SOURCE APPORTIONMENT OF TRACE ELEMENTS IN ANKARA

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ABSTRACT

SOURCE APPORTIONMENT OF TRACE ELEMENTS IN ANKARA

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In this study, chemical composition of aerosol samples in Ankara is identified through receptor modeling. Within the scope of the study, 24-hr aerosol samples are collected by ‘Stack Filter Unit’ with using Nuclepore filter for 9 months at Middle East Technical University campus as a suburban sampling location. Collected filters are analyzed for fifty-seven major and minor trace elements, between z=3 Li and z = 92 (U) and black carbon.

Measured concentrations of fine and coarse fractions are compared with corresponding concentrations reported for other cities around the world and Turkey, and also with performed in city of Ankara since 1975. As a result of these comparisons, average concentrations of elements are not significantly different from concentration reported in the literature, and both crustal and pollution derived elements are observed to be decreased significantly compared to1975 in Ankara.

Coarse-to-fine ratio of the soil related elements are usually found higher than 1.0. In contrast, those of the anthropogenic elements are usually less than 1.0 with a few exceptions, including Cu, Ge, Zn Au, U and Li

.

Concentrations of the trace elements show short time and seasonal variations. These variations are explained according to changes in meteorological parameters and source strength.

Positive matrix factorization (PMF) was used to identify source of elements and evaluate contribution of sources to each elements. This analysis indicates 6 sources; contaminated surface soil, a mixed crustal-anthropogenic factor, coal burning, traffic, road dust and subsurface soil.

Key Words: Source Apportionments, Trace Elements, Positive Matrix Factorization

ÖZ

ANKARA'DA ESER ELEMENTLER İÇİN KAYNAK BELİRLEME ÇALIŞMASI

Çelik, İlke
Yüksek Lisans, Çevre Mühendisliği Bölümü
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Bu çalışmada, reseptör modellemesi ile Ankara'daki aerosol kütlesinin kimyasal kompozisyonu belirlenmiştir. Bu amaçla, 24 saatlik günlük aerosol örnekleri yankent bir istasyon olan Orta Doğu Teknik Ünivesitesi kampüsünde 9 ay süresince, Nuclepore filtre kullanılarak toplanmıştır. Toplanan filtreler Li=3 ile U=92'i kapsayacak şekilde 57 eser element için analiz edilmiştir.

Ölçülen konsantrasyonlar, dünyanın ve Türkiyenin çeşitli yerlerinde ölçülen konsantrasyonları ile ve Ankara ilinde 1975 yılından itibaren yapılan diğer aerosol çalışmaları ile karşılaştırılmıştır. Bu karşılaştırmanın sonucunda, literatürde raporlanan ortalama konsantrasyon değerleri ile bu çalışmanın sonucları arasında ciddi bir fark olmadığı ve Ankara ilinde 1975 yılından itibaren hem toprak hem de antropojenik kökenli eser element konsantrasyonlarının dikkat çekici bir şekilde düştüğü görülmüştür.

Toprak kökenli kaba aeresollerin ince aerosollere oranı genellikle 1.0 civarında bulunmuştur. Öte yandan, bu oran Cu, Ge, Zn, Au ve U elementleri haricindeki diğer antropojenik elementler için genellikle 1.0'ın altındadır.

ODTÜ istasyonundaki eser element konsantrasyonlarının mevsimsel ve kısa süreli değişiklikler göstermiştir. Bu gibi değişiklikler meteorolojik parametreler ve emisyon kaynaklarındaki değişiklikler ile açıklanmıştır.

Pozitif Matriks Factorizasyonu (PMF), elementlerin kaynaklarını tespit etmek ve bu kaynakların herbir element konsantrasyonuna katkısını bulmak için kullanılmıştır. Bu analiz kirlenmiş yüzey toprağı, toprakla karışmış antropojenik kirleticileri, kömür yakılmasını kaynaklı emisyonları, trafik emisyonlarını, yol tozunu ve alt toprak kirliliğini işaret etmiştir. ....

Anahtar kelimeler: Kaynak Belirleme, Eser Elementler,Pozitif MatriksFaktörizasyonu

In the memory of the revolutionist I have recently lost...

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CHAPTER 1

INTRODUCTION

1.1. General Introduction to Atmospheric Particles

Atmospheric particles have been given great scientific attention for the last few decades due to their adverse effects on climate, public health and visibility. With increased scientific knowledge, it became evident that size and composition of the atmospheric particles have profound significance. In particular, inhalable fraction (aerosol<2.5 µm diameter) and the trace metal constituents of particulate matter (PM) was related to most of the deleterious health effects (Sathe et al., 2011). Therefore, source apportionment of the atmospheric particles has become an important part of air quality research (Celo and Dabek-zlotorzynska, 2011).

Source apportionment studies have identified the contribution of different emission sources to the particle concentration in a defined receptor site (Sathe et al., 2011). It is also an effective emission control technique in order to meet ambient air quality standards. By this technique, both the source origin and the amount of its contribution can be determined.

While most of the studies carried out in Turkey were focused on PM, only a few of them includes receptor modeling for the aim of source apportionment (Yatin, 1994; Munzur, 2008; Ozturk, 2009; Tokgoz, 2013). In these studies, anthropogenic and natural sources of atmospheric trace elements were identified for rural and urban areas. Atmospheric research conducted in rural sites of Turkey show the effects of long range transport of anthropogenic emissions from Europe and Asia, Saharan dust from North Africa and sea salt from Mediterranean Sea (Tokgoz, 2013). Air research conducted in the urban receptor sites similar to this study; on the other hand, shows fossil fuel combustion for the residential and industrial activities and also traffic as the most important sources (Yumurtaci, 2010; Bayram, 2000; Kindap et al., 2006).

1.2. Aim of the Study

The foremost aim of this study is to identify sources of trace elements contributing to the observed concentrations in Ankara atmosphere. To achieve this aim, aerosol samples were collected in the backyard of the Department of Environmental Engineering in METU Campus from November 2013 to July 2014.

The tasks undertaken are:

- To measure daily PM_{10} - $PM_{2.5}$, hourly PM_{10} and daily Black Carbon concentrations.
- To identify the potential emission sources and the effects of each of them that contributes to the observed concentrations of Black Carbon and Trace Elements by using Positive Matrix Factorization.
- To understand the short term, Weekday-Weekend and Seasonal variations of the natural and anthropogenic components of aerosols and to examine the factors that lead to observed variations.
- To compare aerosol mass concentrations within the studies that performed in Ankara since 1975 and to evaluate the change in $PM_{2.5}$ concentrations within 40 years in the city in relation to air quality management efforts in the city.

CHAPTER 2

LITERATURE REVIEW

2.1. Characterization of the Particulate Matter

Particulate matter (PM) is the mixture of solid and liquid particles suspended in the air. It comprises acids (such as nitrates and sulfates), organic chemicals, metals, soil particles and biological constituents (EPA, 2006). Each of these components is a tracer of a source which can be classified in terms of their formation mechanism as primary and secondary. Primary particles are directly released to the atmosphere from their sources; however, the secondary particles are formed after the chemical transformation of the primary gases (Fierro, 2000; WHO, 2000).

PM is also one of the six common air pollutants (also known as Criteria Pollutants) which was firstly designated by EPA in 1990 : Particulate Matter, Ozone, Carbon Monoxide, Nitrogen Oxides, Sulfur Dioxide and Lead (Fierro, 2000; Hansen, 2010). EPA calls these pollutants 'criteria' due to their adverse effects on the health, environment and properties (EPA, 2012).

Based on human casualties that occurred during air pollution episodes in history, PM could be classified as the most important element among the criteria pollutants. Among those air pollution episodes, London Episode (1952) is known to be the world's worst episode event that caused death of more than 4,000 people. Since this historical disaster, air quality studies have started in order to find epidemiological and toxicological effects of PM (Appel et al., 1967; Waller, 1967; Zweiman et al., 1972). Eventually, health effects were linked to the size distribution of PM and PM analysis has been divided into two parts: PM_{10} and $PM_{2.5.}$ Besides, the stronger potential impact of smaller particles on human health was revealed (Biersteker, 1976; Bevan and Manger, 1985; Quackenboss and Lebowitz, 1989). Today, cardiovascular and pulmonary problems related with PM are well documented and PM_1 air pollution has gotten great attention in the literature (Carbone et al., 2014; Cheng et al., 2014; Titos, Lyamani, Pandolfi, Alastuey, and Alados-Arboledas, 2014). Moreover, recent studies have focused on the interaction of PM with secondary organic particles and volatile organic acids (Kuo et al., 2014; Dutton et al., 2009).

2.1.1. Particle Size Distribution

Particle size distribution has a great importance in understanding of the behavior and generation mechanism of PM (Richardson, et al., 1957). Size distribution of PM based on formation mechanism is represented in Figure 2-1.

PM could be classified as fine and coarse particles according to aerodynamic diameter of its constituents (Munzur, 2008). Aerodynamic diameter of coarse particles is above 2.5 µm while that of fine particles is below 2.5 µm. Besides, fine particles are divided into two range groups as aitken (0.002 – 0.08 µm) and accumulation (0.08 – 2.5 µm) ranges.

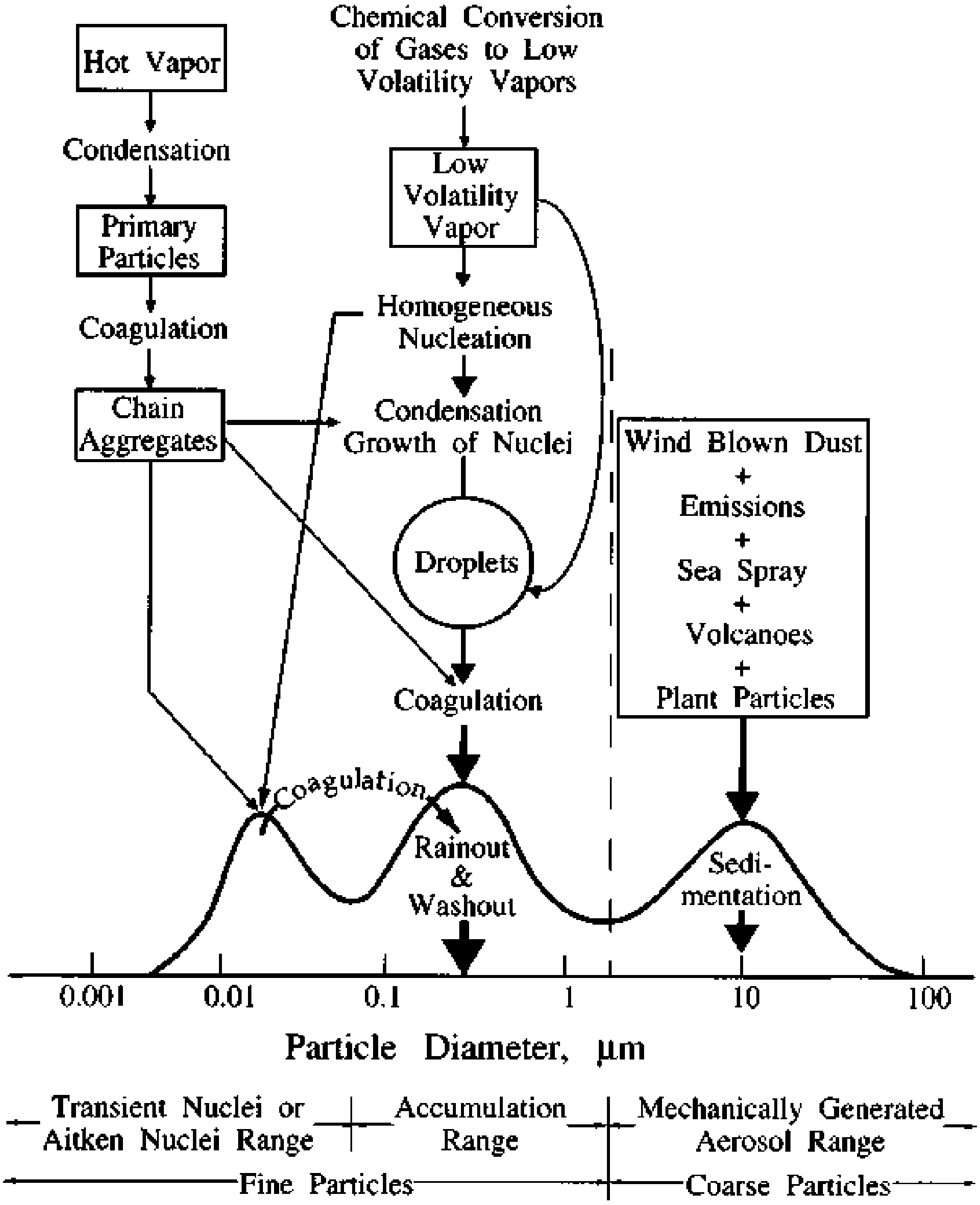


Figure 2-1 Typical size distribution of PM according to generation mechanism (Munzur, 2008)

Size distributions of atmospheric particles classified above give information about the generation mechanisms and sources. First, aitken range particles are emitted directly from the primary sources or they can be produced by the homogenous nucleation of low volatile vapors. Specifically, they are formed as a result of combustion processes, so they have anthropogenic sources. Since these particles are very small, they have short atmospheric life-time. They also account for more than 80% of the number concentration, but their contribution to total mass is negligible. Besides, the aitken range particles are significant for climate since they effect cloud formation acting as cloud condensation nuclei (Warmeck and Williams, 2012).

Second group of the fine particles are in accumulation range. Accumulation range particles are produced by the condensation of the low pressure vapors from combustion processes and coagulation of particles in the aitken range with either themselves or with particles already in the accumulation range. They make up small fraction of number concentration (about 5%) and more than half of the total mass concentration (Munzur, 2008). They have long residence times in the atmosphere and they are scavenged from the atmosphere by both wet and dry deposition. Besides, since they have long residence times, they can be transported over long distances and effect visibility.

Coarse particle, on the other hand, are produced by mechanical processes. Their fraction in PM changes in rural and urban areas. They account for 70 % of the total mass in rural areas while 50 % of that of in urban areas. Since those particles are heavy, they have short atmospheric lifetimes.

2.1.2. Sources of Particulate Matter

After air pollution episodes in the 20th century, atmospheric studies were focused on the source origins of particulate matter. Firstly, composition and sources of aerosols in the urban atmosphere were identified (Negi et al. 1967).

The majority of the global PM concentrations are arisen from the natural resources such as volcanoes, ocean and seas, mineral dust and forest fires (Vallius, 2005). Volcanic ashes released as result of volcanic eruptions are rich in Fe and Mg metals. Besides, they include sulfur salts due to deposition of SO_4^{2-} gases onto the surfaces of these ashes (Witham, et al., 2011). Mineral dust is also a natural source of PM, which can transport by dust storms over continents. Sahara-Sahel region is the largest source of mineral dust which consist of crustal trace elements of Mg, Ca, Al, Fe, Cr and Si (Al-Momani et al., 2008; Argyropoulos et al., 2012; Koçak et al., 2007). Ocean and seas introduce PM in the form of trace elements like Na, Cl, and Mg into the atmosphere via sea spray mechanism (Choi et al., 2013; Clements et al., 2014; Mkomas et al., 2010; Sudheer and Rengarajan, 2012). The last natural way that releases PM is the forest fires. They can be evaluated as biomass burning and lead to an increase in carbonaceous PM (OC and BC) concentrations (Wallace and Hobbs, 2006; See et al.,2006; Verma et al., 2013).

Anthropogenic sources of PM may be divided into two parts as stationary and mobile sources. Mobile sources include transportation related emissions like air, rail, marine, on-road and off road vehicle transportations (BC Ministry of Environment, 2013). Since most of those transportation systems are powered by fossil fuels they release hazardous amounts of heavy metals such as Mn, Fe, Zn, Br, Pb and carbonaceous element (elemental and organic carbon) (Lidia Morawska, 2004; Martuzevicius et al., 2008; Ragosta, et al., 2008). Stationary sources, on the other hand, include fuel combustion for electrical utilities and various industrial processes like steel, petrochemicals, minerals, cement and metal processing (Charron and Harrison, 2006). As a result of these human activities Pb, Fe, Mn, Zn, As, Se, V, Ni are released to the atmosphere (Thurston et al., 2011).

Despite the large number of natural PM sources, their portion in the global PM concentrations is not as significant as anthropogenic sources (EPA, 2005; Fierro, 2000). The reason behind this statement is the difference between their lifetimes due to their sizes. Anthropogenic sources generally release fine particles (aerodynamic diameter<2.5

μm). Since the residence time of the fine particles (from days to weeks) are much larger than that of the natural ones (minutes to hours), particles of the anthropogenic origin are more important considering environmental concerns.

Based on the origin of PM, they can be found all around the world with changing concentrations. Here, in Figure 2-2, global distributions of coarse and fine particles are given in accordance to their concentrations. Yellow color represents coarse particles which can be released from anthropogenic sources; and red color shows fine particles that are released from the anthropogenic sources. The brighter colors indicate the higher concentrations of those particles while dark-gray color indicates the areas with no data.

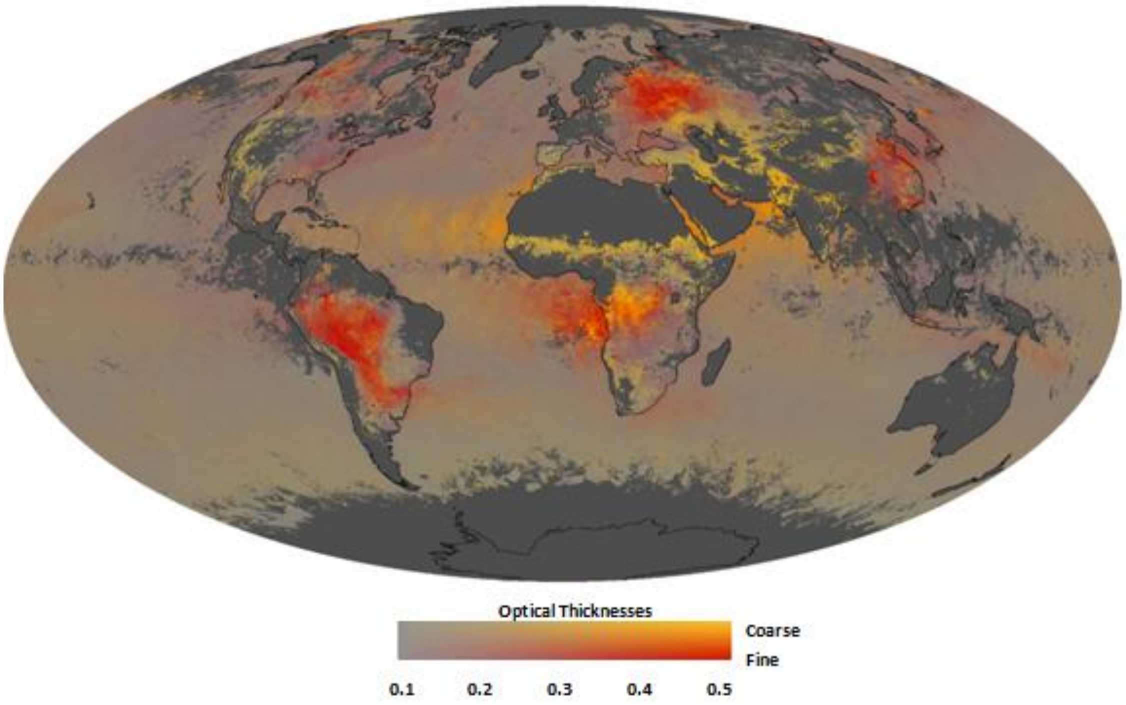


Figure 2-2 Global Distribution of PM in August 2010 (NASA, 2010)

It is seen that the coarse particle resulted from the natural sources are concentrated in the Middle East, North of the Africa and western parts of the North America. Since the snapshot was taken in the summer season, the driest time of the northern hemisphere, coarse particle concentrations are higher due to uplifting of soil and dust storms. Moreover, yellow marks over the oceans and seas are also in relation with the coarse particle release due to sea spray mechanism. Bright red colors, on the other hand, are denser around Russia, South America and Central Africa. This can also be linked with wild fires and agricultural burning (man-made burning to clear land for crops) during the drought season of those fields which makes them very prone to fire. Besides, red color in East Asia indicates the air pollution episodes of that polluted regions which result from the stationary and mobile anthropogenic sources (NASA, 2010).

2.1.3. Effects of Particulate Matter on Environment and Human Health

Adverse effects of particulate matter on environment and human health have become an important issue in the last years. Although the exact mechanisms of health effects of PM have not been revealed yet, it is accepted that particle size and composition have great importance on the health effect (Ozturk, 2009; Tokgoz, 2013).

Stern et. al. (1984) was the first to speak of atmospheric fine particles being responsible for adverse health effects. The reason behind this was explained as; while coarse particle could retain in the upper part of respiratory system, fine particles could not retain as a result of Brownian motion. Therefore, they can accumulate in the lungs and penetrate the ways of respiratory system (Safai et al., 2013). Moreover, smaller particles ($PM_{0.1}$) may even enter the blood and travel throughout the body (Verbrugge, 2004). So, with increasing exposure time, concentrations of the particles that have toxic metals are elevated. Table 2-1 gives these specific trace metals, their sources and health effects.

Table 2-1 Effect of heavy metals constituents of PM on human health (Kimani, 2007)

Heavy Metal	Environmental Source	Minimum risk Level	Chronic exposure toxicity effect
Lead	Industrial and vehicular emissions, paints and burning of plastics, paper etc	Blood lead levels below 10 micrograms per deciliter of blood	Impairment of neurological development, suppression of the hematological system (anemia), kidney failure, immunosupression etc
Mercury	Electronic and Plastic wastes, pesticides, pharmaceutical and dental waste	Below 10 microgram per deciliter of blood; oral Rfd 4 mg/kg/day	Gastrointestinal and respiratory tract irritation renal failure, neurotoxic
Cadmium	Electronic, Plastic, batteries – diet and water.	Below 1 microgram per deciliter of blood	Local irritation of the lungs and gastrointestinal tract, kidney damage and abnormalities of skeletal system
Arsenic	Herbicides and pesticides, electronics, burning of waste containing the element, contaminated water.	Oral exposure of 0.0003 mg/kg/day	Inflammation of the liver peripheral nerve damage neuropathy, cancer of the liver, skin and lungs, irritation of the upper respiratory system – pharyngitis, laryngitis, rhinitis, anemia, cardiovascular diseases.

In addition to the heavy metals listed in Table 2-1, number of studies has linked V, Fe, Zn, Ni, Mn and Cu metals to several health problems such as cardiovascular diseases, nonfatal heart attracts aggravated asthma and lung cancer (Hawas et al., 2003; Sudheer and Rengarajan, 2012).

In addition to the health effects of the trace elements, they are also harmful to the environment due to their influence on global climate, materials and visibility (Jimoda, 2012). Previous studies have linked PM that contains substantial amount of black carbon with global warming by absorbing solar radiation before it reaches the ground. Another adverse effect of PM is the soiling of man-made surfaces. Acid constituents of PM damage aesthetic appearance and materials (Ragosta et al., 2008). Besides, alkaline particles which are prominently composed of dust particles ruins surfaces of walls, doors and automobiles (Jimoda, 2012). Lastly, visibility reduction is one of the obvious impacts of PM. In particular, fine particles with a diameter between 0.3 – 1.0 µm reduce visibility to a great extent by absorbing and scattering light (Sudheer and Rengarajan, 2012; Weingartner et al., 2003).

2.2. Trace Elements

Atmospheric trace elements are significant tracers in identification of air pollution sources. According to the number of studies (Cetin et al. , 2007; Kulkarni et al., 2007; Ozturk, 2009) based on the type of emission trace elements can be detected in almost all aerosol size fractions. Therefore, in order to determine aerosol sources, composition of differentiated size should be identified.

Trace metals can be emitted to atmosphere mainly by releasing from natural sources of emitting from anthropogenic source. Releasing from natural source includes weathering of rocks, mineral deposits, volcanism, wind erosion, forest fires, sea spray and biogenic emission. Emitted trace elements due to those sources are summarized in Table 2-2.

Table 2-2 gives trace element’s source categories according to their strength in annual fluxes. As it can be seen below, windblown dust is a major natural source of atmospheric trace elements. For instance, Cr, Cu, Mo, Ni, Pb and Zn found in windblown dust account for 20-30 % of total fluxes of those metals. Moreover, volcanic eruptions are responsible for 50 % of the total Cd and Hg fluxes and more than 50% of the Se and Mo are emitted from biogenic origins.

Table 2-2 Natural Source of Trace Elements (Pacyna and Ottar, 1989)

Source Category	**Trace Elements**
Windblown dust	Cr, Co, Mn, Zn, Pb, Cu, V, As, Ni
Sesalt Spray	Na ,Cl , V, As
Volcanoes	Cu, Zn, V
Wild Forest Fire	Cu, Zn
Biogenic	
Continental Particulates	Cu
Continental Volatiles	As, Se, Zn
Marine	As, Zn

Secondly, they can be emitted by anthropogenic sources. Most of the industrial processes such as combustion of fossil fuels, auto emission, mining and metal smelting, industrial processes and municipal waste incinerators releases various trace metals to the atmosphere. Emission source of trace elements are listed in Table 2-3.

Table 2-3 Emission sources of anthropogenic trace metals (Morawska et al., 2004)

Emission Source	**Trace Elements**
Road Transport	
Motor vehicle emissions	Br, Pb, Ba, Cl, Zn, V, Ni, Se, Sb, As
Motor wear	Fe, Al
Tyre wear	Zn
Road side dust	Al, Sl, K, Ca, Ti, Fe, Zn
Industrial Facilities	
Coal combustion	Se, As, Cl, Cu, Al, S, P, Ca
Refineries	V
Iron and steel plants	As, In, Cu, Zn, Pb
Copper industry	Cu
Small Scale Burning Industries	
Waste incinerator	Zn, Sb, Cu, Cd, Hg, K, Pb
Wood combustion	Ca, Na, K, Fe, Br, Cl, Cu, Zn
Mineralization And Raw Material Processes	Mg, Al, K, Mn, Fe, Se

As it can be seen, road transport, industrial facilities, small scale burning industries and mineralization and also raw material processes are the main anthropogenic activities that release trace metals. Cu, Pb, Zn and Fe are the most common trace metals that are emitted as a result of these activities.

2.3. Black Carbon

Black carbon (BC) is a significant component of PM which has great influence over visibility, human health and climate. It is basically a solid form of pure carbon that absorbs UV wavelengths and major component of 'soot' which also contains organic carbon (OC) (EPA, 2012).

BC is generally emitted with other particles and gases, such as sulfur dioxide (SO_2), nitrogen oxides (NO_x) and OC as a result of the incomplete combustion of fossil fuels, biofuels, and biomass (C2ES, 2010). A detailed global BC inventory was prepared by Lamarqua et al. (2010) for 2000. According to his report, global BC emission was 7,600 Gigagrams in 2000. The regional distribution of that amount is given below.

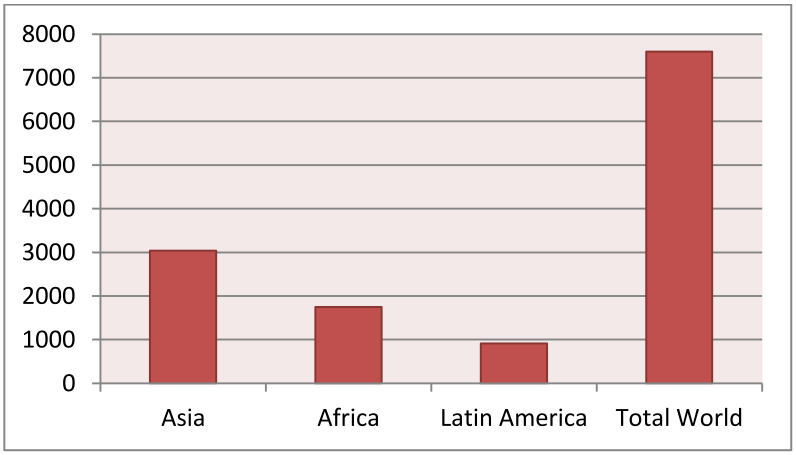


Figure 2-3 BC Emission by Selected World Region, 2000 (Lamarqua et al., 2010)

As it can be seen in Figure 2-3, these three continents are responsible for approximately three quarters of total BC emissions. First, Asian countries such as China, India, Taiwan, Japan and N. Korea accounted for nearly half of worldwide BC emissions. According to EPA (2012), these emissions have mostly anthropogenic origins like industry, energy, transportation and residential. Next, Africa was the second biggest contributor to global BC emissions. However, dominant source of BC in African countries was open biomass burning (includes grassland and forest fires) which could also be classified as a natural source. Similar to Africa, BC emissions in Latin American countries, South America, Mexico, Central America, Argentina, Venezuela, and Brazil, were also dominated by open biomass burning and accounted as the third largest contributor. As we look into BC emission of Turkey, it was around 30 million, less than 0.5 % of worldwide emissions, in 2000. This amount of emission was dominated by anthropogenic sources such as transportation or industry (EPA, 2012).

Widely accepted adverse effect of BC is climatic. It influences the climate as a result of multiple reactions. The direct effect of BC is absorbing both incoming and outgoing radiations that are the starting point of global warming. Besides, BC sediments on snow or ice and makes them darker. This phenomenon is called ice albedo effect which indirectly contributes to global warming (EPA, 2012a). Besides, BC influences the climate by changing distribution of the clouds, their reflectivity, lifetime and stability like other atmospheric particles. The other significant outcome of the atmospheric BC is the health effect. Since the BC is composed of fine particles, they can easily reach the lungs, the body’s major defence cells and possibly the blood circulation. BC causes toxicity in these sensitive body parts and thereby, it is associated with the respiratory system problems, lung cancer and also heart attacks (WHO, 2012).

Unlike other constituents of PM (nitrates, sulfates, and some of trace elements) there is no regulatory standard to restrict BC concentration in ambient air. Therefore, emission inventories based on calculation rather than actual emission measurement are prepared to control BC concentrations (EPA, 2012b). Besides, the fact that BC is a portion of $PM_{2.5}$, it is also considered during BC inventory calculations.

Considering the adverse effects of BC, mentioned above, it can be concluded that achieving BC mitigation will provide numerous benefits for climate, public health and the environment (EPA, 2012). For this aim, global, regional and sensitive region scenarios should be constructed. For instance, improving effective control technologies to reduce usage of diesel engines could be a possible method for the developed countries while restricting grassland burning is an effective way for African countries. Moreover, specific precautions could be taken to protect sensitive regions, like prohibit land based diesel engine usage for the transportation in Arctic region and wood-fired stoves for residential cooking in Himalayas.

2.4. Receptor Modelling

Modelling is an important component of air quality management. Two types of models are typically used: physical models and mathematical models. Since mathematical models can only be proper for small-scale applications, they are utilized frequently in atmospheric studies (Choi et al., 2013; Pekney and Davidson, 2005). Besides, Mathematical models are divided into two groups as Source oriented models and Receptor models. Source oriented models are also called chemical transport models and requires source information such as topography, source of emissions and meteorology to obtain logical results. Receptor models, on the other hand, are utilized for source apportionment of observed concentrations in the receptor sites.

Receptor modeling requires monitoring of atmospheric concentrations. These concentrations are taken into account as natural tracers and these tracers are evaluated statistically in order to find common sources of pollutants (Hopke, 1999; Bozlaker et al. , 2013; Godoy et al., 2009). Moreover, they work with low computational intensity and they are suitable for non-reactive species since the source of evaluation depends on the mass balance equation. Therefore, receptor modelling is more efficiently operated in areas that are closer to the receptors like urban monitoring (Belis and Karagulian, 2011).

Several types of receptor models are available in aerosol studies. Chemical Mass Balance (CMB), enrichment factor (EF), principle component analysis (PCA), factor analysis (FA), positive matrix factorization (PMF) are the most common ones that are utilized in recent years. The choice of the method utilized depends on the available knowledge about the source profile. For instance, if number of sources, composition profile of the sources, elemental mass fractions are known, then CMB is the most proper method for source apportionment. Nevertheless, if only atmospheric concentrations were available, then factor analysis methods like PCA or PMF can be chosen (Ozturk, 2009).

In this study, enrichment factor, source apportionment methods that depend on the ratio of atmospheric concentrations of elements to a reference element, was used for preliminary source apportionment of aerosols. Besides, PMF was utilized for achieving higher resolution.

2.4.1. Enrichment Factor (EF)

Enrichment factor (EF) is a correlation technique which is generally used for source apportionment studies in atmospheric research. In atmospheric studies, the EF is calculated for both crustal and sea salt sources. In order to find crustal enrichment factor (ER_c), a crust is used for reference material; however, a sea salt is used in calculation of marine enrichment factor (ER_m). Al, Fe, and Li are the most common elements which are used as reference element for ER_c. In addition, Na is used for reference element of ER_m. Enrichment factor calculation is done by Equation 2-1.

$$EF = \frac{\left(\frac{C_x}{C_R}\right)_{Aerosol}}{\left(\frac{C_x}{C_R}\right)_{Reference}} \qquad \text{Equation 2-1}$$

In Equation 2-1, C_x corresponds to concentration of an atmospheric element, and Cr is that of reference materials which is explained as above. The ratio of C_x / C_R in aerosol to reference medium gives information about the source of the element. If the ratio is close to unity, it can be concluded that the element has crustal or marine source. Conversely, if the value is much higher than 1, we may conclude that the element has anthropogenic origin since EF generally have geologic or natural origin (Reimann and Caritat, 2000).

2.4.2. Positive Matrix Factorization (PMF)

Positive matrix factorization (PMF) is a widely used technique in source apportionment studies of particulate matter. It is the most recently developed receptor model and the theory behind it is based on conservation of mass principle. PMF was only used in source apportionment and precipitation studies (Al-Momani, 1995). However, currently in addition to these braches, PMF is also used in lake sediments (Comeroa et al., 2014), river sediment, and soil (Dong, et al., 2014) and wastewater (Soonthornnonda, et al., 2008) studies.

PMF has significant advantages compared to the other receptor models. First, it has realistic error estimates, so problematic data such as below detection limits can be introduced into the model (Comero et al, 2009). This helps to evaluate the chemical species more effectively (Munzur, 2008) without loss of data. Besides, non-negativity constraints help to reduce the rotational freedom in factor computations.

EPA PMF 3,0 based on ME-2 algorithm was used in this study. It is a kind of 2-dimentional factor analysis model as it given below.

$$X_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \quad \text{i=1,...,m} \quad \text{j=1,...,n} \qquad \text{Equation 2-2}$$

In Equation 2-1, X_{ij} is the concentration of j^{th} species on the i^{th} day at the receptor site, f_{kj} is the concentration of the j^{th} species emitted from the k^{th} source; g_{ik} is the contribution of the kth source to the ith sample, e_{ij} is the residual for the jth species on the ith day; i is the number of sample and j is the number of measured species; p is the number of independent sources.

In PMF modelling, the only known data is the concentration value (X_{ij}) and its aim is to find contributors (g_{ik}) and their fractions (f_{kj}). Based on this, PMF models atmospheric elements using constrained, weighted, and least square minimization procedure. Constrained part of modeling, which is the most significant feature of PMF that given above, depends on the assumption that contributions and fractions values are non-negative ($g_{ik}>0$ and $f_{kj} >0$). Weighted part of PMF modeling is about uncertainties such as below detection limits value, negative value and missing data. As it given above, it is also one of the advantages of the PMF compared to FA and PCA (Tokgoz, 2013). For least square part, model can be minimized by adding object function (Q).

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right]^2 \qquad \text{Equation 2-3}$$

In Equation 2-2, i=1,...,m elements; j=1,...,n samples; k=1,...,p sources; u_{ij} is the uncertainty of x_{ij} (Gu et al., 2011). Here, if uncertainties are defined correctly, Q should be equal to the number of data points (EPA, 2008).

PMF is a widely used technique in modeling of ambient aerosol samples. Pekney and Davidson (2005) used it to analysis the ambient particulate matter that collects on cellulose filters. Kolker et al. (2013) modeled atmospheric fine particulate matter in coastal New England with PMF. Moreover, Bozlaker et al. (2013) utilized PMF for modeling of PM_{10} sources such as petroleum refineries in Houston, Texas. In Turkey, on the other hand, Munzur (2008) used PMF for defining source of atmospheric particles in the Aegean Region. Ozturk (2009) used it in investigation of short term trends in Eastern Mediterranean aerosol composition. Tokgoz (2013) modeled aerosol composition at northwestern of Turkey with positive matrix factor.

2.5. National and International Ambient Air Quality Standards

National and international air quality standards are prepared in order to protect public health and the environment. Therefore, regulatory standards may vary in accordance to the region, exposure time, or daily-annual average. In this thesis, PM results will firstly get compared with National Standard, Air Quality Assessment and Management Regulation of Turkey (AQAMR). AQAMR has been revised in order to meet with the requirements of the 96/62/EC, 99/30/EC, 2000/69/EC, 2002/3/EC and 2004/107/EC. The requirement of AQAMR and EU are given in Table 2-4 and Table 2-6, respectively.

Table 2-4 Turkish Ambient Air Quality Standards for PM and PM Components (NAAQS, 2008)

Pollutant	Daily	Annual	Unit	From on
PM	50	20	µg m^{-3}	2014
Pb	-	0.5	µg m^{-3}	2014
As	-	6	ng m^{-3}	2014
Cd	-	5	ng m^{-3}	2014
Ni	-	20	ng m^{-3}	2014

As it is given above, PM is not divided into PM_{10} and $PM_{2.5}$. It is only classified for daily and annual averages. All the units are µg m^{-3}, and this standard has been implemented from the beginning of 2014. Other international standards that also take into account are EPA National Ambient Air Quality Standard (NAAQS), EU Air Quality Directives (AQD) and WHO Air Quality Guidelines (AQG). The most remarkable difference between these standards and AQAMR is $PM_{2.5}$. These standards deal with $PM_{2.5}$ separately, as it given in Table 2-6.

Table 2-5 Air Quality Standards of EU

Pollutant	Concentration	Averaging Period	Permitted exceedences each year
PM 2.5	25 µg/m^3	1 year	n/a
SO_2	125 µg/m^3	24 hours	3
PM 10	50 µg/m^3	24 hours	35
	40 µg/m^3	1 year	n/a
Pb	0.5 µg/m^3	1 year	n/a
As	6 ng/ m^3	1 year	n/a
Cd	5 ng/ m^3	1 year	n/a
Ni	20 ng/ m^3	1 year	n/a

Table 2-6 Comparison of $PM_{2.5}$ standard of WHO, EU and EPA

$PM_{2.5}$	**WHO**	**EU**	**EPA**
24 hour average	25	25	35
Annual	10	-	12

CHAPTER 3

MATERIALS AND METHODS

3.1. Sampling

3.1.1. Sampling Locations

Aerosol samples were collected at two stations in Ankara at METU Campus which is classified as suburban station. It was established on the 26th of November 2013 in the backyard of the Department of Environmental Engineering, METU Campus. The coordinates of the station is 39^{0}53’12.05” latitude of North Equator, 32^{0}46’59.76’N longitude east of the Greenwich and 955 m above the sea level. The station is in the parking area of the department and very close to the METU Campus forest. The picture of this station is given in Figure 3-1.

METU Campus is approximately 1.5 km away from the densely populated residential distinct. The campus population is around 15,000 during daytime and the main source of atmospheric particles is the traffic emissions. The population decreases to 2,000-3,000 in the night-time, during that time most of the emissions are formed due to heating facilities of the dormitories. Besides, the campus is surrounded by two crowded highways: Eskisehir highway and 1071 Malazgirt highway. The latter, 1071 Malazgirt Road was opened on the 10th of February, 2014 by clearing more than 3000 trees in the same area. Contribution from this road could also be expected.

(a)

(b)

Figure 3-1 METU sampling station

3.1.2. Sampling Equipment

Daily fine and coarse aerosol samples were collected between November 26, 2013 to April 30, 2014 in the winter season and May 1 to July 7, 2014 in the summer season. The sampling duration was 24 h for all the samples, and samplings were interrupted only to change filters. 117 daily fine and coarse filters were collected during winter in the suburban station, and during summer season in urban and sub-urban stations.

Daily aerosol samples were collected using a ‘GENT’ stacked filter unit (SFU). This unit (Figure 3-2) is made of black polyethylene material and has the dimensions of 10 cm in diameter by 40 cm in length. There is also a PM_{10} pre-impactor in the back of inlet (IAEA, 1994) which has a 50% collection efficiency at 10 µm equivalent aerodynamic diameter (EAD) in order to send the particles with diameters larger than 10 µm away effectively in this stage. The filter holder is placed in the bottom part, and faces the air intake. The upper part of the holder is loaded with a coarse filter and lower part is loaded with a fine filter to collect coarse and fine fraction of aerosols separately. The diameter of the coarse and fine filters equals to 47 mm with a pore size of 8 and 0.4 µm, respectively. The surface of filter that received the air flow is about 12.88 cm^2.

In this study, Whatman Nuclepore track-etched polycarbonate filters were used. These types of membranes have excellent chemical and thermal resistance and have very low background concentrations which are proper for air quality analysis. During the sampling, the shiny side of the filters should be up in order to intake the air easily.

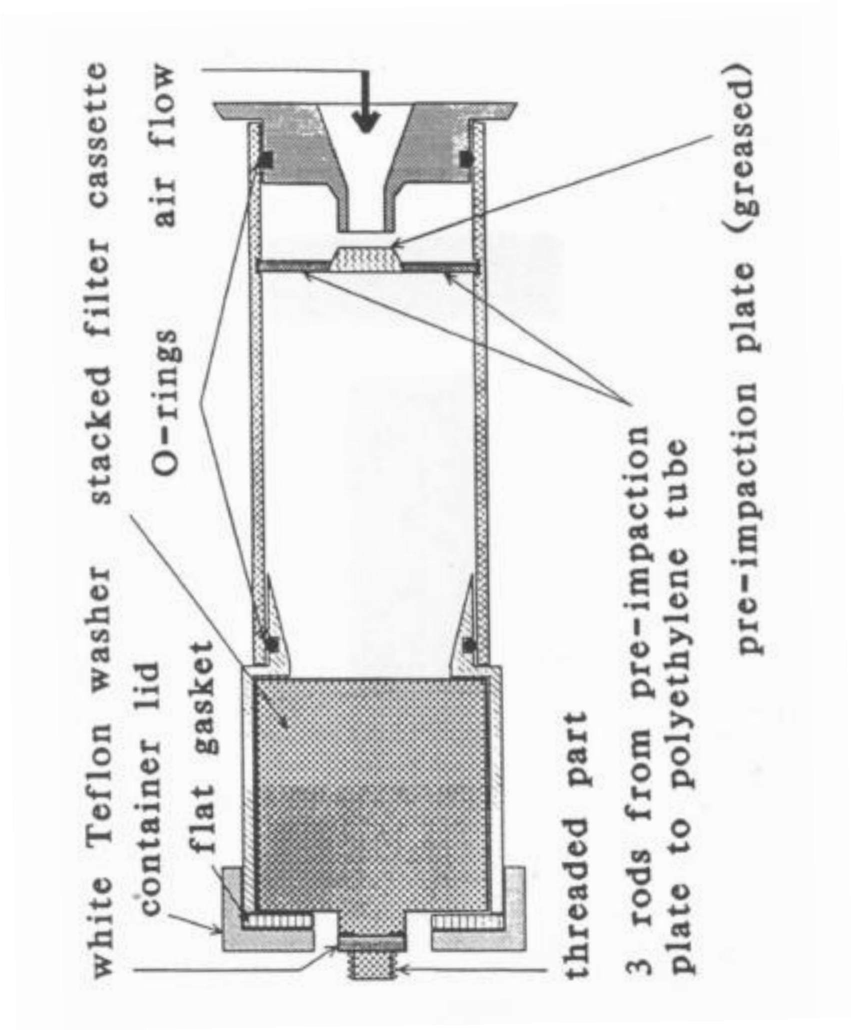


Figure 3-2 SFU Unit (IAEA, 1994)

The SFU unit was connected directly to a pump which provides a fixed flow rate of 16.7 l/min. The pump had a digital monitor which had the units for recording the flow rate, time and total volume. The pump provides necessary flow to collect aerosols on sequential filters. The particles with diameter larger than 2.2 µm were retained in the coarse filter; the others were caught on the fine filter. In this study, although the cut size between fine and coarse is 2.2 µm, fine fraction of aerosols are grouped with $PM_{2.5}$.

Similar low volume air sampling with SFU is a common technique in the.(Munzur, 2008, Yatin et al., 2000, Godoy et al., 2009; Salma et al., 2004),

3.2. Analytical Procedure

3.2.1. Gravimetric Analysis

All coarse and fine filters were kept in the Clean Room of the Department of Environmental Engineering, METU, to remove humidity of the filters before sampling. For this aim, filters were conditioned in a constant temperature (25±5)^{o}C and humidity (26±4)% chamber for at least 24 hours. When they reached a constant humidity, firstly their static electricity was eliminated by an ionizer and the weighing was done using Sartorius MC- 5 microbalance with 0.001 mg sensitivity. Loading of the filters were done under twice HEPA filtered air in the clean room. After sampling, exposed filters were brought to the clean room again, and they were conditioned one more time in order to remove humidity forms during sampling.

3.2.2. Black Carbon Analysis

Black carbon analysis was done using Magee Scientific Aethalometer which is placed in the Air Quality Laboratory of the Department of Environmental Engineering at METU. This measurement was done after the gravimetric analysis. The instrument had a cassette which carried two 47 mm filters (one is for blank the other is for analysis). Field blanks were used during the analysis. BC calculation is done using following equations:

$$Attenuation = 100 * ln\frac{T_0}{T} \qquad \text{Equation 3-1}$$

where T_0= Blank transmission intensity, T = sample transmission intensity,

$$BC\ density\ (\mu g\ cm^{-2}\ ) = \frac{Attenuation}{\sigma}$$ Equation 3-2

where σ =Specific attenuation coefficient,

$$BC\ (\mu g\ cm^{-2}\ ) = \frac{BC\ density(\mu g\ cm^{-2}\ )*A_f}{V_f} * C_f$$ Equation 3-3

where A_f= exposed area, V_f= Total sampling volume.

First of all, transmission intensities (T) of the blank and sample filters were measured. Then, the attenuation was calculated in accordance with Equation 3-1 based on the measured transmission intensity of both the sample and blank (field blank) filters. Here, the assumption was that: filter acts as a perfect diffuse scattering matrix where the light absorbing particles are fixed. Then, one of the two detectors of the Aethalometer measures the light passing through the sample filter and the other measures that of the blank filter. This was done to control variations in incident light intensity and drift in electronics (Weingartner et al., 2003). Besides, black carbon density (μg cm^{-2}) is calculated by dividing attenuation value to the specific attenuation coefficient (σ). This value was given by the manufacturer of the Aethalometer as 16.6 m^2 g^{-1} for 880 nm channel optical BC measurements. Finally, BC concentrations was evaluated by multiplying the exposed area of the filter (A_f) with BC density and dividing the total volume of the sampling (V_f). C_f is the correction factor that is determined by Khan et al. (2010) for Nuclepore filter and equals 1.1

.

3.2.3. Trace Element Analysis

Chemical compositions of the filters were measured using an Inductively Coupled Plasma with Mass Spectrometry (ICP MS) at the Kocaeli University Laboratories. In contrast to neutron a activation method which was frequently used in the past, a destructive method is employed. 57 elements including Li, Be, Na, Mg, Al, P, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ge, As, Se, Rb, Sr, Y, Mo, Cd, Sn, Sb, Cs, La, Ce, Pr, Nd, Eu, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, W, Pt, Au, Tl, Pb, Bi, Th and U are measured on the filters.

3.2.3.1. General Information about ICP MS

ICP MS is a sophisticated instrument that combines inductively couple plasma with a mass spectroscopy. It was developed in 1983 and received great attention due to its advantages over other elemental analysis techniques such as ICP- OEP, ICP AES and ICP AAS(Wolf, 2005). The most important advantages of the instrument is its extreme low detection limits. Besides, its throughput rate is higher than other ICP techniques. Finally, it can work more complex matrices with a minimum of matrix interferences.

For elemental analysis, the sample should be given as aerosol, dissolved form of solid material. Working principle of this instrument is based on converting the atoms of the sample to its ions. The operating conditions of ICP MS that used in measurements of this study is summarized in Table 3-1.

Table 3-1 The operating conditions of ICP MS

a) Instrumental Parameters	
RF power (kW)	1350 Watts
Argon gas flow (L/min)	
• Plasma	15
• Auxiliary	1.2
• Nebulizer	0.99

Table 3-1 (continued) The operating conditions of ICP MS

Peristaltic pump flow (rpm)	20
Sample uptake rate (mL/min)	~1
Skimmer Cone	Pt (1.1 aperture diameter in mm)
Sampling Cone	Pt (0.9 aperture diameter in mm)
b) Data acquisition parameters	
Measurement mode	Standard, Scan Mode: Peak Hopping and DRC (Dynamic Reaction Cell mode) for P,S and As using ultrapure Oxygen as reaction gas 20 ppb Rh and Re internal standart
Number of measurement per peak	50 ms
Mass range (m/z)	5-270 amu
Integration time	1000 ms
Number of repetitions	3
Time per sample measurement	4 min 48 s (including 35 s sample flush)
Rinse time (s)	45 s (plus ~ 15 s read delay)

3.2.3.2. Preparation of the Samples for ICP MS

Polycarbonate aerosol filters were placed into the PTFE (polytetrafluoroethylene) digestion vessels. Then 5.0 ml pure HNO_3 (nitric acid) to destruct crustal elements and 1.0 ml of HF (hydrofluoric acid) for non-crustal elements were added. Since Merck Suprapur analytical grade is 65% HNO_3, the nitric acid should be distilled before the digestion. Next, the closed microwave vessels were put on Microwave (Milestone 900, ETHOS D, US) Digestion Oven. For digestion of polycarbonate filters, three stage programs have been developed by our Air Research Group (Tokgoz, 2013). The properties of the program are given in Table 3-2 below.

Table 3-2 Program used in ETHOS 900 MW

Step	Time(min)	Temperature(^oC)	Power(W)
1	9	100	40 %
2	10	140	80 %
3	9	180	90 %

At the end of the microwave digestion, the vessels were taken and placed in a water bath for cooling. The vessel has to be cooled down to room temperatures, in order to prevent loss of acid. On the other hand, all the HF had to be eliminated with blow since even a small quantity of HF injected to ICP, can etch the silica-based sampling tube of the torch and corrode the Ni cone interference (Tokgoz, 2013). Therefore, after microwave digestion, HF was evaporated on a hot plate under the fume hood and its temperature was kept around 80^oC. The sample was evaporated until one drop of it left and white smoke turned to yellow. At that point, 5 ml of pure HNO_3 was added to vessel and content of the vessel was evaporated again. This procedure was repeated one more time until extracting all of HF content in the solution. Afterwards, the vessels were removed from the hot plate and left to cool down on the laboratory bench with their lids closed.

The remaining solutions were mixed with 1% HNO_3 solution in 50 ml falcon tubes. Then, the diluted solutions were filtered through Sartorius cellulose acetate filter paper which had 0.45 µm pore size in to eliminate soot carbon residue. Finally, they were transferred to 15 ml falcon tubes for ICP MS analysis and kept at 4^oC until analysis.

3.3. Quality Assurance and Quality Control

3.3.1. Blanks

In this study, two blank filters were used, namely laboratory and field blank, for different purposes. The laboratory blank was used to measure the contribution of laboratory procedure to the measured concentrations. Since the previous studies done by our group (Tokgoz, 2013; Ozturk, 2009) shows the effect of laboratory blank is very small, this measurement was done for each box of 100 filters. Field blanks; on the other hand, were utilized with each set (one set contains 10 vessels) of microwave digestion vessel. Field blanks were taken every week during the sampling period since the composition might be changed according to the climatic factors and meteorology. They were kept in the field for only 5 minutes and their PM characterization and digestion were done exactly same as the sample filters. The field blanks give the effect of sample handling and filter itself on measured concentrations. Field blanks were also used to measure the black carbon of the filters.

In this study, quality assurance was confirmed via two ways. First of all, the flow of pumps was controlled by checking measured values by a flowmeter (3-30 LPM - Cole Parmer ®). The calibration graphs of the two pumps are given in Figure 3-3. Here, 2 pumps that used in sampling at METU Station are given.

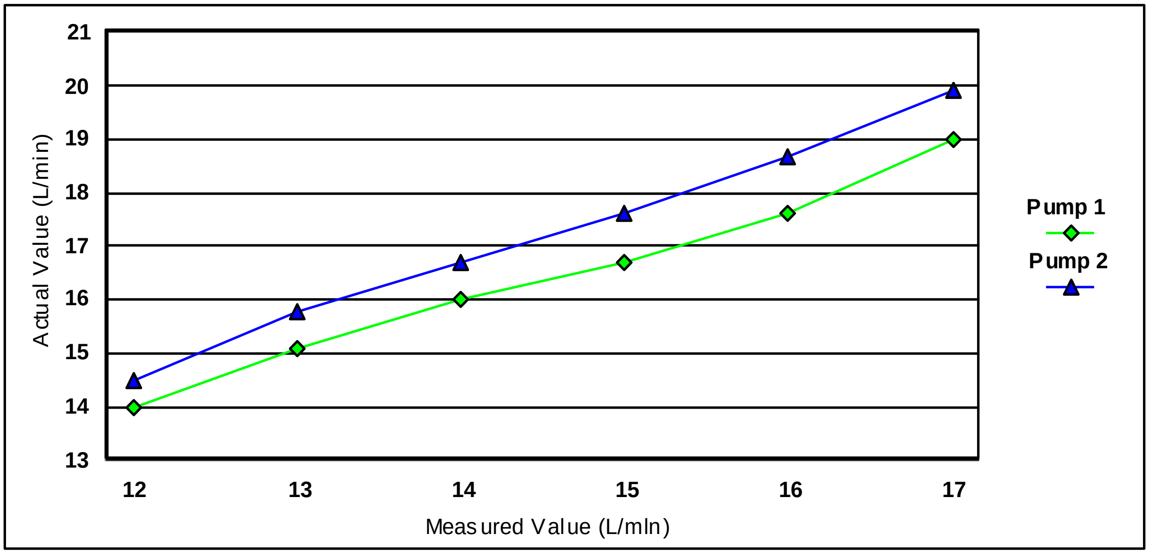


Figure 3-3 The calibration graphs of Pump 1 and Pump 2

As given in part 3.1.2.1 , the required flow for low volume air sampling studies is 16.7 L/min. This calibration was done weekly for each of the stations.

Second, detection limits of each species were calculated 3x of 10 replicates of the field blank concentrations. The calculated values are summarized in Table 3-3.

Table 3-3 Detection limits of each specie

Species	**Limit of Detection (μg/L)**	**Species**	**Limit of Detection (μg/L)**
Li	0.024	Sb	0.007
Be	0.016	Cs	0.001
Na	0.002	Ba	0.125
Mg	0.002	La	0.004
Al	0.014	Ce	0.004
P	5.020	Pr	0.001
S	<0.001	Nd	0.006
K	0.005	Sm	0.003
Ca	0.017	Eu	0.001
Sc	0.026	Gd	0.003
Ti	0.281	Tb	<0.001
V	0.012	Dy	0.003
Cr	0.411	Ho	<0.001
Fe	6.512	Er	0.001
Mn	0.054	Tm	<0.001
Co	0.013	Yb	0.001
Ni	0.215	Lu	<0.001
Cu	0.039	Hf	0.021
Zn	1.336	Ta	0.006
Ge	0.019	W	0.014
As	0.027	Pt	0.003
Se	<0.001	Au	0.039
Rb	0.007	Hg	0.094
Sr	0.099	Tl	<0.001
Y	0.003	Pb	0.032
Mo	0.016	Bi	0.002
Cd	0.010	Th	0.003
In	<0.001	U	0.002
Sn	0.018		

To ensure repeatability of ICP MS measurements, samples were divided into two part and send different times. Finally replicate concentration ratios are found in Figure 3-4.

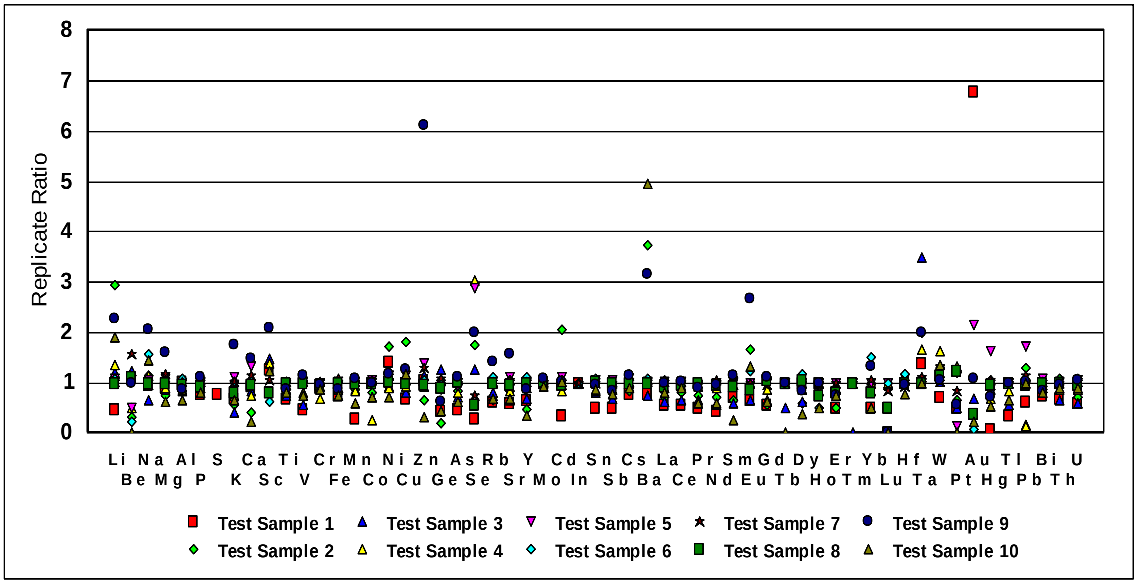


Figure 3-4 Repeatability test for the samples

It is seen that although there are some outlier values for some of the species, they are observed only a few test samples. It means there is no frequent error in measurements of any species. Replicate ratios are generally around 1. This shows that repeatability of the instrument is adequate for our study.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. General Characteristic of Data Set

4.1.1. Data

Fifty-seven major minor and trace elements, between z=3 Li and z = 92 (U) were measured in fine and coarse filters collected at the METU station. Summary statistics of fine and coarse fraction data are given in Tables 4.1 and 4.2, respectively.

The statistical summaries include mean, median, standard deviation, geometric mean, minimum and maximum values of the elemental and black carbon concentrations measured in fine and coarse fractions samples. As will be discussed later in the manuscript, most of the data are log normally distributed, or depicts other forms of right-skewed distributions. This means that data is represented best by median and geometric mean values of elemental concentrations. As a matter of fact these two values are very close to each other for most of the elements. In log-normal or other forms of right-skewed distributions arithmetic mean value does not represent bulk of the data population. In log normal distributions arithmetic mean is generally approximately a factor of two higher than median and geometric mean concentrations of elements. We reported arithmetic mean values of elements, to be able to compare measured concentrations of elements with literature values, because arithmetic mean concentrations of elements are frequently reported in literature. Median and geometric mean values calculated and reported in Table 4.1 and 4.2, as they show where bulk of the data are located. Minimum and maximum concentrations are also computed to depict the ranges of concentrations measured for each element.

Mean concentrations of fine fraction of aerosols are varied between 0.002 ng m^{-3} for Ho and Tb, and 2894 ng m^{-3} for SO_4^{2-} in METU Station. Mean concentrations of coarse fraction species are varied between 0.003 ng m^{-3} for Ho, and 3924 ng m^{-3} for Ca. Standard deviation values are usually high, and they also are higher than average concentrations for most of the elements. This pattern is not unexpected in air quality studies and arises from log-normal and other forms of right-skewed distributions of elements. Few anomalously high concentration values in log-normal distribution of elements strongly affect both concentrations and standard deviations of element. Frequency distributions of elements measured in this study will be discussed in more detail later in the manuscript.

One of the drawbacks of this work is the use of low volume sampler during sampling of particles. Approximately 24 m^3 of air is passed through the filter in 24 hour of sampling. Please note that approximately 1400 m^3 of air is passed through the filter every day when high-volume sampling is performed. We tried to compensate this difference by using cleaner (low-blank) filters in low volume sampling, but detection frequency is still an important problem. This problem also arises from partitioning of elements between fine and coarse size fractions. It is well documented that, crustal and marine particles have diameters > 2.5 μm, whereas anthropogenic particles are generally associated with fine fraction particles (D < 2.5 μm). This means that blank values for crustal and marine elements, such as Al, Fe, rare earth elements and Na will be high in fine fraction (because most of their mass occurs in coarse fraction) and blank values of anthropogenic elements are expected to be high in coarse fraction (because most of their mass occurring coarse fraction). Naturally small amount of air that passed from coarse and fine filters resulted in small amount of particles collected on filters. Please note that, this does not mean that concentrations are low, because small mass collected on filters are divided by similarly small volume. However, low flow-rate used in low volume sampling resulted in low mass of elements, which in turn resulted in fairly large blank subtraction and small frequency of detection for some of the elements.

Twenty-four species, including Tm, Lu, Tb, Ho, Sc, Hf, Ta, Y, Er, Mg, Nd, Ca, Be, Cu, Na, K, Dy, P, Au, Pr, Yb, Ce, Cr, Pt were detected in less than % 60 of the samples; 28 species, including Gd Mo, La, Rb, Eu, Th, U, Cd, Co, Li, SO4, S, W, Se, Sr, Al, Bi, Sn, Pb, Hg, Sm, Ti, Ni, Mn, Ba, Tl, Sb, V, were detected in between 60 % and 90 % of the samples and 5 species, namely Fe, Zn, Ge, As and Cs, were found at least in 90 % of the samples. This frequency of detection is adequate for most of the discussions in the manuscript, but can significantly increase uncertainty of the results in multivariate statistics, such as factor analysis and Positive matrix factorization (PMF).

Table 4-1 Statistical summary of PM, Black Carbon and concentration of elements in fine fraction aerosols

Parameter	Na	Mean ± STDb	Median	Geometric Meanc	Mind	Maxe
PM 2.5	196	14352±45322	8382		416	571557
BC- IR	178	956±930	633		12	4078
SO4	119	2894±2261	2618	2057	66	11911
Li	118	0.370±0.859	0.197	0.168	0.007	7.93
Be	75	0.006±0.005	0.003	0.004	0.001	0.020
Na	79	354±1897	64.2	75	11	16763
Mg	72	104±208	53.8	48	3.62	1624
Al	129	505±588	256	252	7.72	2357
P	91	14±12	12.6	9	0.469	54.2
S	119	965±754	873	619	22	3971
K	81	101±215	46	57	11	1831
Ca	74	2795±2552	2098	1695	60	13740
Sc	58	0.054±0.051	0.049	0.033	0.007	0.198
Ti	141	11.5±25.2	4.76	4.46	0.132	267
V	158	1.63±6.18	0.542	0.511	0.071	58.7
Cr	103	22.7±67.1	4.98	4.40	0.141	487
Fe	175	182±197	141	129	5	1862
Mn	149	4.00±4.62	2.76	2.36	0.117	38.2
Co	117	0.665±1.34	0.184	0.208	0.011	10.2
Ni	144	15.6±41.1	4.40	4.23	0.052	366
Cu	77	8.27±11.2	4.18	4.17	0.198	84.1
Zn	177	260±207	217	193	12	1431
Ge	162	0.051±0.056	0.028	0.027	0.003	0.353
As	162	0.322±0.361	0.195	0.176	0.016	1.68
Se	125	0.159±0.095	0.157	0.122	0.007	0.396
Rb	108	0.160±0.138	0.119	0.107	0.015	0.816
Sr	125	3.14±5.07	2.03	1.74	0.065	46.7
Y	62	0.051±0.053	0.033	0.031	0.004	0.243
Mo	107	1.80±5.16	0.290	0.348	0.002	37.2
Cd	116	0.439±0.815	0.207	0.183	0.011	5.31
Sn	131	0.729±0.845	0.409	0.362	0.006	4.54
Sb	152	0.550±0.542	0.409	0.324	0.013	2.47
Cs	170	0.019±0.015	0.010	0.000	0.005	0.095
Ba	149	59.5±366	21.1	16.4	0.143	4431
La	108	0.123±0.373	0.043	0.023	0.0001	3.75
Ce	102	0.215±0.687	0.076	0.064	0.003	6.80

Table 4-1 (continued) Statistical summary of PM, Black Carbon and concentration of elements in fine fraction aerosols

Pr	93	0.012±0.016	0.005	0.005	0.000	0.095
Nd	72	0.055±0.062	0.035	0.034	0.007	0.351
Sm	141	0.008±0.010	0.005	0.000	0.0002	0.066
Eu	111	0.018±0.116	0.003	0.002	0.0002	1.20
Gd	107	0.011±0.012	0.006	0.006	0.001	0.065
Tb	31	0.002±0.001	0.002	0.002	0.001	0.008
Dy	86	0.007±0.008	0.003	0.002	0.0003	0.042
Ho	38	0.002±0.002	0.002	0.002	0.001	0.008
Er	71	0.005±0.006	0.003	0.003	0.001	0.030
Tm	5	0.003±0.001	0.002	0.002	0.002	0.004
Yb	95	0.004±0.006	0.003	0.002	0.001	0.042
Lu	6	0.004±0.003	0.002	0.003	0.002	0.009
Hf	59	0.190±0.493	0.055	0.049	0.001	3.46
Ta	62	0.020±0.037	0.009	0.009	0.001	0.217
W	123	0.223±0.351	0.113	0.098	0.006	2.91
Pt	105	0.015±0.019	0.008	0.008	0.002	0.139
Au	92	0.397±1.362	0.065	0.080	0.004	12.3
Hg	135	0.495±0.867	0.291	0.270	0.015	7.79
Tl	151	0.028±0.062	0.011	0.000	0.000	0.594
Pb	132	6.67±7.76	3.65	3.22	0.068	39.9
Bi	130	0.071±0.067	0.042	0.050	0.017	0.444
Th	112	0.032±0.039	0.021	0.015	0.001	0.247
U	114	0.032±0.050	0.018	0.013	0.001	0.326

Summary statistics for coarse aerosol fraction in METU station is given in Table 4-2. In this study, PM concentration of coarse fraction had been collected daily in both stations. However, elemental analysis was performed on only 10% of samples which were collected in METU station. Only small fraction of coarse samples were analyzed, because composition and sources are well known and do not change much from one place to another. Soil and sea salt particles make up most of the coarse mass. In places, which are far from the sea, crustal particles dominate coarse fraction aerosol. We analyzed a small fraction to check if there is some unusual modification from this expected pattern.

In the coarse fraction eighteen elements, including Na, Mg, P, S, Sc, V, Cr, Ni, Cu, Mo, In, Eu, Er, Tm, Lu, Ta, W and Pb are detected in < 60% of the samples set. Frequency occurrence of 20 elements were between %60 and 90 % of the samples analyzed and only Al, Fe, Mn and Hg, were measured more than 90 % of the samples. It should be noted that these information on missing data points were based on 25 coarse fraction samples analyzed and the results would be different if all 200 samples were analyzed.

Table 4-2 Statistical summary of PM, Black Carbon and concentration of elements in coarse fraction aerosols

Parameter	N[a]	Mean ± STD[b]	Median	Geometric Mean	Min[c]	Max[d]
PM 10	196	30.2±25.7	22.2	23.4	3.10	205
BC IR	196	159 ±0.212	254	281	1.310	1273
SO_4	6	3159±1329	3474	2592	459	4701
Li	18	0.460±1.19	0.170	0.109	0.007	5.19
Be	17	0.009±0.008	0.005	0.006	0.001	0.030
Na	17	224±261	164	120	21.4	970
Mg	19	101±90.3	110	58.7	9.96	298
Al	23	622±1074	385	346	42.5	5352
P	9	8.01±7.62	5.27	4.89	0.546	21.6
S	6	1053±473	1158	864	153	1567
K	17	121±72.5	103	96.6	21.2	247
Ca	18	3974±2924	3261	2766	267	10961
Sc	12	0.076±0.051	0.073	0.053	0.007	0.162
Ti	24	20.1±15.3	15.1	14	1.23	57
V	24	0.838±0.695	0.558	0.616	0.134	2.68
Cr	5	79.4±139	3.02	8.94	0.646	323
Fe	24	331±372	188	231	59.4	1756
Mn	22	6.76±8.49	3.69	4.27	1.25	37.6
Co	18	0.671±1.57	0.187	0.208	0.031	6.47
Ni	11	55.5±88.5	5.70	11.7	0.883	251
Cu	8	10.8 ±8.28	8.97	8.18	1.76	29.4
Zn	24	459±424	382	332	39.3	2122
Ge	22	0.079±0.077	0.049	0.055	0.006	0.342
As	22	0.257±0.349	0.103	0.125	0.017	1.36

Table 4-1 (continued) Statistical summary of PM, Black Carbon and concentration of elements in coarse fraction aerosols

Se	18	0.123±0.074	0.112	0.097	0.013	0.238
Rb	22	0.278±0.213	0.228	0.210	0.048	0.876
Sr	19	3.36±2.56	3.07	2.28	0.073	10.4
Y	20	0.062±0.051	0.051	0.042	0.011	0.188
Mo	14	2.95±8.15	0.292	0.488	0.042	31.1
Cd	15	0.211±0.485	0.047	0.073	0.019	1.94
Sn	18	0.793±0.995	0.306	0.295	0.007	3.07
Sb	24	0.865±0.951	0.384	0.463	0.015	2.94
Cs	24	0.029±0.019	0.029	0.022	0.008	0.076
Ba	22	7.87±5.31	7.052	6.21	1.47	24.6
La	23	0.094±0.098	0.064	0.036	0.000	0.397
Ce	23	0.159±0.150	0.089	0.091	0.004	0.534
Pr	22	0.022±0.016	0.015	0.017	0.007	0.060
Nd	22	0.072±0.056	0.046	0.052	0.012	0.191
Sm	24	0.020±0.012	0.017	0.016	0.002	0.047
Eu	12	0.004±0.002	0.004	0.003	0.000	0.009
Gd	23	0.017±0.012	0.013	0.014	0.001	0.052
Tb	17	0.003±0.002	0.002	0.003	0.002	0.006
Dy	22	0.013±0.010	0.009	0.009	0.002	0.033
Ho	17	0.003±0.001	0.002	0.002	0.002	0.006
Er	21	0.007±0.006	0.005	0.005	0.001	0.021
Tm	2	0.002±0.0001	0.002	0.002	0.002	0.003
Yb	24	0.007±0.005	0.005	0.004	0.001	0.016
Lu	2	0.002±0.0001	0.002	0.002	0.002	0.002
Hf	17	0.034±0.042	0.030	0.015	0.001	0.178
Ta	8	0.007±0.005	0.007	0.005	0.002	0.016
W	8	0.109±0.179	0.053	0.061	0.031	0.550
Pt	19	0.007±0.004	0.006	0.006	0.002	0.019
Au	19	0.246±0.627	0.105	0.080	0.006	2.81
Hg	23	0.453±0.390	0.330	0.343	0.055	1.82
Tl	24	0.012±0.014	0.006	0.006	0.000	0.046
Pb	13	18.9±41.4	4.05	4.06	0.068	152
Bi	19	0.055±0.047	0.040	0.040	0.016	0.155
Th	24	0.055±0.036	0.049	0.038	0.001	0.147
U	15	0.009±0.006	0.009	0.007	0.001	0.021

N[a] number of samples, STD[b] standard deviation, Min[c] minimum measured value, Max[d] maximum measured value

Annual concentration limits of the European Air Quality Directive 2008/50/EC, which was given in page 20, for $PM_{2.5}$ and PM_{10} are 25 µg/m^3 and 40 µg/m^3, respectively. Average $PM_{2.5}$ concentrations of METU station is 14.3 µg/m^3;, and average PM_{10} concentration of the urban station is 30.2 µg/m^3. PM values of the both stations meet with these limit values. Indeed, permitted exceedences of PM_{10} limit is 35 times each year. In this study, this limit was exceeded 24 times in 9 months. However, sampling of the study was mostly hold in winter season, in which PM_{10} values are less. So, it could be anticipated that the annual averages may exceed annual limit values if the sampling would continue during summer season.

Average Cd, Ni, As, and Pb concentrations are 0.4 ng m^{-3}, 15.6 µg m^{-3}, 0.3 ng m^{-3} and 6.7 ng m^{-3}, respectively. These values also meet the limit values of both Turkish and European Air Quality Direction which were summarized in Table 2-4 and Table 2-5. Moreover, there is no limit value for Black Carbon. However, in the literature it is concluded that BC < 5 µg m^{-3} indicates slightly polluted, 5.0 µg m^{-3} < BC < 10 µg m^{-3} moderately polluted, and BC > 10 µg m^{-3} highly polluted atmosphere (Ozdemir et al., 2013). Mean BC value (956 ng m^{-3}) of METU station is less than these values Even the maximum measured values are below the limit of slightly polluted atmosphere. Therefore, comparison with literature part is excluded from BC discussion.

4.1.2 Comparison with Literature

Elemental compositions of this study are compared with various sampling locations around the world and Turkey. Since this study most of the daily elemental concentrations represent fine aerosol fractions, main discussion in this part involves comparison about $PM_{2.5}$ particles in both urban and suburban sampling sites.

In this part, comparison will be done in three steps. First, fine fraction aerosol in different part of the world will be compared with this study. In the second step, selected trace element concentrations will be compared with the studies performed in different parts of Turkey. Third, concentration changes with time will be compared with other studies previously performed in the city of Ankara.

Brief summary of studies which were included in this comparison are given below:

a) Tito Scalo, Italy – Urban

Daily fine aerosol samples were collected from April 2006 to March 2007 in Tito Scalo, southern Italy. Cellulose filters were analyzed for fourteen elements including Al, Ca, Cd, Cr, Cu, Fe, K and Mg (Caggiano et al., 2010).

b) Al-Hashimya, Jordan – Urban

Coarse and fine fraction aerosols were collected with Stack filter Unit, same as this study, from August 2000 to August 2001. Collected filters are analyzed for 19 trace elements with destructive acid digestion followed by Inductively Coupled Plasma Mass Spectrometry (Al-Momani et al., 2005).

c) Pathumthani, Thailand – Suburban

Fine and coarse fraction aerosols were collected in suburban residential area in Pathumthani, Thailand from September 1993 to August 1994. Similar to this study, nuclepore filters were used in daily sampling, and chemical compositions were determined by Instrumental Neutron Activation Analysis (Chueinta et al., 2000).

d) Mira Loma, Southern California- USA- Suburban

Chemical concentrations of thirty-five elements such as Si, Fe, Ca, Al and Zn were analyzed in fine fraction aerosols. Samples were collected September 2011 to January 2002 in Mira Mora, a suburban area of Southern California (Na and Cocker, 2009).

e) Budapest, Hungary - Urban

Stacked filter units and 47 mm nuclepore polycarbonate membrane filters were used for sampling. Aerosol samples were collected in the non-heating season, at the four urban stations in city of Budapest, a city with almost 2 million inhabitants. X-ray emission spectrometry and instrumental neutron activation analysis were used for determination of elemental concentrations. For comparison, data of a university campus station was used (Salma et al., 2002).

f) Beijing, China – Suburban

An urban and a suburban station were constructed in city of Beijing. Similar to this study, urban station is very near a road site, and suburban station was located near an orchard field. PM_{10} and $PM_{2.5}$ samples were collected in parallel stations. Quartz filters were used for sampling and, acid digestion was performed before ICP MS measurements. Suburban station was used for comparison (Lei et al., 2012).

g) Athens, Greece – Urban

PM10 and PM2 fractions were collected in three stations in Athens, Greece. 47 mm PTFE membrane filters were used daily sampling. After sampling, digestions were done with microwave and similar to this study, HNO_3 and HF were used for extraction of the elements from filters (Karanasiou et al., 2009).

Comparison of concentrations of selected elements measured in this work with corresponding concentrations reported for other cities around the world are presented in Table 4.3.

The table was prepared for a number of selected elements, because it is not possible to find data for all the elements in literature. Average concentrations of elements measured in this study were used for comparison, because average concentrations are generally reported in literature

Table 4-3 Literature Comparison with the studies around the world* (ng m^{-3})

Species	Tito Scalo, Italy[a]	Budapest, Hungary[b]	Mira Mora, USA[c]	Klongha, Thailand[d]	Beijing, China[e]	Al-Hashimya, Jordan[f]	Athens, Greece[g]	*This Study*
	Urban	Urban	Suburban	Suburban	Suburban	Urban	Urban	*METU Station*
Al	114	37	292	356	578	569	101	*505*
K	58	102	213	520	724	128	411	*101*
Ca	996	63	581	439	1852	4239	171	*2800*
Ti	6	3.2	113	-	24	21	-	*11*
Cr	38	<2	11	-	23	2.03	15.7	*22*
Fe	115	62	533	279	721	248	212	*182*
Ni	6	1.2	-	-	1	6.96	7.7	*15*
Cu	4	1.7	-	-	113	26.18	24.2	*8.3*
Zn	6	24	26	70.2	311	323.5	-	*260*
Cd	4	-	33	-	-	4.54	0.56	*0.439*
Pb	-	9	39	-	90	24.28	19.8	*6.68*

[a] Caggiano et al., 2010, [b] Salma et al., 2002 , [c] Na and Cocker, 2009, [d] Chueinta et al., 2000, [e] Lei et al., 2012, [f] Al-Momani et al., 2003, [g] Karanasiou et al., 2009

*Comparison was done for mean elemental concentrations in PM2.5 fraction

Average concentrations of elements measured in this study are not significantly different from concentrations reported in the literature. Crustal elements, Al and Ca concentrations measured in this work are higher than concentrations reported for Italy, Hungary, US, Thailand and Athens, but lower than concentrations reported for Jordan and China. This pattern is not surprising, because concentrations of these elements depends on local re-suspension of soil particles or dust transport from arid regions, particularly from Chad in North Africa, desert areas in the Middle East and Arabic peninsula as well as deserts in the Central Asia. Jordan is under strong influence dust of transport from Middle East and Arabic Peninsula. Higher concentrations of crustal elements are expected in Jordan and China, because they are closer to dust source areas, than Ankara.

Iron do not fit to this pattern of other crustal elements. Concentration of Fe reported for other cities around the world, with two exceptions, are higher than Fe measured in this work. Iron is a typical crustal element and is expected to behave similarly with Al and Ca. Different behavior of Fe can be due to different mineralogy of the dust sampled in this work and that sampled in other studies. This agrees with very high variability in Fe concentrations reported in the table.

Concentrations of anthropogenic elements, namely Cr, Ni, Cu, Zn, Cd and Pb measured in this work are not dramatically different from concentration of the same elements reported for other cities. Concentrations of Pb and Cd are exceptions to this pattern. Concentrations of these elements measured in this work are significantly lower than concentrations reported for other cities in the table. This may be due to two reasons;

1. Concentrations of pollution derived elements depend on anthropogenic emissions in that particular area. Since Ankara is not an industrial city, lower concentrations of anthropogenic elements in Ankara is not surprising

2. Concentrations of pollution derived elements are decreasing most of the developed world with actions taken to reduce their emissions. Because of this concentrations measured depend on the year samples are collected. In constructing the table, we did not pay attention to find trace element data generated at the same time.

h) İstanbul, Turkey – Urban

Fine fraction aerosols were collected with high volume samplers in Istanbul from June 2010 to May 2011. Trace elements determination is done for 21 elements using microwave assisted aqua regia extraction and subsequent ICP MS determination (Szigeti et al. 2011).

i) Mediterranean Coast- Rural

More than 1000 daily PM_{10} aerosol samples were collected from February 1992 to December 2001 at a rural site on Mediterranean Coast of Turkey, using a high volume air sampler onto Whatman-41 cellulose fiber filters. Samples were digested with a HNO_3 – HF mixture using a microwave digestion system and analyzed by ICPMS technique (Ozturk et al., 2012).

j) Norteastern Mediterranean- Rural

$PM_{2.5}$ and PM_{10} aerosol samples were collected at Erdemli, Içel, which is a rural coastal site approximately 5 km to the west of Erdemli. Samples were collected on a daily basis between April 2001 and April 2002, using a stacked filter unit, which is the same sampler used in this study and elemental concentrations were determined by proton induced X-ray emissions technique (PIXIE) (Koçak et al., 2007).

k) Eastern Black Sea Coast- Rural

$PM_{2.5}$ and $PM_{2.5-10}$ aerosol samples were collected onto polycarbonate filters using a SFU between 2011 and 2013. Sampling site is located the Georgian border of Turkey. Elemental concentrations were determined by Energy dispersive x-ray fluorescence technique (XRF) (Balcılar et al., 2014).

l) Zonguldak- Urban

Coarse and fine fraction aerosols were collected December 2004 to October 2009 using a dichotomous sampler. Sampling location was at the center of Zonguldak city, and trace metals such as Mg, Al, Ti, Ca, Cr, Cu, Fe, K, Mn, Ni, Pb, and Zn were analysed using an X-ray Fluorescence spectrometers (Tecer et al., 2012).

Table 4-4 Literature Comparison with the studies performed in Turkey*

Species	Istanbul Urban	Antalya[b] Rural	Erdemli, Mersin[c] Rural	Eastern Black Sea Coast[d] Rural	Zonguldak[e] Urban	*This Study Suburban*
Al	-	546	-	337	94	*505*
K	-	366	116	123	208	*101*
Ca	-	2149	158	550	197	*2795*
Ti	-	40.3	4.1	96.6	12	*11*
Cr	2.8	3.88	1.8	39.9	3.8	*22*
Fe	460	388	53.3	1127	130	*182*
Ni	4	3.03	1.6	8.6	3	*15*
Cu	14	-	-	14.6	61	*8.3*
Zn	72	10.6	4.9	28.4	58	*260*
Cd	0.56	-	-	-	-	*0.44*
Pb	13	37.3	-	13.1	11.9	*6.7*

[a]Szigeti et al., 2011, [b]Ozturk et al., 2012, [c]Koçak et al., 2007, [d]Balcilar et al. 2014, [e]Tecer et al., 2012

*Comparison was done for mean elemental concentrations in PM2.5 fraction

As can be noted in short information about the data sets, all data used in the table is fine fraction data. The only exception to that is data from Antalya station, which is PM_{10}. Data from rural stations, such as Antalya, Eastern Black Sea, Erdemli. had to be included in comparison as trace element data in Turkey is scarce. However, few additional studies were performed in urban areas like Eskişehir, Kütahya, Bolu and Erzurum. Unfortunately those data are not openly available in literature for the time being.

Concentrations of crustal elements, Al, Fe, K are comparable to corresponding concentrations reported for other sites. Small differences in their concentrations between different sites probably reflect how arid the sampling point is. The only exception to this general pattern of crustal elements is Ca. Calcium concentration measured in this study is approximately 2100 ng m^{-3}, which is comparable with Ca concentration reported for Antalya but significantly higher than Ca concentrations reported in all other sites. This is not surprising because Ca concentration vary significantly between sites and depends on the $CaCO_3$ content of soil. Soil in Ankara is known to be very rich in $CaCO_3$ (Yay et al., 2008), which may explain high Ca concentrations measured in this work. Average fine-fraction Cr and Ni concentrations measured in this study are 22 ng m^{-3} 14 µg m^{-3}, respectively. These are high compared to Ni and Cr concentrations measured in other stations in the table. The only reported Cr concentration, which is higher than concentrations reported in this work is the Cr concentration measured at our Torul station on the Eastern Black Sea coast. Chromium concentration reported for Torul is 40 µg m^{-3}. The reason for such unusually high Cr concentration at Torul station is not very clear. One reason may be the transport of pollution derived particles from Russia and Ukraine. Concentration of Cu and Pb measured in this work at the METU station are lower than with their concentration reported for other sites. For Cu this is probably due to suburban nature of our station in METU, compared to data generated at the city center in Istanbul and Zonguldak. For comparison of Pb, smaller concentrations measured in this study is probably because measurement in this work is more recent than Pb measurements performed in other studies. Concentration of Pb had banned decreasing since early 2000 when it was phased out from gasoline. Consequently, Pb concentrations are high in samples collected and analyzed in early 2000 and low in samples collected and analyzed after 2010.

In the last step fine fraction trace element data generated in this study are compared with similar data generated in earlier studies at Ankara. First multi element data set in Ankara was generated in 1975 by İlhan Ölmez (Ölmez and Aras, 1977), then in 1977 (Sabuncuoğlu et al., 1986). More recent data is generated by Mustafa Yatın in 1989 and 1993 (Yatın et al., 2000). Although the second set of data generated in 1977 are not available, we were able to compare concentrations of elements measured in this work with concentrations measured in 1977, 1989 and 1993.

Table 4-5 Literature Comparison with the studies performed in Ankara*

Species	METU 1975[b]	Sihhiye 1989, Winter[a]	Sihhiye 1989, Summer[a]	METU 1993, Winter[a]	METU 1993, Summer[a]	*This study PM10*
		Urban	Urban	Suburban	Suburban	*Suburban*
Al	3400	6900	4420	690	780	*640*
K		590	250	-	180	*148*
Ca	8200	9600	-	1100	-	*5300*
As	14	31	16	14	11	*0,29*
Mn	12	19	10	8	5	*6*
La	2.0	3.1	1.3	3.7	0.3	*0,1*
Na	913	1900	1200	420	360	*227*
Cr	21	17	7	27	5	*8*
Fe	2100	2100	1600	1300	540	*329*
Ni	94	95	49	52	20	*10*
Zn	90	90	45	90	24	*459*
Pb	66	230	320	250	470	*7*

[a]Yatin (1994), [b]Ölmez and Aras (1977)
*Mean values are used for comparison

Conditions under which data in 1989 and 1993 were generated are explained in Yatın et al. (2000). In 1977 total aerosol samples were collected onto Whatman 41 cellulose fiber filter and analyzed by INAA. In 1989 aerosol samples were collected during winter and summer sampling periods, onto polycarbonate filters in a downtown (Sıhhıye) and a suburban (METU) station. In second part of the study, coarse and fine fraction aerosols were separately collected, using a stack filter unit, again in summer and winter period of 1993. Filters were analyzed for approximately 40 trace elements using INAA technique.

Data generated in 1975, 1989, 1993 and 2014 (this work) are given in Table 4-5. This comparison is important as it shows how concentrations of anthropogenic and soil-derived elements have changed over a 40 years period.

It is interesting to note that concentrations of both crustal and pollution derived elements decreased significantly between 1975 and 2014. Concentration of As decreased from 31 ng m^{-3} in 1989 to 0.32 ng m^{-3} in 2014. Similarly Ni and Pb also showed significant decreases between 1975 and 2014. These decreases in As and Ni are probably due to reduced coal and oil combustion for space heating. As is a good marker for coal combustion and Ni is a marker element for residual oil combustion. Both coal and oil were common modes of heating, particularly during winter season. Since then, natural gas replaced both coal and oil as energy source in Ankara, which resulted in a parallel decrease in both Ni and As.

The dramatic decrease in Pb concentration, on the other hand, is due to gradual phasing out of Pb from gasoline, in the beginning of 2000. This decrease in Pb concentrations is a world-wide phenomenon (Yang et al. 2012, Tomasevic 2010).

An interesting point about this table is that not only anthropogenic elements, but also concentrations of crustal elements decrease in time. Concentration of Al, which was 3400 ng m^{-3} in 1975 4000 ng m^{-3} in 1989, decreased to 780 ng m^{-3} in 1993 and to 640 ng m^{-3} in 2014. Similarly, concentration of Fe was 2100 ng m^{-3} in 1975, 1600 ng m^{-3} in

1989 decreased to 540 ng m^{-3} in 1993 and to 329 ng m^{-3} in 2014 other crustal elements such as K and La also show similar trends. This decrease in concentrations of soil related elements is probably due to urbanization around the university, which reduced re-suspension of soil particles, reducing concentrations of crustal elements.

The only element which shows different pattern is Zn. Zinc concentration was between 25 – 90 ng m^{-3} in 1975 and 1993, but its concentration in 2014 is 500 ng m^{-3}. This dramatic increase in Zn concentration in recent years is probably due to increase in vehicle number in Ankara since 1990. Zinc is not an ideal tracer for traffic emissions, because it has other sources as well. However, together with other elements like Cd and Ba, Zn was used as an indicator of traffic emissions (Minguillón et al., 2012; Thurston et al., 2011). Zinc is used in car breaks and emitted to atmosphere from wearing breaks (Johansson et al., 2009). Similar high Zinc values were observed in highly polluted Mexican cities like Zacatecas and Mexico City. In 2006, Mugica et al. measured atmospheric Zinc concentrations between 0.3-0.4 µg m^{-3} in PM2.5 and 0.65-0.60 µg m^{-3} in PM10 samples (2009). Also, Murruni et al. (2009) and Fabian et al. (2010) measured very high Zinc (between 0.30 and 0.65 µg m^{-3}) concentrations in Buenos Aires (Argentine) and explained this by vehicular traffic and motor emissions. Although it is not conclusive evidence, high Zn concentrations in recent years in Ankara may be due to increased number of cars in the city like the studies given previously.

In Ankara, major air quality parameters, including SO_2, NO_2, $PM_{2.5}$ and PM_{10}, are measured by Ministry of Environment and Urbanization based on online techniques. These online measurements are done in 8 stations within the city, including Sincan, Sihhiye, Kecioren, Kayas, Dikmen, Demetevler, Cebeci and Bahcelievler districts. Among these Bahcelievler and Dikmen stations are the closest stations to our sampling locations. Average $PM_{2.5}$(24.9 µg m^{-3}) and PM_{10} (54.9 µg m^{-3}) concentrations reported in these stations were compared with this study. It is found that measured concentrations in METU station is generally lower than those which is thought to be due to the differences in measurement techniques.

These results show that air quality of Ankara city has improved over the last 40 years period significantly. Today, particularly at the sampling point, elemental concentrations of objective air pollutants, including Ni, As, Cd, and Pb, and mass concentrations of PM10 and PM2.5 meet with the limits of the European Air Quality Standards. However, it should be noted that METU is a suburban station, so concentrations measured at this station would not represent the whole city, which are probably higher.

4.1.3 Frequency distribution of elements

The trace elements concentrations in ambient air fluctuate randomly due to atmospheric events and emission sources. Due to these fluctuations, elemental concentrations in the atmosphere changes greatly. Therefore, arithmetic mean concentrations are no longer representative for data population, since they skew right as a result of very high concentrations. So, median values become very different from arithmetic means. Skewness test evaluates the degree of asymmetry of a distribution around its mean (Ozturk, 2008). In contrast to Gaussian distribution, the skewness has tail towards positive and negative values due to the asymmetric distribution it has. If arithmetic mean of a data set is larger than geometric mean and median values, the distribution graph will have positive (right) skewed tail, and the data set is considered as log-normally distributed. On the contrary, when geometric means and median values are larger than arithmetic means, the distribution called negative skewed. Log-normal distributions were observed in many aerosol studies (Al-Momani et al. , 1998; Gullu et al., 1998).

In Figure 4-1, frequency diagrams of a crustal and anthropogenic species, Fe and Zn are given. These two elements represent log-normal distribution best in this study’s data set. As it is known, median values are more convenient parameters for log-normally distributed data sets than arithmetic mean since arithmetic means are deviates from median values. However, most of the elements show neither normal nor log-normal distribution.

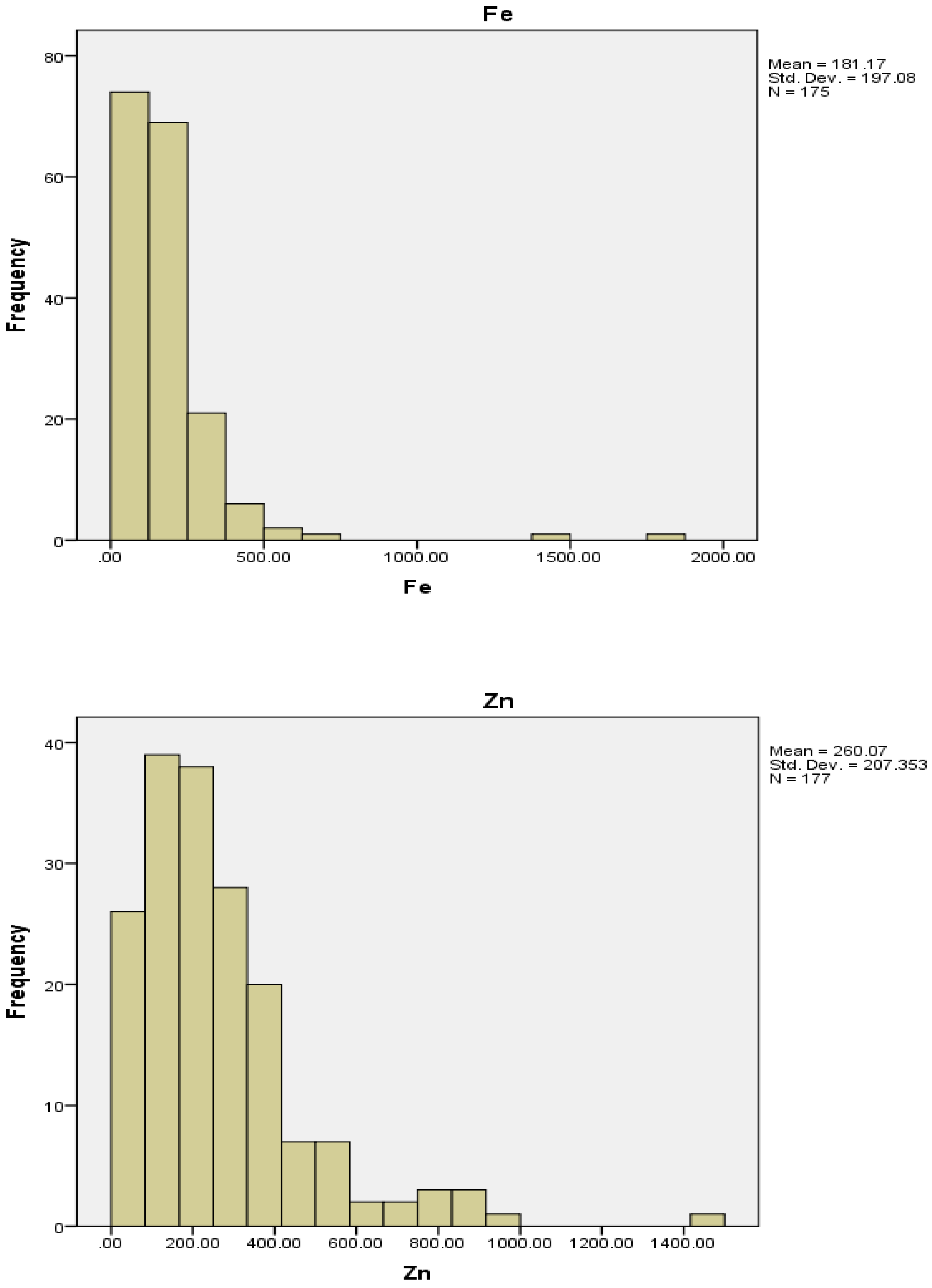


Figure 4-1 Frequency distribution of concentrations for selected species

4.2. Coarse-to-fine concentration ratios of elements

Aerodynamic diameter of trace elements varies according to source of the pollutants. For instance, aerodynamic diameter of soil related elements such as Al, Fe, Si and sea salt tracer Na are large, whereas anthropogenic elements such as Pb, Zn, As, and Se have much smaller diameter, which is generally smaller than 2.5 µm. Therefore, elemental concentrations on the coarse and fine filters, which are known as coarse-to-fine ratio (C/F), give general information about sources of these elements.

Coarse-to-fine of elements at METU station is given in Figure 4-2. Since the data set consist very high values, mean concentrations do not represent whole population, properly. However, median values are less susceptible to effect of extreme values (Jones et al., 2008). Therefore, the bar graph was prepared according to median concentrations of the elements which were collected on coarse and fine filters.

Figure 4-2 shows that C/F of the soil related elements are usually higher than 1.0. This is totally expected and almost always observed in literature (Munzur, 2008). It is clear in the figure, most of the elements whose C/F are larger than 1.0 are soil related tracers. In contrast, C/F ratios of the anthropogenic elements are usually less than 1.0. This common trend is due to coarse nature of soil-related and small diameters of pollution-derived elements. Mass median diameter of Crustal elements, such as Al, Fe is found to be 3.4 μm at a site on the Mediterranean Coast (Antalya), Mass median diameters of anthropogenic elements in the same study varied between 0.6 for Pb μm and 1.5 μm for Zn (Kuloglu and Tuncel, 2005).

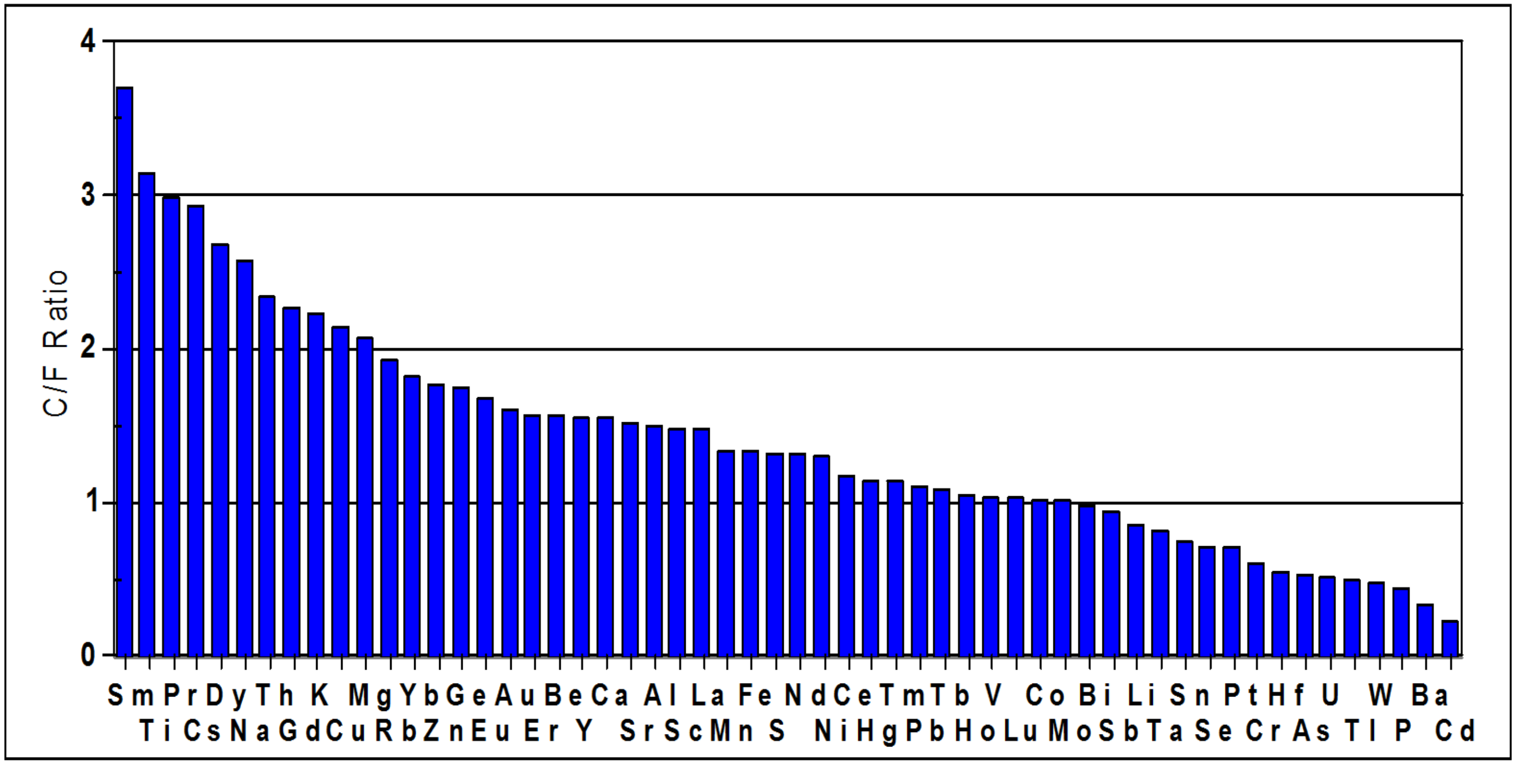


Figure 4-2 Coarse-to-fine ratios of elements

Figure 4-2 also involves a few unexpected results. Coarse-to-fine concentration ratios of some anthropogenic elements, including Cu, Ge, Zn and Au, are higher than 1.0. Also, coarse-to-fine ratios of U, Hf, Li, which are soil related, are less than 1.0. Higher C/F ratios of anthropogenic elements and smaller C/F ratios of lithophilic elements may be due to small number of coarse fraction samples that were analyzed. As explained in the experimental section, since only 10 % of the coarse filters were analyzed; their median values may not be representative for all population. Association of Zn with coarse particles is interesting and can support earlier suggestion that its source may be abrasion of breaks in cars. Normally anthropogenic sources generate fine particles and anthropogenic elements are associated with fine particles. Mechanical processes, such as abrasion of breaks, on the other hand, produce coarse particles. Coarse Zn in this data set confirms traffic source suggested for Zn in Ankara atmosphere.

4.3. Temporal Variations of Pollutant

4.3.1. Short Term episodic variations

Concentrations of elements show episodic changes due to changes in efficiency of ventilation in the urban atmosphere. Concentrations of all pollutants in an urban atmosphere are determined by three factors, namely efficiency of horizontal ventilation, efficiency of vertical ventilation and emissions.

Horizontal ventilation of urban atmosphere occurs by winds, which results in dilution of pollutants and decrease in their concentrations by increasing wind speed. Consequently, short term variations in wind speed can cause episodic changes in concentrations of pollutants.

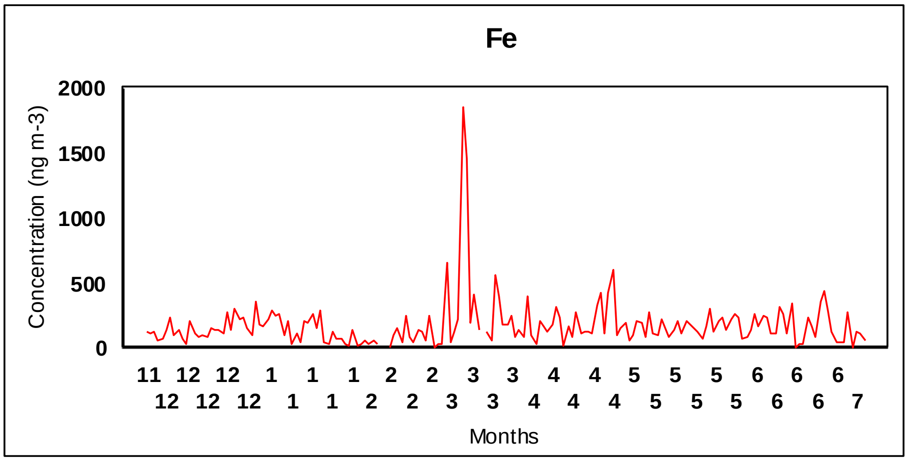
Vertical ventilation of atmosphere in urban areas is determined by stability of atmosphere. As in the case of wind speed, variations in stability of atmosphere, such as setting up of inversions, can generate these episodes. Rain events also can generate observed short-term episodes by washing atmosphere when it rains. Rain can also indirectly enhance short-term variations in soil related parameters by suppressing re-suspension process, which is the most important mechanism for observed concentrations of soil particles and lithophilic elements that are associated with these particles.

Like meteorology, short-term variations in emission strength of pollutants can also generate these episodic changes in concentrations. However, it should be noted that short-term variations in emissions is less likely than short term variations in meteorology. Episodes observed in concentrations of pollutants generally occur by combination of these events.

In addition to these three mechanisms, transport of particles and gases also contribute to measured concentrations of species, but in an urban atmosphere, contribution of distant sources are observable only for very strong transport events, such as episodic dust transport from arid regions of the world. Such transport events are few and their effect is small when compared with effect of ventilation mechanisms and emissions on concentrations of pollutants.

Time series plots of selected crustal and anthropogenic elements are given in Figure 4-3 and 4-4, respectively, to demonstrate short-term variations in their concentrations. The pattern shown in the figure is not unique for these elements, but can be seen in all elements. In Figure 4-3, where temporal changes of Fe and Ni are given over 9 month's period, one major and one minor episodes can be seen in March (11-12th March) and April (26th of April). Since Al, Ca and Ti, the most significant indicators of Saharan dust, did not show episodes during that time, this discussion does not consider influence from a Saharan dust episode. However, episodes in the same days were also observed in concentrations of other anthropogenic and some crustal elements. Therefore, this probably indicates a common source for these crustal elements which is likely to be related to meteorology.

Average wind speed in Ankara was 1.06 m/s, during sampling period. However, wind speed values of 11 and 12th of March were 2.4 and 2.6 m s^{-1}, respectively, which are more than 2 times of mean average wind speed values. So, as it is expected, episodes in concentrations of Fe and Ni were generated by enhanced soil re-suspension, due to relatively high winds. This is a typical demonstration of the influence of emission strength on observed concentrations of elements. Relation between meteorological parameters and episodes in concentrations of elements will be discussed in later sections of the manuscript.



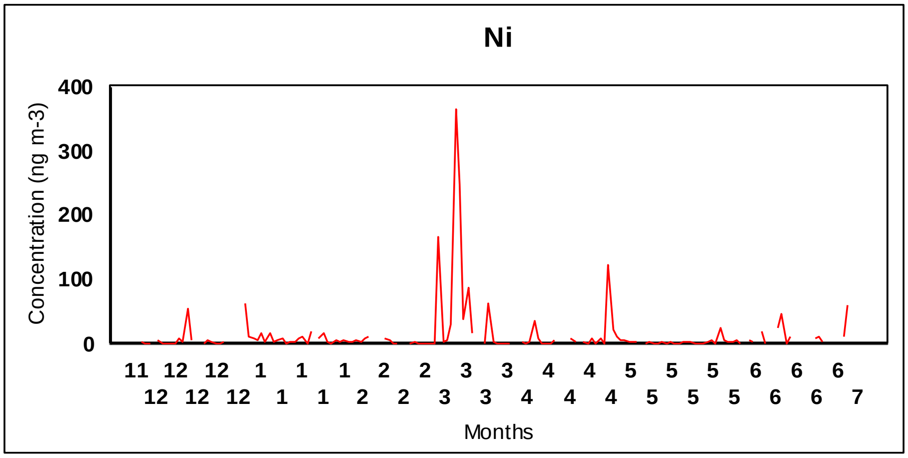
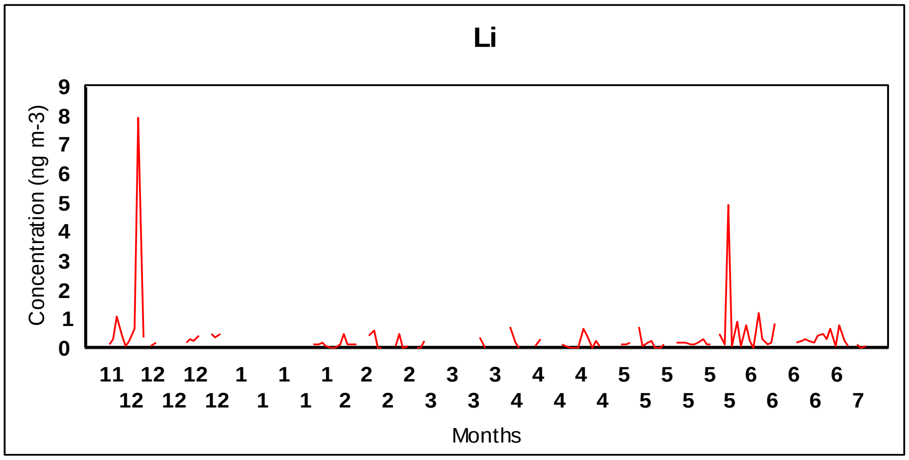


Figure 4-3 Temporal Variations of Fe and Ni



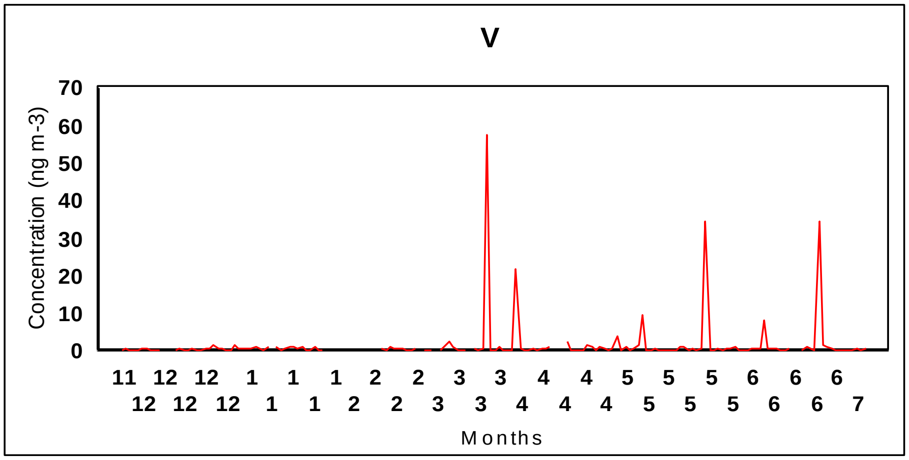


Figure 4-4 Temporal variations of Li and V

4.3.2. Weekday-weekend variations

The ambient aerosols and their elemental content differ in city atmosphere during weekday/weekend (Almeida et al., 2006; Morawska et al., 2002). The reason behind this fact is variation of the human activities through a week. So, based on these activities different elements are emitted to the city atmosphere. For instance, some anthropogenic activities, such as traffic related activities, are denser during weekdays, so their emissions are expected to be higher during the weekdays (Almeida et al., 2006). In contrast, emissions from certain human activities can be more intense during weekends are more frequently done during weekend. Combustion are expected to be higher during weekends. Since fossil-fuel combustion for space heating is one such process, tracers of combustion emissions are expected to be high during weekend (Thurston et al., 2011).

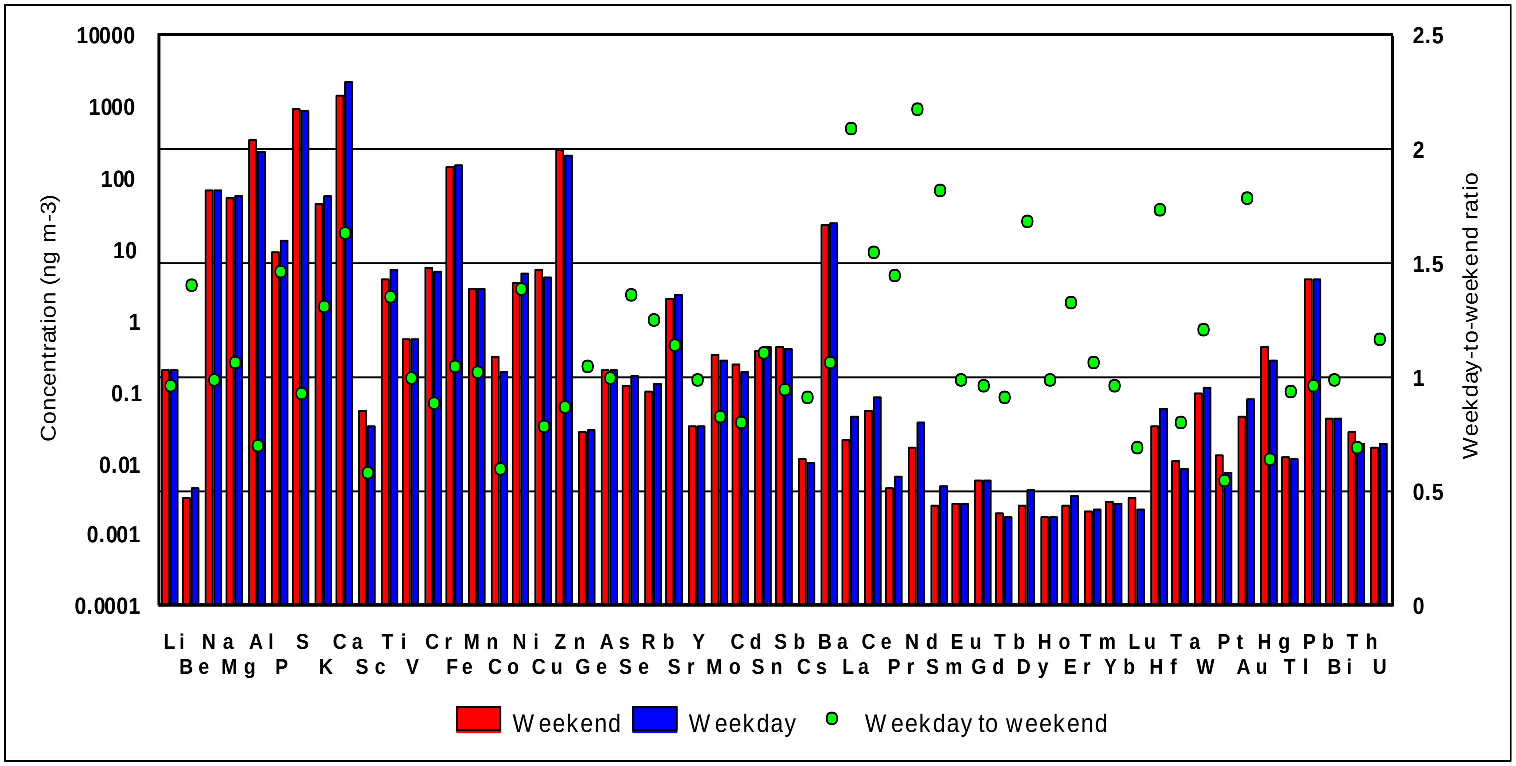


Figure 4-5 Weekday and Weekend median concentrations of selected elements

Therefore, due to the reasons that stated above, comparison of concentrations of elements and ions measured in weekdays and weekends can provide some general information about the sources of the elements.

Weekend and weekday concentrations of selected elements and their weekday-to-weekend concentration ratio are given in Figure 4.3. The average values given in the figure are based on median of the elemental concentrations. In the same way, weekday-to-weekend concentration ratios were also found using median concentrations of species.

Median concentrations of elements, instead of using their average values were used, because as pointed earlier in the manuscript data is right-skewed and median concentrations is better representation of the bulk of the data than average values.

For most of the crustal and anthropogenic elements shown in the figure there is not much difference between their weekday and weekend concentrations. The only two elements that statistically significant higher concentrations during weekday are La and Li. These are minor elements of earth’s crust. It is not clear why their concentrations are high during weekdays, because other markers of soil, such as Al, Fe have rather similar concentrations in weekdays and weekend. Rest of the anthropogenic and soil-related elements have comparable values in weekdays and weekend (their weekday-to-weekend ratios vary between 1.0 ± 0.5).

Concentrations of elements at an urban area in any day is the result of a mixture of a variety of factors, including meteorology, emissions etc. Some of these variations are due to living habits of the population some are not. In the literature there are both examples of similar (Dumka et al., 2013; Xie et al., 2012)and different (Almeida et al., 2006; Madhavi and Badarinath, 2003) concentrations of trace elements in weekdays and weekend days. In Ankara there doesn’t seem to be sufficiently different activities at weekdays and weekend days to generate weekday-to-weekend ratios significantly different than unity.

4.3.3. Seasonal variations

Atmospheric concentrations of the trace elements are affected by seasonal changes. Scavenging and generation mechanisms of the pollutant sources account such variations. So, seasonal variations of measured atmospheric species give significant information about sources, and transportation mechanisms of the pollutants (Tokgoz, 2013).

In this study, data set was divided into two parts in order to represent winter and summer seasons. Winter season includes the months from November, 2013 to April, 2014; while summer season includes the months from May to July, 2014. The division was done by considering temporal and precipitation changes during these months.

The mass and elemental concentrations of species are given in Table 4-6 in order to quantify the differences in between winter and summer season. As it can be depicted in the table, mass and elemental concentrations show different variations according to seasonal change. For instance, mean coarse fraction aerosol is higher than that of winter; while mean fine fraction aerosol is less in summer season. Here, median averages are found more representatives for data set. There median values are used in calculation of summer-to-winter ratios.

Table 4-6 Mass ($\mu g/m^3$) and elemental (ng/m-3) concentrations of species in winter and summer season

	Winter				Summer			
	Fine		Coarse		Fine		Coarse	
	Mean± STD[a]	Med[b]	Mean± STD	Med[b]	Mean± STD	Med[b]	Mean± STD	Med[b]
PM	11.18	8.52	25.64	19.97	9.41	8.05	26.30	21.37
BC	1.02	0.73	0.334	0.295	0.599	0.568	0.239	0.277
Li	0.352±0.952	0.174	0.389±0.700	0.215	0.641±1.38	0.220	0.097±0.087	0.071
Be	0.006±0.952	0.004	0.005±0.005	0.003	0.011±0.008	0.010	0.007±0.005	0.005
Na	494±2333	63.7	98.0±88.3	69.0	214±264	142	243±232	210
Mg	151±2333	56.9	53.9±50.4	32.7	137±92.5	123.3	49.6±42.8	29.5
Al	380±532	159	763±606	509	303±192	231	1120±1534	541
P	15.3±12.8	11.8	12.5±9.58	11.3	11.2±8.08	9.06	4.05±2.52	2.66
S	1112±769	1108	419±297	395	1053±432	1158	n/d	n/d
K	113±261	49.0	82.3±117	42.6	119±62.6	103	122±77.3	119
Ca	2765±2146	2462	2762±2889	1445	3879±3077	3099	4092±2510	3867
Sc	0.062±0.053	0.050	0.025±0.020	0.007	0.082±0.046	0.076	0.007±	0.007
Ti	7.15±11.1	3.83	16.73±37.4	7.14	22.5±17.5	17.9	16.5±8.341	14.0
V	1.40±6.02	0.542	2.05±6.404	0.542	0.870±0.667	0.562	0.784±0.700	0.553
Cr	29.8±81.9	5.75	7.96±13.0	4.45	79.5±124.7	3.022	n/d	n/d
Fe	189±231	136	166±94.2	147	414±437	265	193±67.2	183
Mn	4.59±5.49	2.95	3.00±2.34	2.46	9.06±10.1	4.59	3.46±1.66	2.90
Co	0.887±1.59	0.225	0.222±0.322	0.118	1.05±1.913	0.261	0.197±0.204	0.142
Ni	17.7±48.8	4.95	7.44±11.6	3.40	66.3±89.1	12.6	2.65±1.42	2.65
Cu	9.33±13.2	5.18	6.70±7.76	3.20	10.5±7.75	8.968	n/d	n/d
Zn	205±169	161	370±231	320	447±499	253	478±212	402
Ge	0.060±0.063	0.046	0.035±0.033	0.026	0.100±0.091	0.066	0.049±0.019	0.046
As	0.397±0.411	0.254	0.164±0.112	0.154	0.354±0.394	0.138	0.087±0.061	0.079
Se	0.153±0.095	0.147	0.169±0.092	0.163	0.153±0.067	0.179	0.063±0.036	0.065
Rb	0.159±0.129	0.109	0.160±0.148	0.119	0.316±0.241	0.314	0.224±0.129	0.192
Sr	3.69±6.47	2.12	2.44±2.12	1.84	4.14±2.73	4.29	2.29±1.59	1.58
Y	0.050±0.056	0.023	0.052±0.049	0.034	0.079±0.055	0.075	0.041±0.032	0.034
Mo	2.58±6.76	0.292	0.860±1.435	0.290	4.55±10.1	0.245	0.821±1.00	0.346
Cd	0.536±0.901	0.309	0.104±0.083	0.080	0.357±0.650	0.132	0.083±0.085	0.030
Sn	0.941±0.959	0.578	0.395±0.456	0.269	1.10±1.05	0.428	0.174±0.124	0.200
Sb	0.680±0.626	0.480	0.333±0.235	0.305	1.01±0.953	0.681	0.608±0.830	0.322
Cs	0.019±0.015	0.010	0.020±0.015	0.010	0.032±0.021	0.031	0.023±0.014	0.029
Ba	79.2±469	20.2	28.4±22.3	23.3	8.71±6.00	8.23	6.65±3.35	6.67
La	0.082±0.101	0.043	0.209±0.626	0.045	0.122±0.109	0.103	0.050±0.045	0.040
Ce	0.135±0.163	0.067	0.376±0.164	0.090	0.195±0.164	0.140	0.102±0.091	0.064
Pr	0.012±0.014	0.005	0.013±0.017	0.006	0.026±0.017	0.021	0.016±0.011	0.013
Nd	0.047±0.051	0.024	0.064±0.060	0.036	0.085±0.060	0.086	0.054±0.038	0.033
Sm	0.007±0.009	0.004	0.010±0.014	0.006	0.021±0.014	0.017	0.017±0.007	0.016
Eu	0.030±0.161	0.002	0.005±0.002	0.004	0.004±0.002	0.004	0.002±0.002	0.002
Gd	0.009±0.011	0.005	0.012±0.014	0.007	0.019±0.014	0.016	0.014±0.007	0.012
Tb	0.002±0.001	0.002	0.003±0.002	0.002	0.004±0.002	0.004	0.002±0.001	0.002
Dy	0.006±0.008	0.003	0.007±0.010	0.004	0.015±0.010	0.011	0.009±0.006	0.007

Table 4-6 (continued) Mass ($\mu g/m^3$) and elemental (ng/m-3) concentrations of species in winter and summer season

Ho	0.003±0.001	0.002	0.002±0.001	0.002	0.003±0.001	0.002	0.002±0.001	0.002
Er	0.005±0.006	0.002	0.006±0.007	0.003	0.009±0.007	0.006	0.004±0.003	0.003
Tm	0.003±0.001	0.002	0.002±0.000	0.002	0.002±0.000	0.002	n/d	n/d
Yb	0.004±0.007	0.003	0.004±0.006	0.003	0.007±0.006	0.007	0.005±0.004	0.005
Lu	0.004±0.003	0.002	0.003±0.001	0.003	0.002±0.000	0.002	n/d	n/d
Hf	0.242±0.663	0.042	0.166±0.278	0.056	0.027±0.019	0.031	0.044±0.058	0.017
Ta	0.024±0.042	0.010	0.010±0.011	0.006	0.008±0.004	0.009	0.002±0.000	0.002
W	0.253±0.199	0.113	0.179±0.183	0.108	0.118±0.177	0.056	0.051±0.000	0.051
Pt	0.016±0.010	0.008	0.007±0.006	0.004	0.006±0.003	0.004	0.008±0.005	0.006
Au	0.378±0.201	0.077	0.472±1.11	0.042	0.113±0.081	0.113	0.618±1.10	0.068
Hg	0.515±0.457	0.330	0.411±0.600	0.325	0.472±0.451	0.042	0.520±0.487	0.330
Tl	0.038±0.023	0.015	0.016±0.010	0.011	0.461±0.231	0.262	0.006±0.003	0.004
Pb	8.30±11.33	5.57	34.8±41.1	5.81	0.013±0.011	0.009	3.39±3.01	2.13
Bi	0.084±0.090	0.057	0.070±0.034	0.042	3.82±3.21	2.025	0.022±0.013	0.019
Th	0.018±0.011	0.008	0.048±0.052	0.045	0.046±0.045	0.038	0.066±0.056	0.056
U	0.034±0.031	0.013	0.012±0.011	0.012	0.047±0.034	0.034	0.005±0.004	0.005

STD[a] standard deviation, Med[b] median of measured values

Figure 4-6 shows summer-to-winter (SW) ratio of all trace elements measured in this study. The graph was prepared according to median concentrations of the elements. SW ratios of the elements vary between 4.2 (for Th) and 0.14 (for Sc). It is seen in the figure that SW ratio of crustal and anthropogenic elements separately grouped. As it stated before, since summer is drier, crustal elements becomes more open to re-suspension, so concentrations of crustal elements increase. In contrast, due to the wetness of soil during winter season, crustal elements concentrations in atmosphere decrease. Therefore, SW of crustal elements are expected to be higher than that of anthropogenic elements.

It is depicted in the Figure 4-6 that SW ratio of crustal elements are generally higher than anthropogenic elements, as it is expected. In the same way, SW ratio of anthropogenic elements are usually lower than 1. However, there are some inconsistencies such as very high SW ratio of Zn or low Ca concentration, it could be concluded that the results are consistent with literature.

In addition to SW ratio, monthly average concentrations of crustal elements and rainfall data are depicted in Figure 4-7 for better illustration. It can be seen that, concentrations of Al and Fe are higher in summer season compared to winter season. These two elements have crustal origin, therefore it is expected that with drier season, their concentration consistently increase. This pattern can be shown in monthly median averages of Al. However, in monthly median Fe concentration graph, a peak was observed in March. This may result since the rainfall in March is lowest of all months in sampling period. So, this crustal specie accumulates in atmosphere since no scavenging process decreases its concentration.

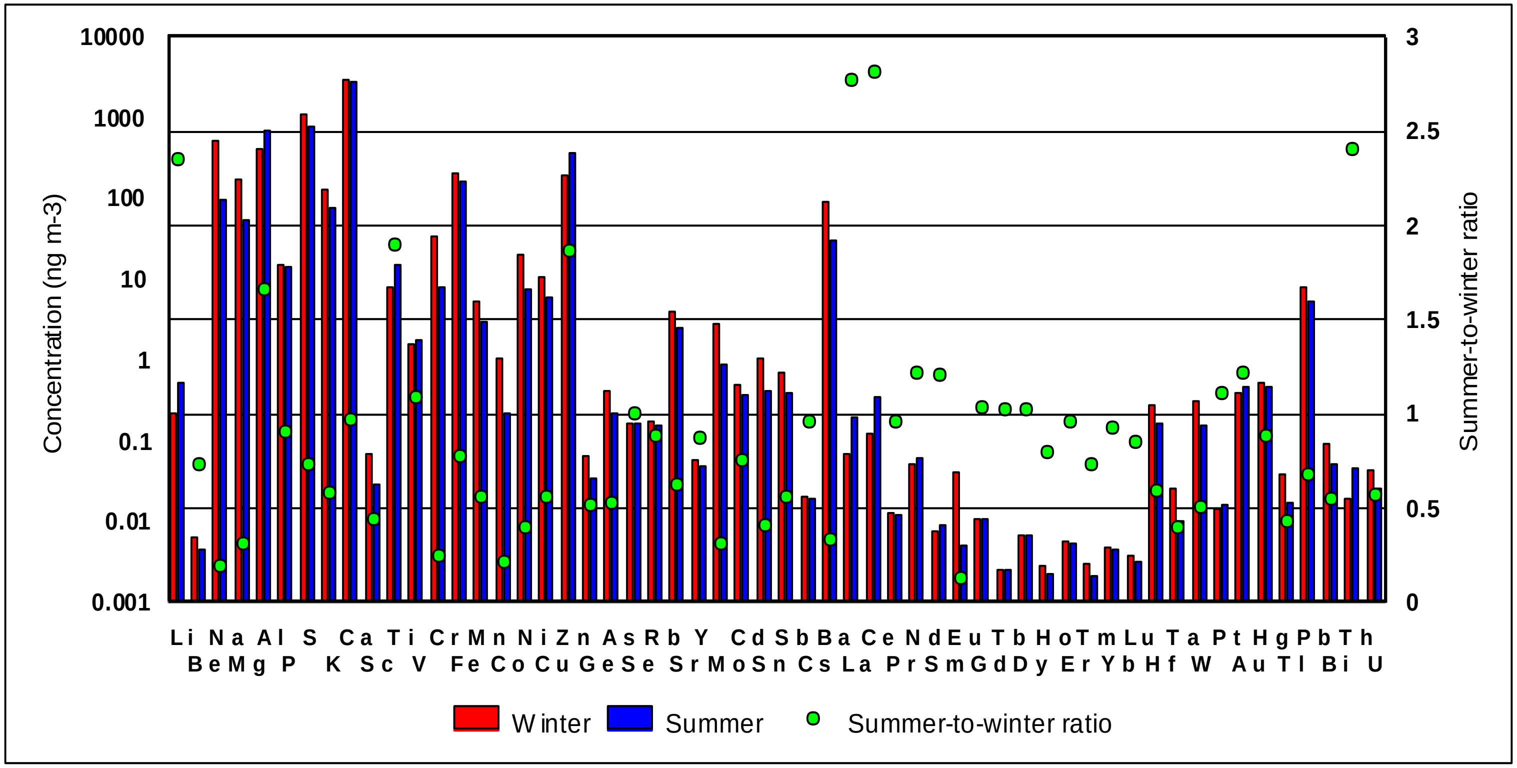


Figure 4-6 Summer-to-winter ratio of species

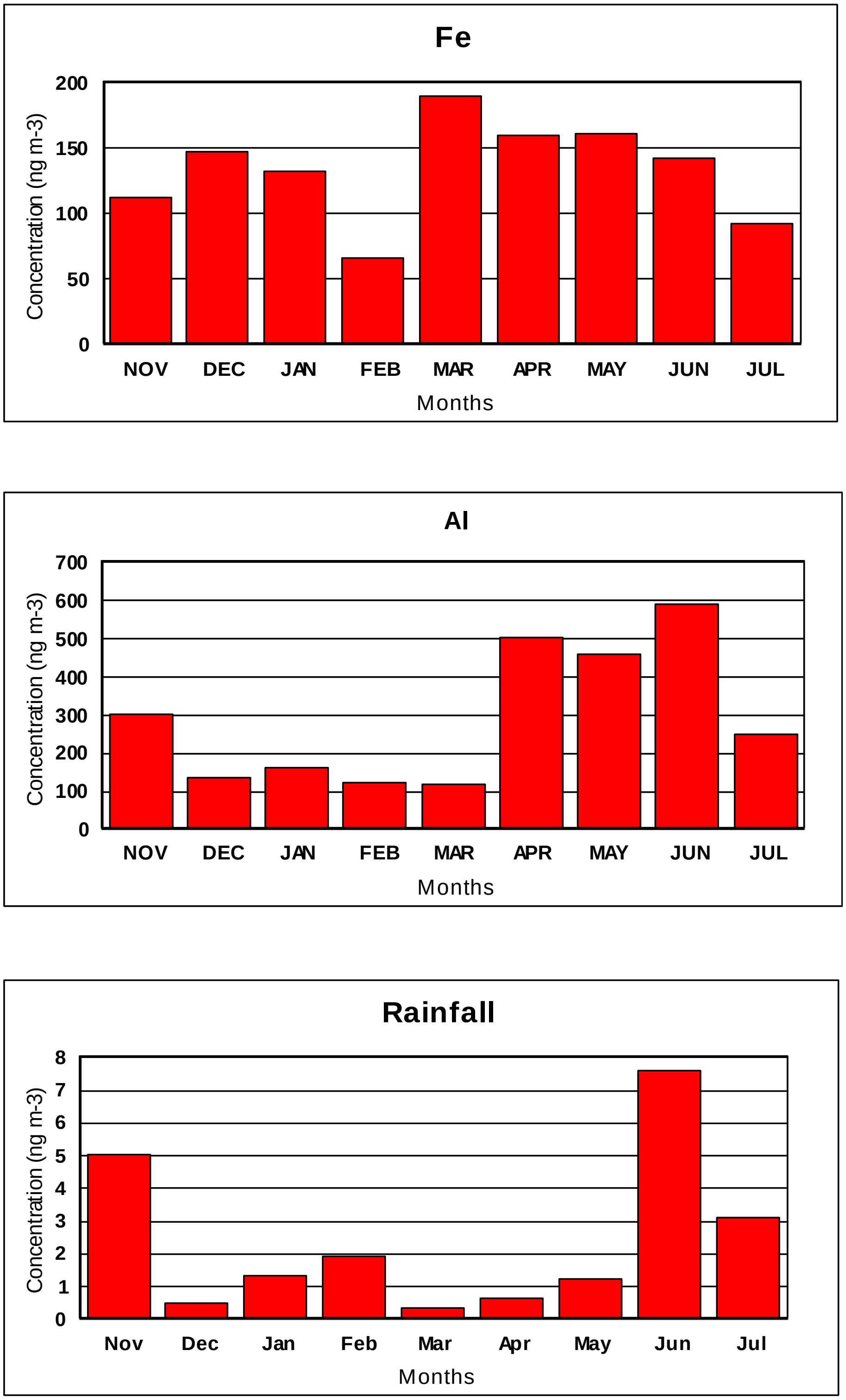


Figure 4-7 Monthly median concentrations of selected crustal species

The monthly median concentrations of selected anthropogenic elements are illustrated in Figure 4-8. As it can be seen, all the selected elements show similar pattern, elements As, Ge, Sn and K have higher concentrations in winter season.

In most of the aerosol studies, it is well documented that anthropogenic elements, including As, Ge, Se, Sn, S and K, have higher concentrations in winter season (Alhaji, 2011; Sudheer and Rengarajan, 2012; Yatin et al., 2000). The result of this study is also consistent with those studies. For instance, As is the good marker of coal combustion marker (Lei et al., 2012; Minguillón et al., 2012; Thurston et al., 2011). Therefore, the decrease in concentration from winter to summer of this marker is reasonable. Similarly, Ge is also high-temperature process related markers (Salma et al., 2002), so the monthly median concentration of this element decreased from winter to summer. In the same way, Sn and Sb are traffic related (brake and tyre abrasion) elements, and they show higher concentrations in winter season (Minguillón et al., 2012, Sternbeck et al., 2002). In addition, K is a good marker of biomass burning (Mkoma and Tungaraza, 2010; Safai et al., 2013). So, its higher concentration in atmosphere during winter season is quite rationale. Last, S is the marker of SO_2 which is emitted to atmosphere by coal consuming of coal for residential heating (Özden et al., 2008).

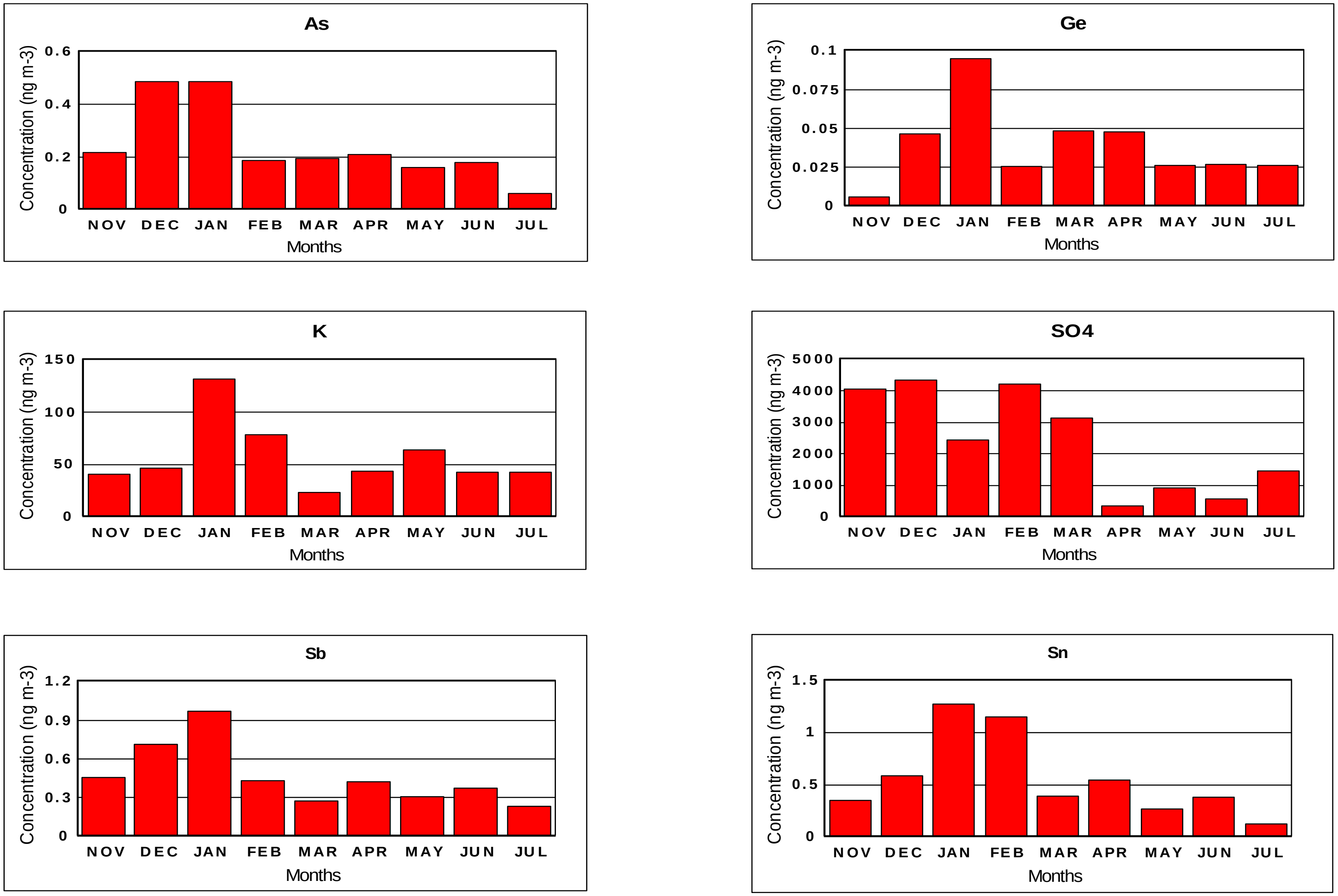


Figure 4-8 Monthly median concentrations of selected anthropogenic element

4.4. Relation between Elemental Concentrations and Local Meteorology

We have to have a good understanding of Meteorology of Ankara because it is one the two most important parameters that affect levels and variations (both spatial and temporal) in concentrations of pollutants in any urban atmosphere (the second one is emission strength).

Data obtained from General Directorate of Meteorology on meteorological parameters including temperature, wind speed, relative humidity, mixing height, and ventilation coefficient, are summarized in Table 4-7.

Table 4-7 Summary of Meteorological parameters during sampling period

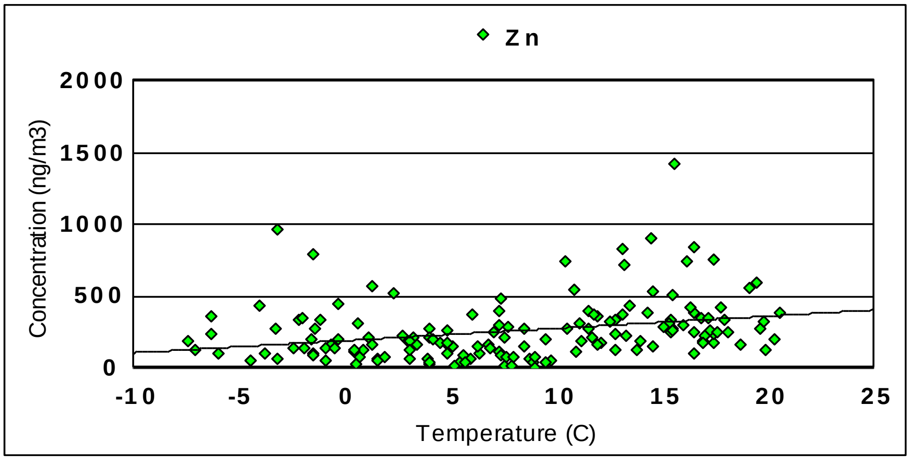
Parameter		Summer	Winter	Annual
Temperature (ºC)	Average	18.7 ± 3.2	4.3 ± 6.2	9.03 ± 7.94
	Min	11.70	-7.10	-7.10
	Max	24.90	19.10	24.90
Wind Speed (m/s)	Average	1.16 ± 0.45	1 ± 0.5	1.06 ± 0.52
	Min	0.40	0.30	0.30
	Max	2.80	2.80	2.80
Relative Humidity (%)	Average	66.5 ± 11.8	69.5 ± 14.2	68.34 ± 13.32
	Min	42.60	39.10	39.10
	Max	93.10	96.70	96.70
Mixing Height (m)	Average	1527 ± 331	1275 ± 1242	1336 ± 1103
	Min	727	83	83
	Max	2159	6481	6481
Ventilation Coefficient (m2/s)	Average	1981 ± 713	1447± 1526	1578 ± 1393
	Min	581	53.7	53.7
	Max	3853	9478	9478

As described previously in the manuscript, winter season includes the period from November 2013 to end of April 2014; whereas summer season includes May and June, 2014. Meteorological data was obtained from the Etimesgut meteorology station, which is the closest meteorological station to our sampling site. Only the days with samples were included in averages.

During our sampling period, temperature changed between -7.1°C in January and 24.9^{0} C in July, with an annual average value of 9.0°C. Temperature can affect atmospheric concentrations of reactive species but do not directly affect observed concentrations of trace elements, which do not react in atmosphere. However, when concentrations of elements are plotted against temperature decreasing and increasing patterns can be observed. Such increase or decrease in concentrations of elements with temperature is due to indirect effect of temperature on elemental concentrations. Examples of both increasing and decreasing concentrations of elements with temperature are depicted in Figure 4.5, for Al and Sb. Other elements, including, Ti, Zn, Y, Sm, Gd and Th showed Al-like patterns and their concentrations increase with increasing temperature. On the contrary, concentrations of elements including S, As, Cd, Sb, Pt, Tl and Bi decreased with increasing temperature, as in Sb in Figure 4.5. None of these variations indicate a direct relationship between temperature and concentrations. They are all due to indirect effect of a totally different parameter on concentrations of elements. Please note that all elements that have increasing concentrations with increasing temperature are crustal elements and all elements that have decreasing concentrations with temperature are pollution-derived elements. Grouping of elements as crustal and anthropogenic depending on their behavior against temperature is not a coincidence. Concentrations of crustal elements increase with temperature, because low temperature corresponds to winter season where the soil is muddy and ice covered and re-suspension of soil particles is expected to be at minimum. As temperature increase in spring and summer soil becomes drier and re-suspension of soil particles and litophilic elements associated with those particles becomes easier. This increases concentration of crustal elements in summer when temperature is high.

Concentrations of anthropogenic elements, on the other hand, are high during winter and decrease towards summer. This variation is due to (i) combustion source of some of the anthropogenic elements, which is strong during winter season and (ii) lower mixing height during winter season.

As mentioned before, although it is commonly believe that Ankara is heated entirely by natural gas, approximately 40% of the residences, mostly in low-income districts of the city, are still heated by coal burning in stoves. Coal combustion is an important source for anthropogenic elements and increases their concentrations in winter season. As temperature increase toward spring and summer concentrations of these elements decrease with less and less burning of coal. As can be understood from this discussion, concentrations of both crustal and anthropogenic elements show seasonal variations due to processes that depend on seasons and thus correlated with temperature change, but these variations are not directly due to temperature variations.



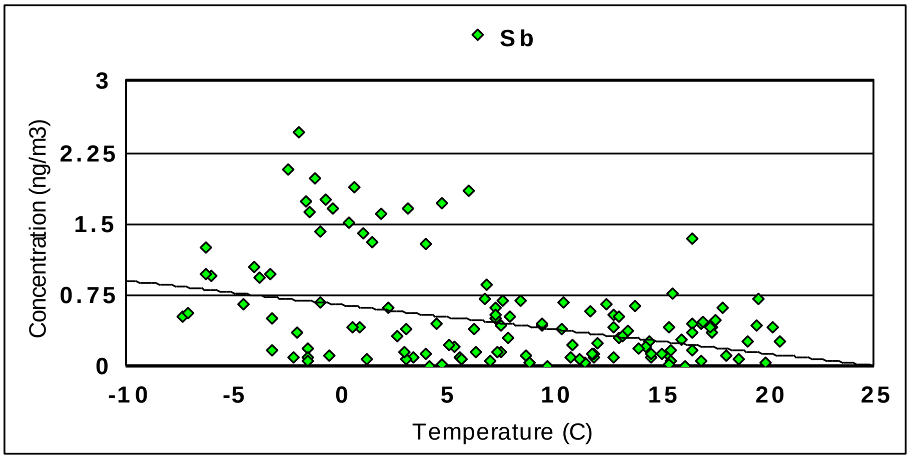


Figure 4-9 Positive and negative correlation between measured concentration with temperature

Frequency of wind flow from each wind direction (average wind rose) for the study period is depicted in Figure 4-10. The wind rose was prepared by Genç et al (2010), using data from Etimesgut met station between 1994 and 2003. In the figure the wind rose is superimposed on the population density map obtained from Ankara Municipality.

Dominant wind directions in Ankara are NE (25%), ENE (21%) and WSW (17%). These three sectors totally accounts for 63% of the total flow. Flows from SSE, SSW, ENE, N and NE were not significant (<10%). Based on this wind pattern, districts Çankaya, Mamak, Bahçelievler, Emek are the districts, which are potential source areas for pollutıon derived species at the METU station.

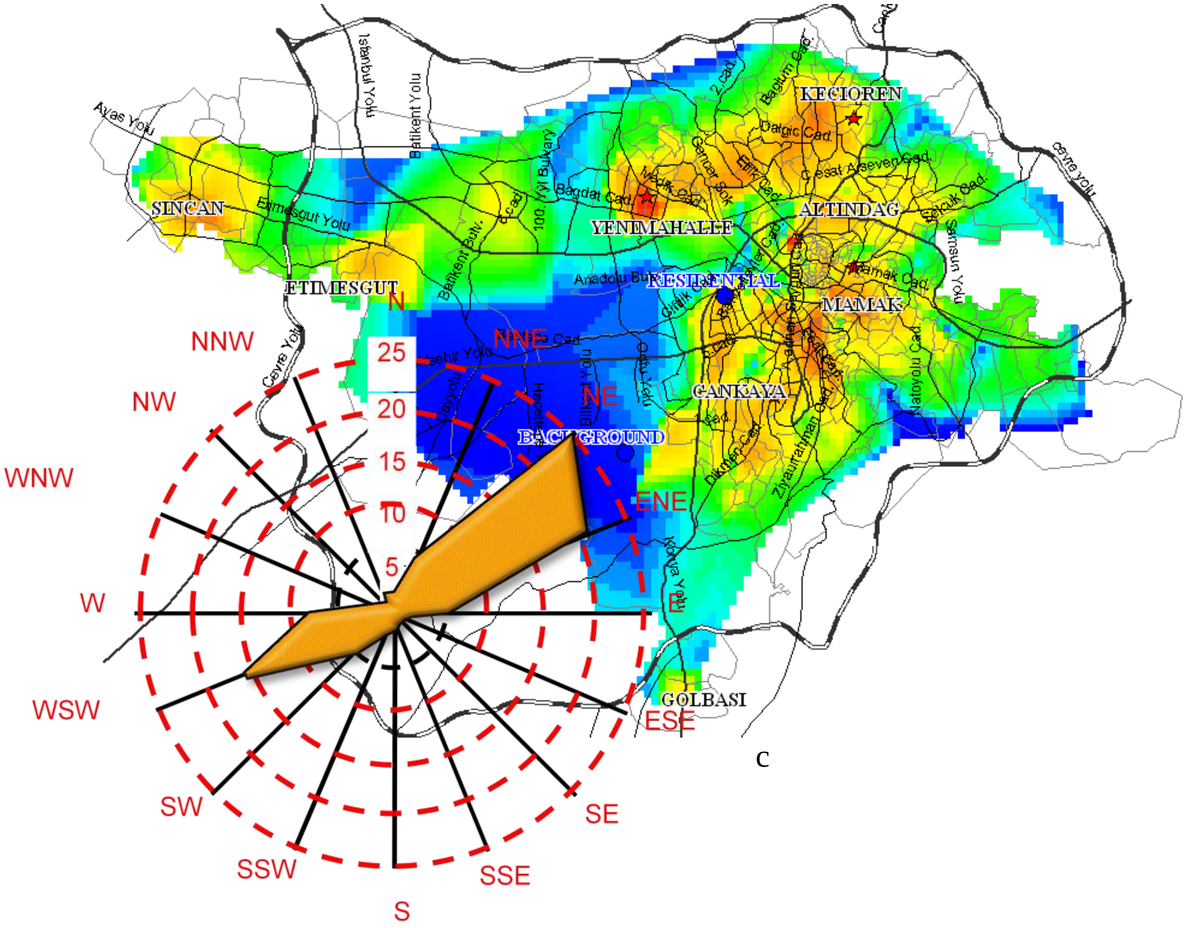


Figure 4-10 The annual wind rose of the Ankara city (during 1994-2003 periods)

Pollution roses, refer to average or median concentrations of pollutants at each wind sector. It is a convenient way of identifying locations of pollutant sources at urban atmosphere. Its use is limited in regional studies where pollutants are transported in upper parts of the atmosphere, but the technique is useful in urban studies, because sources of pollutants are nearby and gases and particles are transported at the surface. In this study pollution roses were prepared for all measured elements. Pollution roses of selected crustal elements are given in Figure 4-11 and Figure 4-12, respectively.

Appearance of the pollution roses for Fe, Al, Sc and La resemble each other and pollution roses prepared for other crustal elements were also not significantly different. Sectors with highest concentrations of crustal elements in general are SW, WSW, W, WNW, NE and ENE. The sector between SSW and NNW is an important source region for crustal elements because exposed land surface from which soil particles can become airborne is larger in that sector. Note that area to the east of the station includes bulk of the city, which is almost entirely covered with asphalt and cement. Consequently, re-suspension of soil particles from exposed land surfaces in the city is limited. Area to the West of the station, includes newer settlement areas, like Bilkent, Ümitköy and settlements around Eskişehir road. The settlements in these areas are not as dense as the settlement within downtown Ankara. This pattern allows for more extensive re-suspension of crustal particles and results in higher concentrations of soil related elements.

This general pattern observed in pollution roses of most of the crustal elements is slightly modified for individual elements. For example, there are very high Fe concentrations in NNW and NNE sectors, and high concentrations of Sc and La in SSW sector, which are not observed in other crustal elements. Similar distribution of crustal elements in wind sectors were also reported for METU by Yatın et al. (2000). This similarity indicates that there is no significant changes in the sectors with highest concentrations of main soil derived elements in 20 year period.

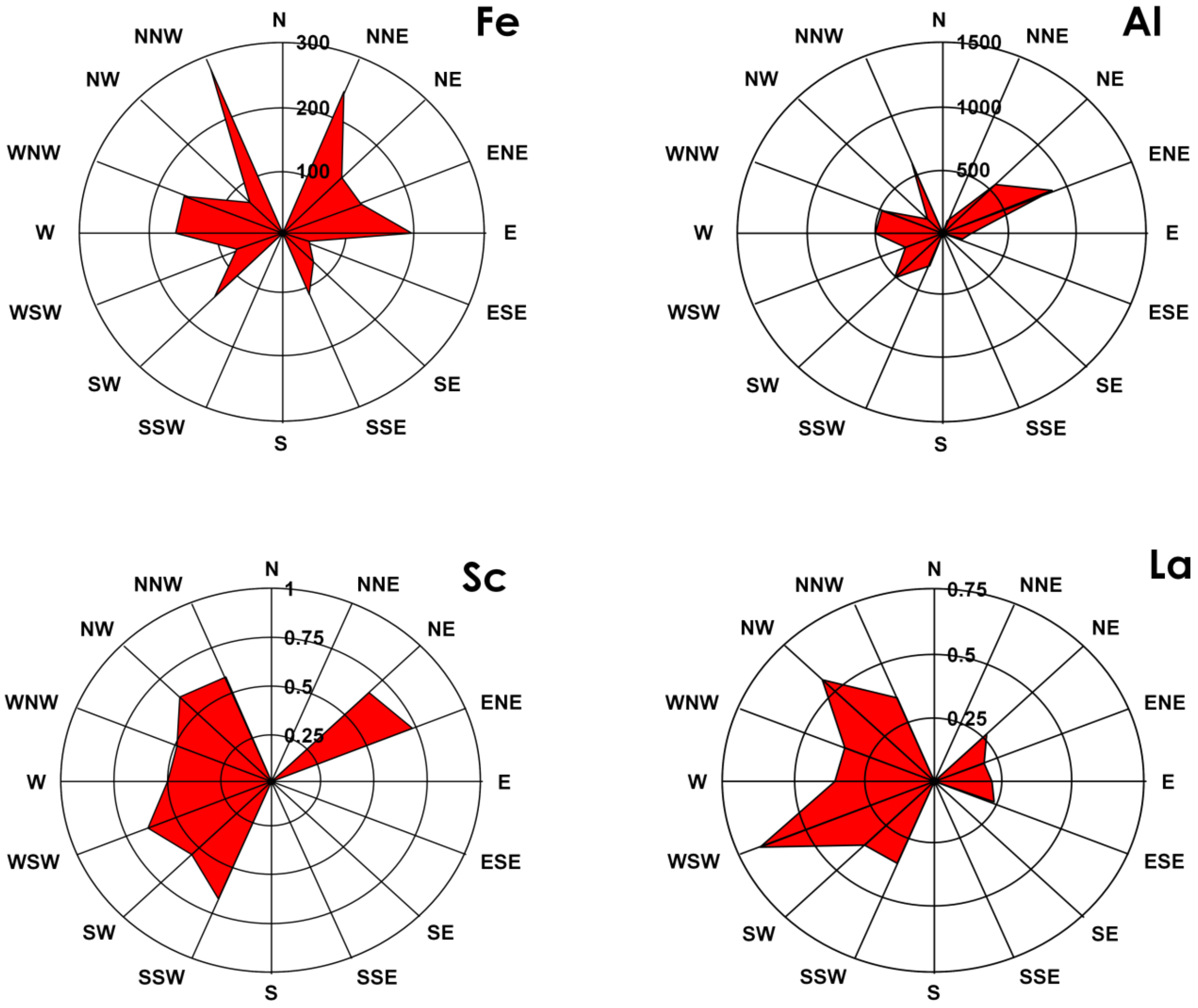


Figure 4-11 Average concentrations of the selected crustal elements at each wind sector

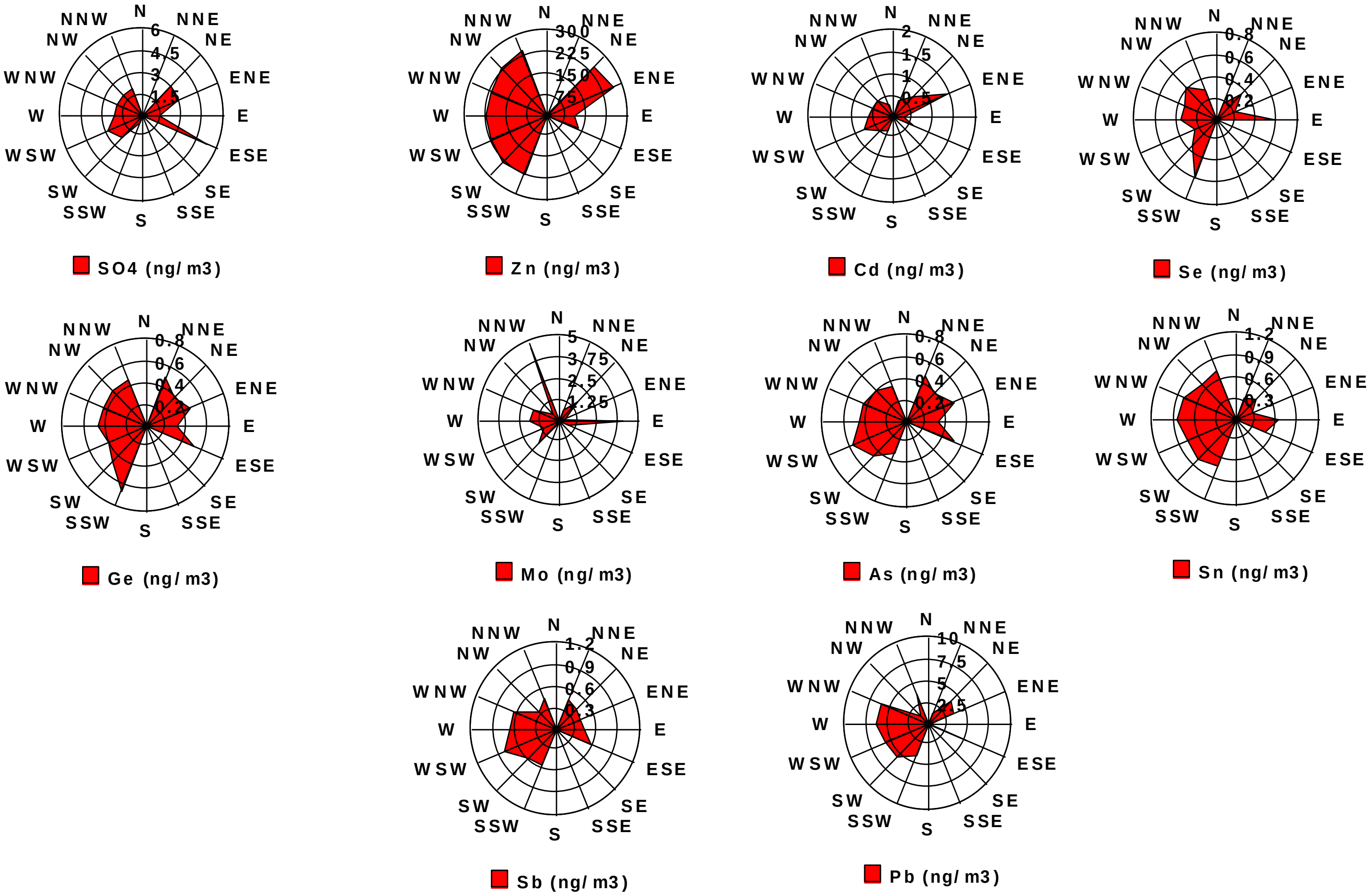


Figure 4-12 Average concentrations of the selected anthropogenic elements at each wind sector

Pollution roses for selected anthropogenic elements are given in Figure 4-12. Essentially roses for pollution-derived elements are not very different from pollution roses prepared for crustal elements, for different reasons. High concentrations of crustal elements in the sector between SSW and NNW were attributed to larger exposed surfaces in that sector. Elements with anthropogenic elements also have high concentrations in those sectors. However, this is not due to exposed land surfaces, but owing to distribution of industries around our station. The districts included in this sector (between SSW and NNW) are given in Figure 4-13 where areas that lied between SSW and NNW sectors (also between NNE and ESE sectors) are plotted using As pollution rose as an example. As can be seen from the figure, most of the industry in Ankara, including OSTIM and Sincan organized district, is located in that sector. High concentrations of pollution derived elements between sectors SSW and NNW are probably due to relatively high intensity of industrial emissions in that sector.

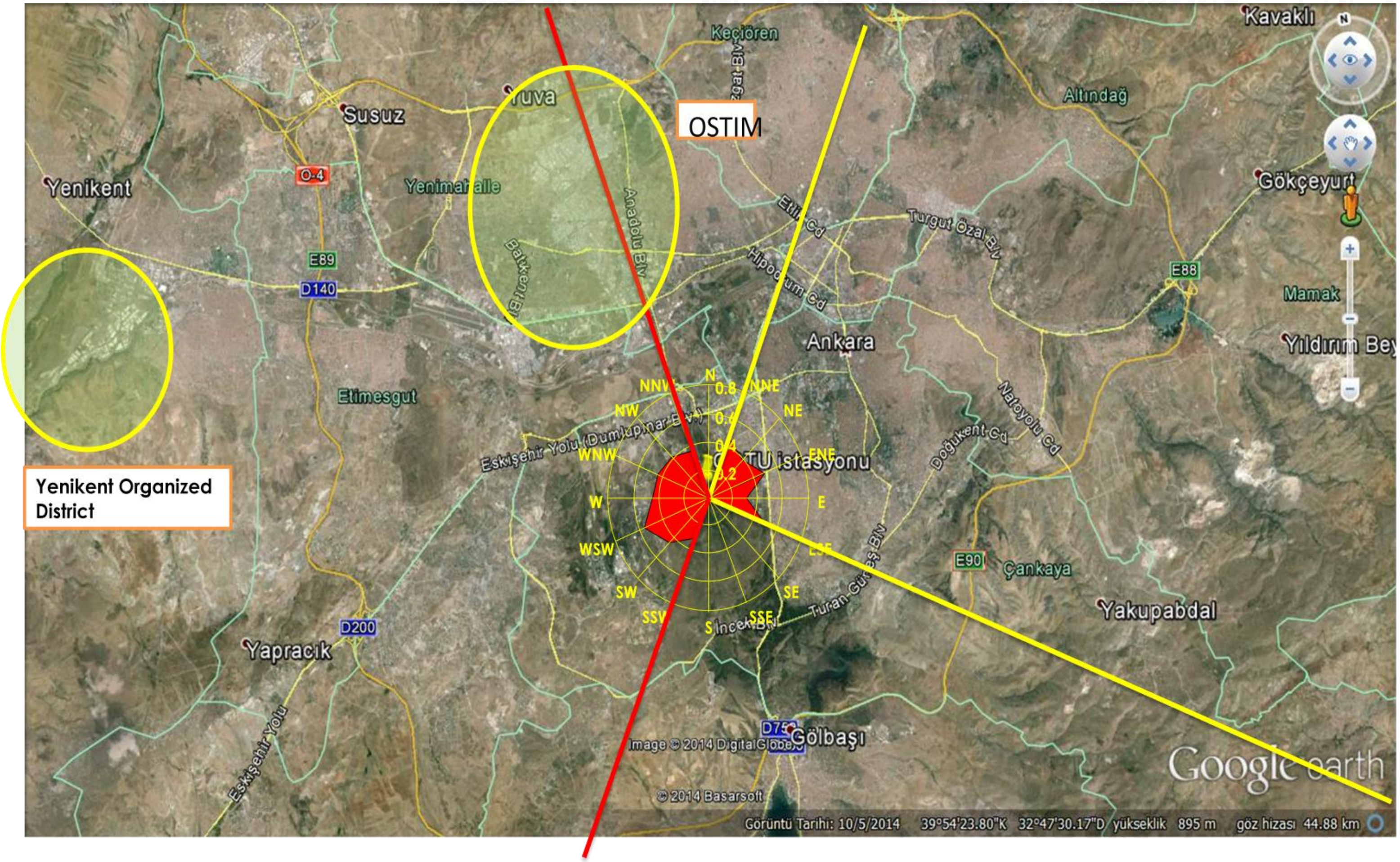


Figure 4-13 Sectors which contributes to As concentrations at METU station

There is one important difference between pollution roses of crustal and anthropogenic elements. Sectors to the east of our station at METU are more important for anthropogenic elements then they are for crustal elements. Concentrations of crustal elements are relatively high in NNE and ENE sectors. This is probably shaped by the frequency of winds from sectors. As can be seen in long term wind rose in Figure 4-10 frequency of wind flow in sectors other than NE, ENE, W and WSW are very small. If an element is not detected in few samples that corresponds to winds from those less frequent sections, the average concentration of that element in that sector appears as zero. Since probability of these zero concentration values are higher in sectors with very low wind frequency, shapes of the pollution roses are to a certain extent is shaped by the wind frequency. This, unfortunately is the limitation of pollution rose approach when there is not sufficient data points available for calculations.

Concentrations of anthropogenic elements are also high in the sector between NNE and SE. This sector includes NE and ENE sectors, which are important for crustal elements, but the sector is wider (extends from NE all the way to SE) and concentrations of anthropogenic species are higher in this sector compared to concentration of soil-related elements. This is reasonable, because, as can be seen in Figure 4-13, the sector includes heavily populated districts in the city that also hosts heavy traffic activity. The exposed land surface, on the other hand, is smaller in the city compared to exposed land surface in SSW – NNW sector, where settlements at Bilkent, Ümitköy and farther SW is not as dense as the settlement in the city. This discussion suggests that, as pointed earlier, sectoral distribution of concentrations of crustal and anthropogenic elements resemble each other, but causes of these distributions for crustal and anthropogenic elements are entirely different.

Concentrations of elements in each wind sector is important to detect sources of that specie in sectors, but it does not provide information on contribution of sectors (and thus sources in that sector) on measured concentrations of elements at our station, because contribution of each sector on concentrations of elements depends not only on concentrations of elements in wind sectors, but also depends on the frequency of wind flow from each sector. For example there may be a very strong source of Ge in one of the factors, but contribution of that source on measured concentrations at the receptor will be zero if there is no wind blew from that sector during the study.

We have calculated frequency weighted pollution roses of elements to be able to determine contribution of each sector on concentrations of elements at our station. Results are presented in Figure 4-14 and Figure 4-14 for crustal elements and in Figure 4-15 for anthropogenic elements.

That's why in this part frequency weighted pollution roses are calculated. For this aim, the average wind speed at each sector was divided the highest wind speed value in whole sector. After, the calculated values are multiplied by the average concentrations in each sector.

Firstly, the frequency weighted graphs of the crustal elements are almost identical with average concentration at each sector. The dominant wind sector of Fe, Al, Sc and La do not change. However, concentrations at the sectors are affected. For instance, frequency weighted pollution rose of Sc and La differs. Figure 4-14 shows that although Sc most frequently comes from WSW sector, although the highest average concentration was at NW sector. Moreover, Figure 4-15 indicates some important differences in highest average concentration sectors. For instance, frequency weighted graph of SO_4 shows that highest concentrations come from WSW sector. However, according to average concentration at sector shows that effect of WSW is less. In the same way, Figure 4-12 shows highest Pb concentration is at the WNW sector, while it is at WSW sector in frequency graph. As a result, meteorological parameters are prevailing factors which affects atmospheric concentrations frequently. In this section, it is seen that temperature, relative humidity and wind speed affects some of the species slightly. In addition, some of the wind sector contributes elemental concentrations of the both anthropogenic and crustal elements.

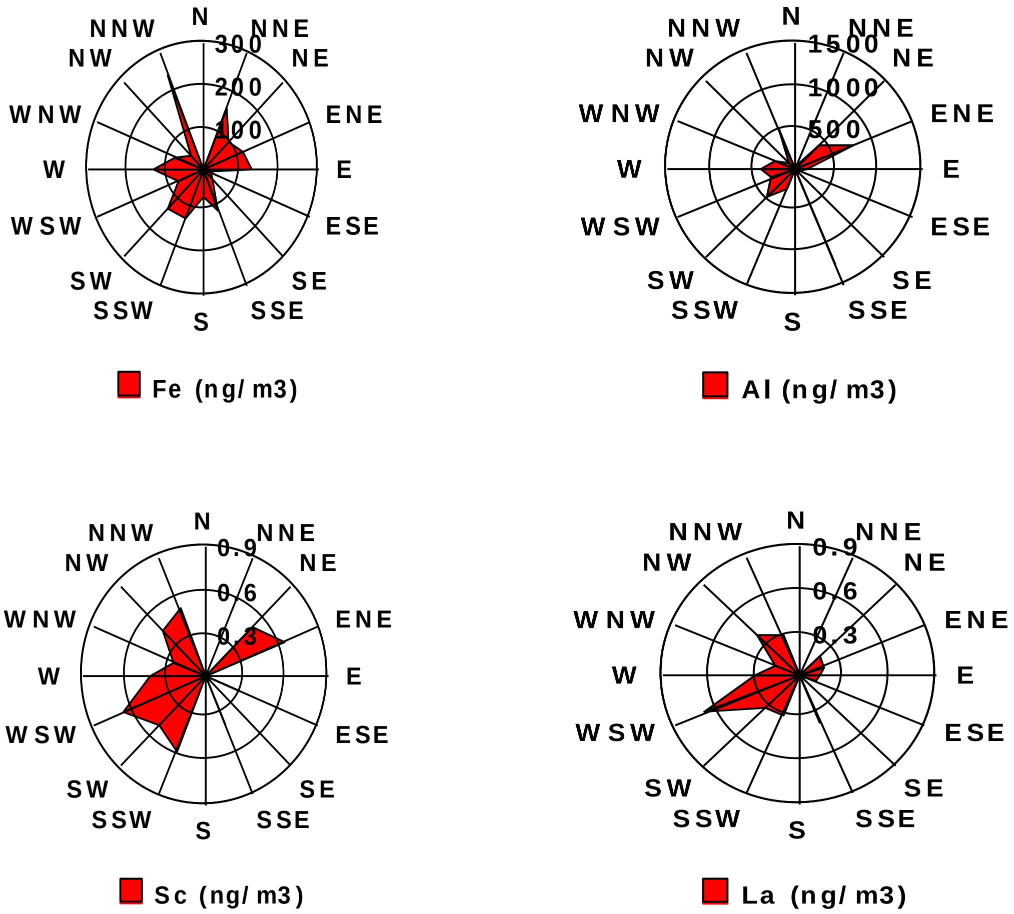


Figure 4-14 Frequency weighted pollution roses of selected crustal element

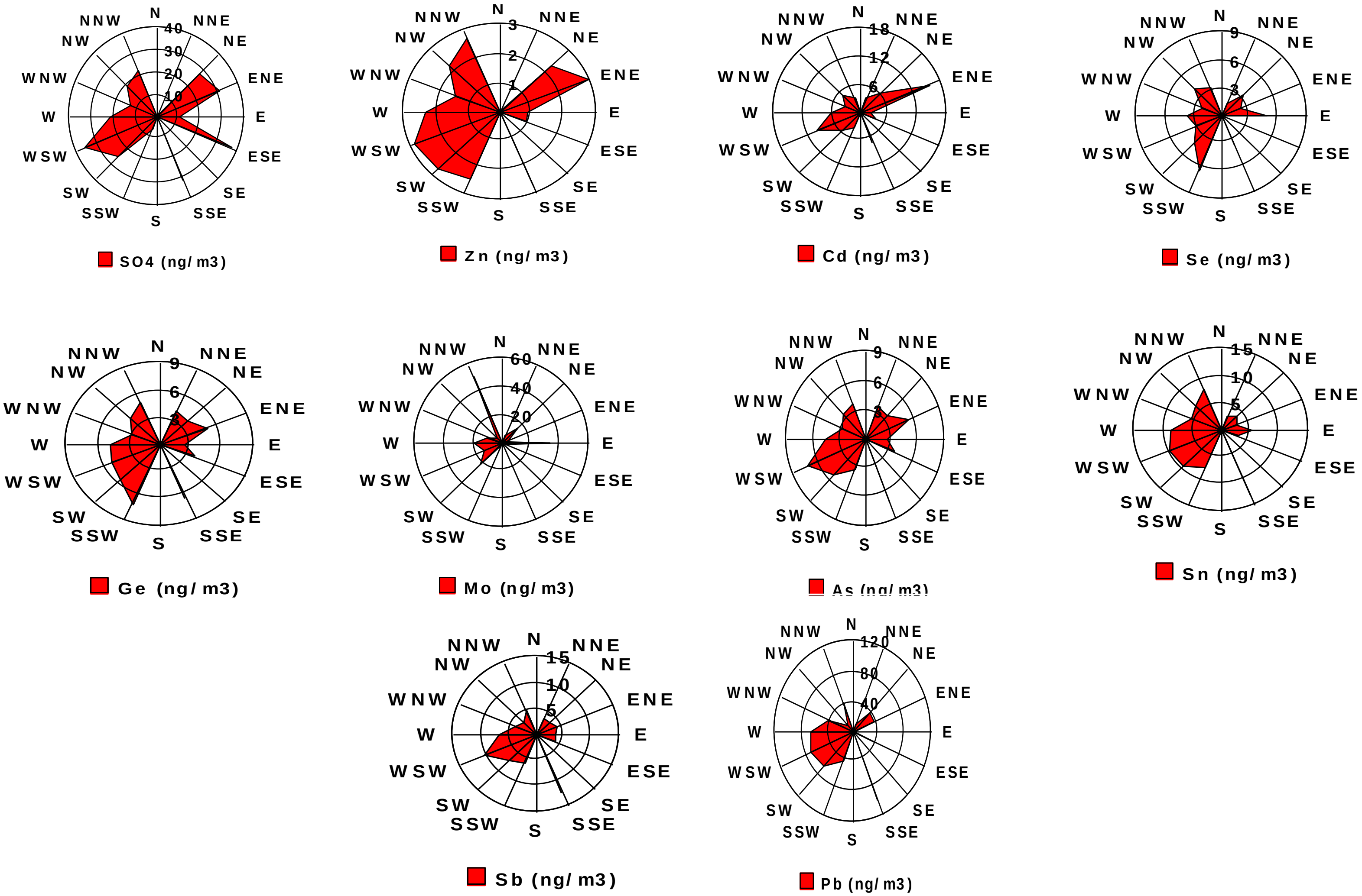


Figure 4-15 Frequency weighted pollution roses of selected anthropogenic elements

Average wind speed in Ankara varied between 0.3 m s^{-1} and 2.8 m s^{-1}, with an average value of 1.0 ± 0.5 m s^{-1}. There is not much difference between summer and winter wind speeds. Calculations of wind speed in each wind direction demonstrated that strongest winds blew from SW during the study period. Average wind speed from this directions was 1.2 m s^{-1},which was followed by ENE (1.1 m s^{-1}). Average flows from other sectors were <1.0 m s^{-1}. These values clearly indicate that wind speed is extremely slow in Ankara, not only during this study, but throughout the year as well. In meteorology ws < 1.0 m s^{-1} is considered as "calm. Annual average wind speed of 1.0 ± 0.5 m s^{-1} indicates that calm conditions prevailed in a large fraction of the time.

Wind speed is another meteorological parameter that affects atmospheric pollutant concentrations. As it could be anticipated, wind speed is expected to have negative correlation with measured concentrations of pollutants (in this case trace elements), because it is a horizontal ventilation mechanism, which carries pollutants away from this city to the surrounding rural atmosphere. In other words, winds dilute concentrations of pollutants during dispersion process. Variation in concentrations of Ge, As, Sn, with wind speed is plotted in Figure 4-16. As expected, concentrations of all three elements depicted statistically significant decrease (within 95% confidence interval) with increasing wind speed. Variations in concentrations of remaining anthropogenic elements with wind speed have weak linear relationship.

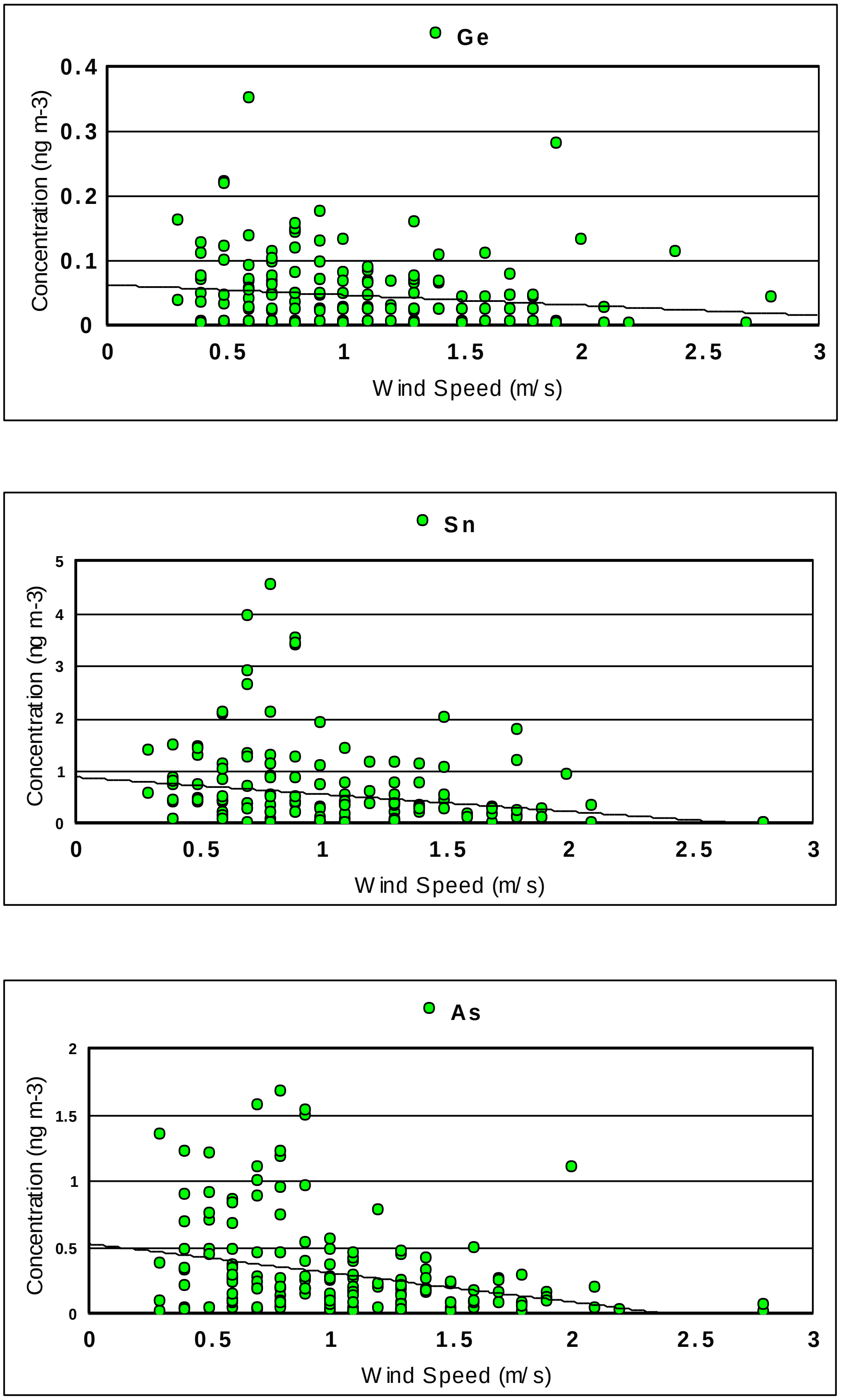


Figure 4-16 Correlation between measured concentrations of selected species with wind speed

Mixing height is an important meteorological parameter as it strongly influences vertical ventilation of pollutants in an urban atmosphere. It refers to the height of the well-mixed lowest lying layer in the atmosphere. Thickness of the mixing height varies diurnally and seasonally, with highest thicknesses occurs in summer and noon-time. When thickness of the mixing height is high pollutants emitted to the urban atmosphere will be dispersed in a larger volume, and thus concentrations we measured at the surface is expected to be low. When mixing height is shallow, emitted pollutants will be confined to a smaller volume and their measured concentrations are expected to be high. The roles of mixing height on temporal variation of pollutants are frequently demonstrated in literature (Karademir, 2006; Safai et al., 2013; Vinitketkumnuen et al., 2002). Diurnal and seasonal variation of the mixing height was calculated by Genç et al. (2010) using a meteorological pre-processor (RAMMET) which is used to prepare meteorological data for numerical modeling. Temporal variation of mixing height in Ankara calculated by Genc et al (2005) is depicted in Figure 4-17. As expected, mixing height in Ankara is low during night (approximately 500 m) but increase during day-time. The highest mixing height occurs between 15:00 PM and 19:00 PM. This maximum value is approximately 2000 m during summer, but can be as low as 600 – 700 m during winter. Day-time average mixing height is 2142 m whereas nighttime average value is approximately 730 m during summer time. However, day-time and night time mixing height depths are approximately 1900 m and 600 m, respectively.

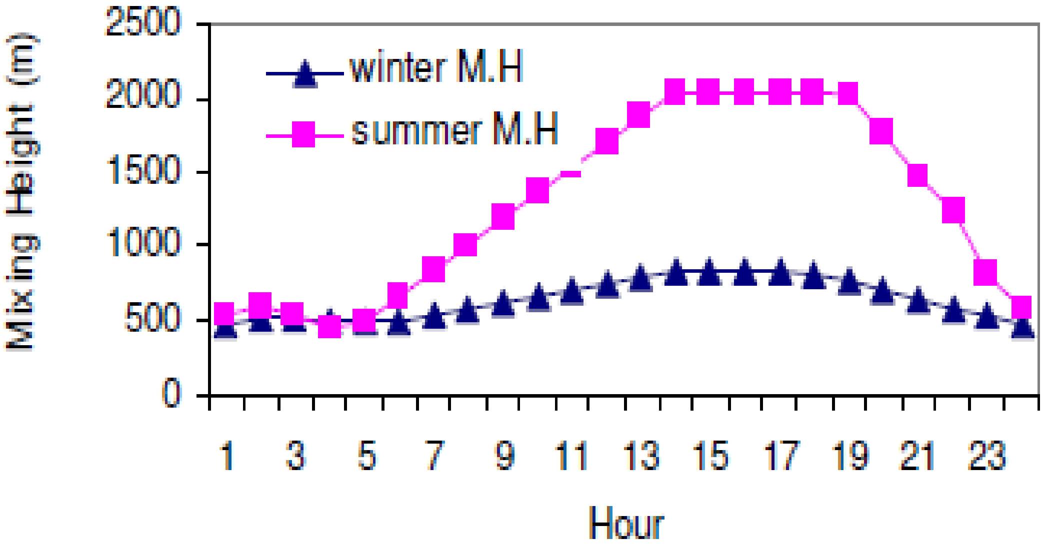


Figure 4-17 Temporal variations of calculated mixing height (Genc, 2005)

Daily average mixing height was calculated during our sampling period using met data obtained from Etimesgut meteorological station and related to measured concentrations of elements in this work. Variation in concentrations of As, Pb, Cd, SO4, Al, Ti, Fe and La is depicted in Figure 4-18. Among these elements As, Pb, Cd and SO_4^{2-} have anthropogenic sources, whereas Al, Ti, Fe and La originate from earth's crust. These two groups of elements depicted two different patterns. Anthropogenic elements showed statistically significant decreases with increasing mixing height. This is normal and expected behavior of elements. As mixing height gets deeper, concentrations of elements decrease due to the dilution in a larger volume of air.

Interesting point in the figure is the variation of concentrations of crustal elements with mixing height. Unlike anthropogenic elements, crustal elements do not show a pronounced decrease with increasing mixing height. Concentrations of most of the crustal elements decrease with increasing mixing height depth, but this decrease is not as sharp as the decrease observed in concentrations of pollution-derived elements. In most cases the decrease is not statistically significant at 95% confidence interval ($p > 0.05$).

Lack of clear relation between concentrations of crustal elements and mixing height is due to temporal variation in source strengths of crustal elements. As pointed earlier, if emission strength of elements (or any other pollutant) is the same in winter and summer seasons, its concentration will be lower in summer due to deeper mixing height. Emission strength of crustal aerosol is higher in summer due to dryer soil, as discussed previously in the manuscript. Summer season is the time when mixing height is deep. This means tendency of low concentrations in summer season due to deep mixed layer is compensated by increased emissions of crustal elements.

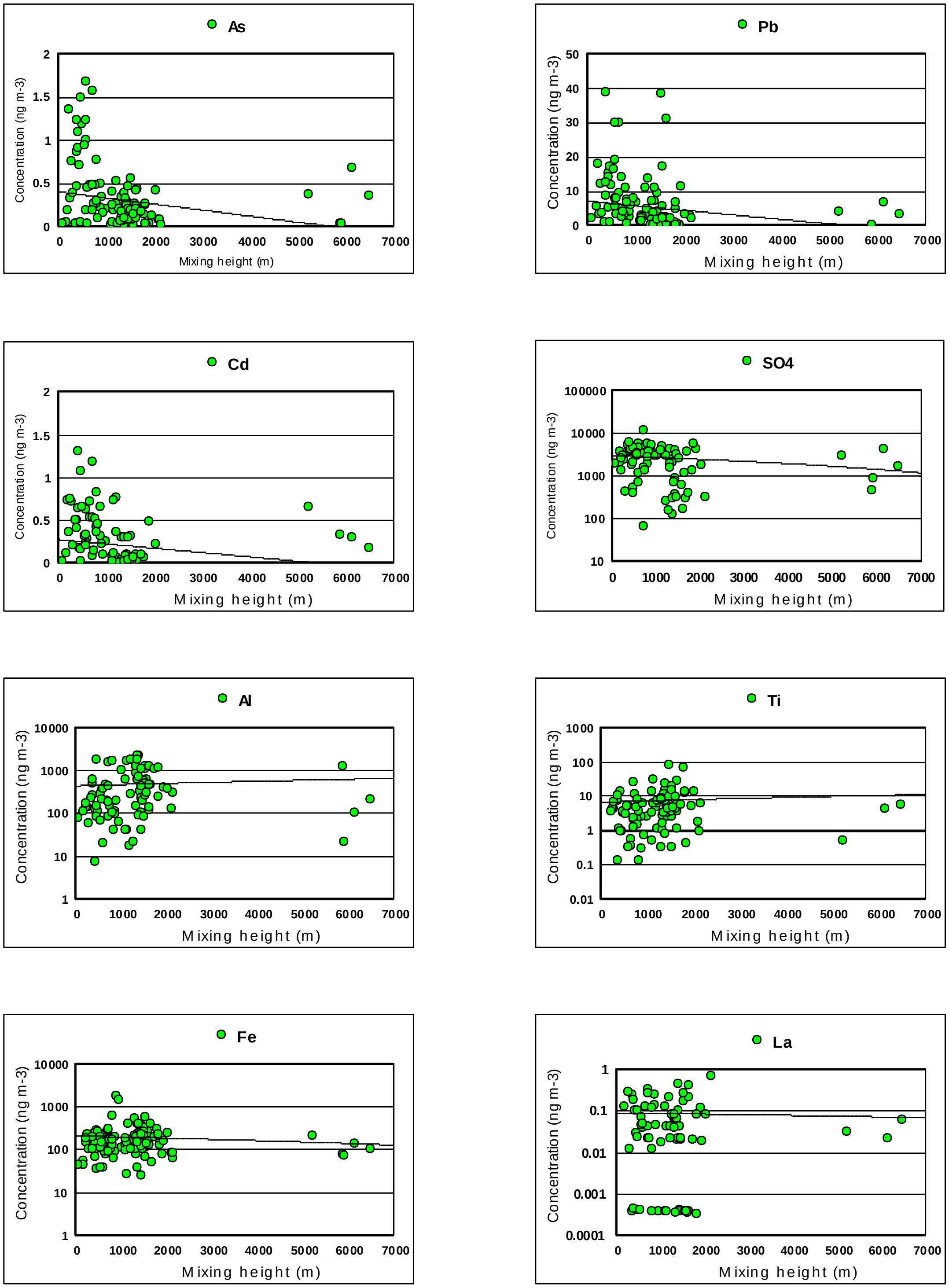


Figure 4-18 Variations of concentrations of crustal and anthropogenic elements with mixing height

The ventilation coefficient is the product of mixing height and average wind speed. It is a measure of the ability of atmosphere to dilute and disperse the pollutants over a region (Iyer and Raj, 2013). The ventilation coefficients for daytime and night also differ from each other, since they are product of mixing height and wind speed. Day-time and night-time ventilation coefficients were calculated to relate these values with concentrations of elements measured in this study. Ventilation coefficients can also be calculated on an hourly basis, but we avoided this because (1) trace elements were measured on a daily basis and (2) although hourly wind speed data were available, mixing height data were calculated twice a day (12:00 noon and 24:00 midnight). Average day-time and night-time ventilation coefficients in summer are equal to 3176 m^2 sec^{-1} and 1034 m^2 sec^{-1}, respectively. Corresponding ventilation coefficients in winter were 6044 m^2 sec^{-1} in daytime, and 1119 m^2 sec^{-1} at night. It should be noted that diurnal and seasonal variations in ventilation coefficient is very similar to variations in mixing height at Ankara, because contributions of wind speed on ventilation coefficient is small due to very small annual average wind speed.

Variations of concentrations of selected crustal (Al and Li) and anthropogenic (Tl, As) elements with ventilation coefficient is depicted in Figure 4-19. Only two elements are selected from each group, because variations in concentrations of all other elements were very similar to each other. Variations in concentrations of crustal and anthropogenic elements with ventilation coefficient are very similar to their variation with mixing height. Such similarity is not entirely unexpected, because contributions of wind speed on ventilation coefficient is small in Ankara compared to other cities owing to generally prevailing calm conditions.

As in mixing height case, concentrations of all anthropogenic elements showed well-defined decreasing trend with increasing ventilation coefficient. Concentrations of crustal elements, on the other hand, did not show similar pronounced decrease with ventilation coefficient. Reasons for these behaviors of crustal and anthropogenic elements are similar to the reasons for variations in their concentrations with increasing mixing height, which was discussed earlier in the manuscript.

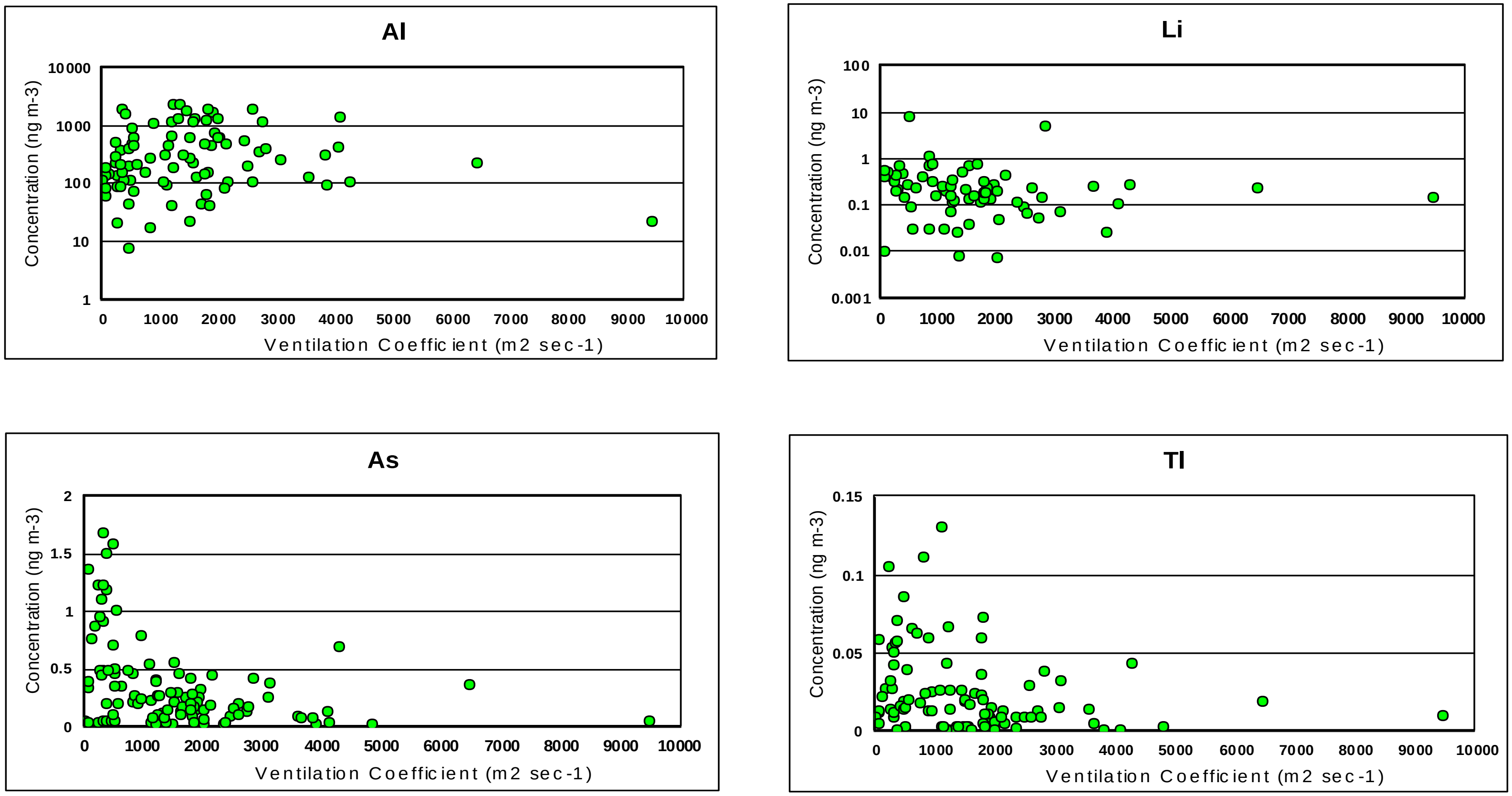


Figure 4-19 Correlation between measured concentrations of selected species with Ventilation Coefficient

4.5. Source Apportionments

4.5.1. Enrichment Factors

Crustal enrichment factor (EFc) is a useful tool to differentiate elements contributed by non crustal sources. Since crustal aerosol is an abundant component of aerosol mass everywhere, calculation of crustal enrichment factors can provide information on the elements and ions, which are contributed by non-crustal sources. These elements that cannot be explained by crustal and marine components of aerosol are generally contributed by anthropogenic emissions. If EFc of any species is higher than unity, it is concluded that the specie originated from pollution derived sources, if not it is assumed that it has crustal origin. Crustal enrichment factor is double normalization technique calculated by the following relation:

$$EF_C = [(C_x/C_{Al})_{sample}]/ [(C_x/C_{Al})sample] \qquad \text{Equation 4}$$

Where (Cx/CAl) of sample is the ratio of the concentration of the test element (X) to that of Al in the sample and (Cx/CAl)crust is the corresponding ratio in Earth's crust.

Al is used as reference element for crustal material. Other elements that are primarily from crustal material, such as Fe, Sc, Si can also be used as reference element. The Al is most widely used, because it can be easily and accurately used by various analytical methods.

Reference soil composition is also important in EF_c calculations. Ideal is to use soil composition in the vicinity of the station. However, such data is not generally available. Also soil material at a rural stations may also come from other regions (such as from North Africa in our case). Compilations of global soil composition reported in the literature (Mason, 1966; Taylor, 1972; Vinogradov, 1959) are commonly used for EFC calculations.

Since there may be differences between the global average soil and local soil actually sampled in the station, EFc values less that 5.0 should not be used as an indication of enrichment. Annual, summer season and winter season EFC values of elements and ions measured in this study are depicted in Figure 4-20.

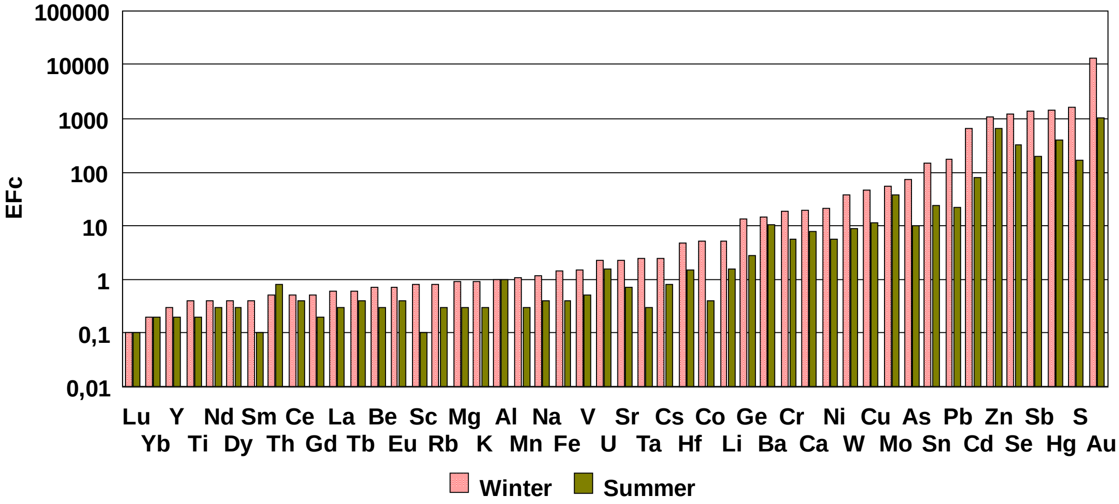


Figure 4-20 Seasonal crustal enrichment factors

Elements formed two very distinct groups in the figure. Elements between Lu and Ba in the x-axis are all crustal elements, without any exception. EF_c's of these elements vary between 0.1 for Lu and 10 for Ba. Slight enrichments of Ba, Ca, Co, is probably due to different composition of soil we intercepted at our station and Mason's soil composition, which was used as reference soil to calculate EF_cs of elements. Elements starting with Cr and including, Cr, Ca, Ni, W, Cu, Mo, As, Sn, Pb, Cd, Zn, Se, Sb, Hg and Au are all anthropogenic elements. They have EFc values varying between 20 for Cr and 10,000 for Au. The only exception to this is Ca which has EFc 20 in winter and which is a well-documented crustal element. Slight enrichment of Ca is due to high $CaCO_3$ content of soil in Turkey. Soil in Turkey, not only in Turkey, but in the Eastern Mediterranean region in general is alkaline, which means have high concentration of $CaCO_3$ in it. Because of this Ca content of soil affecting our station is significantly higher than the Ca content of Masons Soil. This issue is also reported by Güvenç et al. (2003) for soil composition in Antalya.

Please note that samples used in this discussion are fine fraction samples. Since Bulk of the Al occurs in coarse fraction, EF_c values of elements in coarse fraction or in PM_{10} fraction (Coarse + Fine) are expected to be lower than EF_c values given in the figure.

Another point worth pointing in the figure is that enrichments of all elements (crustal and anthropogenic) are higher in winter season. For anthropogenic elements higher enrichments in winter can be due to either their higher concentrations in winter, as discussed in previous sections, or due to decrease in Al concentration in winter, owing to suppression of re-suspension of soil particles in winter from muddy or ice-covered surface soil. Observed higher enrichment of anthropogenic elements in winter probably results from combination of the two mechanisms.

The interesting point in the figure is that winter EF_c values of crustal elements are also a factor of two higher than their summer enrichment factors. This is probably due to higher summer/winter concentration ratio of Al than other crustal elements. Summer-to-winter concentration ratio is 4.2 for Al and less than that for all other crustal elements. This may explain slightly higher enrichments of crustal elements in winter season.

4.5.2. Positive Matrix Factorization

EPA PMF v3.0 was utilized in this study in order to identify sources elements and to evaluate contribution of each source on observed elemental concentrations. Shortly, if data is above detection limit, it can directly be used in PMF, and uncertainty of it is taken as a summation of the detection limits for each element. Data below detection limit was set to half of the detection limit and uncertainty of these data was taken as 5/6 of the detection limits. Missing values in data set were replaced by geometric mean value, and uncertainties were determined as 4 times of geometric mean values.

In the beginning, there were 178 samples included in PMF. However, outliers are dismissed and finally 148 samples were utilized in modelling. The species Na, Al, S, K, Ca, Ti, V, Cr, Fe, Mn, Ni, Cu, Zn, Ge, As, Mo, Sn, Sb, Cs, Sm, Hg, Tl and Pb are included in PMF. Among these species only Fe and Zn are found strong, others were labelled as weak.

Determination of factor numbers is a significant step in PMF analysis (Yurdakul, 2014) and it is determined based on goodness of fit parameter (Q). PMF gives $\mathrm{Q_{robust}}$ in each run. The $\mathrm{Q_{robust}}$ value is compared with $\mathrm{Q_{true}}$, which is theoretical value.

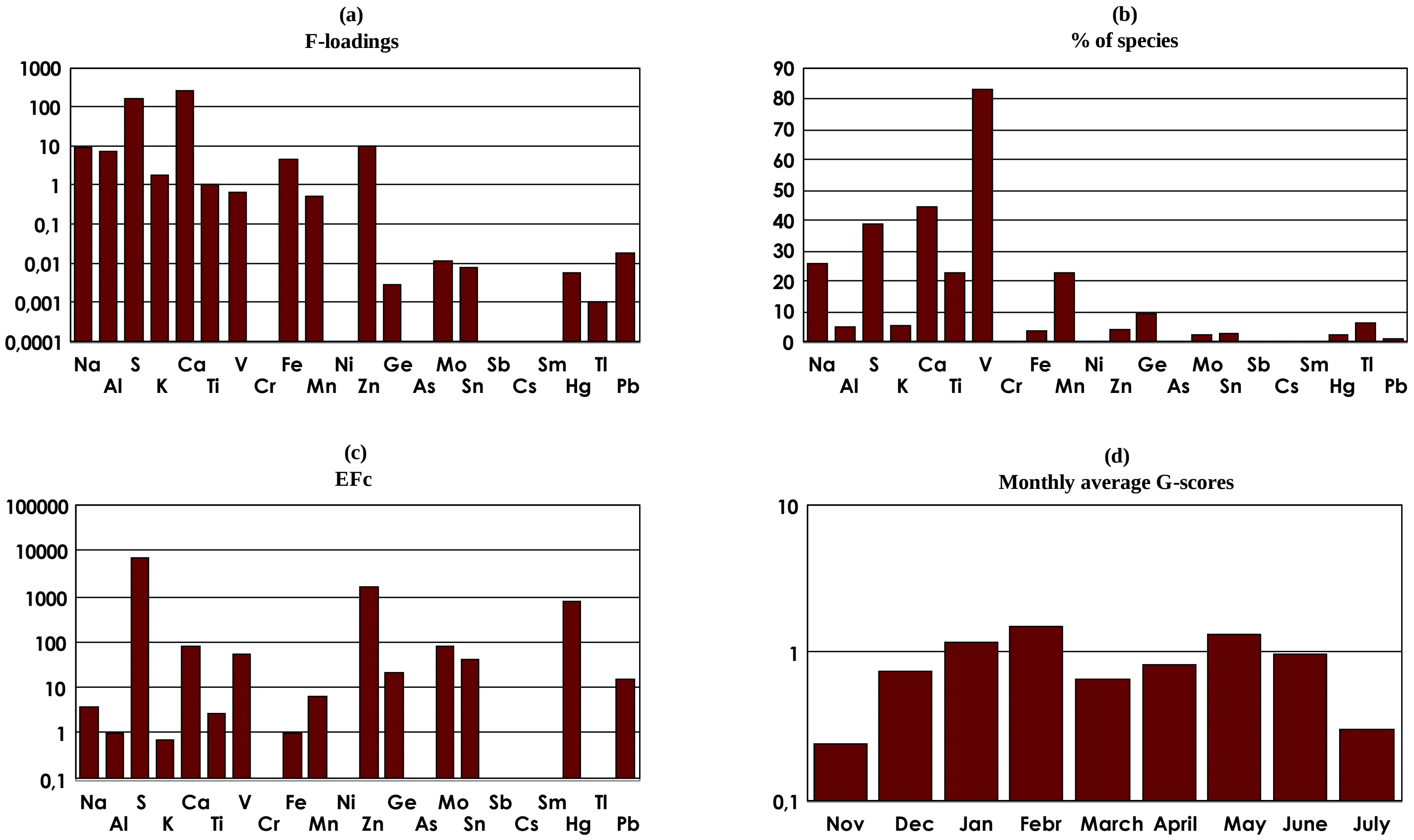
$$Q_{true} = nm - p(n + m) \qquad \text{Equation 5}$$

where n is the number of species used, m is the number of samples and p is the number of factors. Finally, $\mathrm{Q_{true}}$ value should be less than$1.5\mathrm{Q_{robust}}$.

We plotted factor loadings, which show concentration of elements in each factor in ng m-3, percentage of elements associated with each factor, EFc of elements in each factor and monthly average values of G-scores.

Each of these plots was provided pieces of information to identify physical identities of six factors extracted in PMF exercise. Among these percentages of elements associated to factors and EFc values were most informative for the physical identity of factors.

Factor 1 was loaded with Crustal elements Na, Al K, Ca, Ti, V, Fe as well as anthropogenic elements S, Zn, As, Mo, Sn, Sb and Hg. Please note that some of these elements, such as S, Al, Ca, etc have high concentrations in all factors. This is reasonable, because concentrations of these elements are high in the data set. For example S concentration in atmospheric data sets are expressed as μg m-3, whereas most of the other elements have concentrations in ng m-3 level. This means S concentration will be high compared to other element in all factors and this does not mean that S is a marker element in these factors. The same statement is also correct for some of the other elements as well. In this sense percentages of elements associated with factors is a better indicator for the factors which contributes to observed concentrations of elements. EFc values are also fairly informative to identify crustal or anthropogenic nature of factors. Among these parameters, Factor loadings and percentages of elements associated with factors are standard outputs of the EPA PMF version 3.0 software. EFcs and monthly averages of G-scores were not computed by the software. We calculated them for each factor.


(a) F-loadings

(b) % of species

(c) EFc

(d) Monthly average G-scores

Figure 4-21 Factor 1 Parameters, (a) F-loadings, (b) % of species, (c) EF$_c$, and (d) Monthly Average G-score

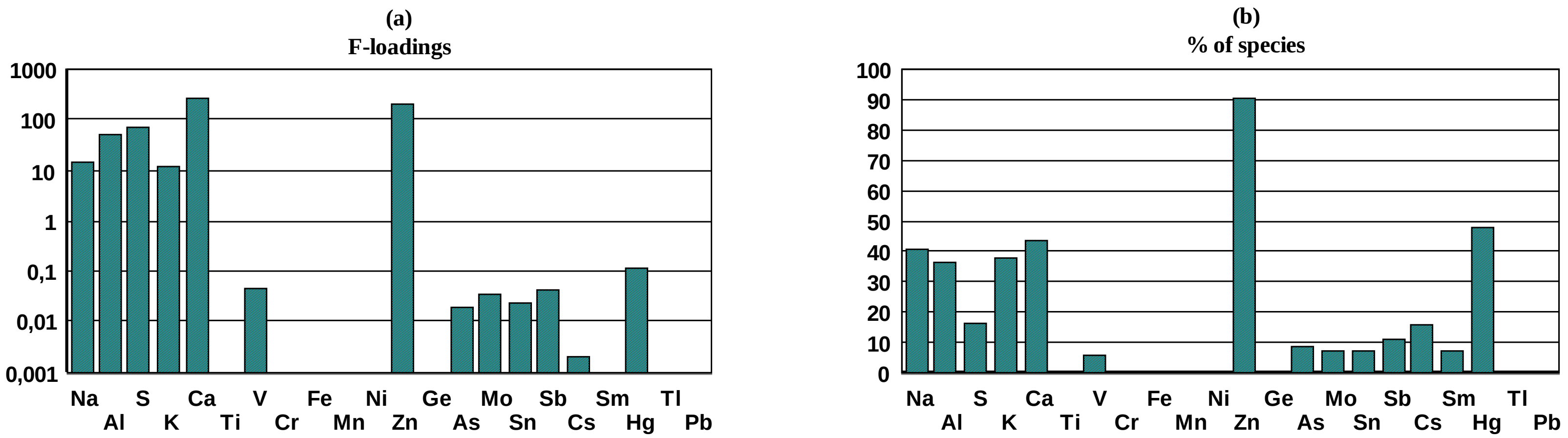
Factor explains approximately 80% of the V concentration in our data set. It also explains more than 20% of the concentrations of Na, S, Ca, Ti and Mn. EFc graph demonstrate that S, Zn, Mo and Hg are highly, Ca, V, Sn are moderately enriched. G-scores were low in November but increased in December and January, remained high in winter and spring and decreased again in July.

Factor 1 is obviously a mixed soil and anthropogenic factor, which includes tracer elements of both of these source categories. However, its assignment to a physical source was not possible Vanadium is generally associated with oil combustion emissions; in a factor that represent oil combustion source one would also see Ni, which is an equally important tracer for oil combustion. Factor 1 does not include Ni.

Factor 2 loadings, percentage of each element associated with Factor 2, Enrichment factors of elements in the factor and monthly averages of Factor 2 scores are presented in Figure 4-22.

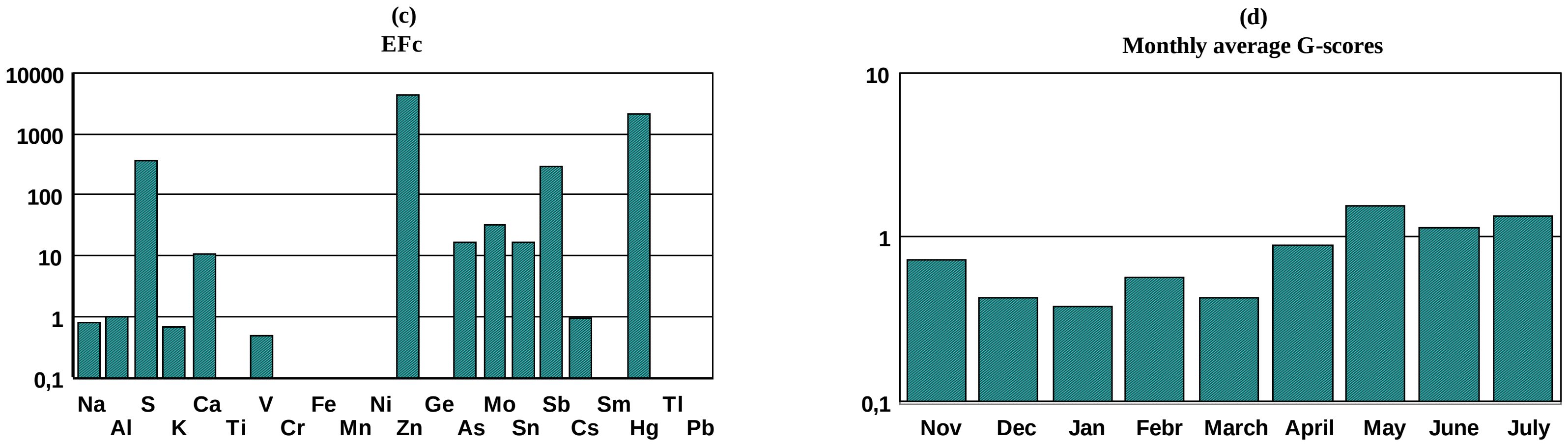
Like Factor 1, Factor 2 is also loaded with both crustal and anthropogenic elements. However, unlike in Factor 1, Factor 2 accounts for approximately 40% of the concentrations of Na, Al, K, and Ca, indicating that its association with soil is much stronger than that of Factor 1. Factor also accounts for 90% of Zn concentration, 50% of the concentration of Hg and approximately 10% of the concentrations of anthropogenic elements As, Mo, Sn, and Sb. Sulfate, Zn and Hg are strongly, Sb is moderately and As, Mo, Sn are slightly enriched. Factor scores are low in winter gradually increase toward summer months.

Factor 2 is a soil factor. Its strong contribution to crustal elements and higher atmospheric loading in summer are clear indications of soil source. However, it also includes some of the anthropogenic elements. It is interesting to note that anthropogenic elements enriched in Factor 2, namely Zn, As, Mo, Sb and Hg are good markers for coal burning. Monthly average g-scores are low in winter and high in summer, which is



(a) F-loadings

(b) % of species



(c) EFc

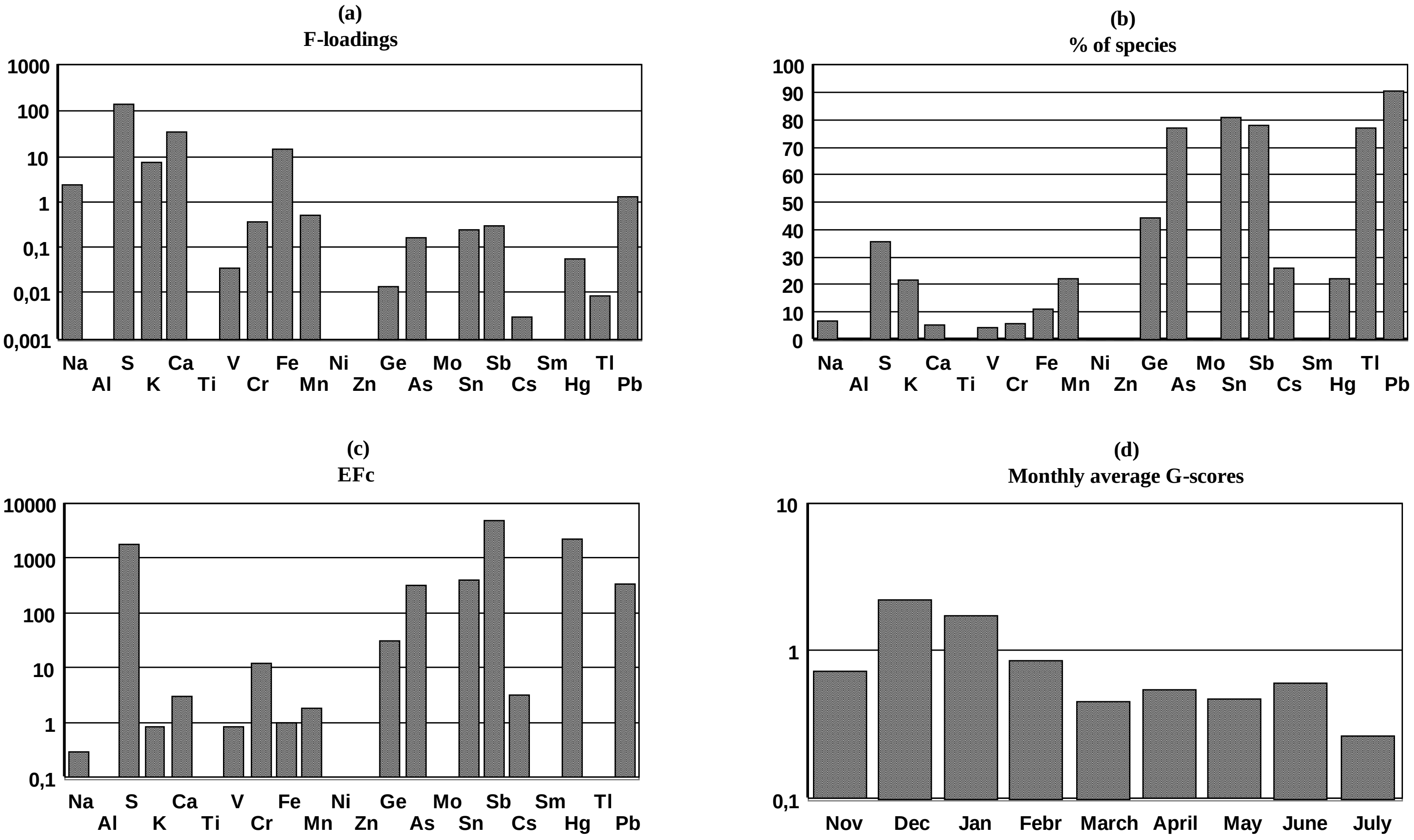
(d) Monthly average G-scores

Figure 4-22 Factor 2 Parameters, (a) F-loadings, (b) % of species, (c) EF_c, and (d) Monthly Average G-score

very typical for soil particles. Factor 2 was identified as surface soil which is contaminated by deposition of anthropogenic particles. Modification of soil composition by deposition of pollution-derived particles was probably occurred in 80's or earlier. Ankara suffered from very serious air pollution before 1990, which gradually improved after 2000. The source of poor air quality was combustion of coal with high sulfur and refractory fraction for space heating. In those years PM and SO_2 levels reaching to several thousand $\mu g\ m^{-3}$ were not unusual. When there is so much particles and metals associated with those particles in the atmosphere, they deposit to the surface and gradually modify the composition of surface soil. Factor 2 is very similar to the soil factor found with conventional factor analysis in 1993 by Yatın, (1993), which was also identified as contaminated surface soil. However, it should also be noted that background Zn concentration values in Turkey is also quite high. Yay et al. (2008) states that Zn concentrations (among some other elements) in Ankara surface soil were significantly higher than the corresponding concentrations in global average soil.

Air quality in Ankara improved substantially in last 5 – 7 years, due to switching, in mode of heating, from coal to natural gas conversion after 1995. Probably deposition of anthropogenic particles onto soil and modifying its composition is no longer a concern, but we will continue to see this factor in the coming years until it is covered with layers of recently generated dust. Considering extremely slow sedimentation rate on the land (1-2 mm in 10 years), complete covering of this layer with uncontaminated soil will probably take centuries.

Factor 3 is a very clear coal combustion factor. It explains approximately 80% of the measured concentrations of As, Sn, Sb, Tl and Pb. It also accounts for 20 – 40% of the measured concentrations of Ge and Hg. These elements are all highly enriched (EFc > 100) in Factor 3. Monthly average G-scores are high in winter months and decrease toward summer. There is not strong association of crustal elements with this factor. Based on these arguments, Factor 3 was identified as coal combustion.



(a) F-loadings

(b) % of species

(c) EFc

(d) Monthly average G-scores

Figure 4-23 Factor 3 Parameters, (a) F-loadings, (b) % of species, (c) EF_c, and (d) Monthly Average G-score

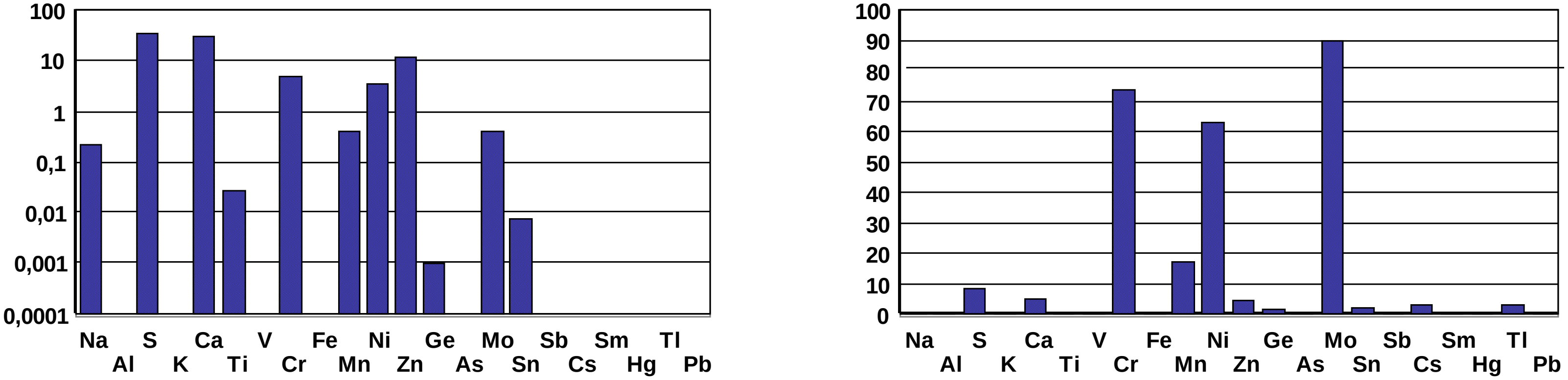
Although it is commonly stated that Ankara is heated by natural gas, data from Municipality demonstrate that natural gas is being used in 60% of the residences in Ankara and coal is being burned in remaining 40% of the residences. In recent years, these percentages had probably changed, in favor of coal, because some of the residences returned to the coal burning with large increases in natural gas prices. Plus, in last 10 years, coal is being distributed free of charge, particularly in low-income districts of the city.

Factor 4 is an anthropogenic factor. It does not explain significant fraction of the concentrations of any of the crustal elements, but explains more than 60% of the concentrations of Cr, Ni and Mo and also a smaller fraction of the concentration of Mn. Note that these are markers of steel production. We do not have a significant Fe and Steel industry in Ankara. These elements are also reported to be emitted from wearing vehicle engines and are being used as tracers of traffic activity in source apportionment studies (Gummeneni et al., 2011; Yatin et al., 2000). Factor 4 G-scores are slightly higher in winter, but the difference is not very significant. Factor 4 is probably a traffic factor. Identification of traffic factor, which was very easy in the past, became difficult task after phasing out of Pb from gasoline, because all of these elements that are associated to vehicle engine also have other sources. In this study we identified Factor 4 as motor vehicle exhaust. Enrichment factors of elements were not calculated for this factor, because there were no concentration values for either Al or Fe, which were the two elements we routinely used as reference element in EFc calculations.

Factor 5 is clear “uncontaminated soil” factor. It accounts for fair amount of the concentrations of crustal elements Al, Ti, K, Cr, Fe, Mn, Cs and Sm. EFc graph showed that Sb and Hg are enriched in this soil indicating that there are mixing of some anthropogenic particles, but this mixing is not as high as the mixing observed in Factor 2. Monthly average G-scores are low in winter and high in summer, which is typical behavior of soil particles, as discussed previously in the manuscript.

(a)
F-loadings

(b)
% of species



(c)
Monthly average G-scores

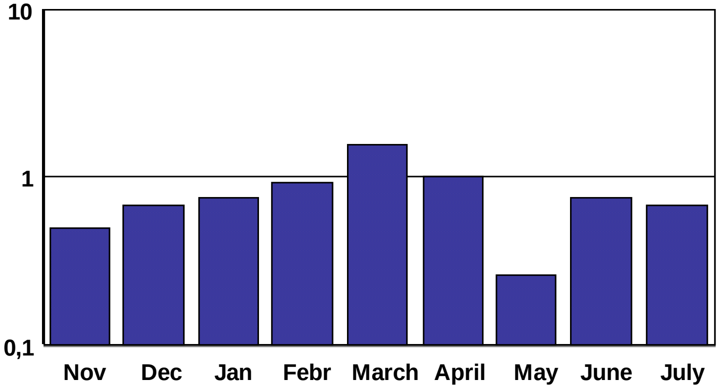


Figure 4-24 Parameters, (a) F-loadings, (b) % of species and (c) Monthly Average G-score

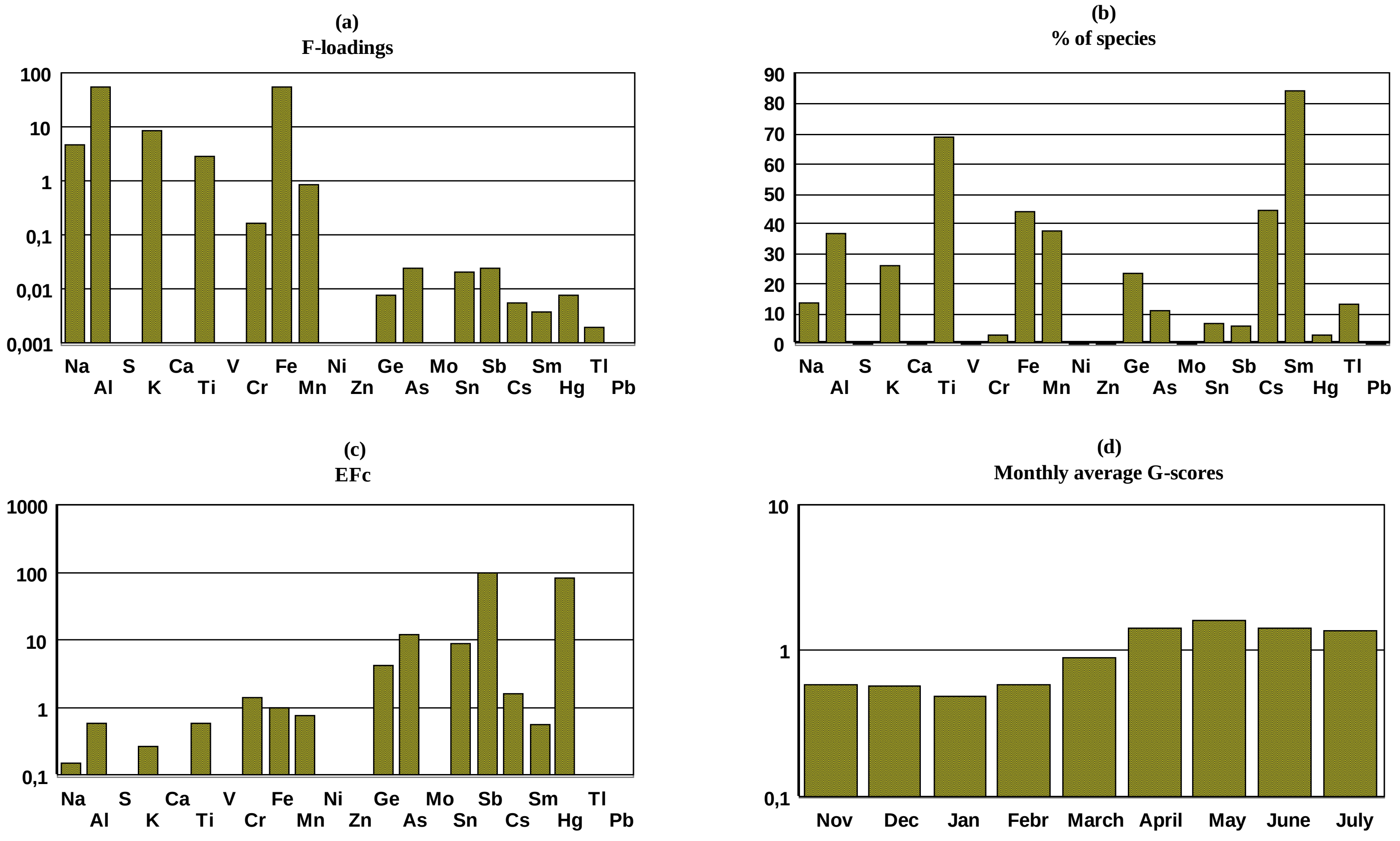


Figure 4-25 Factor 5 Parameters, (a) F-loadings, (b) % of species, (c) EF_c, and (d) Monthly Average G-score

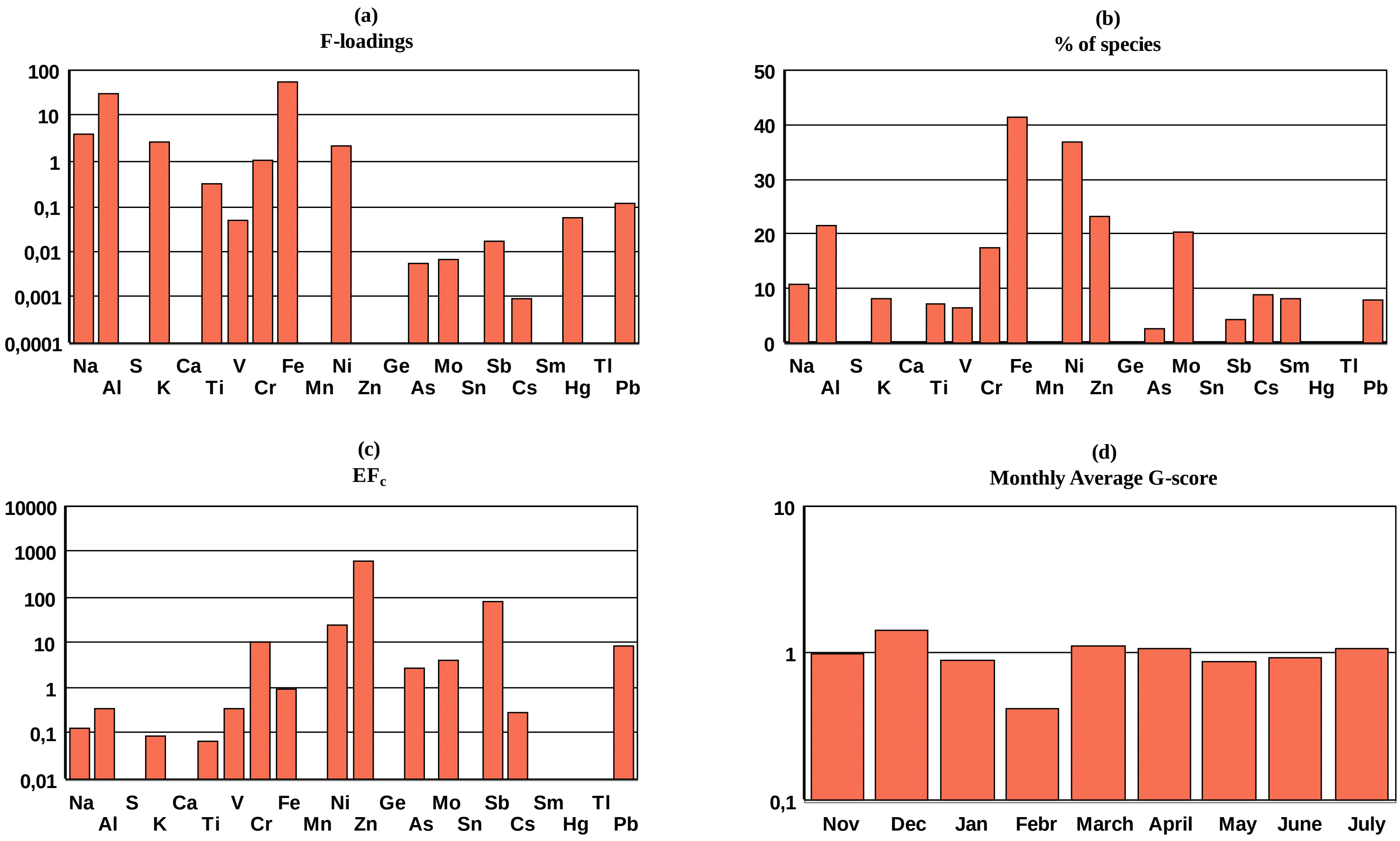


Figure 4-26 Factor 6 Parameters, (a) F-loadings, (b) % of species, (c) EF_c, and (d) Monthly Average G-score

Factor 6 is another mixed crustal-anthropogenic source. It accounts for 20 – 40% of concentrations of crustal elements and also anthropogenic elements Cr, Ni, Mo and Zn. These anthropogenic elements are enriched relative to crustal composition in Factor 6. G-scores of this factor are low in winter but the difference is not consistent and as pronounces as observed in soil related factors. It is worth noting that anthropogenic elements, namely, Cr, Ni, Zn and Mo, associated with Factor 6 are approximately the same with elements associated with Factor 4, which was identified as traffic factor. This similarity in composition with traffic factor and presence an additional crustal elements suggested that Factor 6 represent road dust. Relatively similar G-scores in summer and winter suggest that road dust particles become airborne in all seasons. This is not totally unexpected, because the only mechanism that can re-suspend soil particles is the wind action, which can be effective only when soil is dry. Road dust on the other hand can become airborne by the action of passing vehicles even when dust is not entirely dry. This difference in their generation mechanisms explains the difference between seasonal variation of G-scores of crustal and road dust.

The quality of PMF fit can be tested by comparing measured concentrations of elements with predicted concentrations by the model. This is depicted in Figure 4-27 where measured concentrations of elements are regressed against their predicted concentrations. The agreement between measured and predicted concentrations of elements is reasonable. R2 for the regression is 0.43 and correlation between Σ observed and predicted concentrations is statistically significant at 95% confidence interval. Observed to predicted ratio is 1.1 ± 0.5. All these numbers indicate that the six-factor PMF model applied to fine fraction data set simulated trace element data reasonably good and sources revealed by the model are reliable.

Contribution of factors to total elemental concentrations is depicted in Figure 4-28. Surface soil is the largest contributor to total element concentrations. It accounts for approximately 40% of the concentrations of elements. It is followed by Factor 1 which represents a mixed crustal-anthropogenic factor, which’s physical meaning is not very clear. This source accounts for 29% of the total element concentrations. The only clear anthropogenic factor in this PMF analysis is Factor 3, which represent coal burning source. It accounts for 13% of elemental concentrations. Another anthropogenic source is traffic (factor 4). It accounts for approximately 5% of total concentrations of elements. Road dust and subsurface soil accounts for 8% and 6% of total elemental concentrations.

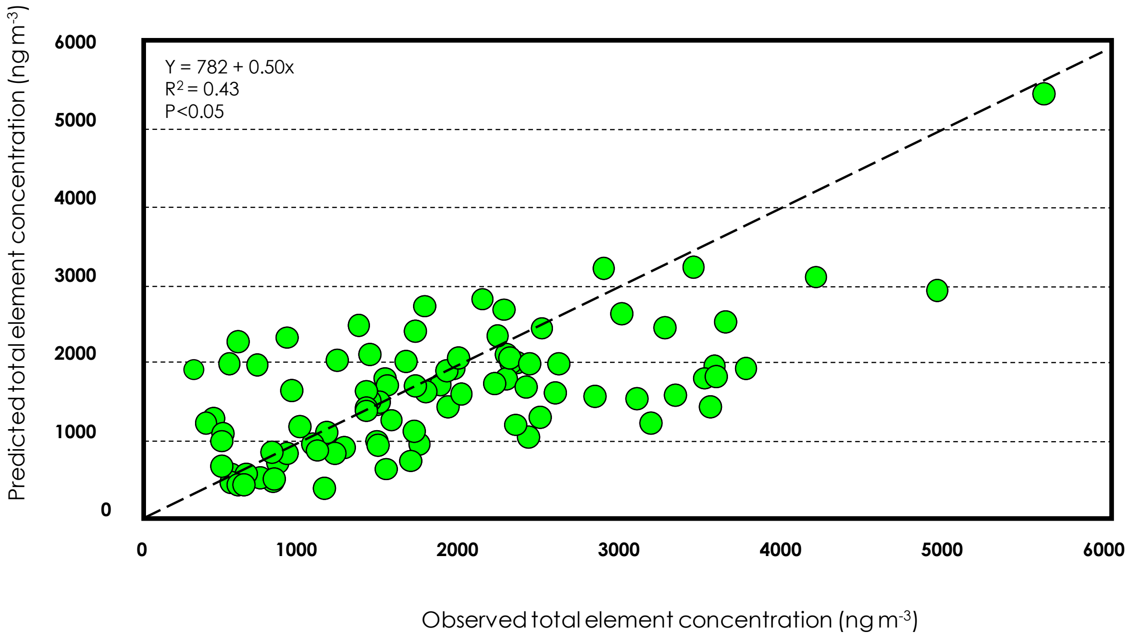


Figure 4-27 Observed vs. predicted concentrations of total elemental concentrations

There is one point to note in this apportionment. Results presented in this study are not apportionment of particle mass concentration. Although PM2.5 mass concentration is measured gravimetrically in this work. It is not included in the PMF modeling, due to its very poor signal-to-noise ratio. Although mass on each filter was measured using a microbalance, which is sensitive to 0.000001 g, uncertainty of mass determination was high due to very small particle mass collected on filters. This is unfortunately drawback of low-volume sampling. Consequently, what apportioned here is the total concentrations of elements measured in each sample. This is the main reason why crustal elements accounts for largest fraction of total elemental mass in fine fraction.

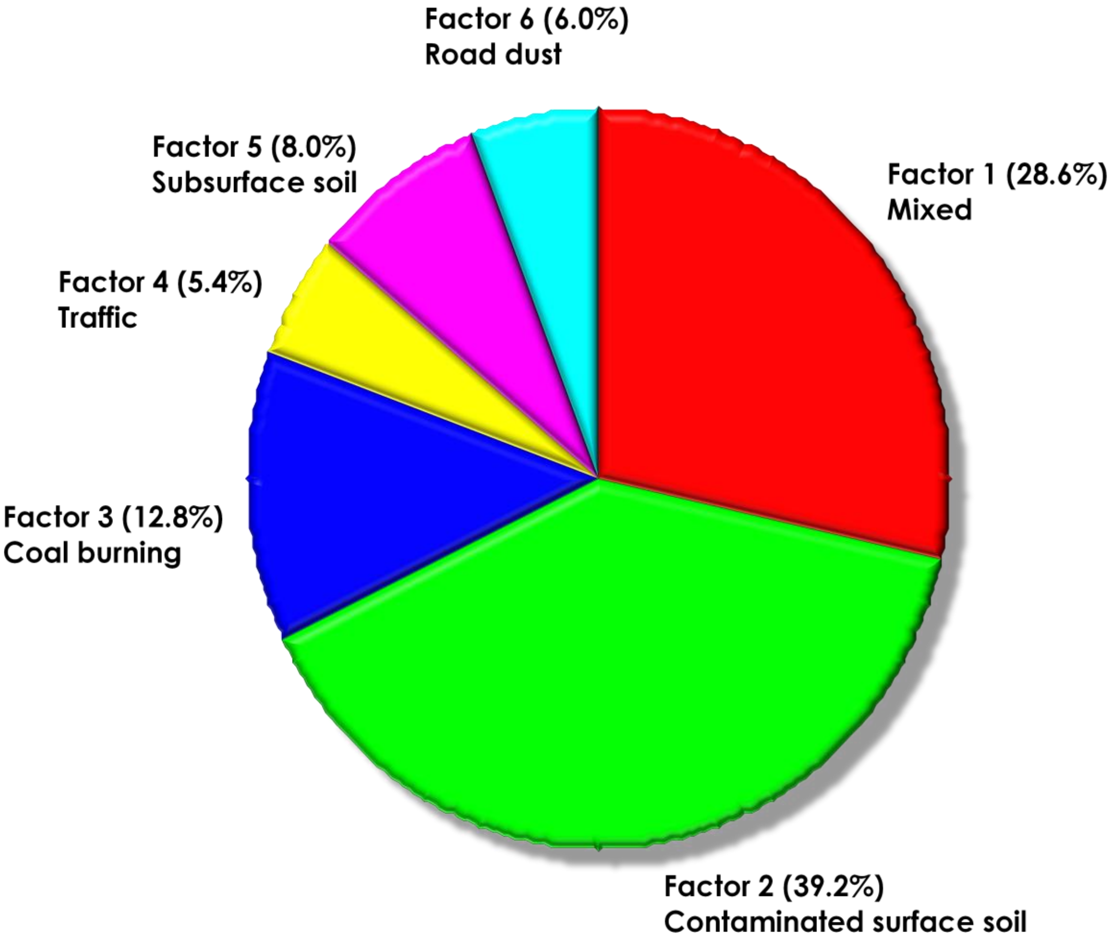


Figure 4-28 Contribution of factors on total element concentration

CHAPTER 5

CONCLUSION

Daily fine and coarse aerosol samples are collected using a ‘Stack Filter Unit’ on polycarbonate filters between November, 2013 and July 2014. Sampling was performed at the Department of Environmental Engineering in METU Campus, which can be considered as a suburban site. Collected samples were analyzed by ICP MS after acid digestion. Approximately 50 elements were measured.

Concentrations of soil-related elements were higher than corresponding concentrations reported for other rural locations around the world, but lower than data reported for arid regions in the Middle East and central Asia. Concentrations of anthropogenic elements measured in this work are not dramatically different from concentration of the same elements reported for other sites of world. Data generated in this work were also compared with trace element concentrations measured at the same location (METU) in 1975 and 1993. Concentrations of pollution-derived elements decreased since 1975 due to actions taken to improve air quality. However, interestingly, concentrations of crustal elements also decreased since 1975. This is attributed to extensive urbanization around the station since 1975, which reduced to expose surface area for re-suspension of soil particles.

Coarse to fine ratios of anthropogenic elements were > 1.0 and those of crustal elements were < 1.0, demonstrating that soil related elements mostly occur in coarse fraction and pollution derived elements in fine fraction, as expected.

Both short- (episodic) and long-term variations were observed in concentrations of most of the elements measured in this study. Episodic variation in concentrations, which lasted for few days were observed frequently and attributed to short term variation in emission strengths, but more importantly to variations in meteorology.

Differences in concentrations of elements between weekdays and weekends were not as pronounced as expected. Probably because (1) weekend and weekday emissions in Ankara is not sufficiently different to generate different levels in weekdays and weekends and (2) sampling locations is at a suburban location and emissions in the city smeared out before they reach to our station.

Coarse fraction particle loading in the atmosphere was higher during summer due to easier re-suspension of soil particles, which make up most of the coarse particles in atmosphere during summer months. Concentrations of fine particles, on the other hand, were higher during winter season owing to higher residential heating emissions in winter.

Elemental concentrations depicted statistically significant decreases with increasing wind speed, mixing height and ventilation coefficient. Concentrations of both crustal and anthropogenic elements were also related to temperature, but the relation was indirect. Dependence of concentrations of anthropogenic elements on wind-direction showed that the highest concentrations of these elements are associated with wind flows from a sector between SSW and NNW, which hosts most of the industrial activity, such as OSTIM and Sincan Organized Districts. Concentrations of pollution-derived elements were also high when wind blew from NNE and NE sectors. Wind flow from this sector transports emissions from densely populated districts of the city.

PMF model applied to fine fraction data set revealed six factors indicating that aerosol population in METU consists of six different components. One of them properly identified, but remaining five factors were assigned to physical sources. Three of these sources were soil related. The most important of these soil related sources was the contaminated surface soil. These soil particles included anthropogenic elements as well as crustal elements. In the days when Ankara suffered from heavy air pollution, particles emitted from residential heating settled to the ground. Over the years deposition process gradually modified the elemental composition of surface soil. Although this mechanism is now insignificant, we still see modified soil particles in the atmosphere, because sedimentation rate is only few mm in a decade. It is also interesting to note that a factor, which is very similar to contaminated surface soil factor found in this study was also found in factor analysis performed by Yatin (1995) again to fine fraction data set generated at METU. That factor was also named as contaminated surface soil.

Elemental concentrations predicted by PMF showed reasonable agreement with their measured concentrations. The relation was statistically significant at 95% confidence interval. Observed-to-predicted ratio of total concentrations of elements is 1.1 ± 0,5, which suggests that difference between observed and predicted total elemental concentrations was within 10%.

In this study, reliable information is generated on levels and temporal variations of crustal and anthropogenic aerosol in Ankara. In addition, factors affecting composition of aerosol population and sources responsible for observed concentrations of elements is established. This information should assist to both Ankara municipality and Ministry of the Environment and Municipality in their efforts to improve air quality in Ankara. In this study, our results indicate that 39.2 % of total elemental concentration is contributed by contaminated surface soil. Subsequently, as an example, we can recommend prevention of re-suspension of contaminated soil for improve air quality in Ankara.

5.1. Recommendation for Future Research

In this study, elemental concentrations of elements were analyzed for fine aerosol fractions mainly. In order to evaluate coarse-to-fine ratios and temporal variations better, coarse fractions should also be analyzed.

In addition, samples were collected between November, 2013 and July, 2014 in this study. Therefore, summer season could not be observed adequately. Longer periods of sampling will provide better understanding of seasonal variations.

Potential Source Contribution Function was not evaluated in this study. In order to identify long range transport of the pollutant, distributions of PSCF should also be considered.

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