not be explained, since occupational exposure contained other toxic elements and substances. Therefore, USEPA classified Cd as a possible carcinogen (ATSDR, 1999).

Chromium: Chromium exists in the environment in two valance states dominantly; trivalent Cr (Cr III) and hexavalent Cr (Cr VI). Chromium (III) is an essential element for human being; it is much less toxic than Cr (VI) (USEPA, 2006c). The respiratory tract is the main target of acute and chronic exposure to Cr (VI) by inhalation (ATSDR, 2000). These effects may occur as coughing, wheezing, and decreased expiratory volume in case of inhalation of large amount of Cr compounds (ATSDR, 2000). Severe effects to liver and neurosystem due to inhaled large amounts of Cr were also reported (ATSDR, 2000). Increase in respiratory system cancers among the workers of Cr processing industries is indicated (ATSDR, 2000). After several studies on the workers and laboratory experiments on animals, USEPA classified Cr (VI) as extremely carcinogenic element for human (ATSDR, 2000).

Copper: Although inhalation of Cu may cause several effects on human systems, it is widely known as a respiratory irritant. The effects differ with respect to exposed concentration and time. The effects can be listed as coughing, sneezing, thoracic pain, and runny nose. Linear pulmonary fibrosis, and in some cases, nodulation among copper sieving workers who are exposed to very high concentrations of Cu was also reported (ATSDR, 2004).

Nickel: The reported effects of inhaled Ni are connected with respiratory and immune systems. The acute and chronic exposure of Ni cause respiratory system diseases like asthma specific for Ni, bronchitis and decrease in lung function (USEPA, 2006d). It was also reported that soluble Ni compounds like nickel acetate are the most toxic compounds whereas the insoluble Ni compounds were the least toxic (USEPA, 2006d). Although USEPA classified the nickel acetate and sulfate as non-carcinogenic after laboratory experiments on animals, it is indicated that the nickel compounds emitted from nickel refineries (mostly nickel subsulfide) are extremely carcinogenic for human beings (USEPA, 2006d). Because, many studies on the workers of Ni refineries clearly showed that there was an increase in lung and nasal cancers among the workers (USEPA, 2006d).

Lead: Lead is one of the most common toxic elements of human interest for many years. Lead has been used widely in industry particularly as an additive to gasoline. Inhalation of Pb compounds causes several serious health effects. These are damage to organs, particularly liver, kidney, brain, nerves etc. Lead is included among causes of osteoporosis (brittle bone disease), reproductive disorders, increase in the blood pressure, increase in heart diseases, and anemia, or weak blood (USEPA, 2006e). The effects on brain and nerves occur as seizures, mental retardation, behavioral disorders, memory problems, and mood changes. It damages the nervous system and brain of children and causes learning deficits and lowered intelligence (USEPA, 2006e). Lead also affects the animals and plants and especially fish, damaging their bodies and decreasing their growth (USEPA, 2006e).

Zinc: Zinc is an essential element for human body. Acute exposure to high levels of zinc oxide may cause respiratory system damage; but, it does not cause chronic lung disease (ATSDR, 2005). The studies performed among workers of Zn industries clearly indicated that Zn compounds do not have a carcinogenic effect (ATSDR, 2005).

2.3.2 Impact on Organisms and Materials

Similar to effects on human health, PM and toxic substances associated with PM may cause several damages to organisms. PM may accumulate on the leaves of plants via dry deposition, decreasing their respiration capacity. Presence of PM in the atmosphere reduces the sunlight; as a result, photosynthesis capacity of the plant decreases (Tunay & Alp, 1996). It was reported that the plant growth was reduced due to PM emitted from cement industry (Tunay et al., 1996). The toxic elements associated with PM may cause of several damages to the plants. These damages depend on the elements, exposure route, time etc. (Baumbach, 1996). Toxic elements can accumulate in several organs of plants.

The effects of PM and trace elements to the animals are generally similar to the effects on humans. Some of the toxic elements can also accumulate in animal bodies (USEPA, 1997). Several events were reported regarding death of grazing animals on grass polluted with toxic elements (Muezzinoglu, 2000). Some toxic elements can accumulate in the sea organisms and enter the food chain (USEPA, 1997).

There were several effects of PM and trace elements on the materials. These effects vary according to chemical structure of PM, type of material (metals, stones, textile etc.) and exposure time etc (Tunay et al., 1996; Baumbach, 1996; Muezzinoglu, 2000).

2.3.3 Impacts to Visibility and Radiation Balance

Particles and water droplets in the atmosphere partially reflect, scatter, refract and absorb the sunlight; and so, the amount of sunlight reaching to surface of the earth decreases (Baumbach, 1996). These mechanisms reduce the visibility, affect the radiation balance of the earth, decrease the photosynthesis capacity of plants; thus, reduce the yield of plants (Baumbach, 1996; Chan et al., 1999; Tsai & Cheng, 1999; Muezzinoglu, 2000; Polissar et al., 2001; Kim, Kim & Oh, 2001; Xu et al., 2002). A decrease of 0.2-0.4 ^{0}C in temperature of the surface due to presence of PM in the air was determined over the last 40 years in China (Xu et al., 2002).

2.4 Atmospheric Concentrations of PM and Trace Elements

The measurements of atmospheric PM and elemental concentrations have been commonly performed all around the world for many years. The PM and trace element levels in the atmosphere strongly depend upon sampling site characteristics (urban, suburban, rural, industrial, etc.). Similarly, PM concentrations and composition are strongly affected by the geographical location, industrialization level, population density, etc. Generally, PM concentrations are higher at the urban sites than suburban and rural sites. City sources, particularly traffic, fossil fuel utilization for residential heating and sometimes industry are the major emitters of PM and their influence decreases with distance from city.

PM concentrations measured around the world are given in Table 2.1. The characteristics of sampling locations are also shown to indicate the effects of level of industrialization and development. Table 2.1 clearly shows that PM and elemental concentrations in the air were much higher in developing countries than developed countries. Yet, some industrialized cities such as Milan and Thessaloniki are polluted in terms of PM and trace elements. It should be emphasized that the degree of success in controlling PM significantly determines the level of ambient air concentrations of PM and trace elements in an area.

Table 2.1 PM and elemental concentrations measured around the world (PM and elemental concentrations are µg m^{-3} and ng m^{-3}, respectively)

Site	Area	Size	Con.,	Cd	Cr	Cu	Ni	Pb	Zn	Reference
Georgia USA	Urban	$PM_{2.5}$	17	-	-	3	-	5	22	Liu et al., 2005
Barcelona Spain	Urban	$PM_{2.5}$	35	-	6	52	6	130	178	Querol et al., 2001
		PM_{10}	50	-	6	74	7	149	250	
Milan Italy	Urban	$PM_{2.5}$	60	-	5	20	5	135	115	Marcazzan et al., 2001
		PM_{10}	85	-	20	65	8	250	210	
Thessaloniki Greece	Urban	$PM_{2.5}$	127	0.9	4.8	168	17	127	521	Manoli et al., 2002
		PM_{10}	107	1.0	7.7	258	23	156	545	
Beijing China	Urban	$PM_{2.5}$	100	3.7	20	40	60	110	320	Sun et al., 2004
		PM_{10}	180	2.4	40	50	40	110	330	
Istanbul Turkey	Suburban	$PM_{2.5}$	21	-	-	-	-	-	-	Karaca et al., 2005
		PM_{10}	47	-	-	-	-	-	-	
Ankara Turkey	Urban	$PM_{2.5}$	-	0.1	3.2	-	3.1	71	16	Yatin et al., 2000
Izmir Turkey	Urban-Industrial	PM_{10}	86	2	52	94	28	98	466	Yatkin et al., 2005
Izmir Turkey	Suburban	TSP*	-	8	11	154	39	111	733	Odabasi et al., 2002

TSP: Total suspended particulates
- : Not reported
Con.: Concentration

Previously, two studies were performed in Izmir: Yatkin et al. (2005) and Odabasi et al. (2002) that measured PM_{10} and TSP, respectively. The results showed that PM and elemental (i.e., Cd, Cu and Zn) concentrations at an urban and a suburban site were mostly higher than other cities except Beijing, Thessaloniki and Milan. Comparison with Ankara indicates that the elemental concentrations in Izmir were much higher than Ankara, which may be attributed to industrial characteristics of Izmir. Comparison with other resembling cities in terms of climate and level of industrialization such as Barcelona and Thessaloniki shows that PM and elemental concentrations in Izmir are higher (Barcelona) or comparable (Thessaloniki).

2.5 Source Apportionment

2.5.1 Methods

Identification of emission sources is critical to develop appropriate control strategies. Since the measurements of PM and elemental concentrations are difficult and expensive, modeling studies are generally preferred for source apportionment. Receptor models that are based on the chemical composition of PM at receptor sites are widely used for this purpose. Chemical composition of PM at receptor sites is mainly determined by the major sources, and a detailed knowledge of the chemical profile of source emissions is needed to determine the sources. This approach is the basis of the receptor models (USEPA, 2006f; USEPA, 2006g). Although knowledge regarding source profiles can be obtained from all around the world, characterization of local sources is highly recommended for modeling purposes.

Factor analysis (FA), Positive Matrix Factorization (PMF) and Chemical Mass Balance (CMB) model are the most common tools used for source apportionment. Details of these tools will be explained in the next chapter.

2.5.2 Previous Studies

Results of several studies on source apportionment of PM are given in Table 2.2. Five studies were performed using FA, PMF and CMB at different places around the world are selected and discussed. The cities were chosen to represent the differences of geographical location, population density, industrial capacity, etc.

Factor analysis and PMF are among receptor models that use chemical profile of PM at receptor sites. The most significant advantage of FA and PMF is that these models do not require a thorough knowledge regarding source profiles; instead, the literature knowledge can be used to identify the sources. However, studies on the source profiles all around the world clearly show that there are significant differences between profiles (Watson & Chow, 2001; Watson, Chow & Houck, 2001; Ho, Lee, Chow & Watson, 2003; Chow et al., 2004). The differences will be discussed in Section 4.4 in detail. Especially, soil, coal and traffic profiles differ significantly from place to place. Using literature data to interpret the factors may be a source of error. The factor results are generally need interpretation by the user; therefore, subjective factors may affect the results. Another significant point regarding FA and PMF is about the measured species. There are several fingerprint elements for different sources such as V and Ni for coal combustion, Se for coal combustion, K for biomass burning, and Na for marine particles. So, species to be measured should be selected by taking possible sources into consideration. In case of inadequate data at a receptor site including appropriate number of samples and species, the sources may not be distinguished using FA or PMF. Cheng et al. (2000) could not distinguish some factors, and reported the source as the mixture of several sources (Table 2.2). To avoid this, the number of samples and species should be appropriate and adequate. On the other hand, FA and PMF are faster tools than CMB, because these are run with whole data set whereas CMB is run sample by sample.

Table 2.2 Selected source apportionment studies from around the world by FA, PMF and CMB

Location	**Tool**	**Sources**	**Reference**
Beijing China	FA	Industry and motor vehicles, road dust, secondary, incineration/coal burning	Sun et al., 2004
Barcelona Spain	FA	Soil, secondary, marine, vehicular,	Querol et al., 2001
Huelva Spain	FA	Soil, marine, petrochemical sources, industry	Querol et al., 2002
Santiago Chile	FA	Transport, soil, oil combustion, As, Cl	Artaxo et al., 1999
Hong Kong China	FA	Marine, vehicle+fossil fuels+incineration+ nonferrous metal smelting, fossil fuel combus., soil	Cheng et al., 2000
Santiago Chile	PMF	Soil, oil combustion, transport, sulfates, copper	Hedberg et al., 2005
Georgia USA	PMF	Wood smoke, nitrate, coal combustion, sulfate, industry1, industry2, soil, vehicles	Liu et al., 2005
Dundee UK	PMF	Marine, soil, secondary PM, incinerator, fuel burning	Qin&Oduyemi, 2003
Beijing China	PMF	Biomass burning, secondary sulfate, secondary nitrate, coal combustion, industry, vehicles, soil	Song et al., 2006
Dhaka Bangladesh	PMF	Road dust, vehicle, construction, soil, marine	Begum et al, 2004
Thessaloniki Greece	CMB	Oil combustion, road dust, gasoline, diesel, construction, industry	Samara et al., 2003
Cairo Egypt	CMB	Road and agricultural dusts, vehicles, vegetative burning, oil combustion, lead smelter, secondary PM, marine	Abu-Allaban et al., 2002
Chicago USA	CMB	Soil, heavy duty diesel, unleaded light duty diesel, coke dust	Paode et al., 1999
W.Macedonia Greece	CMB	Fly ash, soil, gasoline, diesel, vegetative burning, refuse burning, sulfate, oil burning, coal burning	Samara, 2005
Mumbai India	CMB	Road dust, vehicles, marine, coal combustion, metal industries	Kumar et al., 2001

Chemical mass balance model, on the other hand, is generally independent from the subjective factors since data on receptor site and sources are the inputs of the model. It is also generally independent from the number of species and samples. However, the number of species should be adequate to avoid collinearity between the sources. Since performance criteria for CMB are extremely strict (USEPA, 2006f), the criteria may not be met in cases where literature data are used (Paode, Shanin, Sivadechathep, Holsen & Franek, 1999). So, it is highly recommended to characterize and use local source profiles for receptor models, particularly for CMB (Paode et al., 1999).

CHAPTER THREE
MATERIALS AND METHODS

3.1 Study Area

In this study, City of Izmir, the third largest city in Turkey with nearly 3 million inhabitants, was the study area. Izmir is located at the coast of Aegean Sea and surrounded by relatively high mountains (~500-1000 m). There are many industrial activities located in industrial zones such as Cigli Industrial Area (located on northwest of the city), Bornova (east), and Gaziemir Free Zone (south). There are two cement plants and many stone quarries that are important sources in terms of PM in District of Bornova. Izmir is also surrounded by several industrial towns and zones like Kemalpasa (east, ~20 km), Torbali (south, ~30 km), and Aliaga (north, ~40 km). Many industries are located in Aliaga like a petroleum refinery, a petrochemical complex, electric arc furnaces and rolling mills for iron-steel, and fertilizer plants etc.

The PM sampling was concurrently performed at two sites. The first site was at the sampling platform at Dokuz Eylul University Tinaztepe Campus (SUBURBAN) which is located at a suburban area, and the second one was in the city center, near a motorway (URBAN). The locations of stations are illustrated in Figure 3.1.

3.2 Sampling and Analysis

3.2.1 Ambient Air Sampling

The sampling period was between June 2004 and May 2005. The PM was collected by a dichotomous sampler (Rupprecht&Patashnick Inc., Partisol 2025, USA) at the SUBURBAN site. This device allows measuring PM_{10} and $PM_{2.5}$ at the same time. Teflon filters (Whatman Inc., USA) were used to collect PM at this station. This station was also equipped with meteorological sensors. PM sampler (Model PF 20630, Zambelli Inc., Italy) used at the URBAN site collects either PM_{10} or $PM_{2.5}$. Cellulose acetate (Sartorius AG, Germany) filters were used. Sampling height was about 5 m at both sites.

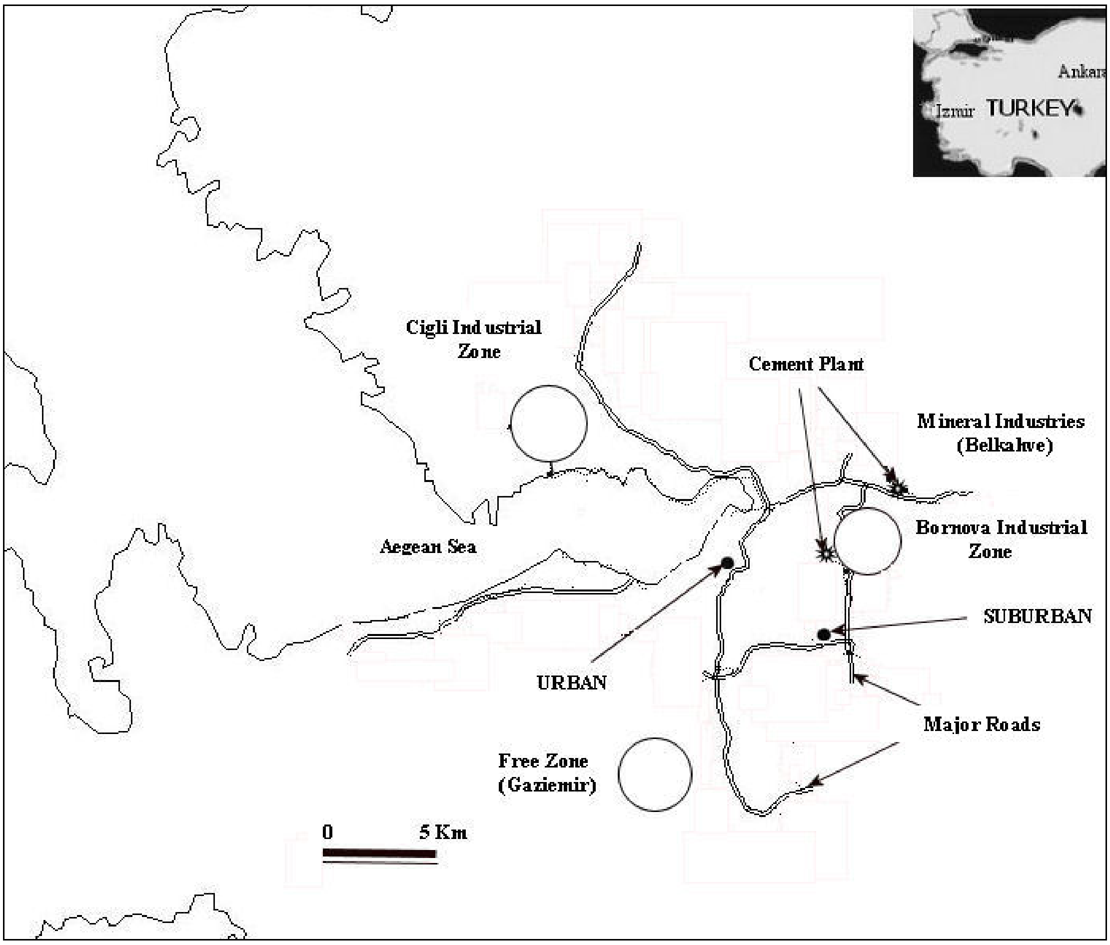


Figure 3.1. The locations of sampling site

Samples were collected every 6 days. Since the sampler at the URBAN site collects only one fraction at a time, samples were collected on two sequential days a week; first day PM_{10} and second day $PM_{2.5}$ was collected. During these two days, sampling was also performed at the SUBURBAN site. As a result, concurrent weekly data on PM fractions were obtained. Sampling duration was 24 h at both sites.

3.2.2 Source Sampling

Industrial Sources: Sampling at selected sources was performed using two devices. The first is an in-stack cyclone (Model PF20357/8, Zambelli Inc., Italy) that collects PM_{10} or $PM_{2.5}$ from the stacks. The design flow of the device was 14.2 l min^{-1}. Photograph of the cyclone is given in Figure 3.2. Many of stack samplings were performed using this device. However, this system is not suitable for temperatures >200 ^{0}C. So, the sampling of such sources was performed by taking deposits from dust control devices (i.e. cyclone, bag filters), then resuspending the collected material in a chamber. Finally, PM_{10} and $PM_{2.5}$ samples were collected in the chamber.

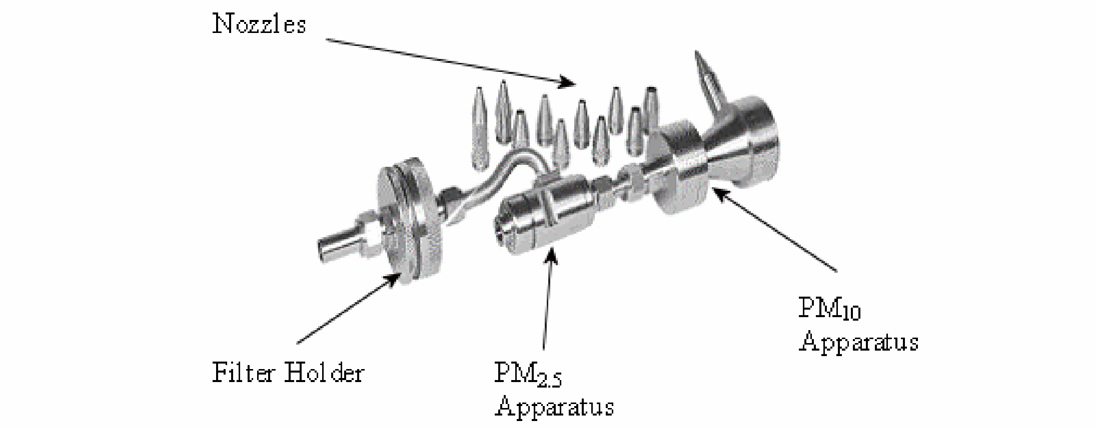


Figure 3.2. Photograph of the in-stack cyclone

Filtered air was used in the resuspension chamber to avoid contamination. After duration of an adequate time to ensure homogeneous dispersion in the chamber, the sampling apparatus was run, and PM samples were collected on filters. The resuspension device is illustrated in Figure 3.3.

Local Soil: To characterize the wind-blown dust from the ground, 29 surface soil samples were collected. These samples were taken from points with different characteristics such as urban areas near main roads, suburban areas, plains, mountains, coasts and farms. The locations of sampling points were chosen taking into account the resuspension potential, especially at areas with weak vegetation. Approximately the same amount of surface soil was collected from at least 20 points in each sampling area. Thus, a mixture of 20 points was obtained for each area. The soil samples were put into high-density polyethylene (HDPE) bottles after passing through plastic sieve (~1 mm mesh size). The samples were homogenized manually prior to resuspension and analysis. Soil samples were resuspended and PM samples were collected in the resuspension chamber.

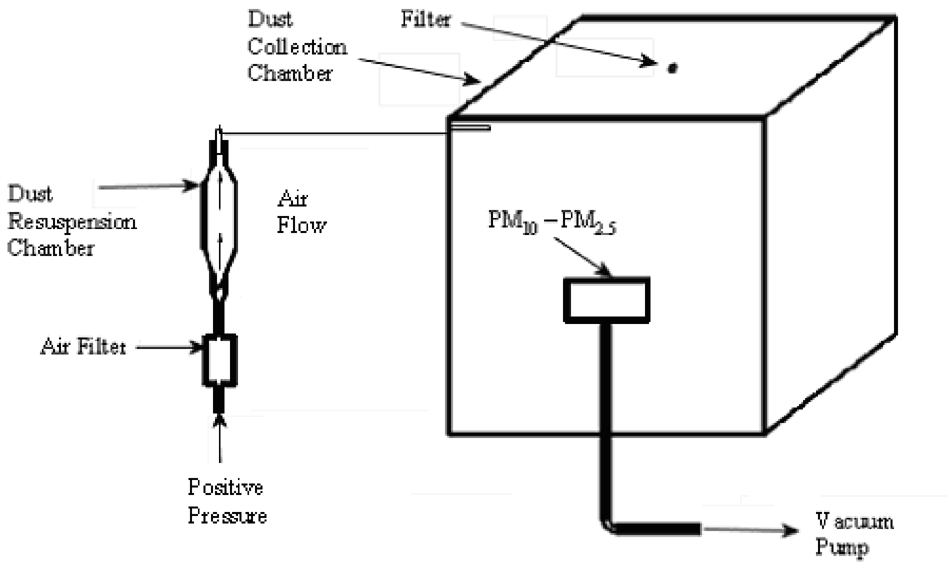


Figure 3.3. Schematic illustration of resuspension chamber

Soil samples have implications in terms of both atmospheric deposition and source characterization. Soil is one of the PM sources due to wind-blown dust; it, also, is a sink for particles through atmospheric deposition. Soil samples were handled in the scope of these two aspects. The soil samples were resuspended in the chamber; and then PM_{10} and $PM_{2.5}$ fractions of soils were collected and analyzed. These data were used for the source apportionment of the ambient air PM and trace elements. On the other hand, the elemental profiles of the top-soil were also determined to asses the pollution level of the soil and possibility of the pollution of the soil derived from man-made activities.

Marine Salt: One seawater sample was taken from Izmir Bay to characterize marine source. Subsequently, the sample was evaporated in a teflon beaker and the evaporation residue was extracted and analyzed.

Traffic: To characterize traffic source, PM_{10} and $PM_{2.5}$ samplings were performed concurrently at a street canyon (Sirinyer junction) between 17.00 and 19.30 during 5-work-day campaign using Zambelli PF 20630 samplers. The elemental composition of traffic source was calculated as the average of these five samples.

Mineral Industries (Belkahve): Belkahve is an area source that encloses limekilns, an asphalt plant, stone quarries and concrete plants. These samples were collected by Zambelli PF 20630 sampler, at ground level (2 m) when wind was blowing from the north to minimize interferences from other sources, since a forest is located at the north side of this area. The sampling was performed at the south of the area to ensure maximum mixture of PM emitted from several sources of the area.

3.3 Chemical Analysis

3.3.1 Extraction Procedure

Extraction of the filters used in ambient air measurements, source measurements, and the top-soils was carried out by hot acid digestion procedure. Hot acid digestion procedure has been commonly used previously (Cook et al., 1996; Gao et al., 2002; Sastre et al., 2002). The filters were placed into HDPE bottles and 5 ml of acid solution (1:3 HNO_3:HCl, Merck Suprapure, Germany) was added. After shaking overnight at room temperature at 250 rpm, 5 ml of 5 times water-diluted acid solution was added and the digests were heated at nearly $100^{\circ}C$, at least for 4 hours. Then the volume of the extracts was adjusted to their final volume using same water-diluted acid solution.

The soil samples were dried in the oven at 60 °C, for 48 h for elemental analysis (Guvenc, Alagha & Tuncel, 2003). Fifty milligrams of the soil were placed into HDPE bottles and 5 ml acid solution (1:3 HNO_3:HCl) and 1 ml HF (Merck) were added. The soil-acid solutions were kept for an overnight, and then digests were heated at nearly 100°C, at least for 4 hours. Repeated additions of HNO_3 were applied to ensure the complete evaporation of HF. Then the volume of the extracts was adjusted to their final volume adding water-diluted acid solution.

3.3.2 Analytical Procedure

Concentrations of Al, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, V and Zn in ambient air and source samples were determined using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) (Perkin Elmer Inc., Optima 2100 DV, USA). In addition, Co and Si were also determined in the top-soil samples. ICP technique is based on creating a plasma (argon flow affected by a magnetic field) to supply the excitation or/and ionization of elements. In this technique, the sample is subjected to very high temperatures, and thus, not only the excitation, but also the ionization of elements can be achieved. OES technology is based on element-specific rays that are radiated while the excited electron returns to the ground state orbital (Boss & Fredeen, n.d.). Two methods can be applied to determine and measure the emissions, i.e., axial and radial states, and thus, elemental concentrations in an ICP-OES instrument. Axial state measures rays along plasma length (~10 cm), whereas radial state measures rays from a split (~0.5 cm) that is located at the right angle of the plasma. Thus, axial reading is much more sensitive than the radial. In this study, concentrations of Ca and Na were determined by radial reading and other elements were read with axial state, because concentrations of the former two were high. All of the analyses were performed drawing 5-point calibration curves for each element, and all readings were repeated twice. The instrumental detection limits of ICP-OES for the elements of interest were 10 (Al), 1 (Ba), 50 (Ca), 1 (Cd), 5 (Cr), 5

(Cu), 50 (Fe), 50 (K), 25 (Mg), 1 (Mn), 50 (Na), 5 (Ni), 10 (Pb), 1 (Sr), 2 (V) and 25 (Zn) µg L^{-1}.

3.4 Quality Assurance/Quality Control

3.4.1 Ambient Air and Source Sampling

The design flow for the Partisol 2025 sampler was 16.67 l min^{-1} and the instrument was equipped with a virtual impactor that splits the main flow into two. The system was capable of cutting the flow and stopping the sampling in case the deviation of the flow was >5% from the design flow continuously for 5 minutes. However, during our sampling campaign such a case did not occur. Leakage tests were carried out monthly to control the leakage along the sampling line. Periodic maintenance and cleaning procedures were applied as described in user manual of the device.

The Zambelli PF 20630 sampler that was also designed for flow of 16.67 l min^{-1} was used with a flow controlled pump. The desired suction rate was adjusted and, a 10% deviation tolerance from this flow was set. In case, a deviation >10% would continue for more than 5 minutes, sampling was automatically stopped. Leak tests were performed manually before each sampling. Periodic maintenance and cleaning were carried out according to the user manual.

In-stack cyclone was designed for a suction flow of 14.2 l min^{-1}. A flow controlled pump was set for the above flow rate, and used to collect samples from stacks. The sampling time was at least 30 minutes. However, in some stacks, such as those with the olive oil residuals (pirina) burning boilers, the filters were plugged and this sampling time could not be achieved. The device was cleaned after each use using de-ionized water and then dried in an oven. The cyclone was kept in its container until the next use to avoid contamination.

The deposits from PM control devices were collected by pre-washed and dried plastic shovel and sieve, and stored in HDPE bottles until delivered into the resuspension chamber. Plastics, cleaned with the same procedure, were used to collect surface soils. The deposits and soils were resuspended in the chamber. The same sampling device and pump that were used for ambient air sampling (Zambelli PF 20630) were employed in the chamber. The resuspension inlet flow was filtered to prevent probable contamination from the supply air. Similarly, the hole of pressure discharge was also equipped with a filter. After each run, the chamber was cleaned by a vacuum cleaner and then washed 3 times by de-ionized water. The chamber was kept closed between the samplings to avoid contamination.

3.4.2 Gravimetric Analysis

The filters were initially weighed using a microbalance (Mettler-Toledo AG, Switzerland) capable of weighing 2 µg, after being left in an oven at 105°C for two hours, and then cooled in a desiccator for an hour. The microbalance was switched on at least 1 hour before weighing. Prior to weighing, internal calibration and external calibration by a certified weight was performed. This procedure was also applied to the filters after sampling. To determine the blank levels for sampling and weighing procedures, three filters from each batch were exposed to the same sampling and weighing steps. Average of the blank values were used for correcting the readings from the balance.

3.4.3 Extraction

All the HDPE bottles and plastic petri dishes that were used for digestion and transportation of the filters were initially kept in acid solution (HNO_3, 10%) at least for 24 h, and then rinsed in triplicate with Type I de-ionized water. Suprapure Grade (Merck, Germany) nitric and hydrochloric acids were used for digestion.

Three aliquots of Urban Particulate Matter (SRM 1648) from NIST (National Institute of Standards and Technology) were extracted and analyzed along with the samples to determine recovery efficiencies of the extraction procedure for the filters. Percent recovery efficiencies were between 70-110% except for Al, K and Cr. The average recoveries of these elements were 42%, 52% and 30%, respectively. The relatively low recoveries of Al and Cr were probably due to their presence in silicate matrices that is difficult to extract (Paode et al., 1999). The recovery efficiency of Ca could not be determined since no certified value is available for this element. Ten blanks were prepared and analyzed for each filter type. Method detection limits (MDLs) were determined by adding 3 standard deviations of the blank readings to the average blank values. All concentrations measured at the URBAN site were higher than the MDLs. However, some elements (Cd, Cr and Ni) were below the MDLs at the SUBURBAN site in a few samples.

The recovery efficiency of the extraction procedure of the top-soil was calculated by three aliquots of SRM 1648. The percent recovery efficiencies of all elements were > 70%.

3.4.4 Instrumental Analysis

The ICP-OES was calibrated daily using a certified standard solution. The analysis of samples was performed only if the r^2 of calibration curve was greater than 0.99. A calibration check solution was prepared using another certified solution and the calibration curves were checked just after the initial calibration and after every 15 samples. If the deviation was more than ±10 %, the instrument was re-calibrated.

The repeatability of the ICP-OES was controlled analyzing some samples, recovery aliquots and calibration check solution. The deviation was less than 10%.

The comparative test of The Scientific and Technical Research Council of Turkey-National Metrology Institute (TUBITAK-UME) was run two times for 7 elements (Cd, Cr, Cu, Fe, Ni, Pb and Zn). These tests were passes twice.

The daily and periodic maintenance programs were followed for the ICP-OES instrument. The sample transfer line, apparatus and optical parts were periodically cleaned as explained in the user manual.

3.5 Calculations

3.5.1 Calculation of Ambient Air PM Concentrations

Ambient air PM concentrations at the SUBURBAN site was calculated using the following equations. These equations were given within user manual of Partisol 2025.

$$C_f = m_f / V_f \tag{3.1}$$

$$C_c = \left[m_c / V_t\right] - \left[(V_c / V_t) C_f\right] \tag{3.2}$$

$$C_t = C_f + C_c \tag{3.3}$$

where;

C_f = Concentration of fine PM ($PM_{2.5}$), µg m^{-3}

C_c = Concentration of coarse PM (PM_{10}-$PM_{2.5}$), µg m^{-3}

C_t = Concentration of PM_{10}, µg m^{-3}

m_f = Mass of fine PM (the difference between final and tare weighing), µg

m_c = Mass of coarse PM (the difference between final and tare weighing), µg

V_f = Volume of air vacuumed through fine PM fraction filter, m^3

V_c = Volume of air vacuumed through coarse PM fraction filter, m^3

V_t = Volume of air vacuumed through both fine and coarse PM fraction filter, m^3

PM concentrations at the URBAN site were calculated by the following equation;

$$C = m/V \tag{3.4}$$

where;

C = PM concentration, μg m^{-3}

m = Mass of PM (m_{final}-m_{tare}), μg

V = Vacuumed air volume, m^3

3.5.2 Calculation of Elemental Concentrations

Ambient air elemental concentrations at the SUBURBAN site were calculated by equations 3.1, 3.2 and 3.3. The masses of elements were used instead of PM to calculate the elemental concentrations in these equations. The mass of element was calculated by the following equation:

$$m_{element} = \left[(C_{sample} . v_{sample}) - (C_{blank} . v_{blank})\right]10^3 \tag{3.5}$$

where;

$m_{element}$ = Mass of element, ng

C_{sample} = Concentrations of element in sample aliquot, μg l^{-1}

C_{blank} = Concentrations of elements in blank aliquot, μg l^{-1}

$v_{sample, blank}$ = Volume of sample/blank, l

10^3 = Conversion factor between μg and ng

Ambient elemental concentrations of the URBAN site were calculated by equation 3.4 where the masses of elements were obtained by using equation 3.5.

3.5.3 Calculation of Elemental Fractions of Sources

As will be explained in Chapter 3.6, CMB model needs elemental fractions ($F_{element}$) for each source as input data. The required elemental fractions were calculated by the following equation:

$$F_{element} = m_{element} / m_{PM} \tag{3.6}$$

where;

$F_{element}$ = Fraction of elements, µg µg^{-1}

$m_{element}$ = Mass of elements, µg

m_{PM} = Mass of PM_{10} or $PM_{2.5}$, µg

Masses of elements were calculated by equation 3.5. Masses of PM were calculated from the difference between final and tare weights. Elemental content of the top-soils were also calculated using equation 3.6.

3.5.4 Calculation of Uncertainties

Uncertainty levels in ambient air concentrations and elemental fractions of sources are entered to CMB model as input data. The uncertainties were calculated by the following equation:

$$U_c = C\left[\sum_{i=1}^{n}(U_i / X_i)^2)\right]^{0.5} \tag{3.7}$$

where;

U_c = Uncertainty of measured concentration, with the same unit of C

C = Measured value, µg m^{-3} for PM and elemental concentrations, and unitless for elemental fractions

U_i = Standard uncertainty value for each component

X_i = Measured value of each component

It should be noted that the U_i and X_i values must have the same units. Then, U_i/X_i term in the equation will be dimensionless.

For ambient air PM concentrations, air volume passed through the filter and filter weights (tare and final) were the components of uncertainty. The uncertainties for air volume of Partisol 2025 and Zambelli PF 20630 were 0.42% and 3%, respectively. These values were declared by the manufacturers. The uncertainty of the calibrated microbalance was ±80 µg. For the uncertainty of PM collected from the sources, equation 3.7 was used. However, air volume component was not taken into consideration, as the concentrations in the air were not determined.

The uncertainties in elemental concentrations were calculated by equation 3.7. Sampled air volume, volume of the aliquot and repeatability of ICP-OES instrument were used as the components in uncertainty calculations. Uncertainties in drawing the calibration curves were not taken into consideration. A calibrated pipette was used to control the final volume of the aliquots. The uncertainty of this pipette was ± 0.03 ml. After the elemental analysis of samples and repetitive determinations, the repeatability of ICP-OES was found to be around 1% for Al, Ba, Ca, Fe, K, Mg, Mn, Na, Sr, V and Zn, and around 10 % for Cd, Cr, Cu, Ni and Pb. Concentrations of the first group were high at the two sampling sites, therefore, their repeatability were very good. However, concentrations of the second group were low, particularly at the SUBURBAN site. Thus, repeatability was less (~10%). The repeatability values were used as 1% for the first group and 10% for the second group. Equation 3.7 was used for determination of elemental mass in order to calculate the fractions of elements emitted in the PM from the sources.

3.6 Data Analysis

Back Trajectory Analysis was used to determine the route of PM plume during the sampling days. Statistical methods (i.e. correlation matrix, factor analysis) and models (CMB and PMF) were used to determine the sources of PM and the degree of their contribution.

3.6.1 Correlation Matrix and Factor Analysis

Correlation matrix is a way of representing the dependence between variables. When the relation among variables is linear, it is possible to denote their correlation by the coefficient r (Berthouex & Finfield, 2002). STATISTICA v 5.0 was used to determine the correlation coefficients r.

FA is a statistical method that determines the factors affecting the changes in variables. FA is a data reduction method that converts dependent data into new, independent and lesser data structure, and also determines and groups the factors that explain these changes (Ozdamar, 2004a). FA method is widely used worldwide to determine sources of PM. Some of the studies involving this method are cited in Table 2.2. SPSS v.13 was used for FA analysis. Principle component analysis with Varimax rotation was applied and the factors with eigen value greater than 1 were taken into consideration.

3.6.2 Positive Matrix Factorization

Positive Matrix Factorization is a receptor model used in source apportionment studies. Recently, it became popular for the source apportionment of PM and volatile organic matter all around the world (see Table 2.2).

Generally receptor models are based on the solving the problem stated by equation 3.8 (Kim et al, 2003).

$$C_{ij} = \sum_{k=1}^{p} g_{ik} . f_{kj} + e_{ij} \tag{3.8}$$

where;

C_{ij} = Concentration of *j*th species measured in *i*th sample

g_{ik} = PM mass concentration from the *k*th source contributing to *i*th sample

f_{kj} = Mass fraction of the *j*th species from the *k*th source

e_{ij} = Residual associated with *j*th species concentration measured in the *i*th sample

p = Number of independent sources

The corresponding matrix equation in order to solve the equation 3.8 is

$$\mathrm{X} = \mathrm{G.F} + \mathrm{E} \tag{3.9}$$

where;

X = $n * m$ matrix with n measurements and m number of species

G = $n * p$ source contribution matrix

F = $p * m$ source profile matrix

E = $n * m$ matrix of residual

Since the possibility of rotation of G and F matrixes may increase infinitely the number of possible solutions of factor analysis problem, PMF uses non-negativity constraints on the factors in order to decrease this rotational freedom (Kim et al., 2003). An object function, Q(E), is described and must be minimized to get the appropriate solution. This function is as follows:

$$Q = \sum_{i=1}^{p} \sum_{j=1}^{m} \left[\frac{C_{ij} - \sum_{k=1}^{p} g_{ik} \cdot f_{kj}}{u_{ij}} \right]^2 \tag{3.10}$$

where;

u_{ij} = Uncertainty estimate in the *j*th element measured in the *i*th sample.

The minimization of Q(E) is achieved iteratively as a weighed linear least squares problem (Kim et al., 2003). The details of PMF can be found elsewhere (Kim et al., 2003; Begum, Kim, Biswas & Hopke; 2004; Qin & Oduyemi, 2004; Kim, Hopke & Edgerton; 2004).

The latest version of PMF as supplied by USEPA (EPA PMF v 1.1) was used in this study for source apportionment. The PMF needs two files as input data, species concentrations at receptor site with date (optional), and uncertainties of these measurements. Factor numbers are selected and the model is run. In order to get physically meaningful results, Q(E) must be minimized and matrices must be converged. Theoretically, Q(E) is equal to the dimension of input data (m*n; m being the number of samples; n being the number of species). When the minimum Q(E) is obtained, model results are given as the profile of each factor and contribution of each factor to each measured (daily, hourly etc.) PM concentration. The contributions are given as normalized values to average contribution that is 1. The details of model are given in the user manual of PMF v.1.1 (USEPA, 2006g)

The sources were selected according to the percentages of different species in the factors. The results given in the source contribution file were regressed with measured PM concentrations. Then, the coefficients of multiple linear regressions were multiplied by the coefficients of related factor score. This process was applied to remove the normalization. Thus, daily contribution amounts of each factor were obtained.

3.6.3 Chemical Mass Balance (CMB) Model

The CMB model is an air quality model, which is to be classified among receptor models applied in air quality management. Receptor models use data obtained from both the sources and the ambient air measurements (receptor) and also include data on physical and chemical characteristics of gases and particles. They are used to identify and quantify source contributions to receptor concentrations (USEPA, 2006f). The CMB model is a solution to the set of linear equations that express each receptor chemical concentration as a linear sum of the contributions of different sources (USEPA, 2006f). The source characteristics (i.e. the mass fractions of a chemical), receptor concentrations, and appropriate uncertainty estimates, are the input data of the CMB model, and it calculates the contribution values of each source type with their uncertainties (USEPA, 2006f).

The CMB consists of the following set of equations:

$$C = \sum_{j=1}^{j} D_j . E_j = \sum_{j=1}^{j} S_j \tag{3.11}$$

where;

C = Concentration of PM during a sampling period of length T

D_j = Dispersion factor depending on wind velocity, atmospheric stability and location of source j with respect to receptor site

E_j = Constant emission rate of source j

S_j = Estimate of the contribution of source j

The advantage of the receptor models is that they do not need exact knowledge regarding D_j. Similar to Equation 3.11, the concentration of elemental component i will be calculated as following:

$$C_i = \sum_{i,j=1}^{i,j} F_{ij} . S_j \tag{3.12}$$

where;

C_i = Concentration of species i measured at a receptor site

F_{ij} = Fraction of species i in emissions from source j

S_j = Estimate of the contribution of source j

i = Number of chemical species

j = Number of source types

These equations have a unique solution only when the number of species is equal to or greater than the number of sources.

The CMB modeling procedure requires: 1) identification of each source type; 2) selection of chemical species for calculation; 3) estimation of the fractions of all chemical species in each source types; 4) estimation of uncertainties of both receptor concentrations and source profiles; and 5) solution of the mass balance equations.

Although many methods have been proposed for the solution of CMB equations by several scientists, the effective variance weighed least squares method by Watson is accepted the best, and generally applied (USEPA, 2006f). The CMB model assumptions are: 1) source profiles are constant during source and ambient sampling; 2) there is no interaction between species; 3) all potential contributing sources of selected species have been identified and their emissions have been characterized; 4) the number of sources is less than or equal to the number of species; 5) the source profiles are linearly independent of each other; and 6) measurement uncertainties are random, uncorrelated and normally distributed.

As these six assumptions are fairly restrictive, they will never be entirely complied within the actual practice. The CMB model can tolerate the deviations from these assumptions, however; as a result, the uncertainties of the CMB model outputs increase (USEPA, 2006f).

The CMB model gives two calculations as the output the contribution amounts of each source, and uncertainties of these amounts. The CMB model helps to explain the receptor measurements but it does not predict ambient impacts of the sources like dispersion models (USEPA, 2006f).

The performance of CMB run is controlled by four parameters: The T-statistics (TSTAT) represents the ratio of the source contribution estimate to the standard error, and should be >2.0 (USEPA, 2006f). The correlation coefficient (R^2) is described as “the fraction of the variance in the measured concentrations that is explained by the variance calculated in the concentrations of species” in the user manual of CMB v.8.2 (USEPA, 2006f). Correlation coefficient should be >0.8 for an adequate result. Chi-square (X^2, should be < 4) is the weighed sum of squares of differences between estimated and measured fitting species concentrations. Percent mass is the percent value of predicted/measured mass concentration (should be between 80 and 120%). The details of the above-mentioned parameters can be found in the user manual of CMB v.8.2 (USEPA, 2006f). It should be indicated that CMB cannot be used with missing data. So, the elemental concentrations below the MDL were replaced by half of the MDL values.

CHAPTER FOUR
RESULTS and DISCUSSION

In this chapter, the temporal and spatial variation of PM/elemental concentrations, the effect of meteorological factors at two the sites is evaluated. Results of statistical analysis (correlation matrix and FA), PMF and CMB are also discussed.

4.1. Experimental Results

In this section, the results of ambient air measurements, the source measurements and the elemental content of the top-soils are given.

4.1.1 PM_{10} and $PM_{2.5}$ Concentrations

4.1.1.1 Seasonal Variation in PM Concentrations

The seasonal concentrations of PM at the two sites are summarized in Table 4.1. The results clearly show that the PM concentrations at the SUBURBAN site in summer are higher than in winter; on the other hand, the situation at the URBAN site is completely the opposite. Shapiro-Wilk W test was applied to check normality of PM concentration distributions according to the seasons and prevalent wind directions. This test checks the normality with W statistics, which varies between 0 and 1. The closeness to 1 indicates that distribution is normal (Ozdamar, 2004b). The test results clearly show that the seasonal distributions and distributions with respect to the prevalent wind directions of PM concentrations were normal at the two sites, as W statistics varied between 0.85 and 0.96. T-tests were run to check whether different samples were coming from the same population or not. The p value of 0.05 was used to indicate the significance statistically.

The results of t-test analyses show that seasonal variations of PM_{10} and $PM_{2.5}$ is significant at the SUBURBAN site. Reason for high concentrations at the

SUBURBAN site in summer might be the influence of re-suspension of surface soil dusts as this station is surrounded by an area that has weak vegetation, and the soil was dry during summer season. In contrast, higher concentrations at the URBAN site are expected in winter, since the urban location most probably affected by fuel burning for residential heating, traffic, and other urban sources.

Table 4.1. Descriptive statistics of seasonal PM concentrations (µg m^{-3})

		Summer				**Winter**			
Station	**Fraction**	**n**	**Mean(SD)**	**Min**	**Max**	**n**	**Mean(SD)**	**Min**	**Max**
SUBURBAN	PM_{10}	60	52.8 (18.4)	19.8	106.4	34	35.8(18.2)	10.0	79.1
	$PM_{2.5}$	60	26.5 (12.7)	7.0	69.6	34	19.9(9.9)	4.8	40.6
URBAN	PM_{10}	30	75.8(24.7)	17.9	133.8	20	91.7(35.8)	46.6	176.3
	$PM_{2.5}$	30	52.5(21.9)	15.1	98.2	20	78.6(54.7)	22.0	224.3

n : Numbers of samples

SD: Standard deviation

The Turkish regulation (The Environment and Forest Ministry-The Regulation for Protection of the Ambient Air Quality, 1986) lists two standards for PM_{10} concentration, but no standard for $PM_{2.5}$. The PM_{10} standard is for daily and annual mean concentrations as 300 and 150 µg m^{-3}, respectively. All the concentrations were lower than these standards at the two sites. However, the European Standard of 50 µg m^{-3} was exceeded at the two sites in all seasons except the SUBURBAN in winter. Similarly, $PM_{2.5}$ concentrations exceeded the European Standard that is 15 µg m^{-3}, in summer and winter at the two sites.

4.1.1.2 The Effect of Meteorological Factors

The effect of meteorological factors (wind direction, wind velocity and precipitation) on PM concentrations is discussed in this section. The SUBURBAN station was equipped with meteorological sensors. The distance between the URBAN and SUBURBAN sites is approximately 8 km. Besides, the topography around the URBAN site differs significantly from the SUBURBAN site. Yet, to have an idea regarding the relations between PM concentrations and meteorological factors, the data obtained from the SUBURBAN site were used for the URBAN site, as well.

The box and whisker plots regarding prevalent wind directions and PM concentrations of the two sites are illustrated in Figure 4.1. Since, the SUBURBAN site is located at the southerly-southeasterly direction of the City of Izmir; it would be reasonable to observe a significant relation between wind direction and PM concentrations. Mainly three directions were observed during sampling periods, which were northerly (N), northwesterly (NW) and southeasterly (SE). In case of N and NW winds, the particles emitted from the urban sources are transported towards the SUBURBAN site. On the other hand, SE winds would bring pollution from the Torbali region located at the southeast of the SUBURBAN site where intense agricultural and industrial activities exist. Torbali has an industrial zone that is approximately 20 km away from the SUBURBAN site. As the result of this situation, high concentrations were measured in case of N direction at the SUBURBAN site. The $PM_{2.5}$ concentrations seemed to decrease in case of SE direction, which is meaningful because of the city location. The concentrations measured in case of N, NW and SE directions were compared. T-test results clearly show that the decrease in $PM_{2.5}$ concentrations in case of SE wind at the SUBURBAN site is statistically significant. On the other hand, PM_{10} concentrations at the SUBURBAN site were different than $PM_{2.5}$. There was no significant difference between N and SE directions. On the other hand, the PM_{10} concentrations increased significantly in case of NW direction at the SUBURBAN site.

On the other hand, the URBAN site was located in the city center, and influenced by several urban sources such as traffic, residential heating sources and industrial plants. As a result, $PM_{2.5}$ and PM_{10} concentrations may strongly be independent from the wind directions that t-test results support this expectation.

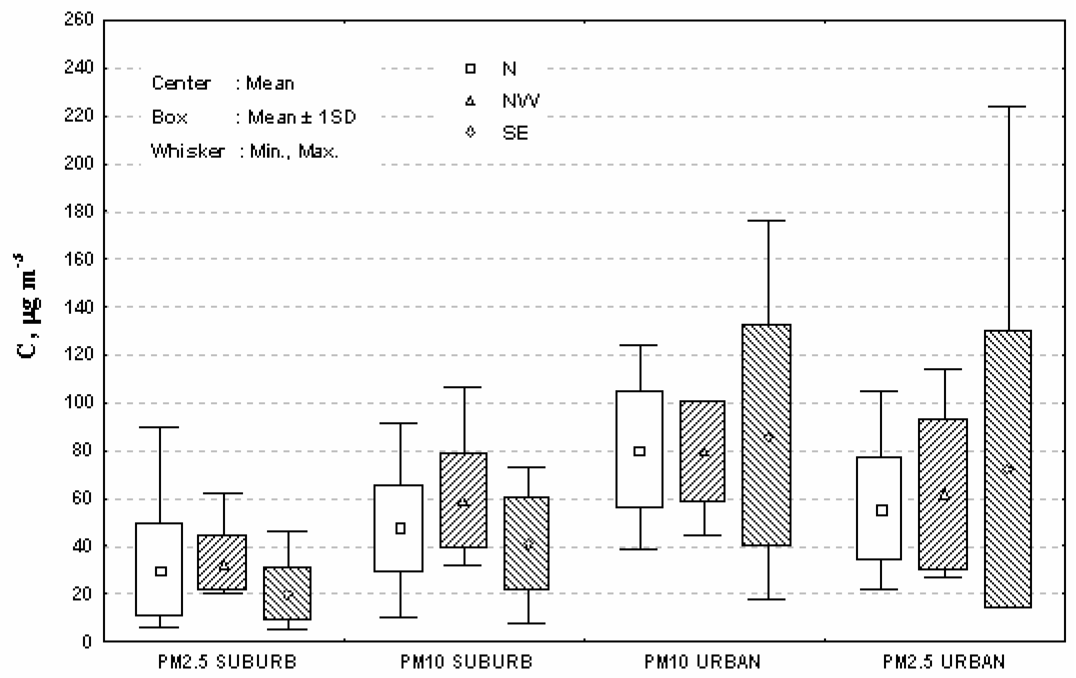


Figure 4.1 The box and whisker plot of PM concentrations according to the prevalent wind directions

Several researchers indicated that the wind velocity is one of the main mechanisms affecting the composition and life of PM in the atmosphere by long-range transport, mixing height and dilution effect (Harrison et al., 2001; Marcazzan, Vaccaro, Valli, and Vecchi, 2001; Chaloulakou, Kassomenos, Spyrellis, Demokritouc & Koutrakis, 2003; Kim, Kim, Hong, Youn and Hwang, 2005). High wind velocity may increase ambient air PM concentrations due to resuspension from surface soils. On the other hand, in case of calm weather conditions, the PM emitted from sources cannot be transported away. Especially, PM concentrations reach to very high levels in winter due to fossil fuel burning in cities (Chaloulakou et al, 2003). In order to evaluate the effect of wind velocity on PM concentrations in Izmir, the scatter plots of concentrations and velocity are given in Figure 4.2.

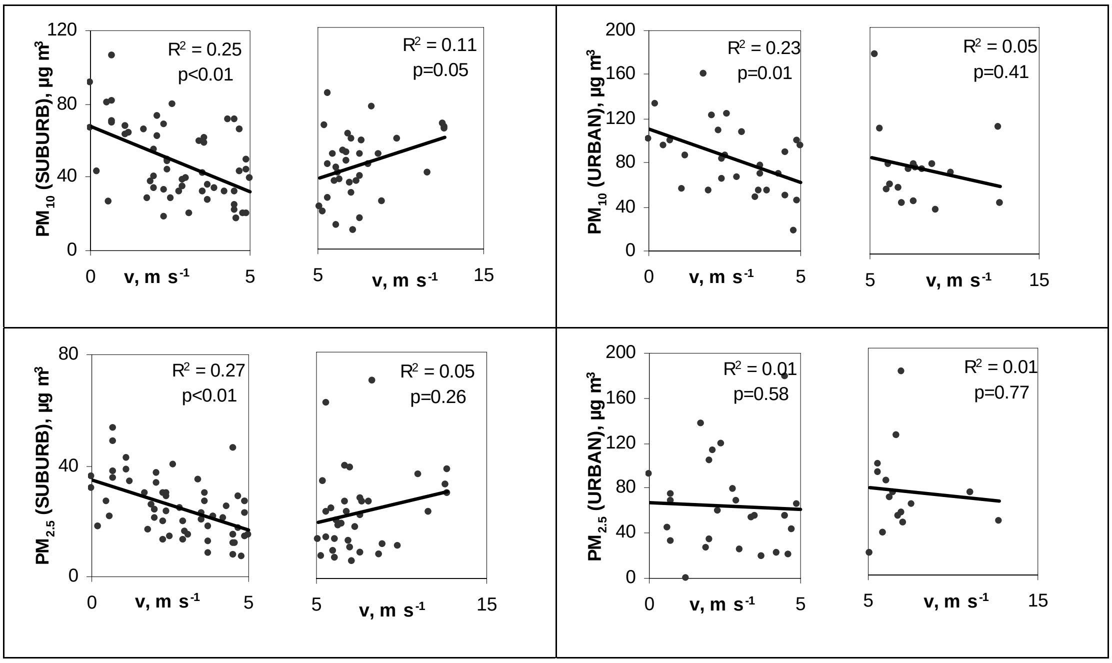


Figure 4.2 The scatter plots of concentrations and wind velocity at two sites

When Fig.4.2 is studied, it is noted that the relationship between PM and wind velocity is quite poor as R^2 values are low. Slight correlations (statistically significant relationships with R^2 values around 0.25 for three of the four regressions) exist at velocities below 5 m s^{-1} showing decreasing concentrations with increasing wind speeds. The concentration decrease in windy conditions may be attributed to the dilution effect. On the other hand, high wind velocities increase resuspension of PM from surface of soil as well as increase the effect of long-range transport (Harrison et al., 2001; Chaloulakou et al., 2003). For stronger winds (> 5 m s^{-1}), weak correlation with an increasing trend was obtained at the SUBURBAN site. This situation may be interpreted as the increased PM was possibly due to resuspension from the surface of the soil at the SUBURBAN site.

There is no statistically significant relationship between the wind velocity and PM concentrations at the URBAN site except PM_{10}. So, it may imply that the URBAN site is not significantly affected by the wind blown dusts.

Some sampling days were very calm with the daily average wind velocities of <1 m s^{-1}. Box and whisker plots were drawn (Figure 4.3) to evaluate the effect of such conditions on the PM concentrations. Since these calm days occurred in autumn just before the residential heating period, the concentration variation was compared to the data obtained in summer. It was clearly seen that calm conditions increased the PM concentrations notably at the two sites under summer conditions. This result is in parallel with the results of several other studies reported in the literature such as Marcazzan et al. (2001), and Chaloulakou et al. (2003).

Precipitation, also, affects the PM concentrations significantly. Decreasing concentrations are seen as the precipitation removes the PM from the atmosphere by wash-out, and also by eliminating the possibility of resuspension of PM from the soil surfaces and roads (Chaloulakou et al., 2003). In general, the precipitation in Izmir occurs during residential heating period. The influence of rain on PM can be seen in Figure 4.4. The figure shows that the PM concentrations at the two sampling sites were significantly decreased with precipitation with the exception of the $PM_{2.5}$ concentration at the URBAN site that increased in rainy days. This was mainly due to a very high (maximum) concentration of $PM_{2.5}$ (224.3 μg m^{-3}) measured on a rainy day. The mean concentration was reduced to 67.3 μg m^{-3} when the maximum concentration was omitted.

In this section, the effects of meteorological factors on the ambient air PM concentrations were evaluated. The data showed that the effect of meteorological factors is significant at the both sites, particularly at the SUBURBAN site. The most dramatic influence is observed in case of calm weather conditions at the both sites.

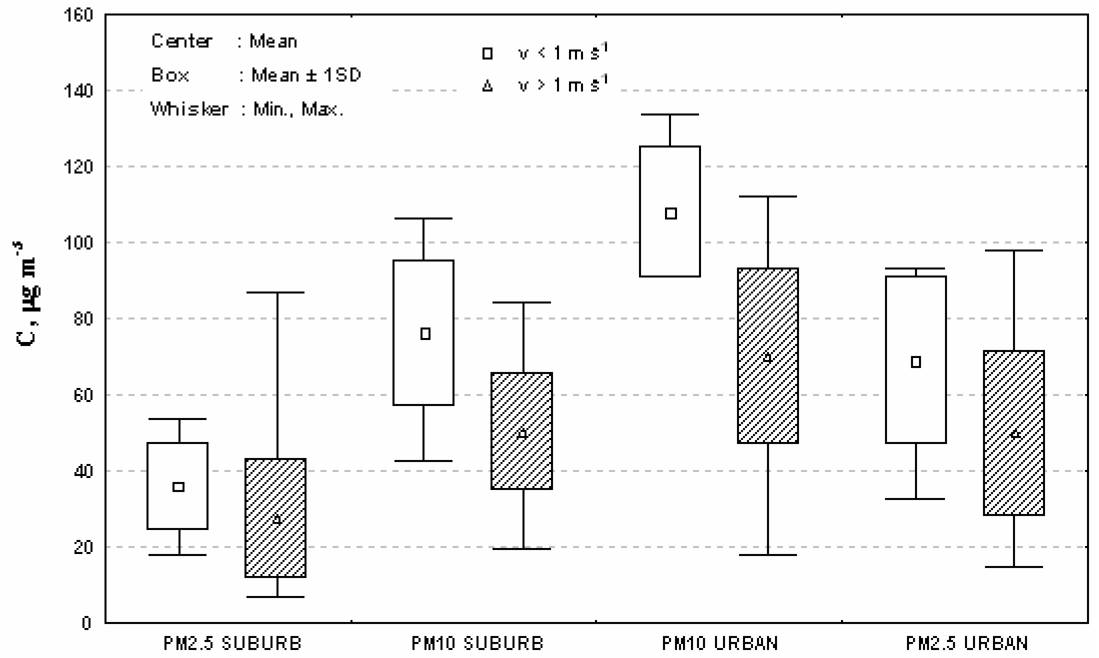


Figure 4.3. The PM concentrations (µg m^{-3}) in calm (v<1 m s^{-1}) and non-calm conditions.

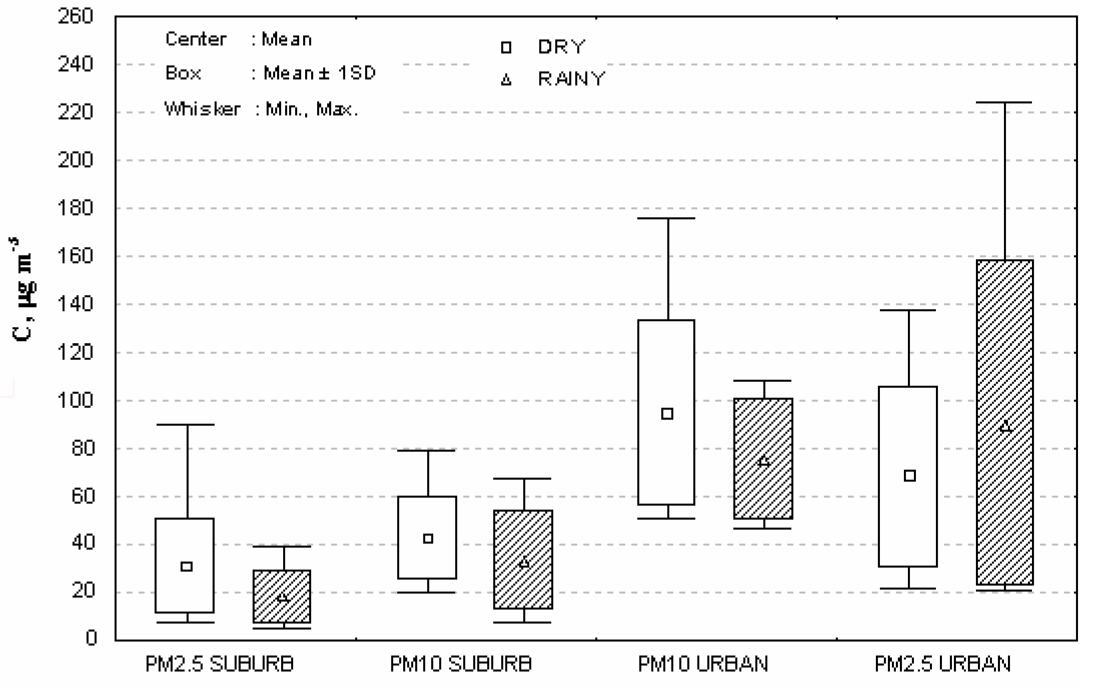


Figure 4.4. The PM concentrations (µg m^{-3}) measured in rainy and dry days in winter

4.1.1.3 Comparison of PM Concentrations at the Two Sites

As concurrent sampling was performed at the two sites, the daily PM concentrations measured at the URBAN and suburban sites could be compared. Ratio of urban to suburban concentrations for PM_{10} and $PM_{2.5}$ are listed in Table 4.2.

Table 4.2. The comparison of concurrent concentrations at two sites

	PM_{10}(URBAN)/PM_{10}(SUBURBAN)		**$PM_{2.5}$(URBAN)/$PM_{2.5}$(SUBURBAN)**	
	Winter	**Summer**	**Winter**	**Summer**
Min.	1.1	0.7	1.0	0.7
Max.	8.6	4.0	46.7	4.0
Mean	2.9	1.6	6.1	1.9
SD	1.9	0.7	10.7	0.9

As discussed in previous section, the summer concentrations were higher than the winter values at the SUBURBAN site, whilst the PM concentrations in winter were higher than the summer values at the URBAN site. Therefore, the ratios at the two sites in winter were much higher than in summer for both $PM_{2.5}$ and PM_{10}. From time to time, the concentrations measured at the SUBURBAN site were higher than at the URBAN site in summer. The maximum ratio occurred for $PM_{2.5}$ concentration in winter (46.7), which was much higher than the others because on the subject day maximum $PM_{2.5}$ concentration was measured at the URBAN site while the concurrent concentration at the SUBURBAN site was one of the lowest values.

4.1.1.4 The $PM_{2.5}/PM_{10}$ Ratio at the SUBURBAN Site

The $PM_{2.5}/PM_{10}$ ratios at the SUBURBAN site under different meteorological conditions are given in Table 4.3. As discussed previously, the $PM_{2.5}$ concentrations in winter were higher than in summer, indicating that PM transport from the city to the SUBURBAN site was more prominent during winter than summer, most probably due to residential heating emissions. However, decreased PM_{10} concentrations in winter might also indicate that the PM emitted from these sources consists of finer particles or alternatively, the fine particles could reach the SUBURBAN site. Also, because winter is the rainy season in Izmir, the effect of resuspension from soil and agricultural activities are significantly decreased due to wetted land in winter. So, the influence of City of Izmir on the concentrations of PM at the SUBURBAN site becomes more significant in winter.

The ratios were slightly increased in case of precipitation. When the wind blown from the city to the SUBURBAN site, which is northwesterly winds, the ratio increased both in summer and winter. The calm weather conditions did not seem to affect the ratio. However, when wind velocity was less than 5 m s^{-1}, the ratio was slightly increased. On the other hand, there is no significant relationship between wind velocity and ratio in winter.

Table 4.3 The $PM_{2.5}/PM_{10}$ percentages in different conditions

	Summer				**Winter**			
Case	**n**	**Mean (SD)**	**Min**	**Max**	**n**	**Mean (SD)**	**Min**	**Max**
Overall	60	49.5(14.1)	16.9	90.5	34	56.6(11.6)	30.9	81.4
Rainy	-	-	-	-	13	60.2(13.8)	30.9	81.4
Dry	-	-	-	-	21	54.4(9.6)	34.3	74.6
N	30	49.3(14.5)	19.8	90.5	16	54.1(9.7)	35.7	74.6
NW	13	53.5(11.0)	33.3	73.8	4	57.4(9.6)	46.4	68.3
SE	10	48.2(19.1)	16.9	67.7	11	54.7(14.8)	30.9	73.6
v<1 m s^{-1}	10	49.9(12.5)	33.3	70.6	-	-	-	-
v>1 m s^{-1}	50	49.5(14.5)	16.9	90.5	-	-	-	-
v<5 m s^{-1}	33	50.3(11.1)	33.3	76.3	26	57.1(12.3)	30.9	81.4
v>5 m s^{-1}	27	48.7(16.9)	16.9	90.5	8	57.4(6.7)	49.6	68.8

4.1.2 Elemental Concentrations

The elemental mean concentrations in aliquots of collected PM at two sites with the sample-blank ratios (S/B) are given in Table 4.4. The S/B values show that the elemental concentrations of Cr and Ni at the SUBURBAN site are very close to blank concentrations. On the other hand, the S/B values of other elements at the SUBURBAN site and of all elements at the URBAN site are higher than blank concentrations adequately.

Table 4.4 The mean elemental concentrations (µg l^{-1}) in aliquots of collected PM at two sites and the sample/blank ratios (S/B)

	SUBURBAN				**URBAN**			
	PM$_{2.5}$		**PM$_{10-2.5}$**		**PM$_{2.5}$**		**PM$_{10}$**	
Element	**Mean**	**S/B**	**Mean**	**S/B**	**Mean**	**S/B**	**Mean**	**S/B**
Al	814.5	7.6	762.5	7.1	923.7	31.0	1439.6	48.3
Ba	8.7	9.0	10.4	10.8	15.0	9.9	25.7	16.9
Ca	2368.1	4.1	2957.1	5.1	2230.5	4.5	5427.0	11.0
Cd	0.9	9.2	0.8	8.1	1.6	2.7	1.6	2.7
Cr	25.4	1.9	20.2	1.5	30.7	5.5	33.1	5.9
Cu	20.0	7.6	17.1	6.5	41.6	7.1	53.9	9.2
Fe	408.3	3.0	464.1	3.5	501.8	6.8	1113.3	15.1
K	214.5	79.0	190.6	70.2	503.2	17.8	541.7	19.2
Mg	128.2	8.5	158.9	10.5	170.7	2.7	381.5	6.1
Mn	15.2	10.4	13.7	9.4	19.1	7.8	34.4	14.1
Na	843.3	3.4	1158.8	4.6	1452.2	11.2	1925.4	14.8
Ni	15.2	1.4	16.8	1.5	69.4	12.0	21.5	3.7
Pb	38.7	43.3	28.4	31.7	107.3	23.1	162.9	35.1
Sr	5.3	4.4	6.3	5.2	5.0	1.5	12.6	3.8
V	7.1	71.3	5.7	57.0	160.1	394.5	16.4	40.4
Zn	140.4	36.9	101.5	26.7	202.8	15.4	323.8	24.5

4.1.2.1 Temporal and Spatial Variation

The seasonal ambient air elemental concentrations are given in Table 4.5. The elemental profiles of PM concentrations in Izmir were dominated by terrestrial elements such as Ca, Al, Fe and Mg and marine salt element, Na at both of the two sites. All the elemental concentrations, except Cr, increased in summer in parallel to the increase in PM concentrations at the SUBURBAN site. Generally, the sharp increase in concentrations of terrestrial elements in summer indicates the significance of re-entrained top soil, and related industries on the concentrations at the SUBURBAN site.

Nearly all of the elemental concentrations of PM$_{2.5}$ at the URBAN site were higher in winter than in summer. Only the terrestrial elemental concentrations of PM$_{10}$ did not differ (decreased) in summer. The increase in elemental concentrations in the fine fraction, particularly the terrestrial elements, indicates the impact of emissions from low quality fossil fuel burning. In Izmir, lignite coal supplied from Soma region is widely used for residential heating, especially, at the part of the city where the URBAN station is located. The elemental compositions of different size fractions from the sources were discussed in Section 4.5. The results clearly showed that PM emitted from the coal burning contained significant amounts of the terrestrial elements, as well as the anthropogenic elements, particularly in the fine fraction. Concentrations of several elements *(i.e.,* Na, Ni, Pb, V, and Zn) were slightly increased in winter. V and Ni are the fingerprint elements of fuel oil burning and their increase may be due to fuel oil consumption for residential heating. However, it was surprising to observe a small increase in V concentrations while the increase in Ni concentrations was considerably high. This may be because of the contribution of other fossil fuels, particularly of coal to Ni concentrations in winter. Similarly, the increase in K concentrations may be due to the biomass burning for residential heating, since biomass is a major source for K just like soil (Park & Kim, 2005).

Elements were grouped according to their possible sources to investigate relationship between their distributions. For example, Al, Ca, Fe and K are markers of soil. Several scientists have shown that Pb, Zn and Cu are indicator elements for traffic emissions (Querol et al., 2001; Manoli et al., 2002; Fang et al., 2003). Vanadium and Ni are the fingerprint elements for fuel oil burning, and Cd and Cr, also, comes from coal burning, as local coals are rich in these elements. The monthly average concentrations of these grouped elements are plotted against the months of the study period in Figure 4.5 and Figure 4.6 for the SUBURBAN and URBAN sites, respectively.

Table 4.5 The seasonal mean and standard deviations (in parentheses) of elemental concentrations (ng m^{-3}) measured at the two sites (The unit of MDL is ng m^{-3})

	SUBURBAN					**URBAN**				
	PM_{10}		**$PM_{2.5}$**		**MDL**	**PM_{10}**		**$PM_{2.5}$**		**MDL**
	Summer	**Winter**	**Summer**	**Winter**		**Summer**	**Winter**	**Summer**	**Winter**	
Al	1523.1(934.5)	581.0(574.3)	739.0(630.9)	249.8(421.4)	142.1	1249.2(677.5)	1416.4(887.8)	769.8(662.8)	946.2(594.5)	102.6
Ba	16.2(14.5)	12.3(15.9)	5.0(4.1)	4.8(9.4)	1.7	21.0(13.6)	21.6(8.7)	14.8(32.7)	5.7(5.3)	4.3
Ca	4133.5(1872.0)	2844.7(2920.0)	945.8(1365.4)	842.4(1472.7)	806.5	4268.4(2677.4)	4346.1(1707.4)	1344.9(866.5)	2208.7(3025.2)	874.5
Cd	1.6(1.4)	0.7(0.5)	1.1(1.1)	0.5(0.3)	0.08	1.5(3.8)	1.6(1.8)	1.0(1.6)	1.7(1.7)	0.8
Cr	16.7(13.0)	20.3(12.8)	6.4(8.0)	13.3(8.5)	5.7	26.9(30.0)	25.5(28.3)	24.2(35.5)	23.6(19.5)	9.2
Cu	32.9(23.9)	16.7(12.1)	19.8(13.8)	9.6(8.0)	5.3	36.6(43.7)	58.0(45.9)	25.5(19.5)	53.7(67.6)	8.2
Fe	849.4(314.7)	581.0(329.1)	302.6(210.2)	222.8(136.0)	95.7	949.1(472.9)	874.1(430.9)	383(239.2)	411.6(426.4)	77.5
K	370.0(210.0)	300.7(187.1)	211.9(188.6)	174.1(120.5)	6.2	384.0(174.4)	594.0(321.3)	273.2(321.1)	822.6(1050.2)	53.4
Mg	273.7(106.0)	142.2(107.5)	82.1(93.9)	38.4(41.9)	27.4	314.2(139.1)	227.8(111.1)	93.8(52.6)	114.0(169.0)	72.2
Mn	27.2(16.8)	14.0(11.6)	12.1(10.1)	6.5(5.4)	2.4	31.8(14.2)	24.8(20.0)	15.4(9.7)	17.3(20.3)	5.1
Na	1505.9(1083.1)	903.1(748.7)	808.1(770.2)	420.9(346.1)	115.7	1144.3(1393.2)	904.2(943.2)	517.3(720.9)	1564.1(3126.4)	128.0
Ni	20.6(13.2)	17.5(4.6)	6.9(1.9)	8.4(5.7)	5.8	14.5(11.2)	18.1(19.3)	10.6(7.3)	24.5(32.9)	8.0
Pb	61.0(54.4)	39.9(45.3)	40.4(35.2)	22.7(27.6)	3.8	114.7(111.2)	184.1(334.7)	77.4(71.9)	118.2(116.7)	10.0
Sr	9.3(3.5)	5.7(3.5)	3.4(2.5)	2.3(2.1)	1.5	12.1(20.2)	5.3(2.8)	2.2(2.3)	3.0(8.8)	2.1
V	12.8(10.9)	7.6(5.3)	9.0(8.8)	4.6(3.8)	0.1	12.8(8.6)	15.5(13.0)	12.2(12.0)	13.0(8.8)	0.8
Zn	214.3(170.6)	148.9(146.2)	137.5(110.9)	82.1(90.9)	10.4	285.4(262.4)	293.9(362.3)	167.7(155.7)	193.0(134.2)	28.5

MDL: Calculated based of the limit of detections (Blank (mean) + 3 SD) of samples determined by ICP-OES.

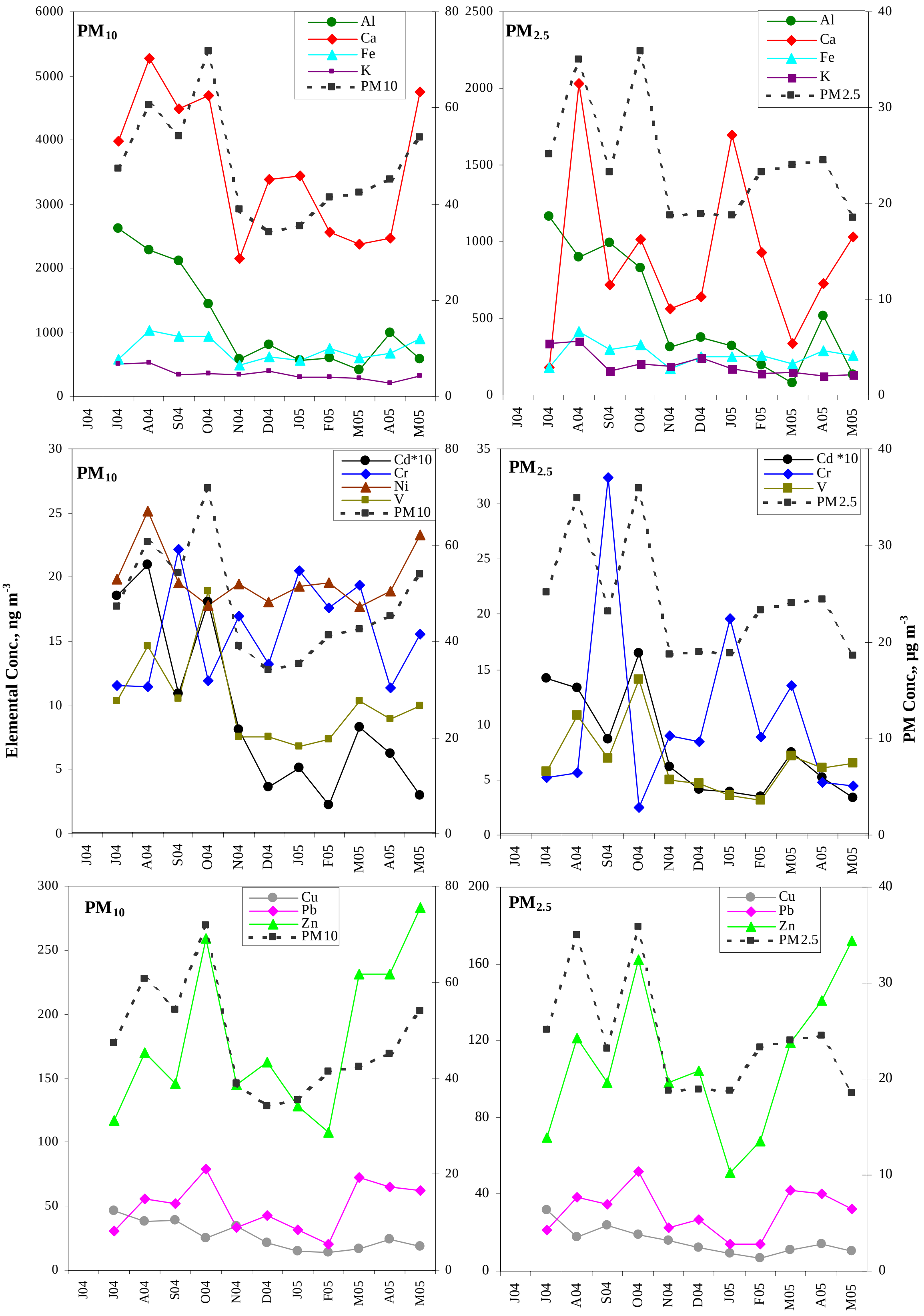


Figure 4.5 Monthly average elemental concentrations at the SUBURBAN site

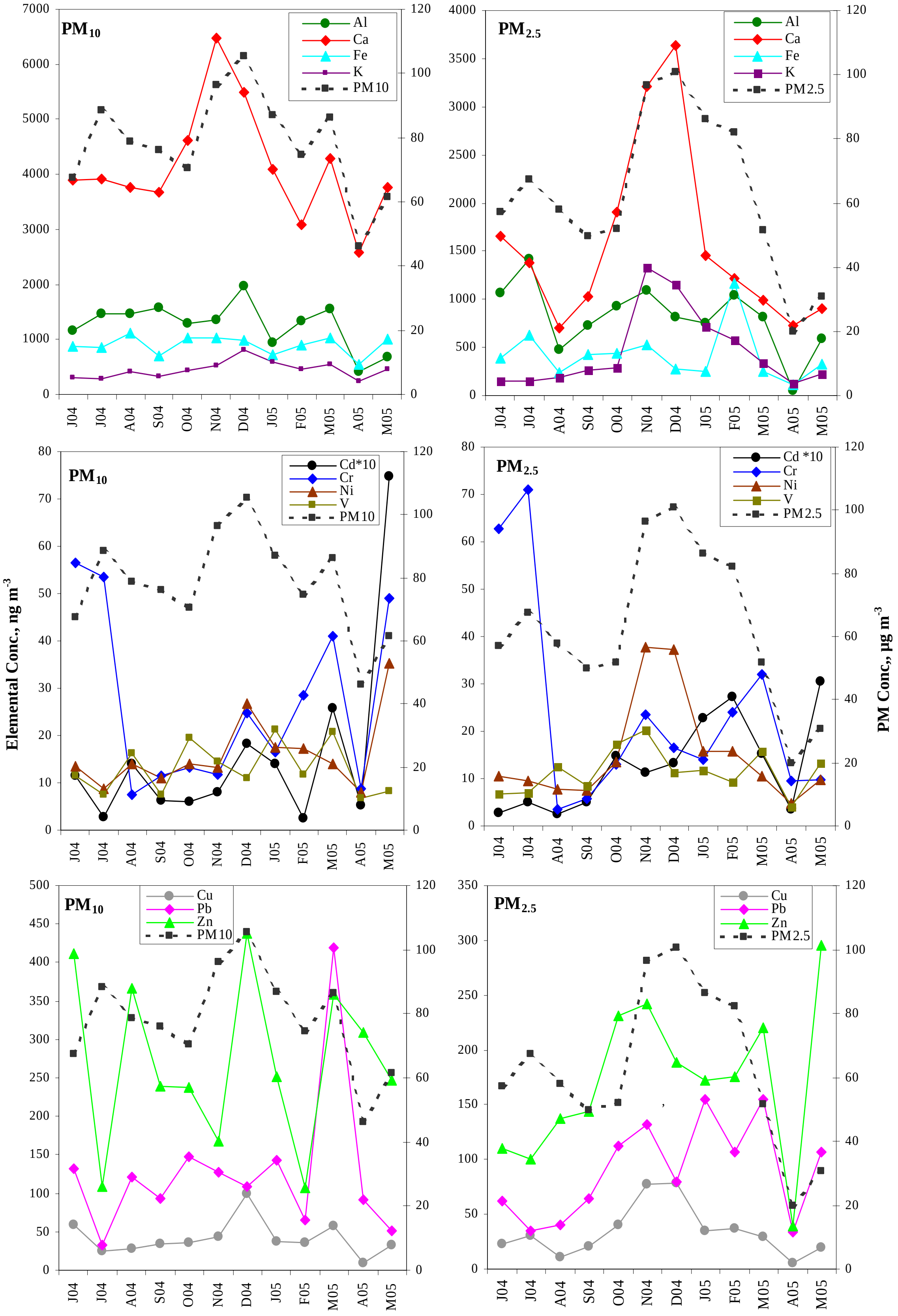


Figure 4.6 The Monthly average elemental concentrations at the URBAN site

It may be noted in Figure 4.5 that the terrestrial elements correlate well in summer, whereas there is no significant correlation in winter for PM_{10} and $PM_{2.5}$ at the SUBURBAN site. This observation suggests that these elements have originated from re-entrained top-soil in summer when the soil was dry. Thus, the concentrations of the terrestrial elements were significantly decreased in winter compared to in summer. However, Al showed a different variation from other terrestrial elements in the both seasons. This suggests that there were other sources of Al. Since there were many samples below the MDL of Ni at the SUBURBAN site, the variation in Ni at this site was not plotted. The metal concentrations at this site were compared. The variations in Zn and Pb were found to be similar. The variations in Cd and V in PM_{10} were also found to be similar, particularly in summer, and the variations in these elements in the fine fraction were similar in winter and summer.

Generally, the variations in terrestrial elements are following similar patterns at the URBAN site for both PM_{10} and $PM_{2.5}$ (Figure 4.6). The $PM_{2.5}$ concentrations approximately doubled in winter, whereas only Ca and K concentrations increased considerably (Ca doubled, K tripled). The increase in K concentrations may be explained by the fossil fuels burning in winter. Potassium has been mainly in the coarse fraction of PM emitted from coal burning but increase of K in PM_{10} was only around 1.5 times. The variations in Fe and Al in $PM_{2.5}$ are similar, whereas there is no correlation between the two for PM_{10}. Vanadium and Ni increased in winter in parallel with the PM concentrations and fossil fuels consumption. The increase in Cd concentration in winter for the both PM fractions may be attributed to the fossil fuels, particularly coal burning. The relatively higher presence of Cd in the fine PM suggests that it exists in the fine fraction of the fossil fuels burning emissions. The concentrations of Cr in summer were generally higher than in winter. However, a sharp decrease was observed in August. The concentrations of Cr began to increase starting from August; however, the increase did not have a regular pattern in winter period. These observations may indicate that there are several sources of Cr. The variations in Zn and Pb are similar probably as the result of their common origin. In some cases, Cu accompanied Pb and Zn. Possibly; Cu has different sources from Pb and Zn at the URBAN site.

4.1.2.2 Elements in the Fractions

The sampler used at the SUBURBAN site allows obtaining concurrent concentrations of coarse ($PM_{10-2.5}$) and fine ($PM_{2.5}$) fractions. Therefore, the existence of the elements in these fractions could be evaluated. Generally, most of the terrestrial elements are expected in the coarse fraction while anthropogenic elements are mainly expected in the fine fraction (Yatin et al, 2000).

The fractional variation of the elements is shown in Figure 4.7. In this study, most of the terrestrial elements were found in the coarse fraction, except for K and Na in winter, and Na in summer. Most of the anthropogenic elements, however, were found in the fine fraction.

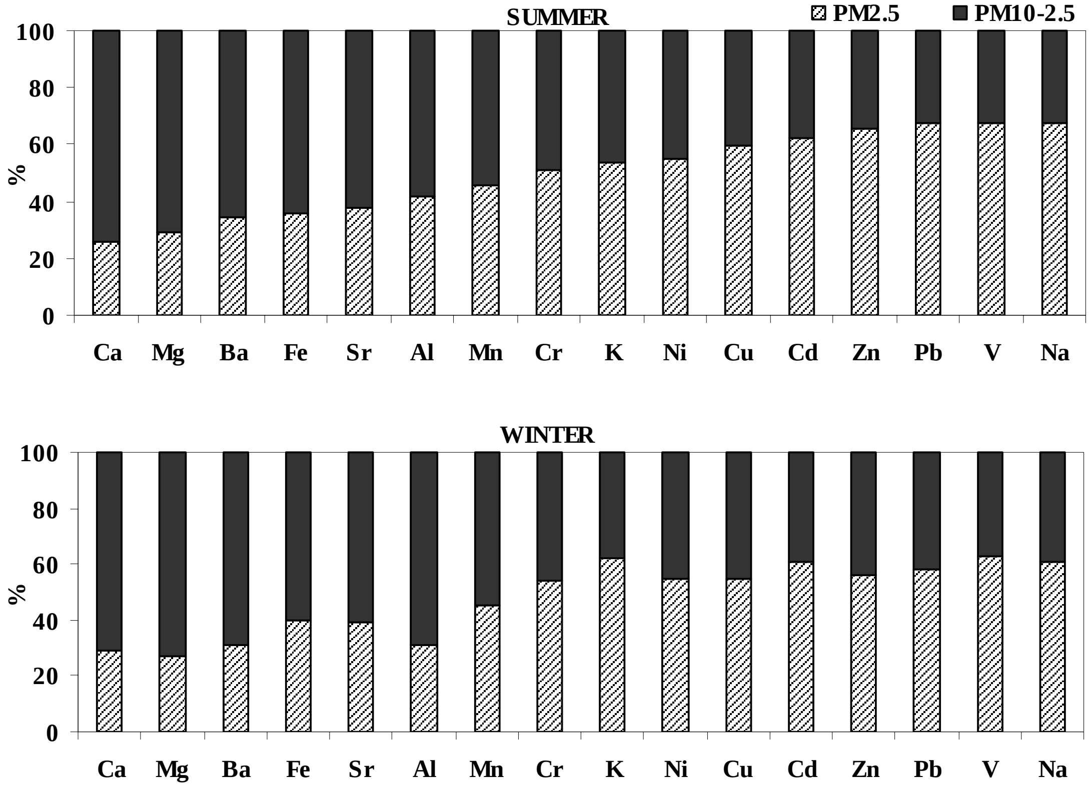


Figure 4.7 The elemental ratios of fine and coarse fractions at the SUBURBAN site

4.1.3 Source Profiles

Fifteen source categories were selected for elemental characterization of important PM sources. These were soil, secondary steel electric arc furnace, ceramic production, car battery recovery furnace (lead), coal burning, fuel oil burning, natural gas burning power plant (Aliaga), coal burning power plant (Soma power plant), biomass burning, mineral industries (Belkahve), aluminum smelting and foundry (wheel rim production), tobacco processing, cement plant, marine salt, and traffic.

Materials from the first five source groups were sampled with the help of the resuspension chamber. Fuel oil burning, natural gas burning power plant, coal burning power plant, biomass burning, mineral industries (Belkahve), aluminum smelting and foundry (wheel rim production) and tobacco processing were sampled using the in-stack cyclone. Marine salt, mineral industry and traffic samples were collected as described in Section 3.3.2.

Biomass burning included burning of wood and olive oil residuals (Pirina). The elemental mass fractions were calculated as the arithmetic mean of values obtained from wood burning in a stove (n=3) and a pirina-burning boiler (n=3).

The soil profile was obtained calculating the arithmetic mean of 29 local samples, also.

PM_{10} and a $PM_{2.5}$ samples were collected from the melting unit (natural gas burning) of rim production unit (aluminum). A sample of PM_{10} and a sample of $PM_{2.5}$ from the paint booth were, also, collected. However, elemental concentrations in samples collected from the stack of melting unit could not be detected. Therefore, only the data obtained from the stack of paint booth was used for CMB modeling.

Samples of fuel oil burning (n=3) were collected from the stack of a boiler that burns fuel oil no. 4 which is the most used fuel oil for residential heating and industrial purposes in Izmir. The elemental mass fractions of fuel oil no. 4 were used for CMB modeling.

The samples of the natural gas burning power plant (n=3) were collected from Aliaga plant. This plant is located at the Horozgedigi industrial region with a power of 1520 megawatts. Flue gas flow rate of the plant is about 10,000,000 m^3 h^{-1} with the PM load of ~7 kg h^{-1}. There are four 95-meters-high stacks in the plant. This plant is the largest plant among natural gas burning plants and boilers in the sampling area.

Marine salt, mineral industry, traffic samples were collected as described in Section 3.3.2. Elemental mass fractions from these sources are given in Table 4.6 with corresponding uncertainties. The uncertainties were calculated using equation 3.7.

Soil: Top-soil profiles were dominated by the terrestrial elements (i.e., Al, Ca, Fe, K and Mg) for both PM_{10} and $PM_{2.5}$. As soil profiles may change substantially with respect to location, the obtained profile was not compared to other soils investigated around the world. In this study, the anthropogenic elements (*i.e.*, Cd, Cr, Cu, Ni, Pb, V and Zn) were generally found in the fine fraction. These elements were enriched approximately by two times in the fine fraction compared to PM_{10}. Similar results were reported in the literature (Ho et al., 2003; Chow et al., 2004).

Steel: Zinc, Fe, Pb, and Mn are the main elements emitted from the electric arc furnaces. The percent contributions of Pb and Zn in this study (~8% for Pb and ~32% for Zn) are notably high when compared to PM profiles from other studies for steel group, such as 0.76% for Pb and 1.2% for Zn (USEPA, 2002). Our data is also greater than the percent contributions calculated in another study in Croatia (Sofilic, et al., 2004). It should be noted that Sofilic et al. (2004) reported these values for PM deposits from dust control devices. Orhan (2005) reported typical PM elemental profiles for steel electric arc furnaces in Kocaeli (Turkey) similar to profiles found in this study. On the other hand, fractions of the other elements in our study are generally lower than those reported for the US (USEPA, 2002). In addition to Pb and Zn, the steel furnaces are one of the major emitters of other trace elements (i.e. Cd, Cr, Cu and Ni). The calculated fractions in this study for PM_{10} and $PM_{2.5}$ indicate that these elements exist in both fine and coarse fractions.

Aluminum: The profile of the aluminum industry showed that Al is the major element emitted from these sources. The Al content of the paint booth was low (~0.8%), which might imply that Al is not significantly emitted during this process. The elemental profile of PM_{10} and $PM_{2.5}$ showed that most of the elements exist in the fine fraction of the dust emitted from the paint booths.

Marine Salt: The marine salt profile was obtained from the sea salt; therefore, fractional separation of PM_{10} and $PM_{2.5}$ could not be obtained. The marine salt contains Na (~30%) and Mg (~1.5%) in significant amounts. The ratio of Mg to Na was used as a fingerprint to identify the marine source.

Mineral Industries (Belkahve Area): PM from the Belkahve area has a profile dominated by Ca. It is quite reasonable as there are several earth and mineral industries (i.e. stone quarries, asphalt plant, lime kilns, concrete plants), and the top-soil contains Ca rich material. Percent Ca content in PM_{10} and $PM_{2.5}$ fractions were ~30% and ~22%, respectively. In conclusion, more Ca exists in the coarse fraction of PM, whereas other elements are found in the fine fraction.

Biomass: Biomass PM emissions profile was based on the average of the elemental fractions of wood burning and pirina burning. Biomass burning is one of the major emitters of K. Potassium content was about 10% overall, 11.4% in PM_{10}, and 10.0% in $PM_{2.5}$ indicating a slightly higher K in the coarse fraction. Literature reported K percentages between 1% and 22% in different types of biomass (Watson et al., 2001; USEPA, 2002, Chow et al., 2004). The higher end of the range (~22%) corresponds to wood burning (USEPA, 2002). Sodium is another major element emitted from pirina burning. In this study, mean Na content was ~8% which is notably higher than the biomass burning results measured elsewhere (Watson et al., 2001; USEPA, 2002, Chow et al., 2004). Similar to K, Na was found more in the coarse fraction.

Ceramic: The profile of the ceramic industry PM was dominated by the terrestrial elements (i.e., Al, Ca, Mg, Fe and K). However, the abundance of Ca (~5%) is lower than soil and the other mineral industries. Profiles for this industry might be strongly dependent upon types of raw materials used in production. The most of the terrestrial elements were in the coarse fraction of PM emitted from the ceramic industries.

Coal: Soma lignite is widely used for residential heating in Izmir. The major contributors to the coal profiles are the terrestrial elements such as Ca, Al, Fe, Na, K, and Mg. The presence of these elements in the $PM_{2.5}$ is greater than in PM_{10}. In other words, most of these elements exist in the fine fraction. Comparison with other studies in the world regarding the elemental profiles of PM from coal combustion reveals that the percentages of the terrestrial elements in the PM emissions from burning Soma coals are generally higher. This is with the exception of Ca contents, which are slightly lower in case of burning Soma coal (Watson et al., 2001; USEPA, 2002, Chow et al., 2004). This can be affiliated with the higher Ca content of some of the coals studied in the literature than Soma coals (Chow et al., 2004). The trace elemental composition showed that Soma coal is a major source of Cr, Cu, Ni, Pb and V. Soma coals contain higher amounts of trace elements compared to the data reported by Watson and friends (2001) and Chow and co-workers (2004). The Cr, Cu, Ni, Pb and V percentages in $PM_{2.5}$ of Soma coal are 0.22, 0.10, 0.16, 0.05 and 0.27%. The Cr, Cu, Ni, Pb and V percentages in $PM_{2.5}$ from coal combustion reported by Chow et al. (2004) were as 0.026, 0.09, 0.02, 0.0055, and 0.079%, respectively. The same percentages were reported by Watson et al. (2001) as 0.005, 0.01, 0.002, 0.006 and 0.04%, respectively. The percentages for Soma coal are significantly higher than these amounts. Similar to terrestrial elements, most of the trace elements were found in the fine fraction in this source group.

Cement: The cement dust emission profile from a coal-fired cement plant was found to be dominated by Ca (~20%), K (~5%), Fe (~1.6%) and Al (~1%). The percentages for these elements in $PM_{2.5}$ were higher than in PM_{10}, therefore, it should be noted that those exist in the fine fraction. Vega et al. (2001), Ho et al. (2003), and Chow et al. (2004) reported several profiles for cement industry dust emissions where the percentages of terrestrial elements differed significantly, which included Ca. The Ca percent for cement industry around the world varied between 19% and 36% of which the profile differed significantly with respect to location. The profiles of trace elements were variable. Percent contents of Cd, Cr, Cu, Pb and V in this study were all greater than the reported values by Vega et al. (2001), Watson et al. (2003) and Chow et al. (2004). Particularly, Cd content is significantly higher with a percentage about 0.01%. This shows that the cement industry in Izmir is one of the major Cd emitters. Similar to terrestrial elements, most of the trace elements were in the fine fraction.

Fuel Oil: In addition to the terrestrial elements, V and Ni are the major elements emitted from sources that burn fuel oil. The fractions of V and Ni were around 9% and 3%, respectively. Since the fractions in PM_{10} were higher than in $PM_{2.5}$, we can conclude that V and Ni mainly exist in the coarse fraction. It was reported in the literature (USEPA, 2002) that the contents in the fine fraction were higher than in PM_{10}. It is known that the more complete the combustion, the lower the soot emissions and higher fine particle formation (Baumbach, 1996). It was reported that nearly 80% of PM emitted from fuel oil burning power plants consisted of coarse (>2.5 µm) particles (Baumbach, 1996). The contradiction between this study and literature (Baumbach, 1996) might be attributed to the difference in efficiency of the burning systems. The most of the terrestrial elements are, also, in the coarse fraction. Comparison with the literature (USEPA, 2002) shows that the fuel oil burning profile highly resembles to the reported value. The reported V and Ni percentages, on the other hand, were 4.5% and 2.0% in $PM_{2.5}$, respectively, corresponding to lower contents than in the fine PM in Izmir. Similarly, the content of the trace elements in the fuel oil burning significantly resembles to the reported composition (USEPA, 2002).

Lead: The lead recovery furnaces (secondary furnace for car battery melt-down) are considered as main responsible sources for Pb emissions. The percentages of Pb in PM_{10} and $PM_{2.5}$ fractions were about 75% and 32%, respectively, which indicated that the most of Pb exist in the coarse fraction. Comparison of the Pb content in the fine fraction to the reported values (USEPA, 2002) shows that the Pb content (~32%) in Izmir is lower than the reported value (~50%). The lead recovery furnace is also a significant emitter of Cd (~0.04%). This value is considerably lower than reported content of 0.7% (USEPA, 2002). The differences in Pb and Cd profiles might be attributed to the difference in the recovered scrap materials between the two countries.

Natural Gas Burning Power Plant: The most surprising profile was obtained from the natural gas burning power plant. The elemental profile was dominated by Ca (~7%), Al (~5%), Fe (~2%), Na (~2%), and Mg (~0.9%). This profile resembles significantly to the profiles of coal and soil. This profile is most probably due to the PM content of the combustion air, since the power plant is located in the heavily polluted Aliaga Industrial region. The reported Al, Ca, Fe, Na and Mg percents are 0.22, 1.04, 0.09, 2.13 and 0.00, respectively (USEPA, 2002).

Soma Power Plant: Soma power plant is located approximately 100 km far away to the City of Izmir at the north. The power of the plant is 990 MW and the flow of flue gas is about 10,000,000 $m^3 h^{-1}$. There are two stacks with heights of 150 m and a stack with height of 250 m. All the turbines are equipped with electrostatic filters. The PM flow is around 3,000 kg h^{-1} when nearly half of the capacity is used. The coal with low calorific content is used as the fuel. The elemental percentages show that the profile resembles significantly to Soma coal that is used for the residential heating in Izmir. However, significant differences were obtained for the content of Al and Ca. Al content (11.2%) in PM_{10} collected from the plant stack was slightly higher than the coal used for residential heating, whereas the Ca content of the former (~5.0%) was significantly lower than the latter. Most of the terrestrial elements were found in the coarse fraction. Surprisingly, the trace elemental content of the plant PM was considerably lower than the coal used for residential heating.

Table 4.6 Elemental mass fractions (F) in PM_{10} and $PM_{2.5}$ from 15 source groups together with uncertainties (Xu) and standard deviation (SD)

Source	Size	n		Al	Ba	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Sr	V	Zn
SOIL	PM_{10}	29	F	3.97681	0.02616	8.85488	0.00085	0.00696	0.00478	4.33103	0.96992	0.92778	0.13811	0.24779	0.01245	0.07028	0.01375	0.00906	0.03030
			Xu	0.06426	0.00042	0.12673	0.00005	0.00036	0.00025	0.06925	0.01570	0.01451	0.00216	0.00416	0.00065	0.00365	0.00021	0.00047	0.00051
			SD	0.01351	0.00011	0.08255	0.00001	0.00004	0.00004	0.01856	0.00379	0.00372	0.00108	0.00263	0.00001	0.00181	0.00012	0.00003	0.00016
	$PM_{2.5}$	29	F	4.61231	0.03062	8.79683	0.00139	0.01037	0.00621	4.74951	1.23028	0.92444	0.14436	0.27429	0.01678	0.10442	0.01419	0.01099	0.06321
			Xu	0.11738	0.00079	0.18617	0.00009	0.00061	0.00035	0.12470	0.03277	0.02381	0.00340	0.00783	0.00100	0.00772	0.00032	0.00064	0.00191
			SD	0.01719	0.00013	0.08842	0.00002	0.00019	0.00006	0.01963	0.00526	0.00408	0.00148	0.00217	0.00012	0.00261	0.00011	0.00004	0.00078
STEEL	PM_{10}	1	F	0.90383	0.05283	1.83758	0.12076	0.71589	0.56094	24.7086	3.61828	0.35124	1.62831	3.97200	0.24006	8.44367	0.00319	0.00812	32.8902
			Xu	0.06426	0.00042	0.12673	0.00005	0.00036	0.00025	0.06925	0.01570	0.01451	0.00216	0.00416	0.00065	0.00365	0.00021	0.00047	0.00051
			SD	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	$PM_{2.5}$	1	F	0.62030	0.05052	0.72940	0.12578	0.22550	0.46200	21.6170	3.71500	0.26810	1.50110	3.98570	0.02014	9.03920	0.00223	0.00683	35.8674
			Xu	0.01562	0.00127	0.01837	0.00693	0.01242	0.02545	0.54435	0.09355	0.00675	0.03780	0.10037	0.00111	0.49790	0.00006	0.00038	0.90319
			SD	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
RIM PROD. (ALUMINUM)	PM_{10}	2	F	0.78278	0.06185	0.52565	0.00026	0.01381	0.01608	0.53478	0.05958	0.11035	0.00928	0.43333	0.01041	0.04761	0.00304	0.00345	0.19817
			Xu	0.02348	0.00186	0.01577	0.00001	0.00041	0.00048	0.01604	0.00179	0.00331	0.00028	0.01300	0.00031	0.00143	0.00009	0.00010	0.00595
			SD	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	$PM_{2.5}$	2	F	0.82502	0.14760	0.41522	0.00021	0.03609	0.01521	0.49854	0.04318	0.26213	0.00712	0.06949	0.02454	0.01016	0.00510	0.00285	0.05346
			Xu	0.02475	0.00443	0.01246	0.00001	0.00108	0.00046	0.01496	0.00130	0.00786	0.00021	0.00208	0.00074	0.00031	0.00015	0.00009	0.00160
			SD	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
MARINE	*	1	F	0.00110	0.00005	0.31673	0.00004	0.00007	0.00000	0.00098	1.06398	1.50491	0.00004	22.93119	0.00009	0.00010	0.00468	0.00002	0.00033
			Xu	0.00001	0.00000	0.00318	0.00000	0.00000	0.00000	0.00001	0.01070	0.01510	0.00000	0.23000	0.00000	0.00000	0.00005	0.00000	0.00000
			SD	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

n : Number of samples; NA: Not available; * : The data obtained from the sea salt residual

Table 4.6 (Continued)

Source	Size	n		Al	Ba	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Sr	V	Zn
MINERAL IND. (BELKAHVE)	PM_{10}	3	F	0.78995	0.00663	30.50410	0.00020	0.00415	0.00240	0.42375	0.13473	0.18601	0.01234	0.18272	0.00338	0.00621	0.01915	0.00372	0.01846
			Xu	0.00905	0.00007	0.34664	0.00001	0.00021	0.00012	0.00486	0.00155	0.00211	0.00014	0.00201	0.00017	0.00031	0.00022	0.00019	0.00021
			SD	0.08221	0.00129	1.71647	0.00001	0.00009	0.00084	0.02259	0.04157	0.02335	0.00070	0.01443	0.00025	0.00384	0.00256	0.00108	0.00709
	$PM_{2.5}$	3	F	1.44326	0.01017	22.91579	0.00158	0.00439	0.00164	0.71940	0.23685	0.22258	0.01701	0.26473	0.01829	0.02342	0.01450	0.00613	0.03778
			Xu	0.05056	0.00032	0.72715	0.00010	0.00026	0.00009	0.02470	0.00803	0.00694	0.00052	0.00753	0.00104	0.00139	0.00045	0.00036	0.00112
			SD	0.06170	0.00283	3.11230	0.00001	0.00114	0.00109	0.05541	0.01169	0.03887	0.00775	0.05312	0.03458	0.00134	0.00163	0.00379	0.00028
BIOMASS	PM_{10}	6	F	0.37834	0.00791	0.85937	0.00217	0.05212	0.01469	0.27009	11.27769	0.11397	0.00519	4.33065	0.01084	0.01154	0.00973	0.00001	0.27529
			Xu	0.01225	0.00026	0.02784	0.00007	0.00169	0.00048	0.00875	0.36529	0.00369	0.00017	0.14027	0.00035	0.00037	0.00032	0.00000	0.00892
			SD	0.12599	0.00656	0.92243	0.00089	0.05699	0.00102	0.11004	2.36451	0.12328	0.00329	0.74738	0.02138	0.00139	0.00641	0.00000	0.01584
	$PM_{2.5}$	6	F	0.77133	0.00258	0.78087	0.00254	0.01735	0.01558	0.22694	9.92337	0.03209	0.00115	3.56307	0.00556	0.00905	0.00949	0.00003	0.20693
			Xu	0.01942	0.00006	0.01966	0.00006	0.00044	0.00039	0.00571	0.24988	0.00081	0.00003	0.08972	0.00014	0.00023	0.00024	0.00000	0.00521
			SD	0.19335	0.00123	0.39570	0.00112	0.00446	0.00688	0.09506	2.17285	0.01632	0.00049	2.13395	0.00344	0.00475	0.00443	0.00000	0.12051
CERAMIC	PM_{10}	1	F	4.45166	0.02155	5.79558	0.00082	0.00598	0.00907	0.97104	0.55244	1.85049	0.01471	2.45755	0.01013	0.00619	0.03909	0.00497	0.04809
			Xu	0.05150	0.00025	0.06705	0.00001	0.00007	0.00011	0.01123	0.00639	0.02140	0.00017	0.02840	0.00012	0.00007	0.00045	0.00006	0.00056
			SD	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	$PM_{2.5}$	1	F	7.23211	0.02850	3.89393	0.00080	0.00409	0.00483	1.30976	0.58745	1.36455	0.01682	0.47396	0.00512	0.00971	0.04644	0.01024	0.04113
			Xu	0.11987	0.00047	0.06454	0.00001	0.00007	0.00008	0.02171	0.00974	0.02260	0.00028	0.00786	0.00008	0.00016	0.00077	0.00017	0.00068
			SD	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
COAL	PM_{10}	2	F	8.73716	0.10240	12.67946	0.00078	0.10525	0.12286	5.19712	0.93496	0.74375	0.04283	4.51743	0.07178	0.06221	0.08806	0.24271	0.22474
			Xu	0.50001	0.00507	1.14637	0.00006	0.01620	0.01890	0.19249	0.07294	0.04081	0.00351	0.30339	0.01040	0.00814	0.00271	0.01315	0.02720
			SD	1.61564	0.00987	0.44185	0.00005	0.00022	0.00228	1.12704	0.34095	0.04852	0.00639	0.26445	0.00416	0.01168	0.00251	0.01983	0.03262
	$PM_{2.5}$	2	F	9.35152	0.11811	14.2845	0.00127	0.22079	0.10313	5.65004	0.63451	0.77413	0.07511	4.10399	0.16185	0.04960	0.09478	0.27487	0.27221
			Xu	0.93289	0.01062	2.83065	0.00022	0.04968	0.02299	0.56632	0.06215	0.07326	0.01265	0.39062	0.03581	0.00903	0.00603	0.02305	0.05278
			SD	0.64241	0.00811	0.32945	0.00008	0.00591	0.00497	0.11300	0.10260	0.11680	0.01215	0.32606	0.00120	0.00000	0.00900	0.03835	0.01000

Table 4.6 (Continued)

Source	**Size**	**n**		**Al**	**Ba**	**Ca**	**Cd**	**Cr**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Ni**	**Pb**	**Sr**	**V**	**Zn**
CEMENT	PM_{10}	3	F	0.96149	0.03628	19.81598	0.01223	0.11899	0.01110	1.70991	4.62222	0.33714	0.01939	0.69421	0.06340	0.01535	0.05172	0.04106	0.29422
			Xu	0.10599	0.00400	2.18448	0.00148	0.01435	0.00134	0.18850	0.50955	0.03717	0.00214	0.07653	0.00765	0.00185	0.00570	0.00495	0.03243
			SD	0.44860	0.02104	7.15543	0.00439	0.03043	0.00754	0.45114	1.77675	0.12186	0.00691	0.21694	0.04169	0.01096	0.01961	0.06131	0.14578
	$PM_{2.5}$	3	F	1.12928	0.03180	23.06500	0.00998	0.15114	0.01110	1.63552	6.75756	0.46844	0.02365	1.18436	0.08101	0.02811	0.02593	0.00973	0.54696
			Xu	0.16615	0.00468	3.39352	0.00155	0.02344	0.00172	0.24063	0.99423	0.06892	0.00348	0.17425	0.01256	0.00436	0.00382	0.00151	0.08047
			SD	0.20357	0.00765	4.10008	0.00239	0.03973	0.00761	0.36061	1.28471	0.07999	0.00501	0.23616	0.03254	0.01111	0.01930	0.00486	0.05996
FUEL OIL	PM_{10}	3	F	2.32163	0.01664	7.24752	0.00098	0.15580	0.02263	1.19200	2.40864	1.38465	0.02132	6.56327	3.18935	0.02255	0.02510	9.49917	0.49619
			Xu	0.12669	0.00068	0.20319	0.00006	0.01171	0.00183	0.05842	0.04620	0.03600	0.00084	0.39077	0.25648	0.00176	0.00061	0.77029	0.02919
			SD	1.15940	0.00039	6.74163	0.00005	0.07110	0.02120	0.23830	3.39014	1.44005	0.00665	5.03408	2.84656	0.01585	0.02824	9.00828	0.36154
	$PM_{2.5}$	3	F	1.79259	0.02490	2.53061	0.00233	0.04210	0.00830	0.72809	1.83564	1.59583	0.03330	2.06391	2.61648	0.01330	0.01650	8.54244	0.60800
			Xu	0.61653	0.00208	0.40682	0.00101	0.00356	0.00192	0.17385	0.06746	0.12673	0.00081	0.35945	0.90669	0.00130	0.00096	3.18890	0.01370
			SD	1.14387	0.02518	1.31608	0.00014	0.05041	0.00016	0.01952	2.39395	1.65075	0.04611	0.89850	1.52020	0.01475	0.01923	6.51607	0.84787
LEAD RECOVERY	PM_{10}	1	F	0.14533	0.00167	0.04000	0.04219	0.00324	0.15053	0.29009	1.17333	0.00033	0.00013	0.53347	0.00403	75.05653	0.00133	0.00466	0.43742
			Xu	0.00209	0.00002	0.00057	0.00215	0.00017	0.00768	0.00416	0.01684	0.00000	0.00000	0.00765	0.00021	3.83148	0.00002	0.00024	0.00628
			SD	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	$PM_{2.5}$	1	F	0.26207	0.00018	0.02143	0.03593	0.03625	0.00107	0.34521	0.52093	0.00714	0.00011	0.22193	0.00212	32.6551	0.00143	0.00256	0.19064
			Xu	0.00506	0.00000	0.00041	0.00189	0.00191	0.00006	0.00666	0.01006	0.00014	0.00000	0.00428	0.00011	1.71952	0.00003	0.00014	0.00368
			SD	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
NAT.GAS BURNING PP	PM_{10}	2	F	4.78325	0.08194	9.71635	0.00300	0.21957	0.25133	1.62354	0.31516	0.96436	0.04164	2.04195	0.18055	0.09397	0.04192	0.01606	0.46390
			Xu	1.01454	0.01720	1.71394	0.00023	0.09024	0.06362	1.08231	0.12240	0.25390	0.01306	0.47843	0.07974	0.02176	0.01491	0.00733	0.11616
			SD	0.01357	0.01470	3.00398	0.00063	0.00997	0.08379	0.08139	0.16969	1.09047	0.01064	2.13639	0.06691	0.05708	0.01734	0.00562	0.27703
	$PM_{2.5}$	2	F	6.81822	0.05542	6.90867	0.00000	0.21854	0.20888	2.87914	0.42875	0.81084	0.03601	1.76398	0.19841	0.07152	0.04486	0.02660	0.39673
			Xu	1.01554	0.01740	1.74938	0.00023	0.09368	0.06643	1.08410	0.12587	0.25605	0.01369	0.47935	0.08221	0.02344	0.01614	0.00743	0.11742
			SD	1.42702	0.01849	2.45340	0.00063	0.11923	0.00141	0.57026	0.12781	0.13080	0.00846	0.45163	0.09329	0.00033	0.00139	0.00562	0.05219

Table 4.6 (Continued)

Source	**Size**	**n**		**Al**	**Ba**	**Ca**	**Cd**	**Cr**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Ni**	**Pb**	**Sr**	**V**	**Zn**
COAL BURNING PP	PM_{10}	3	F	11.17977	0.04857	5.01499	0.00110	0.01638	0.00646	2.04824	1.04425	0.53913	0.01707	0.72639	0.01943	0.01806	0.02714	0.03924	0.05889
			Xu	0.12207	0.00053	0.05476	0.00006	0.00082	0.00032	0.02237	0.01140	0.00589	0.00019	0.00793	0.00098	0.00091	0.00030	0.00197	0.00064
			SD	0.66389	0.01679	0.81892	0.00013	0.01253	0.00135	0.25250	0.63021	0.28006	0.00492	0.29160	0.00886	0.00589	0.00402	0.01409	0.03194
	$PM_{2.5}$	2	F	6.64366	0.06599	3.13080	0.00091	0.02185	0.00798	1.15683	2.95476	1.23975	0.01067	3.96362	0.01129	0.01176	0.03147	0.02135	0.07009
			Xu	0.11659	0.00116	0.05494	0.00005	0.00114	0.00042	0.02030	0.05185	0.02176	0.00019	0.06956	0.00059	0.00061	0.00055	0.00111	0.00123
			SD	5.22013	0.06330	2.33929	0.00068	0.01329	0.00611	0.78635	2.16849	1.11411	0.00517	4.18640	0.00289	0.00625	0.02379	0.00655	0.03319
TOBACCO	PM_{10}	3	F	2.68736	0.01549	4.18714	0.00016	0.01554	0.01869	2.57183	0.70756	0.88535	0.04835	0.23963	0.01856	0.00429	0.00779	0.00335	0.01157
			Xu	0.10749	0.00062	0.16749	0.00001	0.00062	0.00075	0.10287	0.02830	0.03541	0.00193	0.00959	0.00074	0.00017	0.00031	0.00013	0.00046
			SD	1.31555	0.00311	0.58069	0.00019	0.01212	0.02091	0.34397	0.11630	0.18364	0.00509	0.37840	0.00679	0.00411	0.00113	0.00052	0.00734
	$PM_{2.5}$	2	F	2.91403	0.01598	7.03253	0.00035	0.01940	0.02332	2.52717	0.65284	0.90204	0.05108	0.20560	0.01803	0.00532	0.00499	0.00210	0.07962
			Xu	0.03570	0.00020	0.08616	0.00002	0.00098	0.00118	0.03096	0.00800	0.01105	0.00063	0.00252	0.00091	0.00027	0.00006	0.00011	0.00098
			SD	1.07415	0.00461	3.84182	0.00026	0.01638	0.01147	0.34922	0.11619	0.13803	0.01027	0.03822	0.00744	0.00025	0.00187	0.00016	0.07464
TRAFFIC	PM_{10}	5	F	0.39639	0.02127	2.98239	0.00048	0.01717	0.01861	0.53918	0.41359	0.18198	0.01492	0.62897	0.01090	0.02644	0.00733	0.00434	0.06949
			Xu	0.05050	0.00273	0.38200	0.00001	0.00230	0.00266	0.06910	0.05310	0.02330	0.00149	0.08070	0.00150	0.00360	0.00094	0.00059	0.00890
			SD	0.08995	0.00605	3.09709	0.00026	0.00869	0.00841	0.12943	0.08904	0.07074	0.00602	0.31149	0.00581	0.00855	0.00308	0.00161	0.02624
	$PM_{2.5}$	5	F	0.25843	0.01076	1.53740	0.00048	0.02483	0.01350	0.34291	0.35284	0.09823	0.01879	0.47438	0.01271	0.03073	0.00513	0.00380	0.05704
			Xu	0.06220	0.00258	0.37100	0.00002	0.00610	0.00332	0.08270	0.08520	0.02370	0.00454	0.11400	0.00313	0.00756	0.00124	0.00059	0.01380
			SD	0.07841	0.00311	0.44399	0.00036	0.01863	0.00644	0.07700	0.07102	0.03864	0.01805	0.10772	0.00701	0.01377	0.00068	0.00084	0.03314

Tobacco: The profile of tobacco processing was also dominated by the terrestrial elements. The percentages of Ca, Al, Fe, Mg, and K were 5.0, 2.7, 2.5, 0.9, and 0.6, respectively. Generally, the contents in $PM_{2.5}$ were slightly higher than in PM_{10}. Similarly, most of the trace elements were found in the fine fraction of the tobacco processing dusts.

Traffic: Studies on characterization of the traffic source are generally performed near a main road or in a tunnel around the world. Thus, the composite profiles of road dust and exhaust emission are obtained (Watson et al., 2001; Watson & Chow, 2001; Chow et al., 2004). Naturally, the terrestrial element contents differ significantly according to location. Watson & Chow (2001), Watson et al., (2001), and Chow et al., (2004) reported several profiles for traffic emissions, which are significantly different in terms of elemental profile. Watson et al. (2001) found that the content of the terrestrial elements were below 0.01%, whereas Chow et al., (2004) reported values between 0.2% and 1.5%. The reported values (generally >1%) by USEPA (2002) are significantly higher than these values. Thus, it is concluded that profile of the traffic emissions, particularly road dust, differs significantly with respect to location. However, it should be noted that profile of the traffic emissions is dominated by elemental and organic carbon (Funasaka, Niyazaki, Kawaraya, Tsuruho & Mizuno, 1998; Watson et al., 2001; Watson & Chow, 2001; Chow et al., 2004; Giugliano et al., 2005; He et al., 2006). In this study, the measured contents of Ca, Al, Fe, K, Na, and Mg were ~2.0%, ~0.3%, ~0.4%, ~0.3%, ~0.4%, and ~0.2%, respectively. Percentages of the terrestrial elements in PM_{10} were higher than in $PM_{2.5}$ in Izmir indicating that most of the terrestrials exist in the coarse fraction. The elemental fine and coarse fractions are given in Figure 4.8. Sodium, Cr, Zn, Mn, K, V, Cd, Ni, and Pb were mainly found in the fine fraction.

The concurrent traffic measurements (n=5) clearly showed that the emitted PM was mainly fine. Average $PM_{2.5}/PM_{10}$ ratio was 81.2±14.9%. Many studies supported the fine character of the traffic emissions (Sturm et al., 2003; Gouriou, Morin & Weill, 2004; Samara & Voutsa, 2005; Fang, Wu, Rau & Huang, 2006).

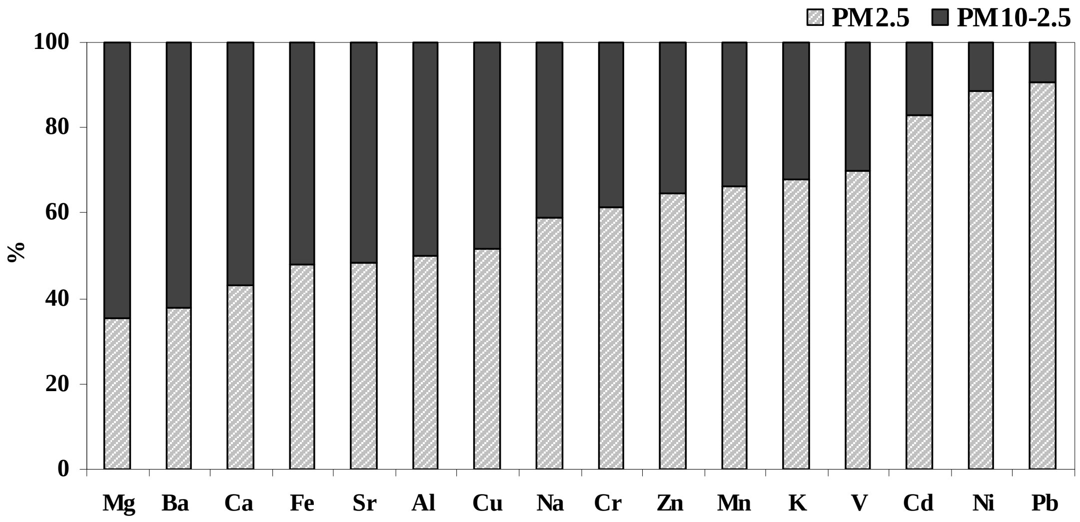


Figure 4.8 The elemental fine ($PM_{2.5}$) and coarse ($PM_{10-2.5}$) fractions emitted from the traffic source

4.1.4 Estimated Elemental Dry Deposition Fluxes

Dry deposition flux is described as the settled amount of a substance in a certain time onto surface of soil or water body. Dry deposition flux can be calculated using the following equation:

$$F = V_d . C \qquad (4.1)$$

where;
F : Dry deposition flux, mg m^{-2} day^{-1}
V_d: Dry deposition velocity, m day^{-1}
C : Ambient air concentration of substance, mg m^{-3}

The calculated dry deposition fluxes of Al, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Sr, V, and Zn for PM_{10} at two sites are given in Table 4.7 with estimated dry deposition fluxes in Bursa (Tasdemir, Kural, C., Cindoruk, S.S. & Vardar, N., 2006), measured overall dry deposition fluxes of total suspended particles (TSP) in Izmir (Odabasi et al., 2002) and measured overall deposition of the elements in Izmir (Yatkin et al., 2005). It should be noted that the dry deposition velocities of Al, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, and Zn in TSP measured at the SUBURBAN site were used to calculate the dry deposition fluxes at two sites. The dry deposition velocity of Mn was used for Ba and Sr, whereas the velocities of Ni, Mg and Ca were used V, K and Na, respectively. It should also be noted that the dry deposition fluxes by Odabasi et al. (2002) were measured at the SUBURBAN site whereas the overall (dry + wet deposition) deposition fluxes by Yatkin et al., (2005) were measured at an urban site around a cement plant in Izmir.

The sequences of the dry deposition flux levels were Ca>Fe>Na>Zn>Al>K>Mg>Pb>Ni>V>Cu>Mn>Cr>Ba>Sr>Cd at the SUBURBAN site, and Ca>Fe>Na>Zn>Al>Pb>K>Mg>Ni>Cu>V>Mn>Cr>Ba>Sr>Cd at the URBAN site. The most deposited anthropogenic elements at the two sites were Pb, Ni, V and Cu. Comparison with the fluxes of TSP measured at the SUBURBAN site by Odabasi et al. (2002) showed that fluxes of the terrestrial elements such as Ca, Al, Mg and Fe estimated in this study are considerably lower than TSP. In conclusion, we may infer that the particles with d_p>10 μm contain significant amount of the terrestrial elements. The fluxes of the overall deposition fluxes measured by Yatkin et al. (2005) support this inference. On the other hand, the fluxes estimated in this study are significantly similar those estimated in an urban site in City of Bursa (Tasdemir et al., 2006).

4.1.5 The Elemental Profile of Top-soils

The soil surface is one of the major sources of atmospheric particles, and it is exposed to the deposition of atmospheric PM. The deposition of pollution-derived atmospheric PM strongly depends on the locations of the major sources such as industries, traffic, residential areas, etc. Agricultural activities, particularly utilization of pesticides and fertilizers, and irrigation with metal polluted waters are the primary sources of trace elements in soil (Guvenc, Alagha & Tuncel, 2003). However, in big cities, deposition of elements from the atmosphere is generally most effective than agriculture-derived elements in soil. Spatial variation of the trace elemental concentrations in soil may be a good indicator of atmospheric pollution derived from anthropogenic activities in cities.

Table 4.7 Estimated elemental dry deposition fluxes in Izmir and Bursa

Dry Deposition Velocity[a], cm s^{-1}		**Average Dry Deposition Flux, mg m^{-2} day^{-1}**				
		This Study		**Izmir[a]**	**Izmir[b]**	**Bursa[c]**
		SUBURBAN	URBAN			
Al	0.4	0.387	0.453	23.5	9.82	NA
Ba	1.2	0.015	0.022	NA	NA	NA
Ca	1.5	4.641	5.569	43.1	171.42	5.633
Cd	3.4	0.003	0.004	0.024	0.0005	0.001
Cr	1.2	0.016	0.027	0.016	0.0851	0.014
Cu	1.5	0.034	0.058	0.124	NA	0.533
Fe	6.0	3.807	4.775	12.09	10.84	1.992
K	0.8	0.235	0.320	NA	NA	NA
Mg	0.8	0.150	0.195	3.1	4.12	0.682
Mn	1.2	0.022	0.030	0.135	0.16	0.213
Na	1.5	1.617	1.367	NA	2.63	NA
Ni	4.8	0.081	0.066	0.129	0.06	NA
Pb	2.8	0.126	0.340	0.22	0.099	0.109
Sr	1.2	0.008	0.010	NA	NA	NA
V	4.8	0.044	0.057	NA	0.051	NA
Zn	4.6	0.737	1.147	1.91	0.367	0.635

[a] Odabasi et al. (2002) (SUBURBAN, TSP)

[b] Yatkin et al. (2005) (urban, overall)

[c] Tasdemir et al. (2006) (urban, fine + coarse)

Since Izmir has intensive industrial and agricultural activities, it is difficult to distinguish the sources of trace elements in the soil. However, nearly all the agricultural activities are performed at the suburban sites particularly at North and South of the city. The median, arithmetic mean, standard deviation and skewness of the elemental concentrations at the urban and suburban sites of Izmir are given in Table 4.8. Shapiro-Wilk test was applied to check the normality of the distribution of the elemental concentrations in the soil. The results show that the elemental concentrations are normally distributed except for Cu, Ni, Pb, and Zn. Thus, to represent these elements, the median values are, also, listed in the table.

Since the trace elements in soils of big cities mainly arise from anthropogenic activities, the distribution of these elements is highly influenced by the locations of these sources. Thus, the trace elemental concentration of soil varies significantly with respect to location. Skewed frequency distribution and high arithmetic mean-to-median ratios are among the indicators used to identify highly variable concentrations, thus, the pollution derived from man-made activities. The terrestrial elemental concentrations are expected to distribute uniformly. Ca, Cu, Ni, Pb, and Zn have skewed distribution at the urban sites with skewness coefficients (>2), indicating that the sources of these elements are mainly man-made activities at the urban sites. Although a terrestrial element, high Ca concentrations were measured in the urban soil, which might be attributed to the influence of the mineral industries such as cement plants and Belkahve region. Comparison the concentrations in the urban and suburban soils showed that concentrations of Cr, Cu, Fe, Ni, Pb, and Zn in the urban soil were higher than in the suburban soil in the study area. However, the differences between the elemental concentrations of urban and suburban soils are not so large. This situation is mainly resulted from the industrial activities near agricultural sites at the suburban sites. Thus, the suburban soil might be polluted due to these industrial activities.

Spatial distribution plots of some elements were prepared to evaluate the man-made derived soil pollution in the study area. The plots were drawn using ArcGIS v.9.1. The plots of Al, Cd, Co, Cr, Cu, Fe, Ni, Pb, V and Zn are given in Figure 4.9. Al and Fe were plotted to represent the terrestrial elements.

The distributions of Al and Fe in the study are fairly similar, and the transition between one concentration level to another one is gradual. These distributions might indicate that the variation of terrestrial elements in the region is resulted from different mineral types. Similarly, the distribution of Zn is not consistent with the locations of anthropogenic sources; therefore, it may imply that the variation of Zn is mainly determined by the mineral types.

Table 4.8 Descriptive statistics of the elemental concentrations (μg g^{-1}) in the urban and the suburban soils

	Urban				**Suburban**			
	Median	Mean	SD	Skewness	Median	Mean	SD	Skewness
Al	43480.0	48201.6	16169.1	0.2	52431.8	50053.6	13346.7	0.1
Ba	272.4	299.9	149.7	1.7	302.8	328.4	167.3	0.5
Ca	27433.0	44055.4	48704.6	2.4	43595.3	67777.3	65915.1	1.5
Cd	1.8	1.8	0.3	0.2	1.7	1.8	0.7	1.5
Co	17.0	17.6	6.0	0.3	17.8	16.9	6.8	-0.5
Cr	110.1	127.9	62.1	0.9	77.5	86.8	41.9	0.0
Cu	47.8	57.0	43.3	2.3	26.6	29.1	13.9	0.6
Fe	25635.1	28712.3	11191.5	0.6	25491.4	23759.6	9147.9	-0.7
K	15872.5	15275.8	4918.3	0.0	14505.0	15633.6	5851.3	1.0
Mg	3969.3	5205.2	3047.1	1.0	5592.0	6649.2	4472.4	0.7
Mn	610.2	716.8	384.6	1.2	869.4	829.3	330.3	0.2
Na	7029.6	7338.4	3186.0	0.7	9629.0	9963.1	6638.3	0.8
Ni	51.0	70.9	65.7	2.8	52.3	48.8	29.2	0.4
Pb	36.5	41.7	26.5	3.8	36.5	40.4	27.9	3.1
Si	150754.3	149746.0	48117.7	-0.5	140115.8	131494.0	47148.1	-0.1
Sr	82.1	108.1	65.9	1.0	110.7	130.2	89.7	1.5
V	51.3	55.5	17.8	-0.2	63.0	62.1	23.4	-0.9
Zn	382.9	4884.8	11940.0	3.0	243.5	2482.9	7476.4	3.6

Spatial distributions of the trace elements, on the other hand, are fairly consistent with the locations of anthropogenic sources. The concentrations of Cd, Co and Pb in the city center and in Torbali region are higher than the other sites. The concentrations of Cr, Cu and Ni are high in the city center. The concentrations of nearly all elements are high at Yesildere region that is influenced highly by the traffic emissions and other urban sources. On the other hand, high Cu concentrations found at Northeast of Izmir Bay may be resulted from the structure of the local soil. Although these regions are residential areas, there is no significant source of Cu. The Cu concentration decreases with increasing distance from the Bay. There are several rivers in the region, which may be the source of the high concentrations of Cu through the soil carried downstream. The variation of V concentrations did not have a regular pattern.

Crustal-Enrichment Factors: To quantify the pollution levels of the soil, crustal-enrichment factors (EFc) for each element were calculated. Crustal-enrichment factor is calculated using following equation:

$$EF_c = (C_x / C_{Si})_{sample} / (C_x / C_{Si})_{crust} \tag{4.3}$$

where;

$(C_x / C_{Si})_{sample}$: The ratio of the concentration of the test element (x) to that of Si in the sample

$(C_x / C_{Si})_{crust}$: The same ratio in the reference soil

Silicon was used as the reference element since there is no anthropogenic Si source. A sample collected from rural site approximately 10 km far from the city center was used as the reference soil. Calculated EFc values are shown in Figure 4.10.

The crustal-enrichment factors of the terrestrial elements are generally close to unity except Ca. The relatively higher EFc of Ca might be attributed the enrichment around the mineral industries located at Belkahve region.

On the other hand, the trace elements such as Cd, Co, Cr, Cu, Ni, Pb, V and Zn are enriched in the soil of the study area. The EFc of these elements are generally <5 except for Zn. As mentioned previously, extremely high concentrations of Zn is attributed the mineralogy of the local soils. The enrichment of other trace elements might arise from the contribution of man-made activities in Izmir area.

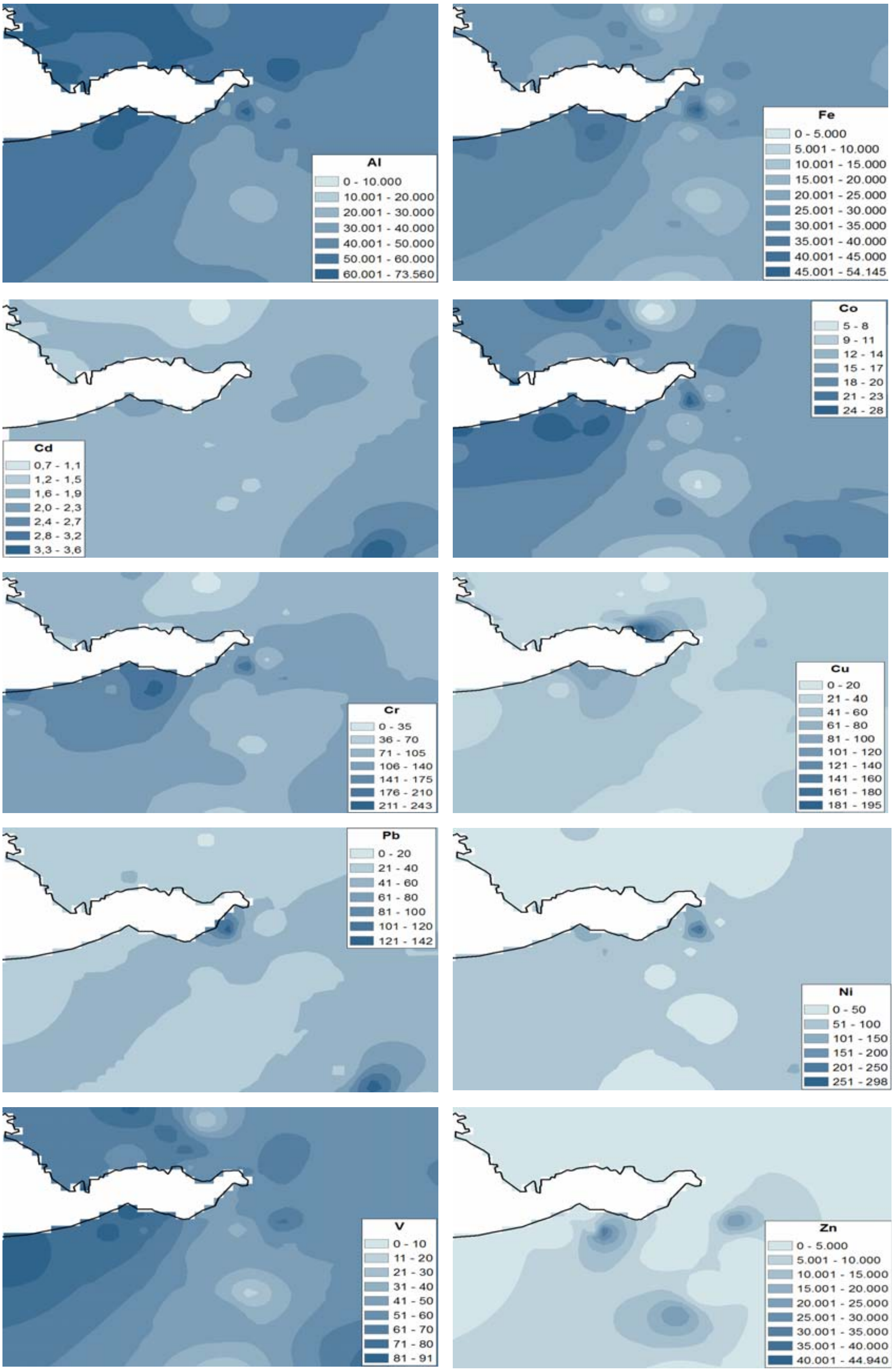


Figure 4.9 The distribution of some elemental concentration (μg g^{-1}) in the study area

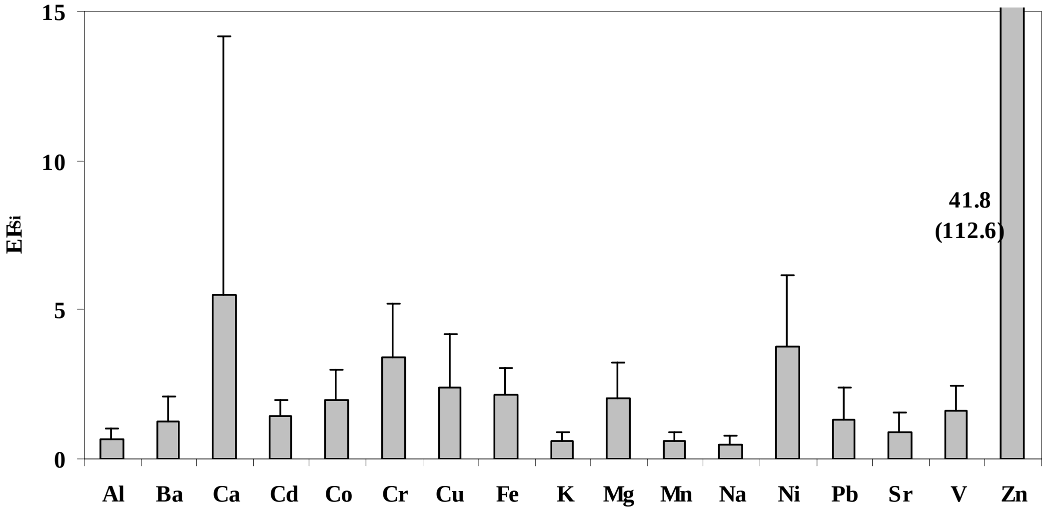


Figure 4.10 Crustal-enrichment factors of the elements in the study area. Error bars represent one standard deviation. The values of Zn are mean and one SD (in the parenthesis).

Spatial distributions of EFc of the trace elements are plotted in Figure 4.11. Comparison of Figure 4.9 with Figure 4.11 shows that the trace elements are generally enriched where their elemental concentrations are high. This might be another indicator that these elements arise from the man-made activities. However, some of the trace elements may be in natural content of the local soil appearing as enriched at the suburban sites, which were Cd, Co, Pb, and Zn. EFc vs Si diagrams for these elements were plotted in Figure 4.12 to evaluate this possibility.

EFc values of Ni and Zn do not seem to be correlated with Si concentrations, which are typical for elements of soil origin (Guvenc et al., 2003). It was mentioned previously that the enrichment of Zn in the soil is mainly due to the difference in the composition of local soils in the study area. Surprisingly, the enrichment of Ni is also because of the natural content of the soil. However, since EFc of Ni at the urban sites of the city (Figure 4.9) were higher than at the suburban sites, it might be concluded that a certain contribution from the man-made activities to Ni concentration in the soil is apparent particularly at the urban sites of the study area.

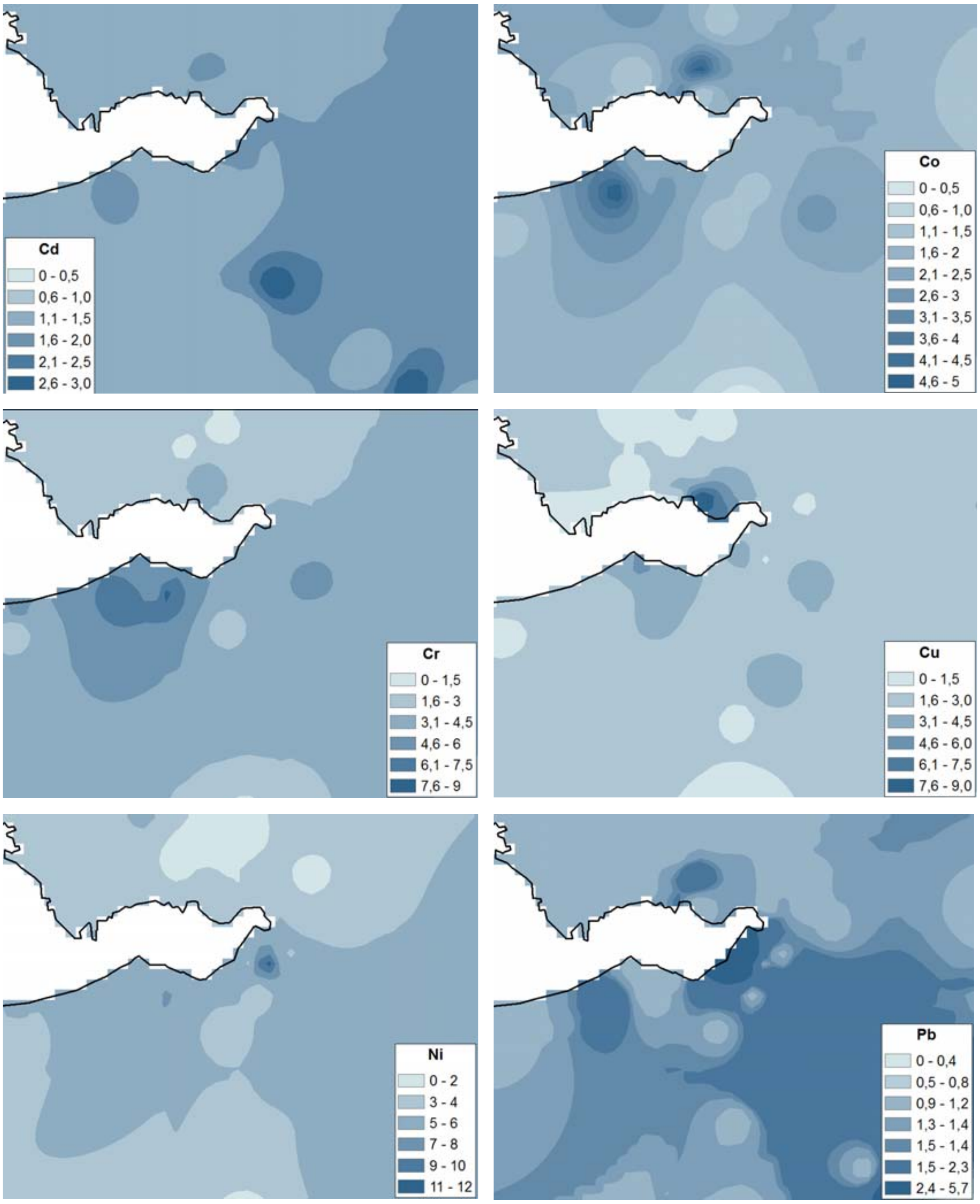


Figure 4.11 Distribution of EFc of some trace elements in soil of the study area

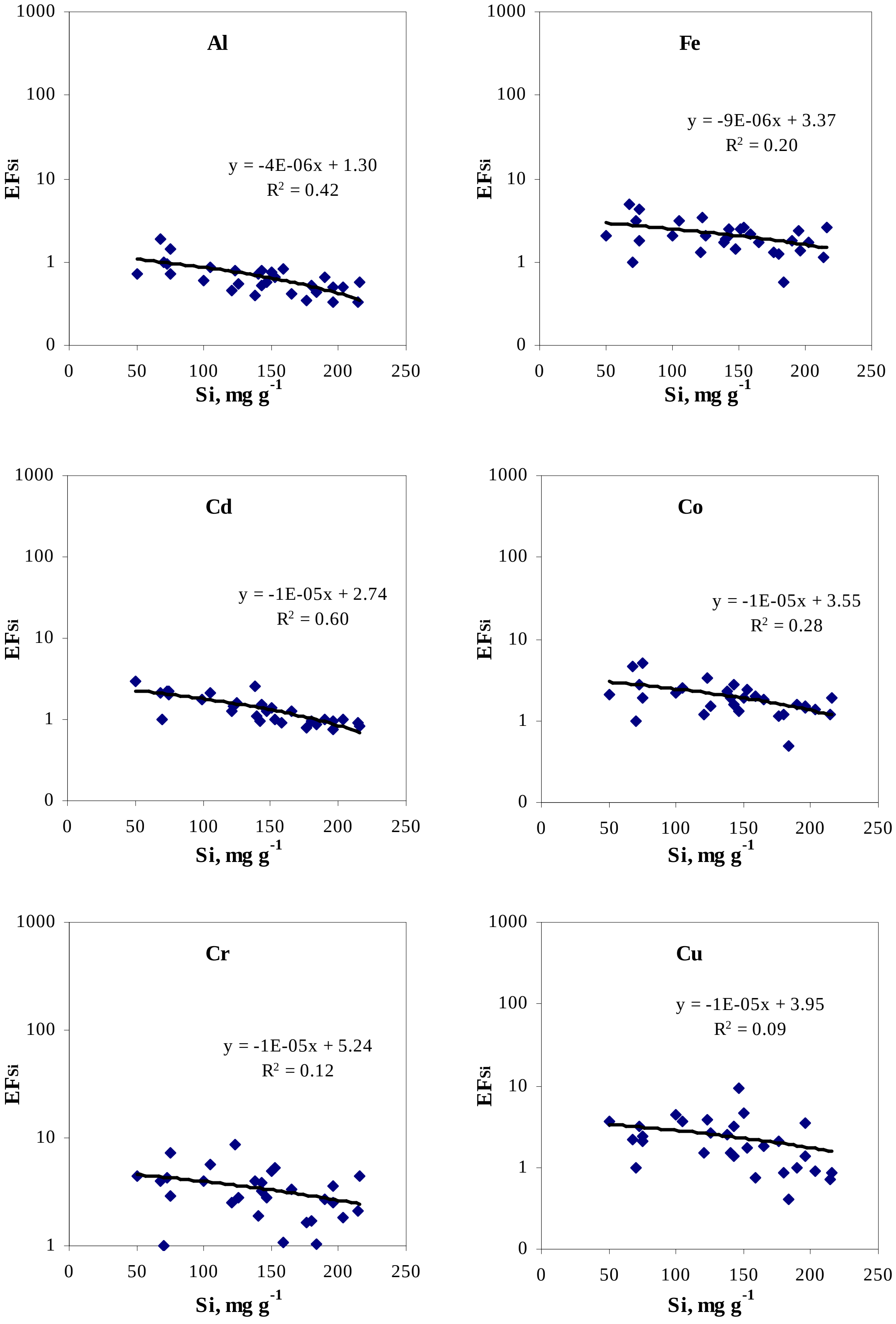


Figure 4.12 The EFc vs Si concentration plots of some elements

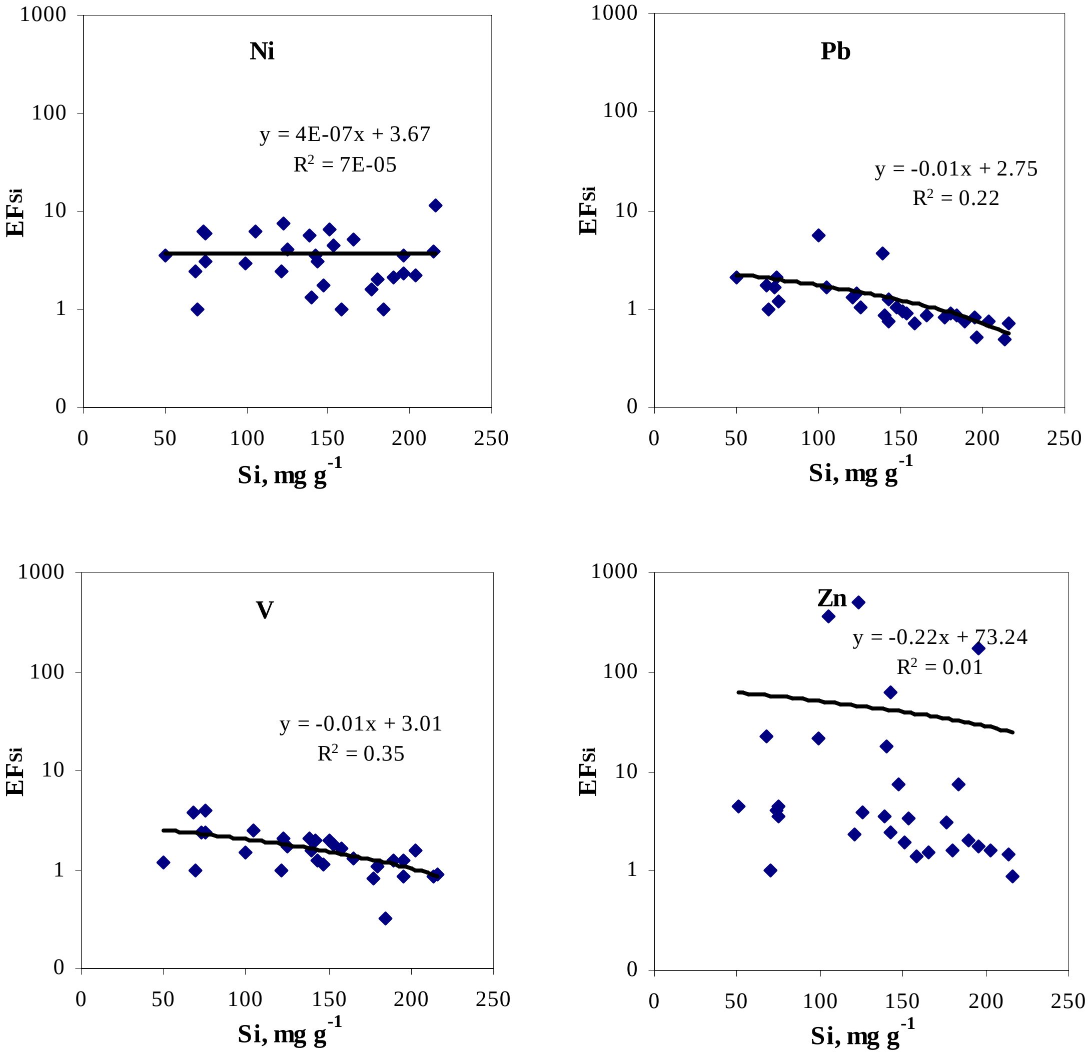


Figure 4.12 (Continued)

EFc of Al, Fe, Cd, Co, Cr, Cu, Pb, and V decrease with increasing Si concentrations as shown in Figure 4.12 indicating that the enrichment of these elements are due to the man-made activities in Izmir area. However, since Al and Fe are among terrestrial elements, and not significantly enriched in the soil, the decreasing EFc with increasing Si concentrations might be attributed the difference in the mineralogy of local soils. On the other hand, since the EFc of the Cd, Co, Cr, Cu, Pb and V are <5, it is concluded that the soil of Izmir region is not highly polluted due to the man-made activities. In conclusion, the man-made activities slightly altered the composition of the soil particularly at the urban sites of the city.

Factor Analysis: Factor analysis (FA) was performed to obtain groups that contain elements with similar pattern, and the results are given in Table 4.9. The analyses were performed by using Varimax rotated principle component analysis (Eigenvalues>1). Only the loadings over than 0.4 are listed in the table.

Table 4.9 The results of factor analysis for the soil data

Element	**Factor 1**	**Factor 2**	**Factor 3**	**Factor 4**	**Factor 5**	**Factor 6**
	Fossil Fuels	**Soil 1**	**Soil 2**	**Soil 3**	**Traffic**	**Soil 4**
Al	0.46	0.71	0.40			
Ba		0.95				
Ca			-0.86			
Cd					0.85	
Co	0.77					
Cr	0.83					
Cu						0.90
Fe	0.86					
K		0.47	0.63			
Mg	0.61				0.48	
Mn				0.83		
Na		0.64	0.55			
Ni	0.89					
Pb					0.84	
Si			0.79			
Sr		0.90				
V	0.55	0.51				
Zn				0.80		
Var. %	**22.7**	**19.9**	**13.6**	**11.2**	**11.2**	**6.8**
Cum.%	**22.7**	**42.6**	**56.2**	**67.4**	**78.6**	**85.4**

Six factors were extracted from the FA analysis and the explanation of the system variance (85.4%) was good. First factor that explains 27.7% of the variance contains some terrestrial elements such as Al, Fe, and Mg, and some trace elements such as Co, Cr, Ni, and V. Nickel and V are the fingerprint elements of fuel oil burning, the Soma coals, also, contain significant amounts of V and Ni. Since the Soma coal burning is a significant source of Al and Fe, the first factor was selected as the fossil fuel burning emissions.

The second and third factors contain the terrestrial elements. Thus, these factors represent the two different types of the soils in the study area. The fourth factor contains only Mn and Zn. As discussed previously, Zn content of some types of soil are extremely higher than the other soils. A simple linear regression analysis was performed for Zn vs. Mn concentrations in the soil, which resulted in a slope of 13.8 with $R^2=0.23$. Thus, it is concluded that this factor represents the third type of the soil.

The fifth factor clearly represents the contribution from man-made activities, since Cd and Pb are found in this factor. Lead is the indicator of the traffic emissions until Year 2003 when the utilization of Pb as fuel additive was forbidden. Thus, this factor might represent the traffic emissions in the past.

The last factor contain only Cu. As discussed previously, this factor may represent the soil type that carried downstream by the rivers that are located at Northeast of Izmir Bay.

In conclusion, the elemental profile of Izmir soil is mainly determined by the different soil types. On the other hand, the man-made activities, particularly fossil fuels burning and the traffic emissions are significant contributors to the trace elemental content of the soil in the study area.

4.2 Results of the Statistical Methods and Models

In this section, results of factor analysis, Positive Matrix Factorization and Chemical Mass Balance models applied to ambient air PM are discussed.

4.2.1 Results of Factor Analysis

Correlation matrixes were calculated to quantify the relation between the elemental concentrations. The correlation matrixes of the elemental concentrations in PM_{10} and $PM_{2.5}$ at the SUBURBAN site are given in Table 4.10. The significant correlation coefficients ($p<0.05$) were highlighted by bold fonts. High levels of correlations between the terrestrial elements in PM_{10} at the SUBURBAN site were obtained. Aluminum was, also, correlated with some terrestrial elements (i.e., Ba, Ca, Fe, K, Mg, Mn and Sr), and a few anthropogenic elements (i.e., Cd, V and Zn).

Similarly, Fe correlated with the same elemental groups (terrestrial and anthropogenic). These results suggest that the sources of the terrestrial elements are most probably soil, soil-related industries, and anthropogenic sources, particularly fossil fuels burning (coal and fuel oil). The correlation between Na and Mg indicate that a certain part of PM was originated from marine salt. Vanadium and Zn were, also, correlated well with some of the terrestrial and anthropogenic elements supporting the finding of the contribution of the fossil fuels burning on the both elemental groups (terrestrial and anthropogenic groups). Nearly excellent correlations between Zn and Pb-Mn may indicate at a same source, which may be the steel furnaces.

The r-values for elemental correlations in $PM_{2.5}$ were much higher than in PM_{10} at the SUBURBAN site for the same confidence level ($p<0.05$). The correlations were significant if only r is >0.7. Therefore, the numbers of elements with significant correlations in PM2.5 were significantly lower than in PM_{10}. It may show that the sources of $PM_{2.5}$ were limited compared to PM_{10} at the SUBURBAN site. Aluminum is correlated well with only Ni and Cr. This may suggest that there was no contribution of the natural sources on Al concentrations in the fine PM. On the other hand, there were high levels of correlations between Fe and the terrestrial elements (i.e., Ba, Ca, Mg and Sr). Thus, the sources of Fe were mainly soil and the soil-related industries. Chromium was correlated with some terrestrial (K and Mn) and anthropogenic elements (i.e., Pb, V, and Zn), however, r-values were negative. As in the case of PM_{10}, the relationships between Zn and Pb-Mn were almost perfect, and point to the steel furnaces. The significant difference from PM_{10} was regarding Fe. No-relationships between Zn, Pb, and Mn, and Fe strongly showed that Fe mainly existed in the coarse fraction of PM emitted from the steel furnaces. Similar high levels of relationships between V and Zn, and Pb and Mn showed the contribution of fossil fuel burning and the steel furnaces.

Table 4.10 The correlation matrixes for the elemental concentrations in PM$_{10}$ and PM$_{2.5}$ at the SUBURBAN site

PM$_{10}$	**Al**	**Ba**	**Ca**	**Cd**	**Cr**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**Na**	**Ni**	**Pb**	**Sr**	**V**	**Zn**
Al																
Ba	**0.58**															
Ca	**0.46**	**0.68**														
Cd	**0.51**	0.09	0.15													
Cr	0.00	-0.30	-0.2	0.18												
Cu	0.26	0.27	0.17	**0.56**	0.3											
Fe	**0.64**	**0.73**	**0.75**	0.22	-0.2	0.16										
K	**0.55**	**0.44**	**0.47**	**0.69**	0.2	**0.76**	**0.53**									
Mg	**0.51**	**0.62**	**0.44**	0.17	-0.1	0.14	**0.74**	0.35								
Mn	**0.60**	**0.55**	**0.44**	0.41	-0.1	0.29	**0.74**	**0.50**	**0.65**							
Na	0.22	0.31	0.28	0.00	0.2	0.13	0.41	0.32	**0.56**	0.15						
Ni	0.33	0.09	0.04	0.17	0.0	0.04	0.08	0.16	0.00	0.04	0.39					
Pb	0.39	0.41	0.27	0.39	-0.3	0.29	**0.55**	**0.50**	0.41	**0.84**	0.01	0.03				
Sr	**0.68**	**0.59**	**0.70**	**0.47**	-0.2	0.11	**0.75**	0.39	**0.70**	**0.73**	0.11	0.06	**0.44**			
V	**0.51**	**0.46**	0.22	**0.53**	-0.3	0.30	**0.51**	**0.43**	0.41	**0.81**	0.08	0.16	**0.82**	**0.53**		
Zn	**0.46**	**0.43**	0.33	**0.48**	-0.2	0.34	**0.63**	**0.56**	**0.48**	**0.89**	0.11	0.04	**0.97**	**0.52**	**0.84**	
PM$_{2.5}$																
Al																
Ba	0.49															
Ca	0.31	**0.92**														
Cd	-0.20	0.00	-0.10													
Cr	0.63	0.00	-0.10	**-0.70**												
Cu	**0.90**	0.28	0.11	-0.10	0.45											
Fe	0.49	**0.89**	**0.88**	-0.10	0.00	0.42										
K	-0.20	0.20	0.00	**0.72**	**-0.70**	-0.10	0.10									
Mg	0.37	**0.93**	**0.97**	0.08	-0.10	0.22	**0.94**	0.13								
Mn	-0.30	0.19	0.16	0.49	**-0.80**	0.00	0.37	0.67	0.29							
Na	-0.20	0.06	0.34	-0.20	0.02	-0.30	0.04	-0.30	0.21	-0.20						
Ni	**0.96**	0.23	0.07	-0.20	0.65	**0.93**	0.26	-0.30	0.13	-0.40	-0.20					
Pb	-0.40	-0.20	-0.30	0.43	**-0.70**	0.01	0.00	0.55	-0.20	**0.88**	-0.40	0.30				
Sr	0.25	**0.80**	**0.92**	0.26	-0.30	0.14	**0.80**	0.12	**0.94**	0.29	0.40	0.10	-0.10			
V	-0.50	-0.20	-0.20	0.66	**-0.90**	-0.10	0.00	**0.72**	-0.10	**0.91**	-0.30	-0.50	**0.95**	0.00		
Zn	-0.30	-0.20	-0.30	0.64	**-0.70**	0.09	-0.10	**0.72**	-0.20	**0.84**	-0.40	0.20	**0.95**	-0.10	**0.95**	

Numbers in bold represent significant correlations, $p<0.05$

Table 4.11 The correlation matrixes for the elemental concentrations in PM_{10} and $PM_{2.5}$ at the URBAN site

PM_{10}	Al	Ba	Ca	Cd	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Sr	V	Zn
Al																
Ba	**0.31**															
Ca	**0.42**	**0.84**														
Cd	0.04	0.21	0.05													
Cr	**0.29**	0.02	0.12	**0.40**												
Cu	**0.51**	0.24	**0.39**	0.03	0.25											
Fe	**0.52**	**0.63**	**0.66**	**0.45**	0.22	0.27										
K	**0.52**	**0.65**	**0.68**	0.25	0.14	**0.55**	**0.61**									
Mg	**0.38**	**0.42**	**0.56**	0.16	0.18	**0.36**	**0.65**	**0.36**								
Mn	**0.35**	**0.38**	**0.42**	**0.42**	0.11	0.26	**0.72**	**0.42**	**0.48**							
Na	-0.1	-0.1	0.0	-0.2	-0.1	0.1	-0.1	0.1	**0.30**	-0.2						
Ni	**0.44**	0.19	**0.38**	**0.43**	**0.45**	**0.43**	**0.46**	**0.59**	0.25	**0.36**	0.2					
Pb	0.15	**0.50**	**0.39**	0.26	0.21	**0.29**	**0.28**	**0.46**	0.21	**0.33**	-0.2	0.05				
Sr	0.0	0.19	0.06	**0.61**	**0.35**	0.0	**0.29**	0.04	0.12	0.17	-0.1	**0.31**	0.01			
V	0.01	**0.37**	0.25	**0.36**	-0.1	0.04	**0.49**	**0.35**	0.12	**0.73**	-0.3	0.14	**0.36**	0.09		
Zn	0.12	0.11	0.15	**0.39**	0.05	0.18	**0.37**	0.26	0.17	**0.76**	-0.2	0.25	0.25	0.09	**0.60**	
$PM_{2.5}$																
Al																
Ba	0.01															
Ca	**0.40**	0.02														
Cd	-0.0	-0.1	0.00													
Cr	**0.51**	0.07	0.11	-0.1												
Cu	**0.56**	-0.0	**0.92**	0.11	0.12											
Fe	**0.55**	0.05	0.25	**0.32**	**0.36**	**0.30**										
K	**0.37**	-0.0	**0.90**	0.22	0.00	**0.92**	**0.28**									
Mg	**0.45**	0.04	**0.95**	-0.1	0.15	**0.85**	**0.29**	**0.82**								
Mn	**0.36**	-0.0	**0.76**	**0.35**	-0.0	**0.82**	**0.31**	**0.79**	**0.72**							
Na	**0.34**	-0.0	**0.86**	0.06	0.02	**0.91**	0.11	**0.90**	**0.80**	**0.76**						
Ni	**0.43**	0.01	**0.94**	0.13	0.11	**0.96**	**0.28**	**0.94**	**0.88**	**0.82**	**0.9**					
Pb	0.02	-0.1	0.06	**0.71**	-0.1	0.13	0.21	0.25	-0.0	**0.31**	0.05	0.13				
Sr	0.16	0.07	**0.75**	-0.1	0.03	**0.72**	0.01	**0.62**	**0.69**	**0.70**	**0.73**	**0.74**	-0.1			
V	-0.0	-0.0	-0.0	**0.64**	-0.2	0.09	0.17	0.18	-0.0	**0.37**	-0.0	0.07	**0.73**	-0.2		
Zn	0.20	-0.1	0.2	**0.73**	-0.1	**0.34**	**0.34**	**0.38**	0.17	**0.64**	0.25	**0.31**	**0.69**	0.06	**0.80**	

Numbers in bold represent significant correlations, $p<0.05$

The correlation matrixes of the elemental concentrations at the URBAN site are given in Table 4.11. The correlations between the terrestrial elements (i.e., Ca, Ba, Fe, Mg, and Mn) were significant with $p<0.05$ in PM_{10} at the URBAN site. Aluminum was correlated well with some terrestrial elements (i.e., Ca, Ba, Fe, K, and Mg) and anthropogenic elements (i.e., Cr, Cu, and Ni) similar to correlations in PM_{10} at the SUBURBAN site (Table 4.10). However, Al was correlated with Cd, V, and Zn in PM_{10} at the SUBURBAN site, whereas Al was correlated to Cr, Cu, and Ni in PM_{10} at the URBAN site. The correlation of Al with different anthropogenic elements in PM_{10} at the URBAN and SUBURBAN sites may suggest that the anthropogenic sources contributing to Al concentrations were different at the two sites. There were high levels of correlations between Ca and a few anthropogenic elements (i.e., Cu, Ni, and Pb) in addition to the terrestrial elements. This may indicate that the contribution of polluted soil or the soil-related industries to Ca concentrations in PM_{10} at the URBAN site was significant. Cadmium was correlated well with some terrestrial elements (i.e., Fe, Mn, and Sr) and anthropogenic elements (i.e., Cr, Ni, V, and Zn). Manganese and Fe are among elements that are emitted from the steel furnaces in significant amounts, whereas V and Ni are elements arise from the fossil fuels burning. Ferrous was correlated with nearly all elements except for Cr, Cu, and Na that may indicate the contribution of soil and the soil-related industries, and anthropogenic sources to Fe concentrations in PM_{10} at the URBAN site. Sodium was only correlated to Mg as in the case of the SUBURBAN site for PM_{10}, which indicates the contribution of the marine salt to Na and Mg concentrations. Similar to the SUBURBAN site, Zn was correlated well with Fe, Mn, and V; but no correlation was found with Pb.

Similar to PM_{10}, Al was correlated with several terrestrial elements (i.e., Ca, Fe, K, Mg, and Mn) and a few anthropogenic elements (i.e., Cr, Cu, and Ni) in $PM_{2.5}$ at the URBAN site. The correlated anthropogenic elements are the same elements as with PM_{10} at the URBAN site. This may indicate the contribution of the same anthropogenic sources in addition to the terrestrial elements to Al concentrations. Calcium was correlated well with several terrestrial elements (i.e., K, Mg, Mn, and Sr) and two anthropogenic elements (i.e., Cu and Ni), which may suggest the contribution of soil and the soil-related industries or polluted soil to Ca concentrations. There was no relationship between Ca and Pb in $PM_{2.5}$ different from PM_{10}. This may indicate that Pb mainly existed in the coarse fraction of a related source. Similar to PM_{10}, Cd was correlated with elements come from the steel furnaces (i.e., Fe, Mn, Pb and Zn) and fossil fuels burning (i.e., V). Sodium was correlated well with marine (Mg), several terrestrial (i.e., Ca, K, Mn, and Sr), and two anthropogenic elements (i.e., Cu and Ni). This may indicate the contribution of all kinds of source groups. Lead was correlated with Mn, V, and Zn while Zn was correlated with Cd, Cu, Fe, Mn, Ni, Pb, and V. This may show that the main source of Zn in the fine fraction at the URBAN site was anthropogenic sources particularly the steel furnaces.

Factor analysis (FA) was applied to PM_{10} and $PM_{2.5}$ data at the two sites to obtain groups that contain elements with similar patterns to identify possible sources of PM. The analyses were performed using Varimax rotated principle component analysis (Eigenvalues>1). The results of factor analysis of the SUBURBAN site are given in Table 4.12. Only the significant loadings of the factors are given in the table. Identification of factors as sources that are given in the second line of the table was performed according to the loadings of the elements in the factors. Because of missing data, Cr and Ni were excluded for FA analysis at the SUBURBAN site. Three factors were determined in PM_{10}, which explained 72.2 % of the variance. The first factor consisted of Mg, Sr, Fe, Ca, Ba, and Na with high loading levels, and explained 28.9 % of the total variance. This factor clearly indicated soil and the soil-related industries. The second factor may represent the PM emitted from the fossil fuels burning and the steel furnaces, since it consisted of the mixture of these source-related elements. As stated in Table 4.6, the steel furnaces are the major emitters of Zn, Fe, Pb, and Mn, therefore, high loadings of these elements represented these sources. Also, V in the factor with a high loading (0.91) indicated fossil fuels burning sources. The second factor explained 27.9 % of the variance. The third factor was selected as industry, since it contained many anthropogenic elements (i.e., Cd, Cu, Al, and K). It was expected to obtain a factor of the marine salt, since Na only correlated with Mg (Table 4.10). However, Na existed in the first factor with a relatively low loading (0.52). Thus, this result may be interpreted as the limited contribution of the marine salt to first factor.

Traffic emissions seemed to be not a contributor to PM_{10} concentrations at the SUBURBAN site. Because utilization of Pb as a fuel additive was banned since 2003 in Turkey, as a result, Pb could not be used as an indicator of traffic emissions. As mentioned previously, Querol et al. (2001) and Manoli et al. (2002) and Fang et al. (2003) suggested that Zn, Mn, Cu, and Fe are marker elements for transportation in addition to Pb. As stated in Section 4.4, the elemental profile of transportation differed significantly according to the location, particularly the profile of re-entrained dust from roads. As a consequence, it was difficult to distinguish soil and road dusts by just only taking some elements into account. Therefore, profile of the second and the third factors may indicate the contribution of the traffic emissions, since above-mentioned elements existed in these factors. However, it is difficult to distinguish the traffic related sources with the studied elemental profiles.

Four factors were determined for $PM_{2.5}$, which explained a greater percentage of variation (82.8 %) than PM_{10}. The first factor was soil and the soil-related industries similar to PM_{10}, and explained 31.6% of the variation. The second and the third factors were the steel furnaces + fossil fuels burning, and traffic emissions; respectively. The third factor was selected as traffic emissions because Cu was included in the factor. In addition, variance was explained by these factors with 27.0% for the second factor and 12.6 % for the third factor, were very close to the respective factors of PM_{10}. Differently, a fourth factor containing Na and K was obtained for $PM_{2.5}$ that might indicate the marine salt. It was expected to encounter with a factor of marine salt in the coarse fraction, since the PM emitted from sea is mostly in the coarse fraction (Querol et al, 2001). Appearance of the marine salt source in the fine fraction may be attributed to the distance of the SUBURBAN site from the Izmir Bay suggesting that only fine particles are transported to the sampling site.

Table 4.12 Results of factor analysis for PM measured at the SUBURBAN site

	PM_{10}			**$PM_{2.5}$**			
	F1	**F2**	**F3**	**F1**	**F2**	**F3**	**F4**
	Soil	**Steel + Fossil Fuel**	**Industry**	**Soil**	**Steel + Fossil Fuel**	**Traffic**	**Sea Salt**
Al			0.74			0.90	
Ba	0.68			0.86			
Ca	0.80			0.92			
Cd		0.64	0.50		0.60		
Cu			0.87			0.89	
Fe	0.81	0.50		0.88			
K			0.62				0.78
Mg	0.86			0.92			
Mn		0.59			0.77		
Na	0.52						0.83
Pb		0.95			0.96		
Sr	0.82			0.94			
V		0.91			0.91		
Zn		0.91			0.93		
Var.%	**28.9**	**27.9**	**15.3**	**31.6**	**27.0**	**12.6**	**11.6**
Cum.%	**28.9**	**56.8**	**72.2**	**31.6**	**58.6**	**71.2**	**82.8**

FA results for PM_{10} and $PM_{2.5}$ at the URBAN site are given in Table 4.13. For PM_{10}, the first factor explained 35.7 % of the total variance. Pb and the terrestrial elements were included in the factor. The traffic related elements that were used to identify the factors at the SUBURBAN site were not found in the first factor. Despite this situation, the factor was selected as traffic + soil, since the URBAN site is near a main motorway. This factor may contain the PM arising from road dust and exhaust emissions. Since the loadings of the terrestrial elements were higher than Pb, it may be interpreted as the effect of the road dusts were higher than the exhaust emissions. The second factor with 14.0 % of total variance explained, was selected as the steel furnaces + fossil fuels burning since it included Zn, Mn, and V. The third and fourth factors were considered as industries, since many of anthropogenic elements existed in these factors. The last factor was selected as the marine salt due to inclusion of Na and Mg.

Results for $PM_{2.5}$ at the URBAN site are significantly different from PM_{10} ones. Four factors were determined with total variance explained (83.8%) was slightly higher than for PM_{10}. The first factor was determined as the mixture of traffic emissions and the marine salt explaining 45.7 % of the variance. Similar to PM_{10}, most of the terrestrial elements included in this factor. Copper and Mn were, also, included in the factor as the traffic related elements. The presence of Cu and Mn in the fine fraction may be interpreted as the exhaust emissions mainly consist of the fine PM. The second factor was selected as the mixture of the fossil fuel burning and the steel furnaces, since it contained Pb, V, Cd, and Zn. The third factor might be soil and the soil-related industries. The last factor could not be identified since it contained only Ba.

Table 4.13 Results of factor analysis for PM measured at the URBAN site

	PM_{10}					**$PM_{2.5}$**			
	F1	**F2**	**F3**	**F4**	**F5**	**F1**	**F2**	**F3**	**F4**
	Soil + Traffic	**Steel+Fossil Fuel**	**Ind. 1**	**Ind. 2**	**Sea Salt**	**Traffic+ Sea Salt**	**Steel+Fossil Fuels**	**Soil**	**Unkn.**
Al			0.73					0.81	
Ba	0.93								0.99
Ca	0.87					0.95			
Cd				0.80			0.87		
Cr			0.52	0.64				0.80	
Cu			0.81			0.94			
Fe	0.66							0.76	
K	0.62		0.56			0.92			
Mg	0.59				0.46	0.90			
Mn		0.86				0.83			
Na					0.80	0.94			
Ni			0.63	0.45		0.96			
Pb	0.47						0.87		
Sr				0.86		0.84			
V		0.81					0.90		
Zn		0.88					0.89		
Var. %	**35.7**	**14.0**	**11.6**	**7.9**	**7.3**	**45.7**	**20.7**	**11.1**	**6.3**
Cum.%	**35.7**	**49.7**	**61.3**	**69.2**	**76.5**	**45.7**	**66.4**	**77.5**	**83.8**

There were several difficulties with the interpretation of the correlation matrixes and FA results in our study due to the characteristic of studied elements. The main difficulty was to differentiate soil and the soil-related industries (i.e., cement, quarries, concrete plants, and ceramic). Because elemental profiles of soil and the soil-related industries are similar, and there are no distinct fingerprint element(s). The other difficulty for soil was the significant variation in terrestrial element concentrations according to the locations in Izmir area. Two of the most abundant elements in soils are Ca and Al. The content of the soils are dominated by one of these elements locally. This variation made it difficult to select the factors to represent the real sources. Another difficulty was to identify the traffic emissions. As mentioned previously, Pb is no fingerprint element for traffic emissions today. Several researchers have shown that PM emitted from the exhausts contains mainly elemental carbon (EC) and organic carbon (OC) (Funasaka et al., 1998; Watson et al., 2001; Watson & Chow, 2001; Chow et al., 2004; Giugliano et al., 2005; He et al., 2006). Br is also used a fingerprint element of the traffic emissions. Unfortunately, EC, OC and Br were not measured in this study. In conclusion, the number of species should be increased and the fingerprint species should be studied to solve such handicaps in using receptor models and tools.

The correlation matrix and FA are useful tools to estimate possible sources of ambient air PM concentrations. However, these tools cannot determine the contribution amounts of the sources. Further analyses using more sophisticated methods (i.e., Positive Matrix Factorization and Chemical Mass Balance Modeling) are required for more accurate source apportionment estimation.

4.2.2 Positive Matrix Factorization (PMF)

In this section, results of Positive Matrix Factorization (PMF) are evaluated. This evaluation includes the determination of the sources of PM and seven elements (Cd, Cr, Cu, Ni, Pb, V, and Zn), which are indicators of pollution from anthropogenic activities. Since the sources of PM_{10}, $PM_{2.5}$ and the seven elements in the fractions at the two sites are generally the same, only the fine fractions are evaluated. The significant differences in the sources of the fine and the coarse fractions are also evaluated.

4.2.2.1 Performance of PMF Runs

The critical point in a PMF run is to minimize the object function, Q(E), as described in section 3.6.3. Since the number of measurement days at the SUBURBAN and URBAN sites were 85 and 50 with 16 species, respectively, Q(E) was calculated as 1360 (85*16) and 800 (50*16) for the SUBURBAN and URBAN sites, respectively. These were the theoretical values, and to get physically meaningful results, Q(E) should be approximated to these values. The minimized values of Q(E) in this study were 966 and 945 for PM_{10} and $PM_{2.5}$ at the SUBURBAN site, respectively, whereas the values for PM_{10} and $PM_{2.5}$ were obtained as 500 and 635 at the URBAN site, respectively. These values showed that Q(E)s were minimized adequately, because the convergence of the appropriate run was considered as satisfactory by PMF v.1.1. Thus, appropriate numbers of factors were obtained.

4.2.2.2 $PM_{2.5}$ at the SUBURBAN Site

$PM_{2.5}$: Four factors were determined for $PM_{2.5}$ at the SUBURBAN site. The source profile and time series of the factors are given in Figure 4.13. The first part of the figure represents the source profile of the factor. The columns show the mass contribution of the species to the factor in ng m^{-3}, and the diamonds represent the percentage of species in the factor, e.g., if a diamond represents 80% of specie-X in factor-Y, it is 80% of measured X exists in factor-Y. These percents are the major tool to identify the factors as sources. The second part of the figures represents the time series of source (factor) contribution to PM concentrations. They were calculated as described in section 3.6.3. The time series are the auxiliary tool to determine the sources.

The first factor was determined as the marine salt, since nearly 90% of Na existed in this factor. The contribution amount of the marine salt to $PM_{2.5}$ concentration is very limited compared to contribution amounts of other sources. The time series showed that there was no significant seasonal variation in contribution of the marine salt. The time series indicated that the contribution of the marine salt to $PM_{2.5}$ concentration did not have a regular pattern. The mean mass amounts that contributed to PM_{10} and $PM_{2.5}$ by the marine salt at the SUBURBAN site were calculated as 1.52 and 0.74 µg m^{-3}, respectively. Thus, nearly half of the PM originating from the marine salt consisted of fine particles at the SUBURBAN site.

The second factor indicated the mixture of the steel furnaces and fossil fuels burning, since it contained Zn, Pb, Mn, Fe, Ni, and V. Comparison to the same factor obtained for PM_{10} at the SUBURBAN site clearly showed that the percentages of Zn, Pb, Mn, and Fe of the fine fraction were significantly higher than the coarse. It might imply that these elements mainly exist in the fine fraction of PM emitted from the steel furnaces, or mainly fine PM could reach to the SUBURBAN site. Similar higher V and Ni percentages in $PM_{2.5}$ than in PM_{10} might be attributed to the same reason. The average mass contribution of the steel furnaces + fuels to the concentrations of $PM_{2.5}$ and PM_{10} at the SUBURBAN site were calculated as 8.76 and 14.07 $\mu g\ m^{-3}$, respectively, which may indicate that approximately 60% of PM emitted from the steel furnaces + fuels reached to the SUBURBAN site are fine particles.

The third factor is selected as the soil-related industries named MINERAL containing area source of Belkahve region and the cement plant, since it is dominated by the terrestrial elements (i.e. Ca, Mg, Ba, and Sr). As discussed previously, there are several difficulties to distinguish soil and the soil-related industries, because mass fractions of many elements were generally close for soil and the soil-related industries (Table 4.6). The major differences were observed in the mass fractions of Al and Ca. The mass fraction of Al in soil was higher than the soil-related industries, whereas Ca contents of the soil-related industries were much higher the soil. Therefore, Al and Ca were used to recognize soil and the soil-related industries. The factor was chosen as the soil-related industries because Ca was included. Similar to the marine salt factor, the time series of the soil-related industries did not have a regular pattern. The contributed mass amounts of the soil-related industries to PM_{10} and $PM_{2.5}$ concentrations at the SUBURBAN site were calculated as 5.45 and 2.32 $\mu g\ m^{-3}$, respectively. Thus, nearly 40% of PM from the soil-related industries consisted of fine particles at the SUBURBAN site, or, 40% of the soil-related industries emitted PM reached to the site was fine PM. In other words, the PM emitted from the soil-related industries was mainly coarse.

The last factor seems to be the mixture of soil and the traffic emissions. As discussed previously, there were no fingerprint elements for traffic source, since Pb utilization was banned since 2003, in addition, Br, organic carbon (OC) and elemental carbon (OC) were not measured in this study. As mentioned in Section 4.5.2, Zn, Cu, Fe, and Mn can be used as the fingerprint elements for traffic emissions. Elemental ratios of Zn/Cu, Zn/Ni, Zn/Cr, Cu/Cr, Cu/Al, Cu/Fe, and Cu/Ca of traffic emissions that had been obtained from concurrent measurements (Table 4.6) were used to identify the traffic emissions. The ratios were calculated for the factors to determine the representing factor. Zn/Ni, Zn/Cr and Cu/Al ratios of the factor were 1.93, 2.9, and 0.02, respectively, whereas Zn/Ni, Zn/Cr and Cu/Al ratios of the traffic emissions were calculated as 4.3, 2.5, and 0.04, respectively. So, these ratios may show that this factor might contain the PM emitted from the traffic emissions. To investigate whether there is a contribution from soil, Ca/Al, Ca/Ba, Ca/Fe, Ca/Mg, Ca/Mn and Ca/Sr ratios of $PM_{2.5}$ were calculated for soil (Table 4.6) and factor-4. Ca/Al, Ca/Ba, Ca/Fe, Ca/Mg, Ca/Mn, and Ca/Sr ratios are 1.92, 293, 1.85, 9.6, 61, and 628, for soil, and 0.07, 905, 1.2, 3.5, 120, and 45.3 for factor-4, respectively. The ratios might show that there was no contribution from soil. Therefore, factor-4 was selected as the traffic emissions only. The mass contributions of the traffic emissions to PM_{10} and $PM_{2.5}$ at the SUBURBAN site were calculated as 7.69 and 2.51 µg m^{-3}, respectively. This means that 30% of PM emitted from the traffic emissions consisted of fine particles. This result is in contradiction with the previous findings and measurements that majority (~80%) of emitted PM from traffic emissions is fine. This difference could not be interpreted.

A fifth factor that is soil, was obtained in PM_{10} at the SUBURBAN site differently from $PM_{2.5}$. Inclusion of Al in the factor, and a clear seasonal variation that the contribution of the factor to PM concentrations at the SUBURBAN site in summer being significantly higher than in winter were the reasons for selecting the factor as soil. Finding soil as a contributor to PM_{10} concentrations but not to $PM_{2.5}$ might be interpreted as the windblown PM from soil was mainly coarse.

The scatter-plot of measured vs. predicted $PM_{2.5}$ concentrations, and the contributions of four sources at the SUBURBAN site are given in Figure 4.14a and 4.14b, respectively. The performance of PMF in predicting $PM_{2.5}$ concentrations is quite well. r^2 and slope of the simple regression line was 0.50 and 0.53, respectively. On the other hand, the undetermined part was 38%. The contribution percentage of the steel furnaces + fuels (37%) was slightly higher than PM_{10} (32%). These values are consistent with the previous findings that the PM emitted from fossil fuel burning and steel furnaces are mainly fine; or, the PM reached to the SUBURBAN site was mainly fine.

Cadmium: The major contributors to Cd concentrations in $PM_{2.5}$ at the SUBURBAN site were the steel furnaces + fuels (50%), the traffic emissions (33%) and the marine salt (17%). Table 4.6 shows that the major emitters of Cd were the steel furnaces, the lead recovery furnaces, and the cement plant. The traffic emissions and the marine salt were not significant sources of Cd. Contribution of the traffic emissions to Cd concentrations in PM_{10} at the SUBURBAN site was calculated as 40%. The elemental fraction of Cd in the traffic emissions in $PM_{2.5}$ (0.0004%) was higher than in PM_{10} (0.0003%). Thus, the contribution of the traffic emissions to Cd concentration in $PM_{2.5}$ was expected to be higher than in PM_{10}. However, the PMF predicted Cd concentrations at the SUBURBAN site were partially unrealistic, since the traffic emissions and the marine salt were not significant Cd sources.

Chromium: One of the best source apportionment results was obtained for Cr in $PM_{2.5}$ at the SUBURBAN site. The major contributors were the steel furnaces + fuels (64%), the traffic emissions (25%), and the soil-related industries (12%). These sources are consistent with the major emitters of Cr given in Table 4.6.

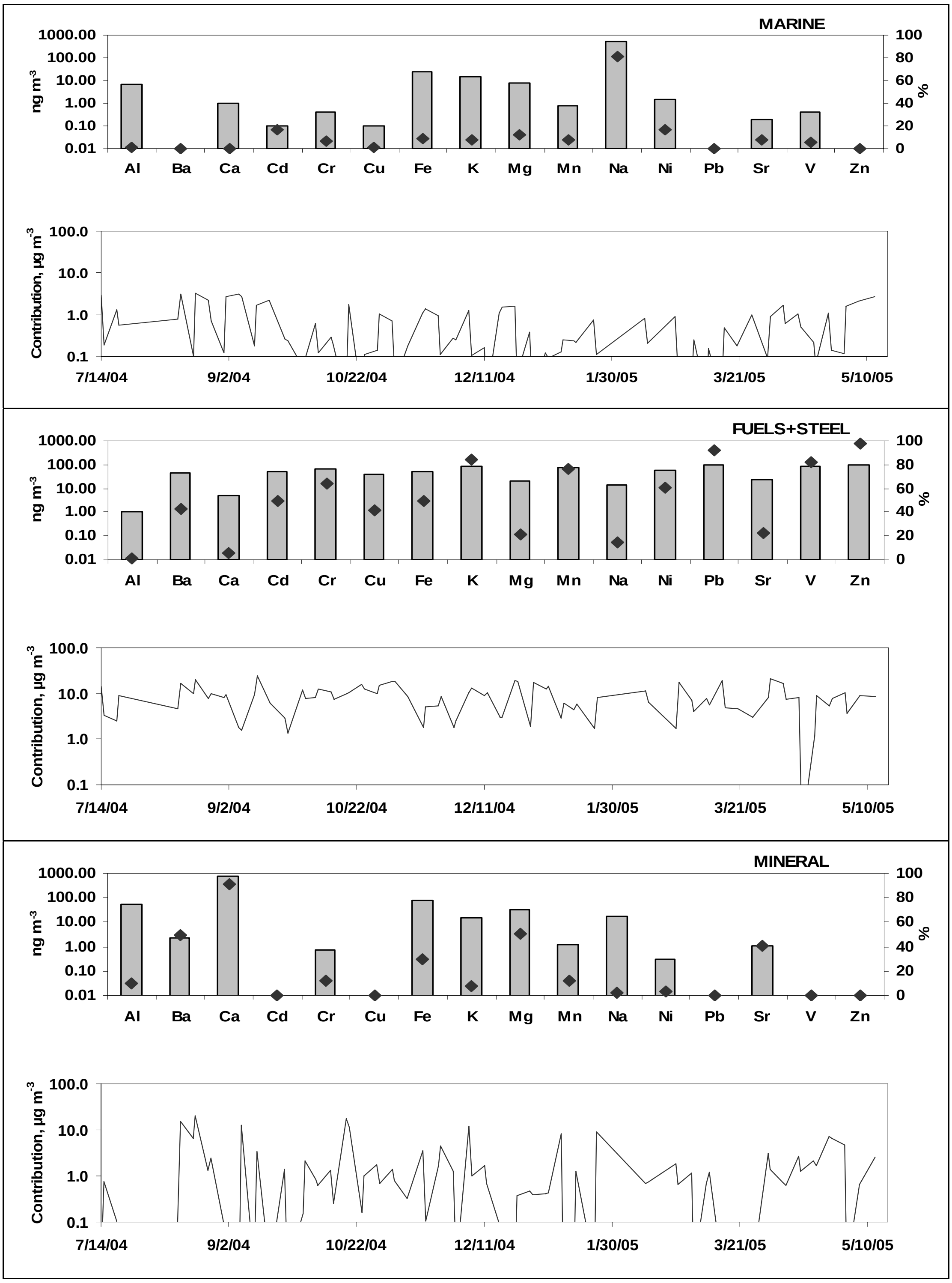


Figure 4.13 The sources and time series of contribution for $PM_{2.5}$ at the SUBURBAN site

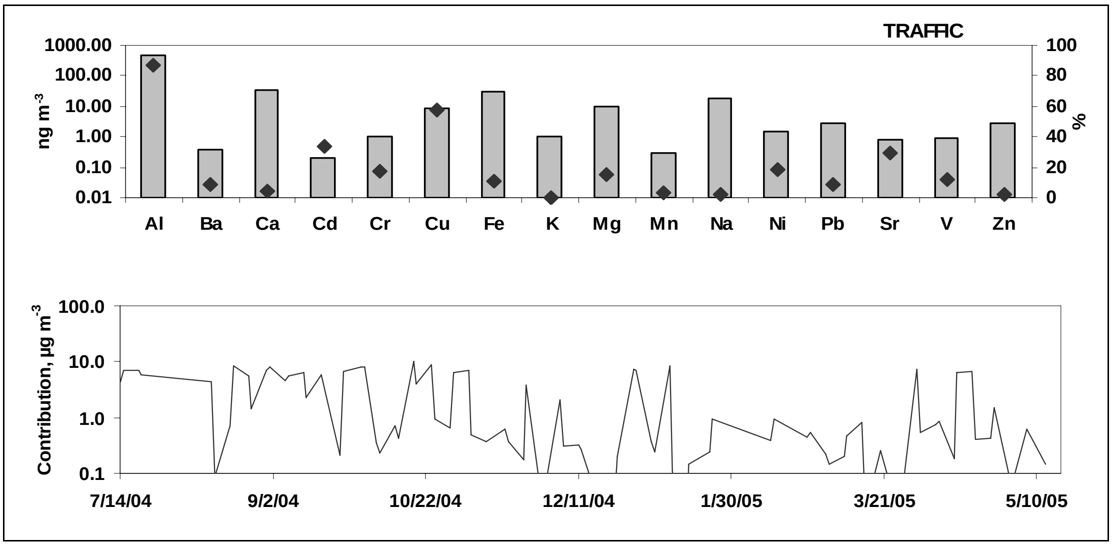


Figure 4.13 (Continued)

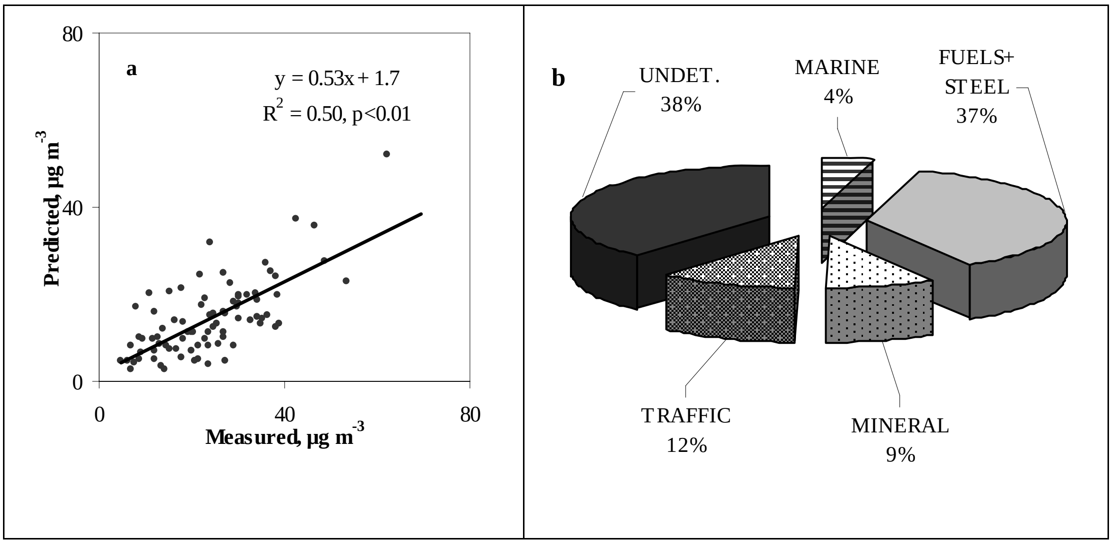


Figure 4.14 (a) Scatter-plot of measured vs. predicted $PM_{2.5}$ concentrations and (b) percentages of source contributions of the four factors at the SUBURBAN site

Copper: Another good result was obtained regarding the contributors of Cu. There were two contributors, the traffic emissions (58%) and the steel furnaces + fuels (42%), which were, also, consistent with the emitters of Cu. The contribution of the traffic emissions to Cu in $PM_{2.5}$ and in PM_{10} were calculated as 58% and 45%, respectively. These values might imply that Cu mainly existed in the fine fraction of the PM emitted from the traffic emissions, or, mainly, fine PM could reach to the SUBURBAN site.

Nickel, Pb, V, and Zn: The contributors to Ni, Pb, V, and Zn concentrations in $PM_{2.5}$ at the SUBURBAN site were the same. The major contributor to these elemental concentrations was the steel furnaces + fuels, whereas the traffic emissions were the minor contributors. The calculated contribution level of the steel furnaces + fuels to these elemental concentrations in $PM_{2.5}$ was significantly higher than in PM_{10}. It might strongly indicate that these elements mainly existed in the fine fraction of PM emitted from these sources, or, mainly fine PM could be transported to the site.

4.2.2.3 $PM_{2.5}$ at the URBAN Site

$PM_{2.5}$: Four factors were determined for $PM_{2.5}$ at the URBAN site. The profiles and time series of the factors are given in Figure 4.15. Similar to the factors of the SUBURBAN site, fuels and the steel industries exist together in the same factor. However, six factors were determined for PM_{10} at the URBAN site, and factors of the steel furnaces and fossil fuels burning could be separated. The contribution profile of the fuels in PM_{10} at the URBAN site had a regular pattern in winter and summer but the profile of the steel furnaces did not have a regular pattern. The contribution of the steel furnaces and the fuels in PM_{10} were calculated as 4% and 27%, respectively. Thus, it might be suggested that the contribution of the fuels to PM concentrations at the two sites are much higher than the contribution of the steel furnaces. It might, also, suggest that contribution profile of the fuels have a regular pattern in Izmir city, whereas profile of the steel furnaces does not have a similar regular pattern.

The second factor was selected as the soil-related industries, since the most of the terrestrial elements, particularly Ca, were included in the factor. Surprisingly, the contribution of the soil-related industries increased significantly in winter compared to summer. The reason for this result may be the meteorological factors, particularly the wind directions. A regular and continuous contribution profile of the soil-related industries is observed in $PM_{2.5}$ at the URBAN site

The third factor clearly indicated the marine salt, because contribution of Na was >90%. The contribution of the marine salt did not have a regular and continuous pattern.

The last factor was selected as the traffic emissions. The Zn/Cr, Zn/Cu, Cu/Al, Cu/Cr, Cu/Fe, and Cu/V of the factor were calculated as 2.4, 4.7, 0.02, 0.58, 0.05, and 4.0, respectively. Zn-Cr, Zn-Cu, Cu-Al, Cu-Cr, Cu-Fe, and Cu-V ratios of the traffic emissions were 2.5, 4.8, 0.04, 0.52, 0.035, and 3.0, respectively. Most of the ratios are similar. The contribution of the traffic emissions in summer was slightly higher than in winter.

Similar to the SUBURBAN site, soil was a contributor to PM_{10} concentrations at the URBAN site but it was not a contributor to the fine fraction. Thus, it is suggested that the PM blown from the surface of the soil was mainly coarse.

Regression analysis for the predicted vs. measured $PM_{2.5}$ at the URBAN site is given in Figure 4.16. r^2 and slope of the line are 0.71 and 0.72, respectively, which is the best fit among the other constructed regression lines. On the other hand, the undetermined part of the prediction (48%) was large. Nearly half of $PM_{2.5}$ could not be predicted by PMF. The major contributor to $PM_{2.5}$ concentrations was, also, the steel furnaces + fuels. However, its contribution (22%) was significantly lower than the contribution at the SUBURBAN site, and than PM_{10} at the URBAN site. The contribution of the traffic emissions is close to the values calculated for the SUBURBAN site but it is notably higher than PM_{10} of the URBAN site. Similarly, the contribution of the marine salt (14%) was three times higher than the SUBURBAN site (4%), and two times higher than PM_{10} of the URBAN site (6%). On the other hand, the contribution of the soil-related industries (1%) was nearly equal to PM_{10} at the URBAN site, while it was much less than $PM_{2.5}$ of the SUBURBAN site (~9%).

Trace Elements: Contribution profiles of the trace elements in $PM_{2.5}$ at the URBAN site were consistent with the emitters. The only significant inconsistency was observed regarding the contribution of Cr. It seemed that there was no contribution from the steel furnaces + fuels. The major contributor for the other elements was the steel furnaces + fuels. The traffic emissions were another significant contributor to the trace elemental concentrations in the fine fraction at the URBAN site. Generally, contribution of the traffic emissions to the elemental concentrations in $PM_{2.5}$ was higher than in PM_{10}. This might indicate the fine character of the PM emitted from the traffic emissions.

Since the measurements of PM_{10} and $PM_{2.5}$ were not performed concurrently at the URBAN site, an evaluation regarding fractional contribution by the sources could not be performed.

4.2.2.4 Evaluation of PMF Results

Generally, r^2 values for PM concentrations at the two sites were around 0.50, whereas the slopes of regression lines vary between 0.4 and 0.7. When these performances of the PMF are compared to other studies in the literature (Kim et al., 2004; Zhao & Hopke, 2006; Qin, Kim & Hopke, 2006), it can be seen that the r^2 values of this study are a bit lower, while the undetermined parts in this study are considerably higher. A lesser number of samples and measured species compared to the literature is most probably the reason for the difference. In addition, more source-specific species (i.e., OC, EC, Br, Se, etc.) were measured in the literature; thus, the separation of the sources could be achieved without any data on local sources. In other studies, the contribution levels are generally >80% and correlation coefficients (r^2) are >0.8. In this study, identification of the factors as sources could be achieved, since the data on the sources of PM including the elemental profiles were measured. In fact, the number and characteristics of the measured elements were not adequate to identify some sources, particularly, the traffic emissions, soil, and the soil-related industries. The sources could be determined with the help of elemental ratios. The same difficulties were encountered in the correlation matrixes and factor analysis.

Unrealistic and unexpected results were found regarding the contribution of the traffic emissions. Since the URBAN site is located near a main motorway, the traffic emissions were expected to be the major contributor to PM concentrations. However, the effect of the traffic emissions on the PM concentrations was very limited. This was most probably because, the dominating species in traffic emissions, OC and EC (Funasaka et al., 1998; Watson et al., 2001; Watson et al., 2001; Chow et al., 2004; Giugliano et al., 2005; He et al., 2006), were not measured in this study. As a result, the traffic emissions were found not to be a major source of the studied elements. The mass ratios of measured elements to PM from the traffic emissions were about 5% in PM_{10} and in $PM_{2.5}$ (Table 4.6). Thus, the determined elemental content of the PM emitted from the traffic emissions took a very little part of the total PM. Therefore, the traffic emissions seem to be not a major contributor to the PM concentrations. On the other hand, the steel furnaces could be identified easily, since some of the elements (i.e., Zn, Pb, Fe, and Mn) were dominant in the emitted PM (Table 4.6). Furthermore, the ratios of the measured elements to PM mass were about 80%. Similarly, the ratios of the fuels, soil and the soil-related industries were much higher than the traffic, therefore, they can be considered as contributors of PM at the two sites. It is apparent that if the number of measured species is increased, the sum of measured elemental mass would approach the mass of PM, and the contribution profile to PM concentrations would considerably change.

The performance of PMF on the source apportionment of the seven trace elements was generally satisfactory except for PM_{10} at the SUBURBAN site. The major contributors of these elements may be the steel furnaces + fuels, and the traffic emissions. The model could separate the sources of the steel furnaces and the fuels only at the URBAN site for PM_{10}. The results at this site clearly showed that the effect of the steel furnaces on PM concentrations is very limited (~4%), whereas the contributions to trace elemental concentrations, particularly Pb, Zn, and Cd, were much higher.

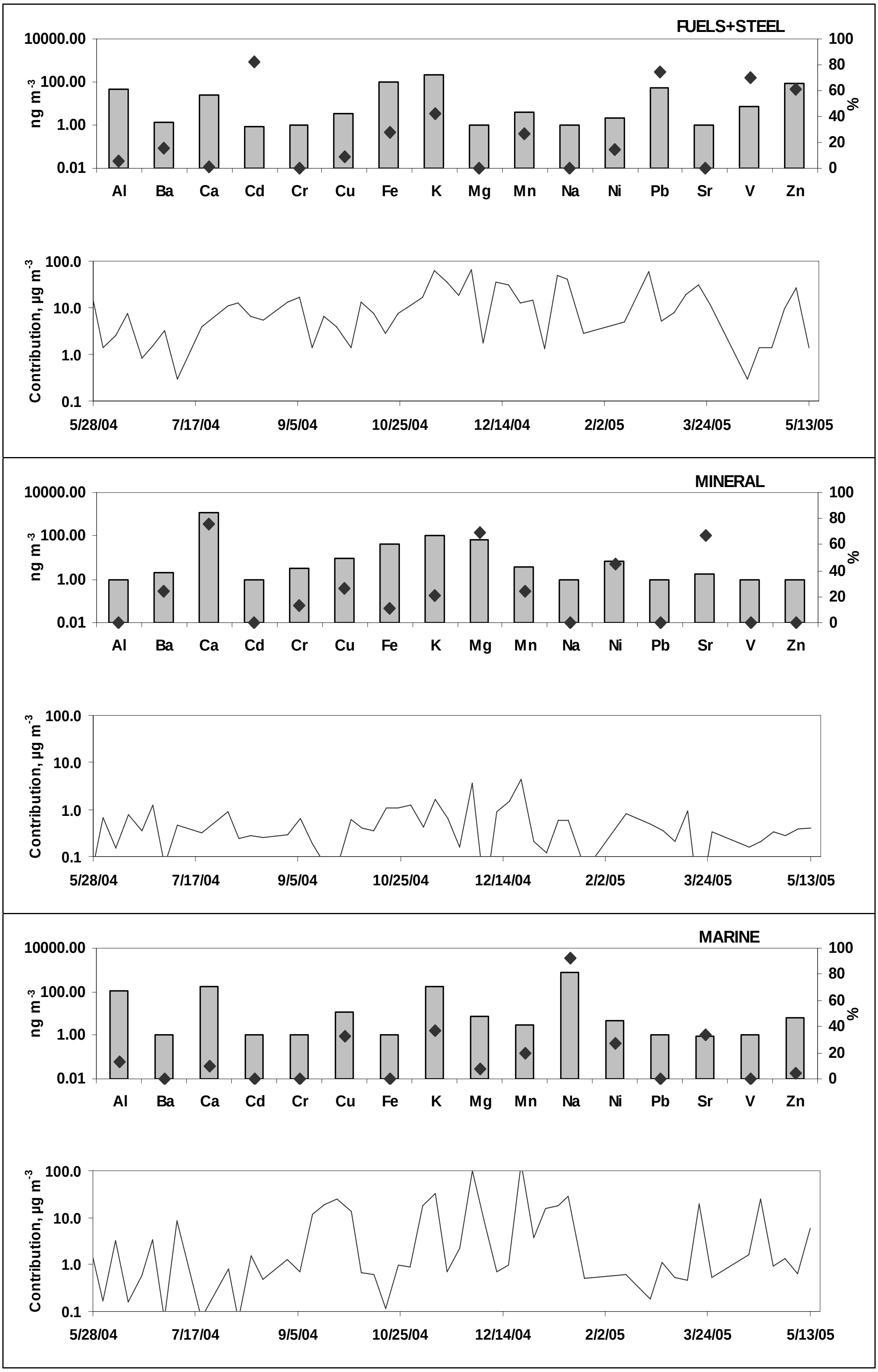
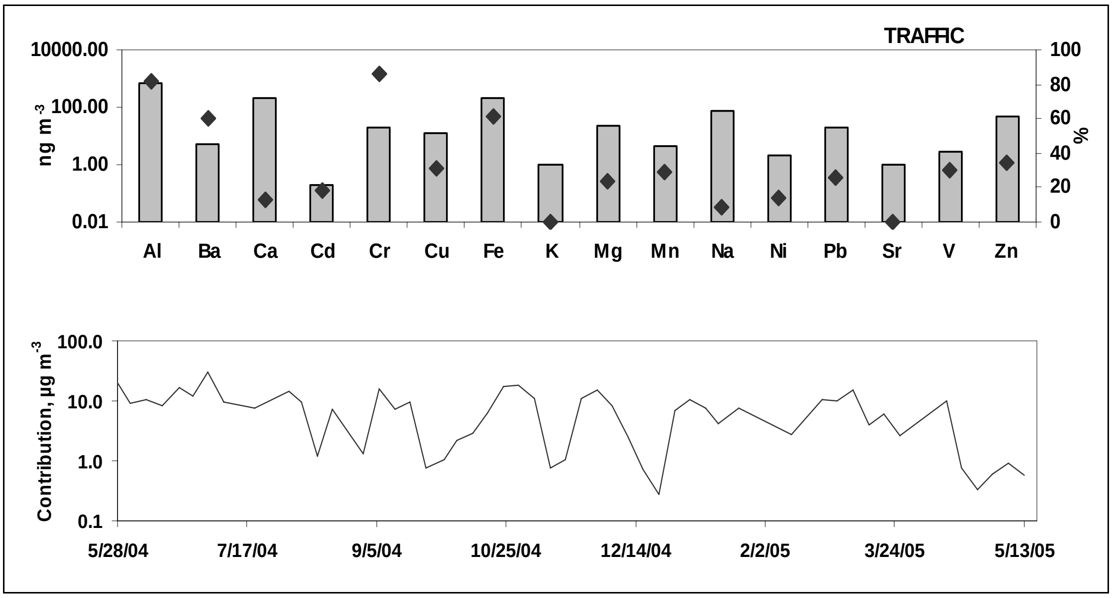


Figure 4.15 The sources and time series of contribution for $PM_{2.5}$ at the URBAN site



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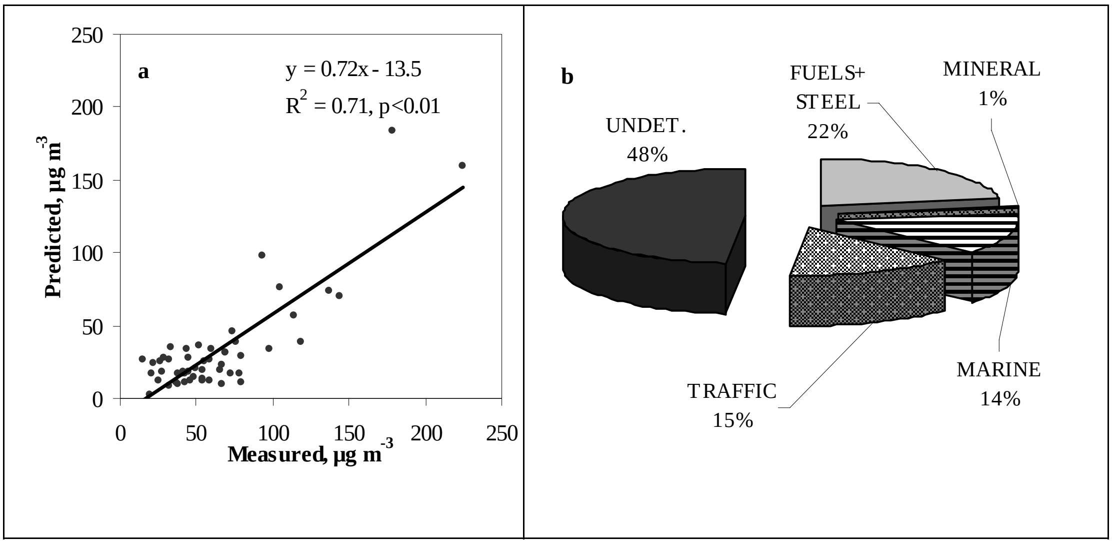

Figure 4.16 (a) Scatter-plot of measured vs. predicted PM_{10} concentrations and (b) percentages of source contributions of the four factors at the SUBURBAN site

Another significant result is regarding the fractional contribution by the steel furnaces + fuels. The contributions of these sources to the trace elemental concentrations in the fine PM at the SUBURBAN site were significantly higher than in PM_{10}. This might be interpreted as these sources generally emit fine PM, or, mainly the fine PM could be transported to the SUBURBAN site. Although measurements of PM_{10} and $PM_{2.5}$ were not performed concurrently at the URBAN site, the results may show that the trace elements mainly exist in the fine fraction of the PM emitted from the traffic emissions, because the contribution of the traffic emissions to the trace elemental concentrations in $PM_{2.5}$ was much higher than in PM_{10} at the URBAN site.

Sources of some elements (i.e., Cr and Pb) could not be separated with PMF. The marine salt seemed to be a major contributor of some elemental concentrations. In fact, the marine salt was not a significant emitter of the related trace elements. Other sources such as the soil-related industries may exist in the marine salt factor. Similarly, the lead recovery furnaces might be in the traffic factor, since the traffic emissions are not an emitter of Pb. Increasing the number of measured species and samples might solve such distinguishing problems.

4.2.3 Chemical Mass Balance (CMB) Model

In this section, results of CMB model are evaluated. This evaluation includes determination of the sources of PM and seven elements (Cd, Cr, Cu, Ni, Pb, V, and Zn) that are important in terms of identifying the pollution from anthropogenic activities. Since the sources of PM_{10}, $PM_{2.5}$, and the seven elements in the fractions at the two sites were about the same, only the fine fraction is evaluated. The significant differences in the sources of the fine and the coarse fractions are also evaluated.

4.2.3.1 Performance of CMB Runs

The cumulative frequency table of X^2 for the two sites is given in Table 4.14. The X^2 values were generally between 0 and 10. More than half of X^2 values were <4 at the two sites. The best X^2 values were obtained at the URBAN site for PM_{10}.

Descriptive statistics of output parameters of CMB runs are summarized in Table 4.15. In addition to the statistics, uncertainties in the calculated and measured PM concentrations (XuPM/PM) are given in Table 4.15.

Table 4.14 The cumulative frequency table of X^2 values calculated by CMB at the two sites

	SUBURBAN		**URBAN**	
	PM_{10}	**$PM_{2.5}$**	**PM_{10}**	**$PM_{2.5}$**
X^2	**Cum.Frequency, %**	**Cum.Frequency, %**	**Cum.Frequency, %**	**Cum.Frequency, %**
2	33	26	41	18
4	56	51	71	51
10	81	81	92	86
20	94	93	96	100

Table 4.15 Descriptive statistics of the CMB results

	SUBURBAN PM_{10}					**SUBURBAN $PM_{2.5}$**				
	Min	**Max**	**Mean**	**SD**	**90%**	**Min**	**Max**	**Mean**	**SD**	**90%**
Xu(mea.), %	3.0	37.0	7.5	5.3	13.3	3.9	56.5	15.1	10.0	29.9
Xu(cal.), %	2.6	60.3	16.5	12.5	34.0	1.5	35.4	14.1	5.9	19.1
r^2	0.82	1.00	0.99	0.03	1.00	0.62	1.00	0.97	0.05	1.00
Ccal./Cmea. %	74.2	133.8	101.0	10.6	111.9	74.4	158.3	101.9	11.0	114.2

	URBAN PM_{10}					**URBAN $PM_{2.5}$**				
	Min	**Max**	**Mean**	**SD**	**90%**	**Min**	**Max**	**Mean**	**SD**	**90%**
Xu(mea.), %	1.5	34.0	4.8	4.7	6.6	2.0	18.1	6.3	3.5	10.4
Xu(cal.), %	5.6	38.5	13.5	6.6	22.8	8.2	43.4	14.4	5.3	18.6
r^2	0.92	1.00	0.99	0.02	1.00	0.83	1.00	0.97	0.04	1.00
Ccal./Cmea., %	83.6	116.1	101.0	7.3	110.3	81.2	119.6	98.7	7.9	109.6

Xu(mea.) : The uncertainty/concentration percentage of the measured PM
Xu(cal.) : The uncertainty/concentration percentage of the predicted PM by CMB
Ccal./Cmea.: Ratio of predicted/measured PM concentrations
90 % : 90th percentile value

Table 4.15 shows that the requirements of CMB model were successfully met at the two sites for the both PM fractions. Uncertainties in the predicted are approximately two times higher than uncertainty in the measured values at the two sites whereas r^2 values were very close to unity. The calculated/measured ratios of PM concentrations at the two sites were generally between 80-120%.

The regressions between measured and predicted $PM_{2.5}$ concentrations, and some elemental concentrations at the two sites are given in Figure 4.17. Since, the plots of PM_{10} and $PM_{2.5}$ significantly resemble, only the fine fractions are assessed. The X-axis represents the measured concentrations.

$PM_{2.5}$ at the SUBURBAN site: Modeling results for $PM_{2.5}$ at the SUBURBAN site were quite good. The slope indicated that the $PM_{2.5}$ concentrations were predicted by CMB with only 1% deviation. The fit of the line (R^2 =0.97) was also good. The residual of the line was very close to zero.

Unfortunately, the results for Cd were not as good. The slope indicated that more than 30% of Cd could not be predicted. The residual value (0.0002) was very high compared to the lowest measured Cd concentration, which was 0.0001 µg m^{-3}. The reason for this discrepancy was most probably the low concentrations of Cd at the SUBURBAN site of which some were below the MDL. Similar results were also encountered with the concentrations of Ni, Cu and Cr.

On the other hand, quite good results were obtained for elements that could easily be detected. The slope for Pb (0.97) indicated that nearly all Pb were predicted successfully. The R^2 value (0.86) was relatively lower than the values for the URBAN site. This is mainly the result of the deviation at low Pb concentrations. Similar results were obtained for Zn in the fine fraction at the SUBURBAN site. However, since the concentrations of Zn in the fine fraction at the SUBURBAN site were lower than at the URBAN site, the slope and R^2 values of the line for the SUBURBAN site was a bit less than the URBAN site.

$PM_{2.5}$ at the URBAN site: The most successful results were obtained for $PM_{2.5}$ at the URBAN site with an R^2 value of 0.98 for the measured vs. predicted regression. However, the highest slope value (1.04) was also calculated for $PM_{2.5}$ at the URBAN site. Again, the residual value was high (2.54) but it was much less than the minimum $PM_{2.5}$ concentration (15.1 µg m^{-3}).

Again, the best fit among the regression lines of measured vs. predicted Cd concentrations was obtained for the fine fraction at the URBAN site (R^2=0.81). However, the slope was low (0.66). The residual value (0.0003) was relatively high, since the measured minimum Cd concentration in fine fraction was 0.0002 µg m^{-3}.

Performance of the model was excellent (R^2=0.99 and slope=1.01) for Pb. The best slope value among the plots of measured-predicted Zn concentrations was obtained for the fine fraction at the URBAN site (slope=1.01). However, the fit of the line was not so good (R^2=0.84). Similar to the regressions for Zn at the SUBURBAN site, the model deviated at low concentrations.

In conclusion, the CMB resulted in quite fine predictions for PM concentrations at the two sites of this study. The main aim of CMB modeling was to calculate the apportionment of the sources on the PM concentrations at receptor sites. This aim was achieved at both of the sites of this study. On the other hand, the model deviated in apportionment of some elements (i.e., Cd, Cr, Cu, and Ni) particularly at the SUBURBAN site. Performance of the model for the URBAN site was much better than the SUBURBAN. The main reason for that was the low elemental concentration with a number of days below the MDLs (especially Cr and Ni). In case of high concentrations, for example at the URBAN site, better model performances were obtained. The slope values were around 0.6-0.7 at the URBAN site where higher R^2 values was the case. This might be interpreted as there are some sources of these elements (Cd, Cr, Cu, and Ni) that were not characterized in this study. However, the contribution of these sources on PM concentration was very limited while contribution of these sources on concentrations of Cd, Cr, Cu, and Ni may be significant. Except for these four elements, the model performed well, particularly for the terrestrial elements, and some trace elements such as Pb and V.

4.2.3.2 Source Apportionments of $PM_{2.5}$ and Trace Elements

The sources and their apportionment for PM and seven trace elements (Cd, Cr, Cu, Ni, Pb, V, and Zn) are discussed in this section. Seasonal variation, effect of wind direction and velocity are evaluated. Since the effect of wind velocity was significant depending on being lower or higher than 5 m s^{-1} as discussed in Section 4.1.2, the same wind velocity value was used for evaluation. Again, only the fine fractions are discussed, however, significant differences from PM_{10} are indicated.

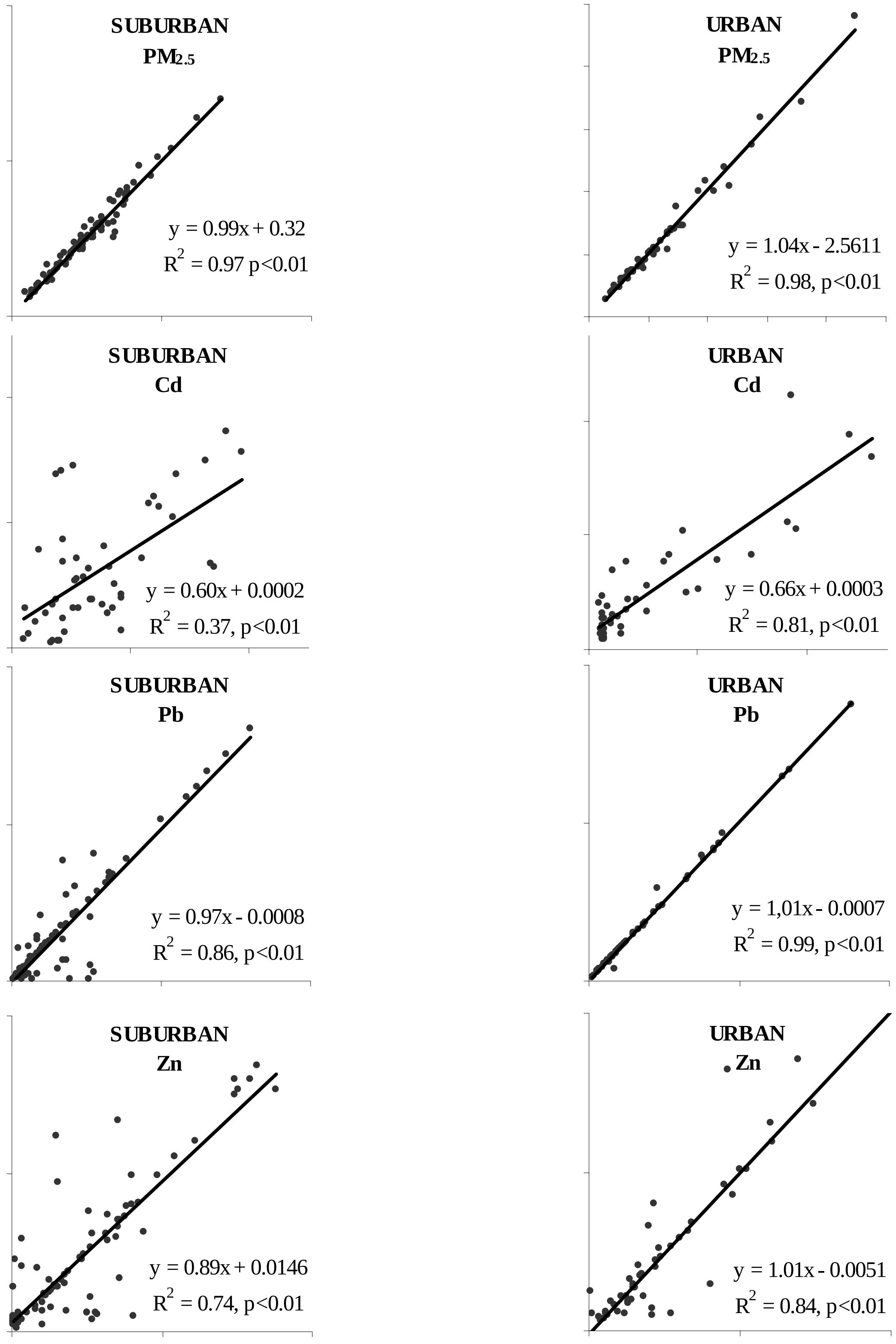

Figure 4.17 Scatter plots of measured and predicted concentrations of $PM_{2.5}$ and some elements at the two sites (x-axis represents the measured concentrations).

4.2.3.2.1 Sources of $PM_{2.5}$ and Trace Elements at the SUBURBAN Site. Seasonal variation in source contribution for $PM_{2.5}$ and seven trace elements are given in Figure 4.18. The variation according to the seasons and prevalent wind directions are shown.

$PM_{2.5}$: The major contributors to $PM_{2.5}$ concentrations at the SUBURBAN site were traffic emissions, the mineral industries (cement, quarries and ceramic), fossil fuels burning (coal + fuel oil), and the marine salt. The contribution of traffic emissions to $PM_{2.5}$ concentrations at the SUBURBAN site was about 65%, whereas the contributions of other three sources were around 10%. The contribution of traffic emissions to PM_{10} concentrations at the SUBURBAN site was estimated as ~35%. So, it is clear that PM from traffic emissions that could reach the SUBURBAN site was mainly the fine particles. Because, the average mass contribution of the traffic emissions source to PM_{10} and $PM_{2.5}$ concentrations were 18.5 and 18.1 µg m^{-3} in summer, respectively, indicating that nearly all PM from traffic emissions transported towards the SUBURBAN site was fine particles. The situation in winter was the same. The average mass contributions in winter were 14.14 and 14.13 µg m^{-3} for PM_{10} and $PM_{2.5}$, respectively. The contribution of the fuels increased in winter, as expected. On the other hand, the contributions of the mineral industries and the marine salt in summer were higher than in winter. As discussed previously, the marine salt was found to be a source of the fine fraction at the SUBURBAN site according to the results of the correlation matrices, FA and PMF. The contribution of the marine salt to $PM_{2.5}$ and PM_{10} were calculated as 2.2 and 2.5 µg m^{-3}, respectively. Thus, most of the PM arising from the sea salt at the SUBURBAN site was fine particles.

As discussed in Section 4.1.2, there was no significant difference between $PM_{2.5}$ concentrations of N direction and NW direction, whereas the concentrations were decreased in SE direction cases. The contribution of traffic emissions to $PM_{2.5}$ concentrations of N and NW directions were 66% and 72%, respectively. The average mass contribution of the traffic emissions source for N and NW directions were calculated as 16.8 and 22.7 µg m^{-3}, respectively. The contributions of traffic emissions increased slightly in the cases of NW winds compared to N winds. On the other hand, the contribution of traffic emissions in SE winds was 57%, and the mass contribution was 10.8 µg m^{-3}. In other words, contribution of the traffic emissions source decreased significantly with SE winds. A similar pattern was observed regarding the contribution of traffic emissions to PM_{10} concentrations at the SUBURBAN site. The contribution profile of the fuels (coal + fuel oil) to $PM_{2.5}$ concentrations according to the prevalent wind directions resembles significantly to the traffic emissions source. These results are consistent with the location of the Izmir city. Similarly, the contribution of the sea salt increased in NW winds compared to the other directions, which is also meaningful since Izmir Bay is located at NW direction of the SUBURBAN site. As opposed to traffic emissions, the fuels and the marine salt, contribution of the mineral industries increased with northerly winds compared to northwesterly winds. Figure 4.18 shows that the highest contribution from the mineral industries occurred in cases of SE winds. In fact, the highest contribution from the mineral industries as mass was calculated for N direction. It is reasonable because these industries are located north of the SUBURBAN site. The contributions of the steel furnaces and the natural gas burning power plant to $PM_{2.5}$ concentrations at the SUBURBAN site were increased in northwesterly winds compared to the other directions, which are consistent relative locations of these sources.

Wind velocity influenced contribution of the traffic emissions, the mineral industries and the marine salt sources. Contribution of traffic emissions decreased in case of windy conditions (v>5 m s^{-1}), whereas higher wind velocities increased contribution of the mineral industries and the marine salt at the SUBURBAN site. High velocities may dilute PM concentrations originating from traffic emissions, while amount of PM arising from the sea and the mineral industries, particularly the stone quarries, may increase due to high wind velocity.

Cadmium: The major contributor to Cd concentrations in $PM_{2.5}$ at the SUBURBAN site was the steel furnaces. More than half of the Cd came from the steel furnaces. These industries are located approximately 50 km far from the

SUBURBAN site at NW direction. It was surprising to encounter with a contribution of 50% to Cd concentrations from these industries, since the contribution to $PM_{2.5}$ concentrations was <1%. This situation might be due to the high Cd content (~0.1%) of PM emitted from the steel furnaces. Although, the contributed Cd mass by the steel furnaces doubled in summer, the increase in percent contribution was not as much. The contribution amounts to Cd in PM_{10} and $PM_{2.5}$ were compared to the mass contribution in order to estimate fractional Cd contribution from the steel furnaces at the SUBURBAN site. The mean contribution of the steel furnaces to Cd concentrations in PM_{10} and $PM_{2.5}$ were calculated as 0.00062 and 0.00041 $\mu g\ m^{-3}$ in summer, respectively. Thus, nearly 65% of Cd was in the fine fraction of the PM emitted from the steel furnaces. The percentage value in winter was almost the same. Therefore, Cd was mainly in the fine fraction of PM but some was also found in the coarse fraction. This result is consistent with the contribution of the steel furnaces to PM concentrations at the SUBURBAN site. The $PM_{2.5}$ /PM_{10} contribution ratio by the steel furnaces was ~0.75 in both summer and winter. The mineral industries, particularly the cement plant, are the other sources with a contribution of about 15%. Different from PM_{10}, traffic emissions contributed to Cd concentrations in the fine PM in significant amounts (~ 15%), which supported the results of PMF for $PM_{2.5}$ at the SUBURBAN site. The significant contribution to Cd concentrations from traffic emissions at the SUBURBAN site was mainly due to the huge contribution of the source to $PM_{2.5}$ concentrations (~65%). This situation was, also, observed for almost all the other elements. Soil was a significant contributor to Cd concentrations in PM_{10} at the SUBURBAN site (~10%) but it was not in the fine fraction.

The contributions of the sources to $PM_{2.5}$ at the SUBURBAN site according to the prevalent wind directions pointed to the effect of the steel furnaces. In the cases of northwesterly winds, the contribution of the steel furnaces was approximately 76%, whereas the contribution was ~58% for N winds. When the average mass contribution was taken into consideration, the contribution of the steel furnaces in case of NW winds was nearly 2 to 10 times higher than N and SE directions, respectively. On the other hand, the contribution of the mineral industries increased in cases of N winds. The contributions of all the sources decreased in $v>5\ m\ s^{-1}$.

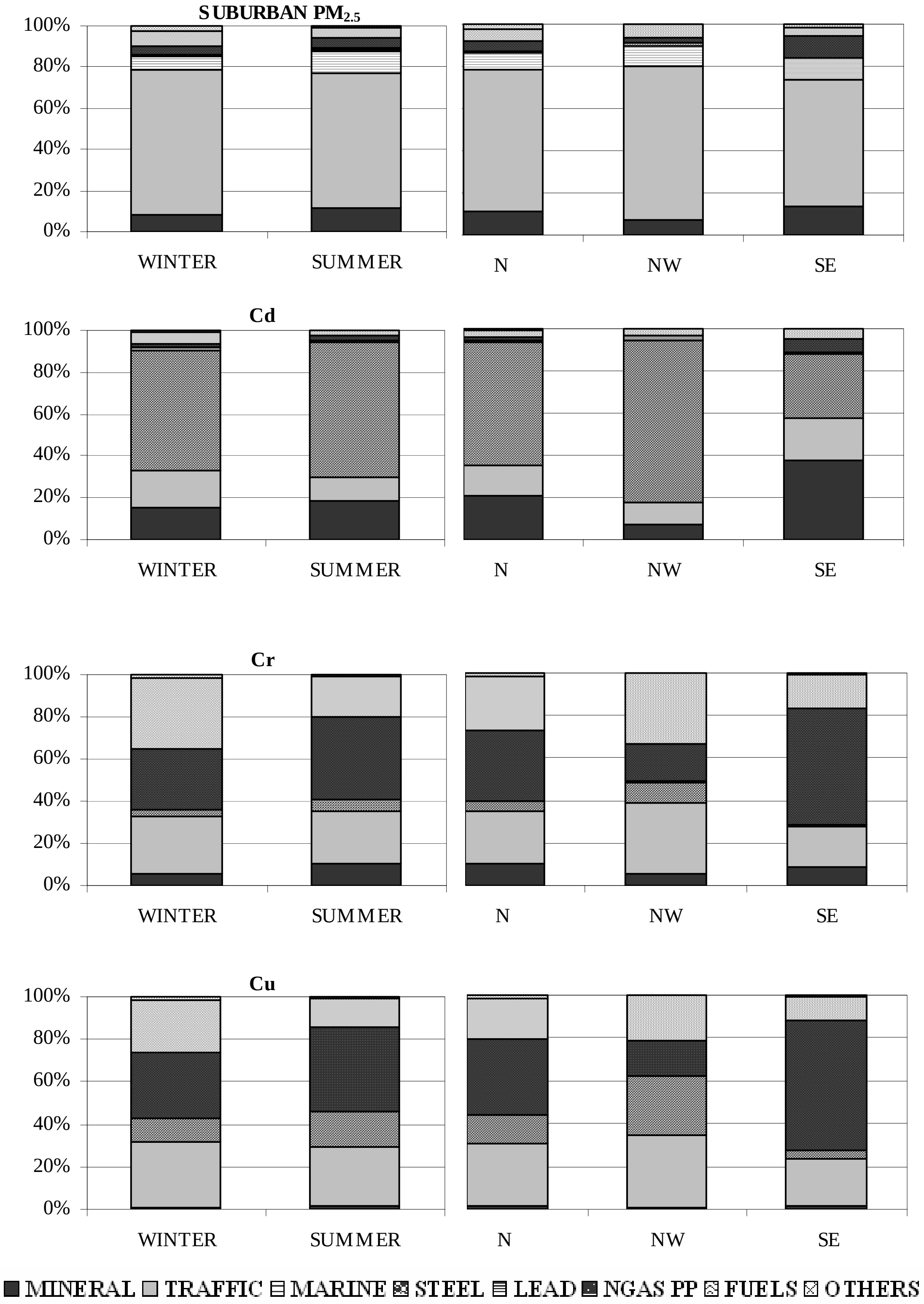

Figure 4.18 Variation in source contribution to the concentrations of $PM_{2.5}$ and seven elements at the SUBURBAN site according to seasons and prevalent wind directions.

NGAS PP : Natural gas burning power plant (Aliaga)

FUELS : The sum of the coal burning and the fuel oil burning

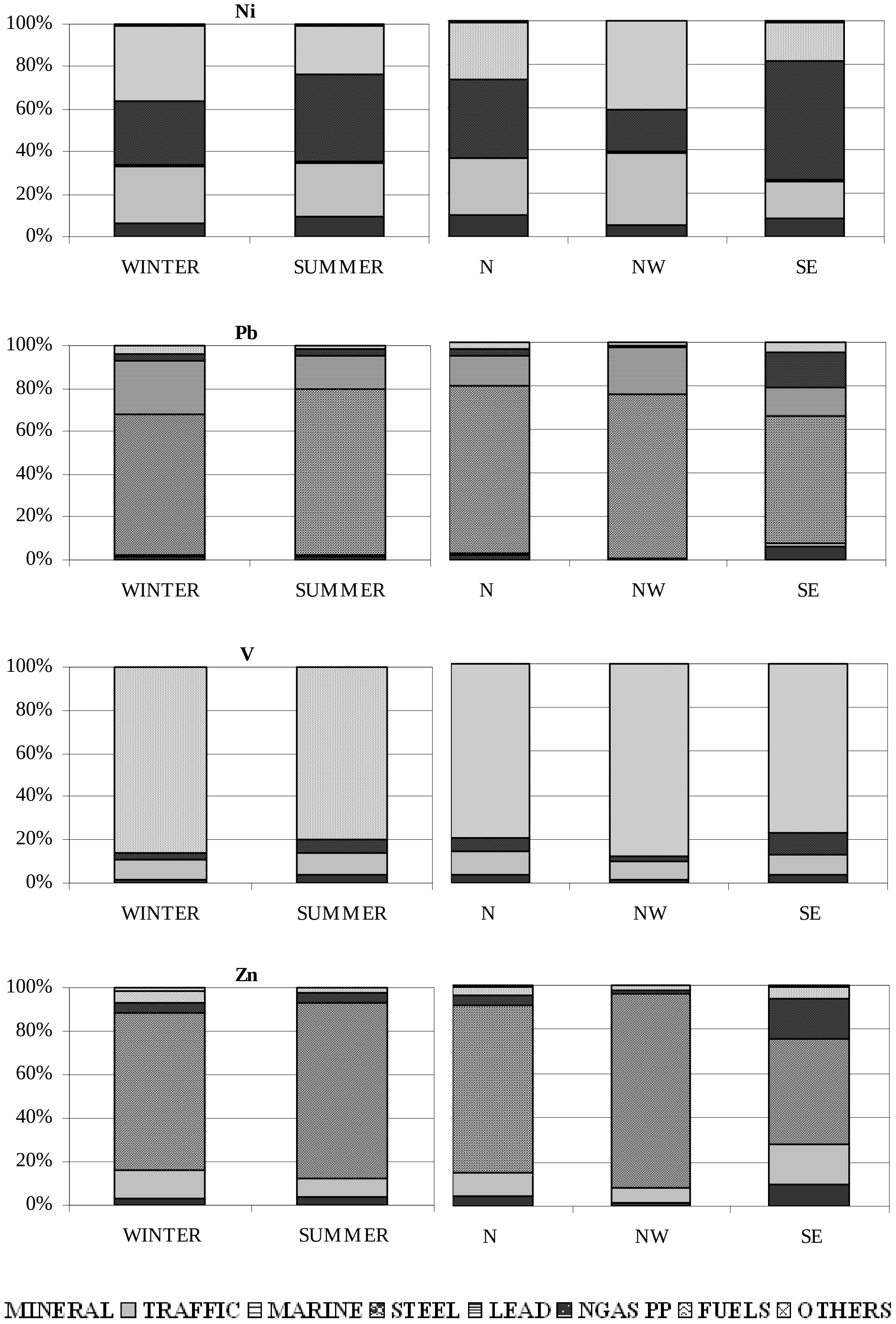

Figure 4.18 (Continued)

NGAS PP : Natural gas burning power plant (Aliaga)

FUELS : The sum of the coal burning and the fuel oil burning

Chromium, Cu and Ni: Since the sources and contribution profiles of Cr, Cu, and Ni were similar in $PM_{2.5}$ at the SUBURBAN site, they were treated as a group. The major contributors to these elemental concentrations in $PM_{2.5}$ at the SUBURBAN site were the natural gas burning power plant, the fuels, traffic emissions, the mineral industries, and the steel furnaces. Contributions of the natural gas burning power plant and the fuels to Cr and Ni concentrations were approximately 30%, whereas the contribution of the fuels to Cu concentrations was estimated as about 20%. Contribution of traffic emissions to Cr, Cu, and Ni concentrations were ~25%. Contribution of the mineral industries to the concentrations of Cr and Ni were calculated as ~7%, and ~2% for Cu. Contribution of the steel furnaces to the concentrations of Cr, Cu, and Ni were ~5%, ~13%, and ~1%, respectively. There were no significant seasonal variations in the contributions of these elemental concentrations in $PM_{2.5}$ at the SUBURBAN site except for the fuels. The contribution of the fuels in winter was significantly higher than in summer.

The contributions of the traffic emissions, the fuels and the steel furnaces were increased during northwesterly winds compared to northerly, whereas the contribution of the mineral industries in N direction was higher than in NW direction. The mass contribution of the natural gas burning power plant was generally increased in case of NW winds compared to the other directions. In conclusion, the variations in the contributions of these sources to the elemental concentrations in $PM_{2.5}$ with the prevalent wind directions are consistent with the locations of the major contributors. The contributions of all sources were decreased during windy conditions.

Lead: Lead was mainly arisen from two sources in $PM_{2.5}$ at the SUBURBAN site: the steel furnaces and the lead recovery furnaces. Approximately, 70% and 20% of Pb originated from the steel furnaces and the lead recovery furnaces, respectively. Very limited contributions from the soil, the fuels, the mineral industries and the natural gas burning power plant were found. The $PM_{2.5}/PM_{10}$ ratios for mean mass contribution of the steel furnaces to Pb concentrations at the SUBURBAN site were approximately 55% and 80% in winter and summer, respectively. These results clearly showed that most of Pb was in the fine fraction of the steel furnaces PM at the SUBURBAN site. However, the coarse fraction also contained a significant amount of Pb. As mentioned previously, the $PM_{2.5}/PM_{10}$ ratios of contributed amounts from the steel furnaces were ~0.75 in both winter and summer.

When the wind was from NW, the contribution of the steel furnaces to the elemental concentrations in $PM_{2.5}$ at the SUBURBAN site increased significantly compared to the other wind directions. The same was also observed for Pb. On the other hand, one of the lead recovery furnaces is located at the NW of the SUBURBAN site, approximately 5 km far away. As a result, contribution of the lead furnace, in cases of northwesterly winds, was nearly two times the N direction. During windy conditions, the contribution of the lead furnaces was significantly decreased, whereas the contributions of the soil, the mineral industries, and the fuels increased. Although, mass contribution of the steel furnaces to Pb concentrations decreased significantly in case of high wind velocities, there was no significant change in the percent contribution.

Vanadium: The major contributor to V concentrations in $PM_{2.5}$ at the SUBURBAN site was the fossil fuels burning emissions with >80%. The results clearly showed that the coal burning was one of the major sources of V, due to the V content of Soma coals. In addition to the fuels, traffic emissions were the other major contributor with about 10%. Wind direction and velocity did not significantly affect the contribution profile.

Zinc: The major contributor to Zn concentrations in $PM_{2.5}$ at the SUBURBAN site was the steel furnaces with >70%. The contribution in summer was slightly higher than in winter. Similar to Pb and Cd, while the mean mass contribution of the steel furnaces to Zn doubled in summer, the increase in percent contribution was very limited. The $PM_{2.5}/PM_{10}$ ratios for the average Zn concentrations of the steel furnaces were 55% and 70% in winter and summer, respectively. This result showed that the main part of Zn was in the fine fraction, however, the coarse faction also contained a certain part of Zn. The other significant contributors to Zn concentrations were traffic emissions with 10%, the fuels with 8%, and the mineral industries with 4%. The effect of wind to contribution profile considerably resembled to Pb and Cd.

In summary, for CMB results at the SUBURBAN site, the major contributors to PM concentration were traffic emissions, the fuels, and the soil-related industries. Especially, the contribution of the traffic emissions source to $PM_{2.5}$ was significantly higher than to PM_{10}. It is meaningful, since the PM emitted from the traffic was mainly fine particles, which is supported in the literature (Sturm et al., 2003; Gouriou et al., 2004; Samara et al., 2005; Fang et al., 2006). Although the traffic was the major contributor to PM concentrations at the SUBURBAN site, it did not dominate the contribution to the elemental concentrations. This is reasonable, since, as several researchers indicated, exhaust emissions mainly contain elemental and organic carbon (Funasaka et al., 1998; Watson et al., 2001; Watson & Chow, 2001; Chow et al., 2004; Giugliano et al., 2005; He et al., 2006). The measurements of traffic emissions also support this finding. The sum of 16 elemental concentrations was calculated as 5% of the total PM, therefore, elemental content of the PM emitted from the traffic was very low. Another result supporting the contribution profile of the traffic was the sum of ambient elemental concentrations. The sum was <20% of the total PM. It can be interpreted that most of the measured PM, particularly $PM_{2.5}$, consisted of EC and OC at the SUBURBAN site. Nevertheless, traffic emissions were one of the major sources of few elements (i.e., Cr, Cu, and Ni), particularly in $PM_{2.5}$, due to the considerably high contribution from the traffic to $PM_{2.5}$. Contribution of soil to PM_{10} concentrations was significant, whereas it was very limited for $PM_{2.5}$. This might imply that the wind blown PM from the surface of soil were mainly coarse particles. The steel furnaces were not among the major contributors of PM concentrations at the SUBURBAN site, however, those dominated the contribution profiles of Cd, Pb, and Zn concentrations. The contribution ratios of PM_{10} and $PM_{2.5}$ to the elemental concentrations clearly showed that not only the fine particles but also the coarse particles from the steel furnaces were transported to the SUBURBAN site. Since Fe and Mn are the other elements emitted from the steel furnaces in significant amounts, the mass contributions of these furnaces to Fe and Mn concentrations were calculated, and then compared to Cd, Pb, and Zn. The results showed that the contribution to Mn and Fe were very close to Cd, Pb, and Zn. The contribution of the fuels to ambient PM concentration varied between 10% and 20%, while the contribution to Cr, Cu, Ni, and V was much more greater. Variation in contribution profiles according to prevalent wind directions was consistent with the locations of the sources. The contribution of the urban sources (the traffic and the fuels) during northwesterly winds increased compared to the other wind directions, whereas the contribution of the mineral industries was higher than the other directions in northern winds. The effect of the steel furnaces on the ambient elemental concentration doubled in case of NW direction compared to N direction. Generally, high wind velocities ($v>5$ m s^{-1}) decreased the contribution of all sources except for soil.

4.2.3.2.2 Sources of $PM_{2.5}$ and Trace Elements at the URBAN Site. Seasonal variation in source contribution of $PM_{2.5}$ and the seven trace elements are given in Figure 4.19 The figure also includes plots that show variation with prevalent wind directions.

$PM_{2.5}$: The major contributors to ambient $PM_{2.5}$ concentrations at the URBAN site were traffic emissions with 80%, the mineral industries with 5%, and the fuels with 5%. The mass contribution of the traffic increased significantly in winter compared to in summer; however, no increase was observed in the percent contributions. The reason for this increase in winter might be the increase in time spent in traffic due to winter conditions, particularly precipitation. The contribution of the fuels in winter was two times higher than in summer. Surprisingly, the contribution of the mineral industries doubled in winter compared to in summer. The contribution of the steel furnaces was less than 1%.

The contribution of traffic emissions increased significantly in case of SE winds compared to N and NW winds. The average mass contribution of the traffic in SE winds (63.0 µg m^{-3}) was considerably higher than the N (44.8 µg m^{-3}), and NW (44.4 µg m^{-3}). Izmir-Aydin Road (Yesildere Street) is located at SE of the URBAN site (Figure 3.1), which might be the reason for the increase in the contribution of traffic emissions at the site. The average $PM_{2.5}$ concentration during SE winds (70.5 µg m^{-3}) was significantly higher than the concentrations in N and NW winds, which were about 55 µg m^{-3}. The difference may be attributed to the contribution of traffic emissions. The mineral industries are located at the NE of the URBAN site. Thus, the contribution of the mineral industries significantly increased in case of N winds compared to the other directions. Similar to the SUBURBAN site, the contribution of the steel furnaces in case of NW direction was two times higher than the N direction. Also, the contribution of the fuels significantly increased in NW winds. The reason for this huge increase might most probably be the very closely located houses at NW of the URBAN station. Wind velocity, however, decreased the contributions of all sources.

Cadmium: The source contribution profile of Cd in $PM_{2.5}$ at the URBAN site significantly resembled to the profile at the SUBURBAN site. The major contributors of Cd were the steel furnaces (~50%), the traffic (~20%), the mineral industries (particularly the cement plant, ~10%), the lead recovery furnaces (~5%), and the fuels (~5%). The contributions of all the sources in winter were higher than in summer.

Relationship between the source contribution to Cd in $PM_{2.5}$ and wind direction at the URBAN site clearly indicated the locations of the major sources. During northwesterly winds, the contribution of the steel furnaces was significantly increased compared to the northerly, similar to at the SUBURBAN site. SE winds increased the contribution of the traffic compared to the other directions. The contribution of the mineral industries in case of N direction was two times higher than the NW direction.

The effect of the wind velocity on Cd concentrations significantly resembled to the SUBURBAN site. Generally, the windy conditions decreased the source contribution of all sources. Because this result was also found for almost all other elemental contributions, the results regarding wind velocity are not mentioned further to avoid repetition.

Chromium, Cu and Ni: Source contribution profiles of Cr, Cu, and Ni in $PM_{2.5}$ at the URBAN site were similar; therefore, those are discussed together. The major contributors of these elemental concentrations are traffic emissions (~40%), the fuels (~30%), the natural gas burning power plant (~15%), the steel furnaces (~10%), and the mineral industries (~5%). Seasonal variations in the contribution of these sources were similar to $PM_{2.5}$ and Cd. The source contribution profile according to the prevalent wind direction was, also, similar to $PM_{2.5}$ and Cd.

Lead: The major contributors to Pb concentrations in $PM_{2.5}$ at the URBAN site were the lead recovery furnaces (~50%) and the steel furnaces (~40%). The contribution of the lead furnaces in winter was higher than in summer, whereas the contribution of the steel furnaces in summer was higher than in winter. Since the southerly winds transport the PM emitted from the lead furnace towards the URBAN site, the contribution to Pb increased in case of SE direction compared to the other directions. The contribution of the steel furnaces increased sharply in case of NW winds compared to the other directions.

Vanadium: The major contributors to V concentrations in $PM_{2.5}$ at the URBAN site were the fuels (~80%) and traffic emissions (~10%). Similar to $PM_{2.5}$ concentrations, average mass contribution from the fuels to V in winter was two times higher than in summer. However, the increase in the percent contribution was not as much. Average mass contribution from the traffic emissions in winter (0.051 $\mu g\ m^{-3}$) was higher than in summer (0.048 $\mu g\ m^{-3}$). On opposite, the percent contribution in winter (~9%) was estimated as less than in summer (~15%). The variation in contribution profile of these sources according to prevalent wind directions significantly resembled to $PM_{2.5}$ and the other elements.

Zinc: The major contributors to Zn concentrations in $PM_{2.5}$ at the URBAN site were the steel furnaces (~70%), traffic emissions (~18%), and the fuels (~5%).

Although, the average mass contribution of the steel furnaces in winter (0.164 μg m^{-3}) was higher than in summer (0.128 μg m^{-3}), the percent contribution in winter (~66%) was less than in summer (~74%). Similar to $PM_{2.5}$ and the other elements, the average mass contribution of the traffic in winter was two times higher than the summer. The variation in the contribution profile of these sources to Zn according to prevalent wind directions was similar to $PM_{2.5}$ and the other elements.

In brief, the traffic emissions were a major contributor to PM concentrations. Since PM emitted from the traffic mainly consisted of fine particles, the contribution to $PM_{2.5}$ was higher than PM_{10}. The traffic emissions source was also a significant contributor to concentrations of the seven elements except for Pb in $PM_{2.5}$. Thus, it might strongly be suggested that these elements mainly existed in the fine fraction of PM emitted from the traffic sources. Average mass contributions from the traffic to PM and the elemental concentrations significantly increased in winter compared to in summer. This might be due to the increase in time spent in traffic because of the winter conditions, particularly precipitation. Similarly, the contribution of the fuels significantly increased in winter. The contribution of the fuels to $PM_{2.5}$ was higher than PM_{10}, which might suggest that fossil fuel burning sources mainly emitted fine PM.

Significant differences were observed in the contribution profiles of $PM_{2.5}$ with prevalent wind directions. The contribution of the traffic was higher in SE winds. This is reasonable due to the location of the Yesildere Street. The contribution of mineral industries was higher in cases of N winds because of the location of these industries. The contribution of the steel furnaces during northwesterly winds was higher similar to the SUBURBAN site. Generally, the windy conditions decreased the contributions of the sources.

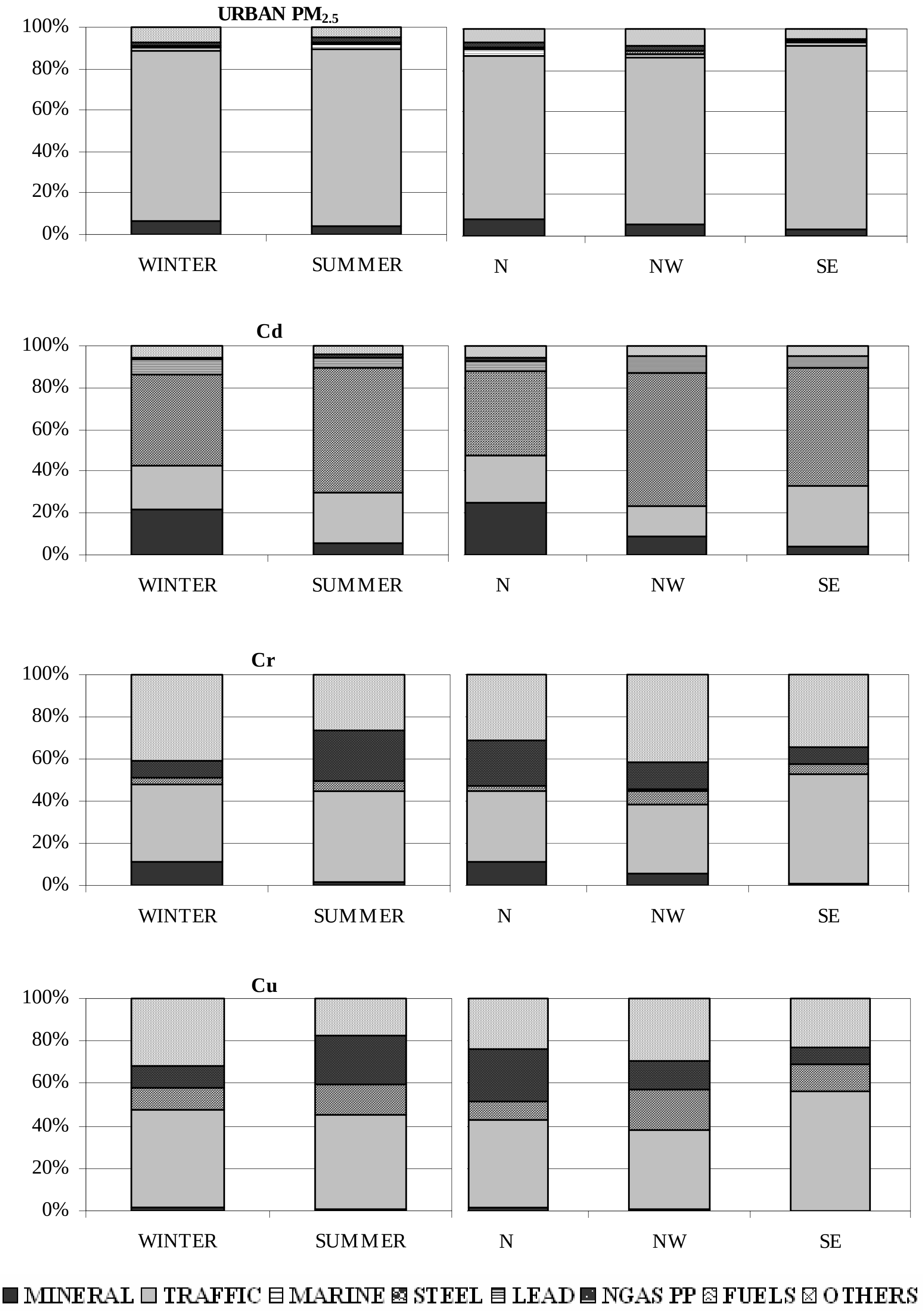

Figure 4.19 Variation in source contribution to concentrations of $PM_{2.5}$ and the seven elements at the SUBURBAN site according to seasons and prevalent wind directions.

NGAS PP : Natural gas burning power plant (Aliaga)

FUELS : The sum of the coal burning and the fuel oil burning

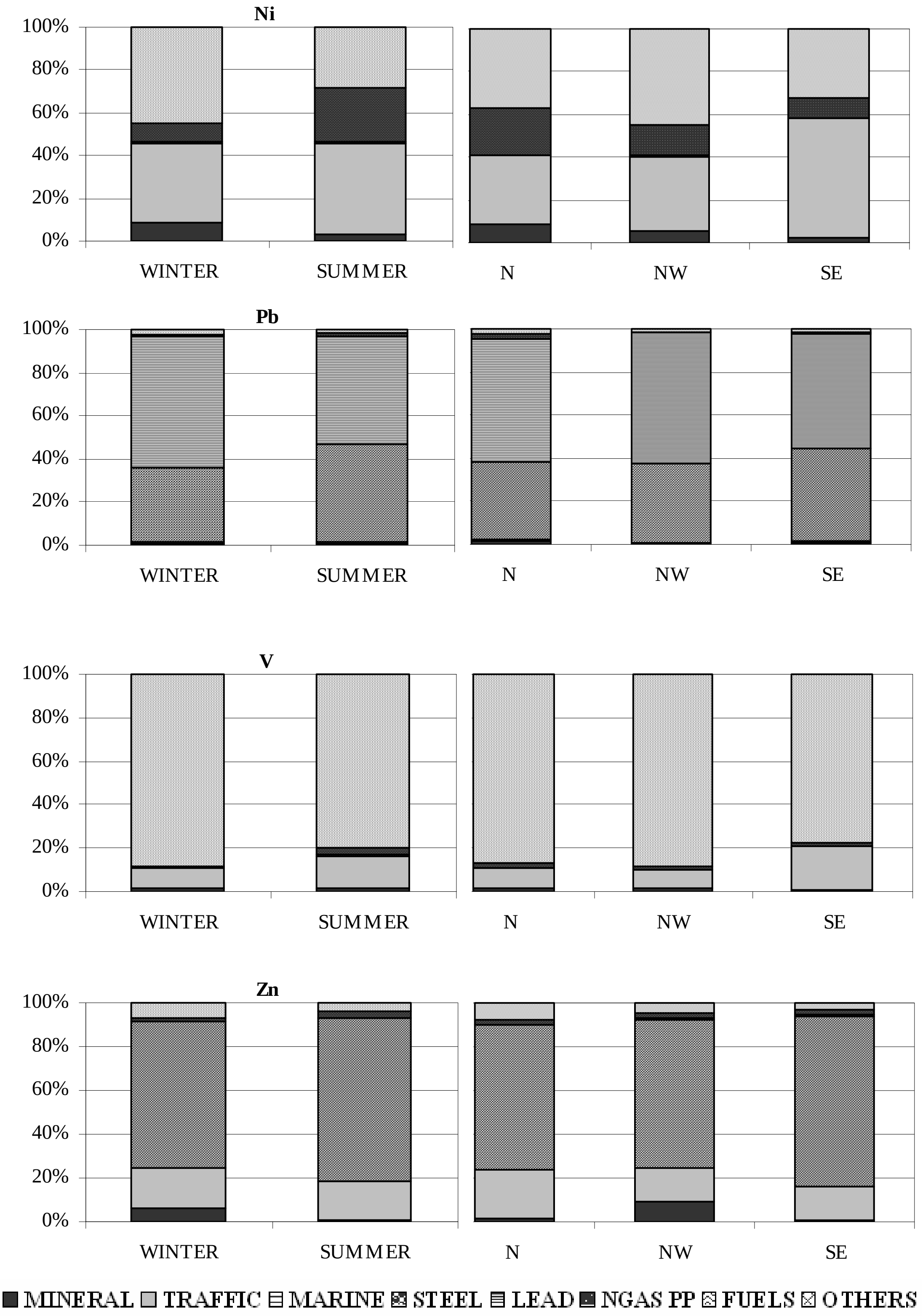

Figure 4.19 (Continued).

NGAS PP : Natural gas burning power plant (Aliaga)

FUELS : The sum of the coal burning and the fuel oil burning

4.2.3.3 Evaluation of CMB Results

The major contributor to PM concentrations was traffic emissions at the two sampling sites, particularly at the URBAN site. The contribution of the traffic to $PM_{2.5}$ was significantly higher than PM_{10}. Thus, it might be concluded that the PM emitted from the traffic sources was mainly fine.

The steel furnaces were the dominant contributors to concentrations of Cd, Pb, and Zn at both of the sites, although the contributions to PM was <1%. The contribution of the steel industries to PM and the elemental concentrations at the URBAN site was slightly higher than the SUBURBAN. Ratio of the contributions from the steel furnaces to the SUBURBAN and URBAN sites varied between 0.8 and 0.9. The effect of the steel furnaces on the PM and the elemental concentrations significantly increased in NW winds.

The lead recovery furnace is one of the major contributors to Pb concentrations at the both sites, particularly at the URBAN site. The contribution level in $PM_{2.5}$ was higher than in PM_{10}. Fossil fuels burning, particularly the coal burning, are the dominant contributors of V, Ni, Cu, and Cr concentrations at the two sampling sites. Approximately one half of these elements originate from the fossil fuel burning sources, except for V (60% - 85%).

Surprisingly, the mineral industries, particularly the cement plants, contributed to Cd concentrations at both of the sites in significant amounts. Cd is among anthropogenic-originated elements, although one of its significant sources is mining activities (ATSDR, 1999). The mineral industries were also among the contributors of Cr, Ni, and V, particularly in PM_{10}.

The contribution profiles according to the prevalent wind directions were generally consistent with the locations of major sources at the two sampling sites. Similarly, the effect of the wind velocity may be significant on the contribution profiles. The windy conditions generally decreased the contribution of the sources, except for soil, via dilution effect. High wind velocities generally increased the resuspension of PM from the surface of soil. The PM emitted from the soil surface was mainly coarse.

CHAPTER FIVE

SUMMARY, CONCLUSIONS, and SUGGESTIONS

5.1 Summary and Conclusions

The mean concentrations of $PM_{2.5}$ and PM_{10} were measured as 24.1 ± 12.2 and 46.9 ± 20.1 $\mu g\ m^{-3}$ at the SUBURBAN site, and 64.4 ± 38.5 and 80.0 ± 30.2 $\mu g\ m^{-3}$ at the URBAN site, respectively. The temporal and spatial variations were significant. The concentrations in summer at the SUBURBAN site were higher, whereas the concentrations at the URBAN site were increased in winter. The effects of wind direction and velocity, and precipitation on the PM concentrations were, also, considerable. The most significant influence was observed when the wind velocity was <1 $m\ s^{-1}$. The mean $PM_{2.5}/PM_{10}$ ratio was approximately 0.5 at the SUBURBAN site. The relatively low ratio indicates that soil and the soil-related industries affected PM concentrations at the SUBURBAN site.

Concentrations of Al, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, V, and Zn were determined in PM_{10} and $PM_{2.5}$ at the both sites. The elemental compositions at the two sites were dominated by the terrestrial elements. The trace elemental concentrations were mostly higher at the URBAN site than the SUBURBAN. It is concluded that the trace elements mainly found in the fine fraction at the SUBURBAN site.

Fifteen sources were characterized in terms of the elemental composition. These were the surface soil, the steel furnaces, the aluminum industry (rim production), the marine salt, the mineral industries (area source including the stone quarries, the concrete plants, the lime kilns, and the asphalt plant), biomass burning (the wood and pirina), the cement plant, the ceramic industry, the coal burning, the fuel oil burning, the natural gas burning power plant, the lead recovery furnace, the coal burning power plant (Soma), the tobacco processing plant, and traffic emissions. The produced data were used as input to CMB model, and used to interpret the results of the correlation matrices, FA and PMF.

The correlation matrices and FA were applied to determine the possible PM sources. The results showed that the natural and anthropogenic sources were influencing the PM concentrations at the two sites, particularly at the SUBURBAN site. Five factors were obtained in PM_{10} at the URBAN site, which are the traffic emissions, the steel furnaces + fossil fuel burning, industry 1, industry 2, and the marine salt. These factors explained 76.5 % of the variation. The factors for $PM_{2.5}$ were significantly different from the PM_{10} at the URBAN site. Four factors, the traffic emissions + marine salt, the steel furnace + fossil fuel burning, soil, and unknown source were determined with a better explanation (83.8%). Three factors were obtained for PM_{10} at the SUBURBAN site. These are soil, the steel furnace + fossil fuel burning and industry, with 72.2% of the variation explained. The factors for $PM_{2.5}$ were soil, the steel furnace + fossil fuel burning, the traffic emissions and the marine salt explaining 82.8% of the variation. There are several mineral industries located in and around the city. Since there are no fingerprint elements to distinguish the contributions of soil and the soil-related industries, these could not be separated using FA and correlation matrices. Ca and Al were used to distinguish these sources. The fingerprint species of traffic emissions (i.e., OC, EC, and Br) were not measured in this study, therefore, interpretation of factors was problematic. The steel furnaces emit several metals (i.e., Zn, Fe, Mn, and Cu) that were suggested for use as fingerprint elements of traffic emissions by several researchers (Querol et al., 2001; Manoli et al., 2002; Fang et al., 2003), which make the interpretation of factors more difficult. The elemental ratios were used to distinguish the sources at receptor sites. In fact, these might have been a serious source of error, if only the elemental profiles of the sources were not obtained in this study.

PMF is the second tool that was used for PM and the trace element source apportionment. The results of PMF are generally consistent with the results of

FA. The fossil fuels + steel furnaces, the mineral industries, the marine salt, and traffic emissions were determined as sources for $PM_{2.5}$ at the URBAN site. The sources of $PM_{2.5}$ at the SUBURBAN site, on the other hand, were the marine salt, the fossil fuels + steel furnaces, the mineral industries, and the traffic emissions. The same difficulties in interpretation of FA results were encountered with in PMF results. The elemental ratios were used to overcome these difficulties. The PMF performed well in apportionment of the PM sources. However, there were some unrealistic contributors to some trace elemental concentrations. The steel furnaces and the fossil fuel burning sources could not be distinguished using PMF. The possible reason for this may be the inadequate number of the collected samples and the studied species. A better performance can be expected with more species and samples.

This study planned to apportion the sources of PM and the trace elements using the CMB model. The CMB results were considerably good in source apportionment of PM as well as the trace elements except for Cr and Ni. Problems in Cr and Ni might be attributed to the number of samples below the MDL. The major contributors to PM were the traffic, the soil-related industries, the fossil fuels burning, and the marine salt at the both sampling sites. The contribution of the traffic to $PM_{2.5}$ concentrations was higher than PM_{10} at the two sites. This result is consistent with the fine characteristic of PM emitted from the traffic emissions source. On the other hand, the traffic emissions were generally not a major contributor to trace element concentrations except for $PM_{2.5}$ at the URBAN site, which is meaningful, since the elemental composition of traffic emissions are dominated by OC and EC, not trace elements (Funasaka et al., 1998; Watson et al., 2001; Watson & Chow, 2001; Chow et al., 2004; Giugliano et al., 2005; He et al., 2006). The sum of 16 elements in the traffic emissions was found as only about 5%. On the other hand, the steel furnaces were one of the major contributors to the elemental concentrations (Cd, Pb, and Zn) although their contribution to PM concentrations was less than 1% at the both sites. The contribution of the steel furnaces to the PM and elemental concentrations at the two sites in summer was higher than in winter. In conclusion, there was a limited transportation from Aliaga

Industrial Zone (Horozgedigi) to Izmir city (< 1% for PM), whereas the contribution to the elemental concentrations of Cd, Pb, and Zn was much more than PM.

5.2 Suggestions

The number of species should be increased, and if possible, all the constituents of PM should be determined. Particularly, the major constituents (i.e., organic carbon, elemental carbon, SO_4 and NO_3) should be measured. The complete characterization of the sources should be performed. The data would be very useful for the future source apportionment studies.

Source characterization was one of the most important parts of this study. The constructed source profiles would be employed in future source apportionment studies in Turkey. Because some sources (i.e., soil and coal) may differ significantly with respect to location, such sources should be characterized locally.

Use of HF for digestion of the samples was avoided because the available purity was not high as HNO_3 and HCl. As a result, the recoveries of some elements (i.e., Al, Cr, and K) were low (<50%) in this study. HF should be utilized in the future studies to assure complete digestion of PM. The use of advanced digestion techniques (e.g., microwave digestion) can be suggested for higher recovery efficiencies. In this way, the lost of some volatile elements can, also, be avoided.

More sensitive analytical instruments (i.e., ICP-MS) should be used to decrease the number of sample below detection limits, and to increase the number of the detected species as well.

The CMB model results show that there are significant sources of some elements (i.e., Cr, Cu, and Ni) that are not characterized in this study. The effects of these sources on the PM concentrations at the two sites may be very limited, and could be neglected. On the other hand, these sources seemed to be significant sources of some of the elements. So, these sources should be determined and characterized.

Horozgedigi Industrial Zone (steel furnaces) is one of the major contributors to the most of the trace elements at the two sites, whereas the contribution to the PM concentrations is less than 1%. Studies on the transportation of PM from this region should be performed to determine the pathways.

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