IDENTIFICATION AND SOURCE APPORTIONMENT OF TRACE ELEMENTS IN URBAN AND SUBURBAN AREA OF ANKARA

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ABSTRACT

IDENTIFICATION AND SOURCE APPORTIONMENT OF TRACE ELEMENTS IN URBAN AND SUBURBAN AREA OF ANKARA

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In this study, Chemistry and Composition of Atmospheric fine aerosol particles in urban and suburban stations in Ankara are identified and generated data set are used to determine sources of fine particles, using receptor modeling. For this purpose, 24-hr aerosol samples were collected on Nuclepore filters using a ‘Stack Filter Unit’. Sampling continued for 15 months from July 2014 to October 2015. Samples were collected at two stations. One of the stations was located at Ankara university campus, which is an urban location, and the second station was located at METU campus, which can be considered as a suburban location. Collected filters were analyzed for 63 major, minor and trace elements, with atomic numbers ranging between 3 for Li and 92 for U.

Measured concentrations elements are compared with corresponding data generated in other urban and suburban locations around the world, Turkey, and with performed studies 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. Concentrations of both crustal and pollution-derived elements decreased significantly between 1975 and 2015 in Ankara.

Concentrations of elements show short- and long-term variations. Some of these variations are due to temporal variations in emissions and some due to temporal variations in meteorology. Meteorological parameters wind speed, wind direction, mixing height and ventilation coefficient strongly affect measured concentrations of elements. Relation between measured concentrations of elements did not show a meaningful relationship with wind direction at urban station, because sources were all around the station. However, relationship between measured concentrations of elements and wind direction was very clear in suburban station. Conditional probability function calculations demonstrated that Mamak area and OSTIM are two important source areas affecting composition of particles at METU.

Positive matrix factorization (PMF) was used for source apportionment of elements to identify sources contributing to measured concentrations of them. This analysis indicates 6 sources for both stations; contaminated surface soil, a crustal factor, coal burning, oil combustion, diesel, and traffic for METU, and crustal factor, coal combustion, Road dust, traffic, contaminated soil, and diesel.

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

ÖZ

ANKARA’DA ESER ELEMENTLER İÇİN KAYNAK BELİRLEME ÇALIŞMASI

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Bu çalışmada Ankara atmosferindeki ince (fine) parçacıkların eser element kompozisyonları belirlenmiş ve ölçülen elementler kaynakların doğal izleyicileri olarak kullanılmış ve aerosol kaynakları belirlenmiştir. Aerosol örnekleri 24 saatlik sürelerle ve “stack filter unit” (SFU) olarak tanımlanan bir örnekleyici yardımıyla toplanmıştır. Kullanılan SFU, ard arda yerleştirilmiş, farklı gözenek boyutlarına sahip iki filtreden oluşmaktadır. Örnekler birisi kentsel istasyon özellikleri taşıyan diğeri ise banliyö (suburban) istasyonu olarak tanımlanabilecek iki istasyonda toplanmıştır. Kentsel istasyon Keçiören’deki Ankara Üniversitesi, Ziraat Fakültesi arazisinde, banliyö istasyonu ise ODTÜ, Çevre Mühendisliği bölümünde kurulmuş ve Temmuz 2014 – Ekim 2015 arasında 15 ay boyunca çalıştırılmıştır. Toplanan örneklerde ICPMS tekniği kullanılarak 60 dolayında elementin konsantrasyonları belirlenmiştir.

Ölçülen element konsantrasyonlarının daha önce Ankara'da yapılan çalışmalarda elde edilen konsantrasyon değerleri ile karşılaştırılması hem toprak kökenli hem de antropojenik kökenli element konsantrasyonlarının zaman içerisinde azaldığını göstermiştir. Bu çalışmada Ankara'nın iki farklı bölgesinde ölçülen element konsantrasyonları, literatürde başka şehirler için rapor edilmiş konsantrasyonlarla genel anlamda uyumludur. Ankara atmosferindeki element konsantrasyonları gerek kısa süreli ve gerekse uzun dönemli değişimler göstermektedir. Bu değişimlerin bir bölümü emisyonlardaki değişimlerden kaynaklanırken bir bölümü de meteorolojik parametrelerdeki zamansal değişimlerden kaynaklanmaktadır.

Ölçülen element konsantrasyonlarının meteorolojik parametrelerle ilişkili olduğu görülmektedir. Özellikle, karışım yüksekliği, rüzgar hızı, ölçülen konsantrasyonlardaki değişimleri belirleyen meteorolojik parametrelerdir. Rüzgar yönünün element konsantrasyonlarına etkisi "conditional probability function" olarak bilinene bir istatistik yöntemle incelenmiştir. AU istasyonunda, kaynakların istasyona göre her yönde bulunmasından dolayı, rüzgar yönü ile ölçülen konsantrasyonlar arasında anlamlı bir ilişki görülememiştir. Buna karşılık METU istasyonunda Mamak bölgesinin ve organize sanayi bölgesinin etkileri açıkça görülmüştür.

Çalışmanın son bölümünde Ankara'da aerosol popülasyonunu oluşturan bileşenlerin neler olduğu incelenmiştir. Her iki istasyonda da aerosollerin altı farklı bileşenden oluştuğu görülmüştür. Bunlardan beşi her iki istasyonda da aynıdır. Birer tanesi ise istasyonlara mahsus bileşenlerdir.

Anahtar Kelimeler: Eser elementler, atmosfer, hava kirliliği, reseptör modellemesi, Positive Matrix Factorization

To two women of my life….

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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, Y., Ayare, A., and Srinikethan, 2011). Therefore, source apportionment of the atmospheric particles has become an important part of air quality research (Dabek-Zlotorzynska, 2011).

Source apportionment studies have identified the contribution of different emission sources to the particle concentration in a defined receptor site (Sathe, Y., Ayare, A., and Srinikethan, 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, Tokgöz 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 (Tokgöz, 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 (Yumurtacı, 2013, Bayram, 2000, Kindap, T. *et al*. 2006).

1.2 Aim of the Study

The main purpose of this study is to measure the concentration of the trace elements available in the aerosols in urban and suburban of Ankara, and finally identifying the sources contributing in these measured concentrations. In this regard, particle samples have been collected and analyzed in two stations located at Middle East Technical University and Ankara University in Ankara from July 2014 to August 2015.

CHAPTER 2

LITERATURE REVIEW

2.1 Characterization of the Particulate Matter

Particulate matter (PM) is the combination of liquid and solid particles suspended in the air and is a major segment of urban air pollution, having adverse effects on human health, climate change, and visibility (Fierro, 2001). These particulate matters have different natural and anthropogenic sources. Natural sources include dust storms, volcanic eruptions, living vegetation, forest and grassland fires, and sea spray. Anthropogenic sources are mainly traffic, power plants, domestic heating, and different industrial activities. The chemical combination of particles is highly complex and differs based on the source of emission, their size and aerodynamic diameter, and meteorological conditions. (Pražnikar and Pražnikar, 2012). It contains acids (like sulfates and nitrates), organic chemicals, soil particles, metals, and biological components (Fierro, 2001). Each of these constituents is a tracer of a certain source that can be categorized as primary and secondary, based on their formation mechanism. Primary particles are the ones which are directly discharged to the air from their sources; but the secondary particles are built by the chemical alteration of primary gases (WHO, 2000).

As Peter Wiederkehr and Yoon (1998) grouped the air pollutants, they can be categorized into major and trace or hazardous air pollutants. Major air pollutants includes six classical pollutants: airborne particles, sulphur dioxide (SO_2), carbon monoxide (CO), nitrogen dioxide (NO_2), ozone (O_3), and lead (Pb). Trace or hazardous air pollutants have very smaller concentrations compared to major ones and comprise different physical, chemical, and biological agents, such as volatile organic compounds (VOCs), micro-organisms, and radio-nuclides. (Langner, Draheim and Endlicher, 2011)

The aerosols in the atmosphere influence the quality of air, and thus, ecosystem well-being and human health, also having an essential effect on the climate system of Earth (Fowler *et al.*, 2010). Air pollution was ranked eleventh, in the Western Europe ranking of the risk factors for diseases based on their attributable burden, in which smoking tobacco was ranked first (WHO, Henschel and Chan, 2013).

PM can be categorized as the most significant factor among the criteria pollutants, after high human casualties that happened during the various air pollution episodes in the history. London air pollution episode, which happened in 1952, was the most severe episode in the World's history, causing above 4,000 deaths. Wide investigations on identifying the epidemiological and toxicological consequences of PM have started since that event (Appel *et al*., 1967; Waller, 1967; Zweiman *et al*., 1972), and at the moment, around 1500–2000 papers per year are getting published on the topics related to atmospheric aerosols (Fuzzi *et al.*, 2015).

Several epidemiological studies have demonstrated that exposure to PM of varying size fractions is associated with an increased risk of respiratory and cardiovascular diseases. The most severe effects in terms of overall health burden include a significant reduction in life expectancy by a several months for the average population, which is linked to long-term exposure to moderate concentrations of PM. Nevertheless, numerous deaths and serious cardiovascular and respiratory problems have also been attributed to short-term exposure to peak levels of PM. (Pražnikar and Pražnikar, 2012).

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 as they are able to penetrate deeper into the lung (Biersteker, 1976, Bevan,D. and Manger, 1985, James J.Quackenboss, 1989). Today, cardiovascular and pulmonary problems related with PM are well documented and $PM_{2.5}$. Air pollution has gotten great attention in the literature (Carbone *et al.*, 2014;Cheng, H. *et al.* 2014; Titos *et al.*, 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 major importance in realizing their behavior, adverse effects and generation mechanism. Particulate matters can be categorized as fine and coarse particles based on their aerodynamic diameter (Munzur, 2008). The aerodynamic diameter of the coarse fraction of the particles (PM_{10}) can be between 2.5 µm and 10 µm. Mechanical infraction (e.g. crushing, granulating, and erosion of surfaces), dust suspension in the air, and evaporation of sprays can form them. Coarse particles are composed of aluminosilicate and different oxides of crustal components. Main sources of PM_{10} are industrial activities, absconder dust from roads, construction and destruction, agriculture, and fly ash coming from fossil fuel combustion. Coarse particles can stay in the atmosphere from minutes to hours, and they can travel to distances from less than 1 km up to 10 km. (Fierro, 2001).

Fine particles have an aerodynamic diameter less than 2.5µm ($PM_{2.5}$). Their chemistry and sources are different from PM_{10}. $PM_{2.5}$ is composed of different mixtures of nitrate, sulfate, organic and carbon compounds, hydrogen ion, ammonium; particle bound water, and metals such as Ni, Mn, Fe, Zn, Cu, Cd, V, etc. They are formed from gas and condensation of high-temperature vapors during combustion, therefore fossil fuel combustion, metal smelting, and vegetation burning are their main sources. Fine particles can remain in the air from days to weeks, and they can travel to distances from hundreds of kilometers up to thousands. $PM_{2.5}$ contributes in reducing the visibility in many cities around the world (Kindap, T. *et al*. 2006) . Moreover, fine particles are divided into two groups named Aitken with aerodynamic diameters between 0.002 – 0.08 µm and Accumulation group with aerodynamic diameter in 0.08 – 2.5 µm ranges. Size distribution of PM based on formation mechanism is represented in Figure 2-1.

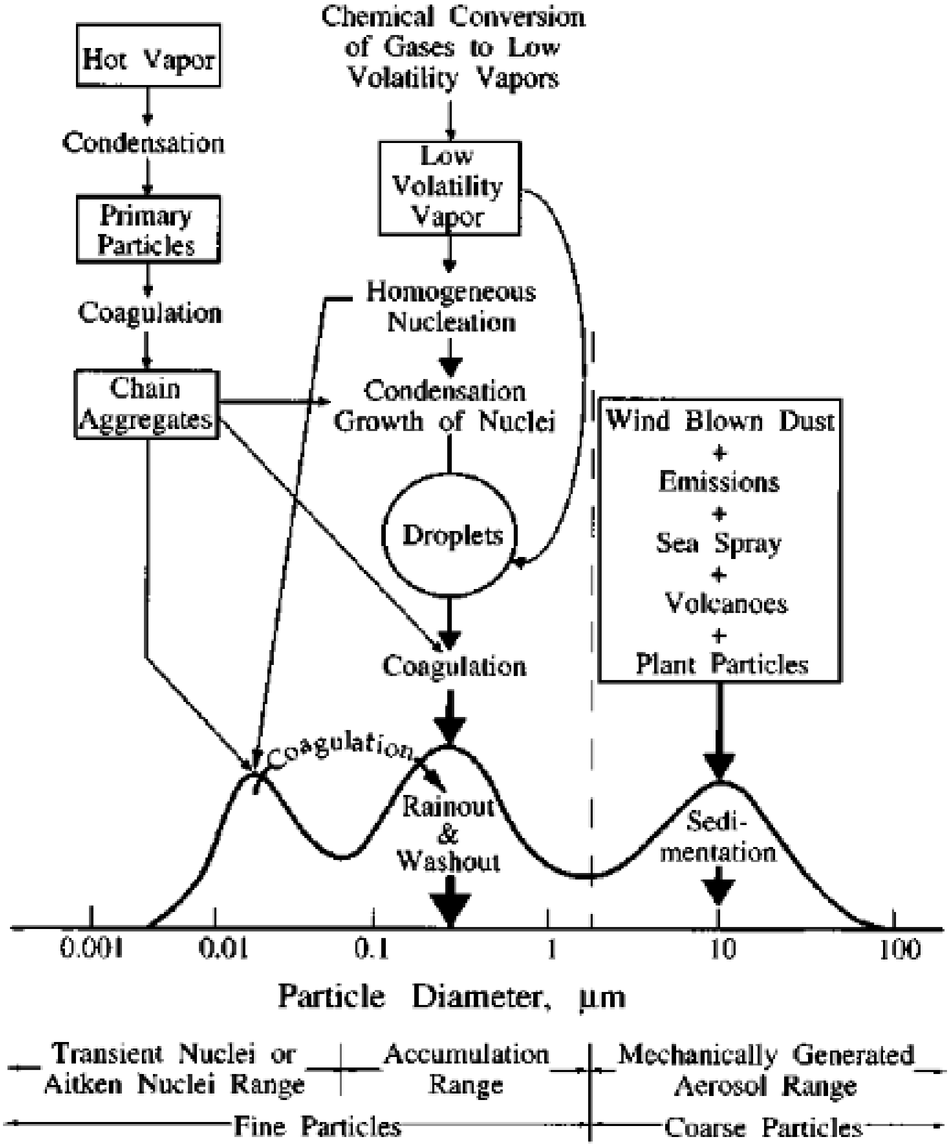


Figure 2- 1 Size distribution of PM according to their generation mechanism (Munzur, 2008)

2.1.2 Sources of Particulate Matter

The atmospheric studies started to focus mostly on the origin and sources of the particulate matters after the air pollution episodes in 20th century, that were explained above occurred. Sources of aerosols and their composition in an urban atmosphere were identified firstly (Negi, B. S.; Sadasivan, S.; Mishra, 1967).

Atmospheric aerosol particles originate from a wide variety of natural and anthropogenic sources. Primary particles are directly emitted as liquids or solids from sources such as biomass burning, incomplete combustion of fossil fuels, volcanic eruptions, and wind-driven or traffic-related suspension of road, soil, and mineral dust, sea salt and biological materials (plant fragments, microorganisms, pollen, etc.). Secondary particles, on the other hand, are formed by gas-to-particle conversion in the atmosphere (new particle formation by nucleation and condensation of gaseous precursors) (Marko Vallius, 2012, Finlayson-Pitts BJ, 1997, Seinfeld, J. H. and Pandis, 1998).

Particles in the atmosphere arise from natural sources as well as anthropogenic activities. The former source includes windborne dust, sea spray, volcanic activities and biomass burning, while emissions of particles attributable to the activities of humans arise primarily from four source categories: fuel combustion, industrial processes, nonindustrial fugitive sources (e.g. construction work), and transportation sources (e.g. automobiles). Natural aerosols have probably 4 to 5 times larger aerodynamic diameters than anthropogenic ones on a global scale, but regional variations in man-made pollution may change this ratio significantly in certain areas, particularly in the industrialized Northern Hemisphere (Titos *et al.*, 2014).

Once airborne, particles can change their size and composition by condensation of vapor species or by evaporation, by coagulation with other particles, by chemical reaction, or by activation in the presence of water supersaturation to become fog and cloud droplets. Particles are eventually removed from the atmosphere by two mechanisms: deposition at the Earth’s surface (dry deposition) and incorporation into cloud droplets during the formation of precipitation (wet deposition). Because wet and dry deposition lead to relatively short residence times in the troposphere, and because the geographical distribution of particle sources is highly non-uniform, tropospheric aerosols vary widely in concentration and composition over the Earth. Whereas atmospheric trace gases have lifetimes ranging from less than a second to a century or more, residence times of particles in the troposphere vary only from a few days to a few weeks. (Rami Alfarra and Rami Alfarra, 2004)

2.1.3 Effects of Particulate Matter on Environment and Human Health

The detrimental influences of the atmospheric particles on human health and the environment have gained importance in recent decades and been investigated widely. The exact mechanisms of health effects of PM have not been identified yet, but it is known that particles size and composition have great importance on the health effect (Ozturk, 2009, Tokgöz, 2013). The deposition of particulates in different parts of the human respiratory system depends on particle size, shape, density, and individual breathing patterns (mouth or nose breathing).

The effect on the human is also influenced by the chemical composition of the particles, the duration of exposure, and individual susceptibility. All particles smaller than 10 microns in diameter can reach the human lungs, but the retention rate is largest for the finer particles, because coarse particle could retain in the upper part of respiratory system but 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 (PM0.1) may even enter the blood and travel throughout the body (Verbrugge, 2004). That is why recent studies are mostly focused on the fine fraction of the particles. In addition, as stated before, atmospheric particles contain toxic metals, which have harmful effects on human health as the exposure time to them increases. Some of these trace elements, their specification, sources and health effects are given in Table 2- 1 (Kimani, 2012).

Moreover, there are several studies that shows the connection between exposure to other heavy metals such as Fe, V, Zn, Mn, Ni and various health problems like cardiovascular diseases, nonfatal heart attracts aggravated asthma and lung cancer (Hawas *et al.*, 2003, Geiger and Cooper, 2010) . It is estimated that approximately 3% of cardiopulmonary and 5% of lung cancer deaths are attributable to PM globally (World Health Organization, 2013).

Table 2- 1 Effect of heavy metals constituents of PM on human health (Kimani, 2012)

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, immunosuppression, 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.

Despite the adverse health effects of the particulate matters have other harmful influences on the environment by interfering in visibility, global climate, and materials (Jimoda, 2012).

It is evident based on the previous performed studies that the black carbon contained in the PM causes global warming by absorbing the 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 (Weingartner *et al.*, 2003). Besides, alkaline particles, which are composed of dust particles mainly, ruin surfaces of walls, doors and automobiles (Jimoda, 2012). Visibility degradation is one of the most readily perceived impacts of fine particulate matter. In particular, fine particles with a diameter between 0.3 – 1.0 µm reduce visibility largely by absorbing and scattering light (Weingartner *et al.*, 2003, Seinfeld, J. H. and Pandis, 1998). Also, deposition of air pollutants on soils and surface water can cause alteration of the nutrient content of the soil and effect the vegetation and animals’ lives (Jimoda, 2012).

2.1.4 Trace Elements

Different sources have specific emissions in which some of the present chemical species can be used as fingerprints of these specific sources. Atmospheric trace elements are important 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. However, the trace elements coming from the anthropogenic sources, which are important for us due to their adverse effects on human health and environment, are mainly in the fine fraction of the aerosols, which are identified in this study.

Trace elements are emitted to the atmosphere from both natural sources and anthropogenic ones. For example, Duce et al. (1975) showed that anthropogenic V in aerosol is a result of combustion of heavy fuel oil containing V-porphyron complex. Sciare et al. (2003) and Alves et al. (2010) demonstrated that potassium can be used as a marker of biomass burning activities i.e., agricultural waste burning and forest fires. The main emission source for trace elements is natural sources, such as weathering of rocks, mineral deposits, volcanism, wind erosion, forest fires, sea spray and biogenic emission. Emitted trace elements due to natural sources are summarized in Table 2- 2.

The elements are categorized in Table 2- 2, based on their presence in annual fluxes. The first source, windblown dust is a significant natural source for atmospheric trace elements to the extent that 20-30 % of total fluxes of some metals such as Cr, Cu, Mo, Ni, Pb and Zn is coming from windblown dust. Volcanic eruptions accounts for 50 % of the total Cd and Hg fluxes and above 50% of Se and Mo is 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
Sea salt 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

Human activities is the other major source for trace elements, forming the second emission source, named as anthropogenic source. 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 these trace elements are listed in Table 2-3.

As it can be seen, road transport, industrial facilities, small-scale burning industries and mineralization, and raw material processes are the main anthropogenic activities that emit trace metals and Cu, Pb, Zn and Fe are the most common trace metals that are emitted to the atmosphere by these activities.

Table 2- 3 Emission sources of anthropogenic trace metals (Morawska, *et al*, 2002)

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

2.1.5 Receptor Modelling

Receptor models as a mathematical modeling method include a range of multivariate analysis methods that use ambient air measurements to identify the source types, locations, and contributions that affect ambient pollutant concentrations. Mathematical modeling is divided into two groups as Source oriented models and Receptor models (Choi et al., 2013, Srimuruganandam and Jose, 2016). Receptor models contrast with source models, which begin with source emissions and calculate ambient concentrations using mathematical representations of meteorological dispersion, chemical transformation, and deposition. Source and receptor models are complementary, and applying both of them to the same situation lead to a better assessment of pollution sources (Morawska, L., et al, 2002).

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, and each one of them has their advantages and weaknesses. Several receptor modeling methods that are commonly used for source apportionment studies and are based on the Chemical Mass Balance (CMB) model are Multiple Linear Regression (MLR), Enrichment Factor (EF), Positive Matrix Factorization (PMF), Principal Components Analysis (PCA), Factor Analysis (FA), Empirical Orthogonal Functions (EOF). Other receptor models include back trajectory, equilibrium, aerosol evolution, cluster analysis, neural networks, and time series.

Depending on the available data and information about the source profile, the modeling method can be chosen. For example, CMB is the most proper method for source apportionment, if number of sources, composition profile of the sources, and elemental mass fractions are known. On the other hand, factor analysis methods like PCA or PMF are better options if only atmospheric concentrations are available (Ozturk, 2009). In this study, enrichment factor (EF) source apportionment method that depend on the ratio of atmospheric concentrations of elements to a reference element was used for preliminary source apportionment of aerosols and Positive Matrix Factorization (PMF) was utilized for achieving higher resolution.

2.1.6 Enrichment Factor (EF)

Enrichment factor (EF) as a double normalization technique, is mainly used for the preliminary source apportionment of aerosol species in the atmosphere. In atmospheric studies, EF is calculated for both crustal and sea salt sources, because crustal and marine particles are the most widely observable particles in the atmosphere. For each element EF can be calculated by the equation 2-1(Chester, R. and Stoner, 1973, Zoller et al., 1974).

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

If crust is used as the reference source, calculated EF is called as crustal enrichment factor (EFc) and if marine source is used as the reference source, then calculated EF is called as marine EF (EFm). Al, Fe, and Li are the most common elements, which are used as reference element for ERc. In addition, Na is used for reference element of ERm. In this formula, C_x represent the concentration of the target element in the atmospheric aerosol, and in the reference medium. C_R represents the concentration of the reference element, which can be chosen as a crustal or marine element as stated above, in the aerosol and reference medium. The ratio close to unity for an element indicates that the element has crustal or marine source. If the ratio is above unity, it can be concluded that element has other anthropogenic sources (Reimann P., 2000).

Mason’s soil composition (Mason and Moore, 1982) was used as the reference crustal source to calculate EFc in this study. Al is being used normally as reference element for crustal material. Although other elements that are primarily from crustal material, such as Fe, Sc, and Si can also be used as reference element. Ideally, the soil composition near each station should be used, but that data is not generally available for the specific sampling locations in which the observation of the study is taking place. In addition, soil material at a rural stations may also come from other regions. Therefore, Compilations of global soil composition reported in the literature (Mason, 1966; Taylor, 1972; Vinogradov, 1959) are commonly used for EFC calculations.

By definition, the enrichment factor close to unity (EF = 1) indicates, that the element originates from the soil. However, scientists argue that the values of EF < 10 are merely the measurement background and are due to the difference between the station soil and Mason's soil composition. Therefore, EFc values less that 10 should not be used as an indication of enrichment.

2.1.7 Positive Matrix Factorization (PMF)

PMF is one of the latest receptor modeling techniques, which is used very frequently in last 15 years. It is developed in late 1990's by Pentti Paatero, 1997 as an alternative to earlier versions of multivariate statistical tools, such as factor analysis (FA), and principal component analysis (PCA).

The theory behind it is based on the idea that time dependency of a chemical species measured at a receptor site is the same for species from the same source. Therefore, species of similar variability are grouped together in a minimum number of factors (sources) that explain the variability of the data set. It is assumed that each factor is associated with a source or source type (Chueinta et al., 2000).

PMF was only used in source apportionment and precipitation studies (Al-Momani, 1995). However, currently in addition to these branches, PMF is also utilized in wastewater (Soonthornnonda, et al., 2008), lake sediments (Comeroa et al., 2014), river sediment, and soil (Dong, et al., 2014) studies. The most important advantage of PMF compared to the other receptor models is that, it uses both sample concentration and user-provided uncertainty associated with the sample data to weight individual points. So, problematic data like the ones, which are below detection limits can be introduced into the model with the associated uncertainty adjusted to them to reduce their influence on the solution (Comero et al, 2009). Chemical species can be evaluated more effectively because of this (Munzur, 2008) without loss of data. In addition, non-negativity constraints help to reduce the rotational freedom in factor computations.

PMF solves the general receptor modeling problem using constrained, weighted, least-square minimization scheme, assuming that there is p sources contributing in the measured data, and linear combinations of the impacts from the p factors rises to the measured concentrations of the different species. It is a type of 2-dimentional factor analysis model as given below.

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \qquad \text{Equation 2-2}$$

In this equation, *i* is the number of samples and *j* is number of chemical species, and p is number of independent sources (factors). Xij, is the concentration of jth species on the ith day at a receptor, gik is the contribution of the kth factor on the ith day, fkj is the fraction of the kth factor that is allocated to species j, and eij is the residual for the jth species on the ith day.

PMF assumes that contributions (g_{ik}), and fractions (f_{kj}) are not negative, and that is the feature that makes is advantageous compared to conventional FA. In FA, source contributors can be negative, which is physically meaningless. In PMF modelling, the only known data is the concentration value (X_{ij}) and the goal is to find contributors (g_{ik}) and their fractions (f_{kj}), and Q value, which is the object function in the problem, will be minimized using by squares solution, as given below in equation 2-3.

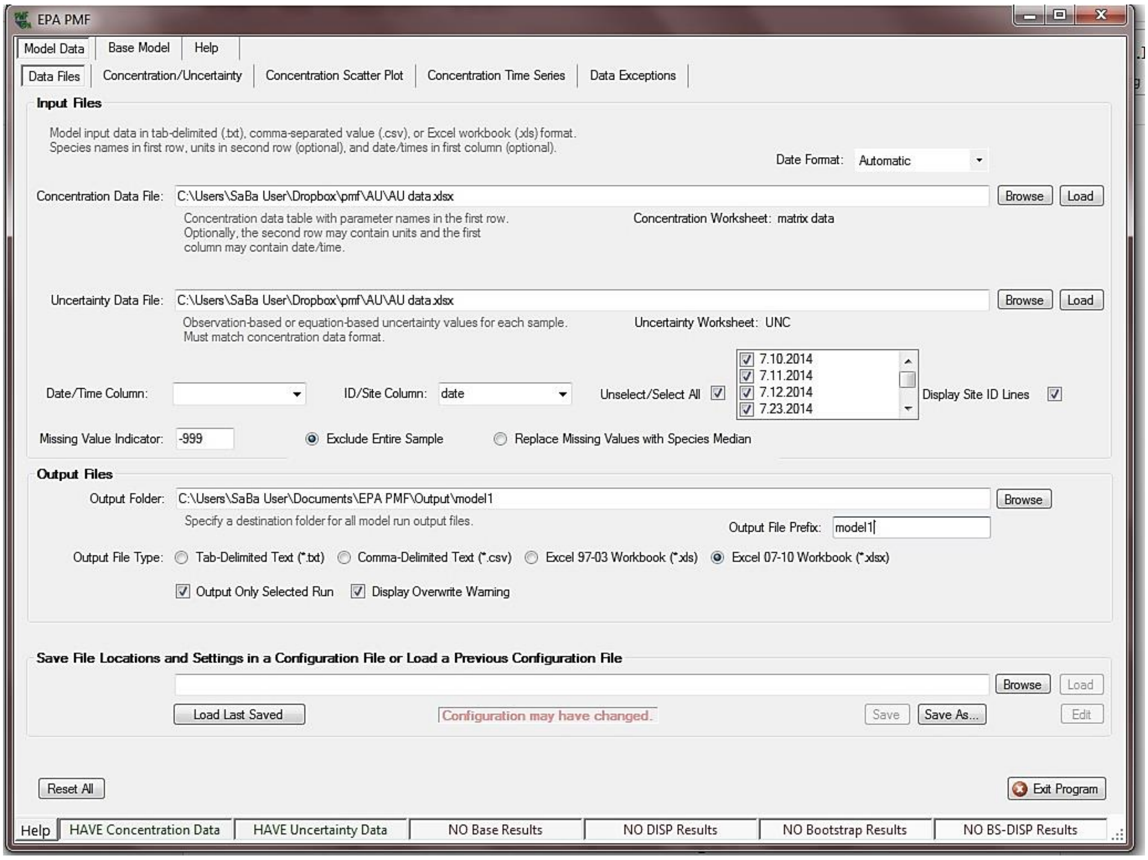
$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{X_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{S_{ij}}\right)^2 \qquad \text{Equation 2-3}$$

S_{ij} is the uncertainty in the j^{th} species for i^{th} day. If uncertainties are correctly defined, Q has to be equal to the number of data points (EPA, 2008).

PMF has been used world widely, in order to model the atmospheric aerosol samples. Ziad Ramadan (2000) identified the Sources of Phoenix Aerosol by PMF. Kim, et al, (2003) used it to identify sources of aerosols in Atlanta by collecting 662 fine particle samples. MuhayatunSantoso (2008) utilized PMF for sources identification of the atmospheric aerosol at urban and suburban sites in Indonesia. Kolker et al. (2013) modeled atmospheric fine particulate matter in coastal New England with PMF. In Turkey, Munzur (2008) used PMF for identify sources 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 the composition of the aerosols at northwestern of Turkey by positive matrix factor, Balcilar *et al.*, (2014) used it to define chemical composition of Eastern Black Sea aerosol.

Positive Matrix Factorization has some advantages over earlier multivariate receptor modeling tools. First of all, results of PMF are quantitative, whereas FA and PCA results are not. Factor loadings (which represents composition of particles emitted from a particular source) can take negative values. This is a problem because negative concentration value does not make sense. In PMF, factor loadings cannot be negative. Maybe the most important advantage of PMF over all other multivariate tools is that it can operate on data sets with missing data. This was a very serious problem in earlier multivariate statistical tools. In atmospheric trace element data sets, there are large amounts of missing data, due to very low concentrations of elements. In FA, for example, only the samples in which there is concentration value for all elements can be included in the analysis. This criterion generally leaves us with very few samples, because in any atmospheric data set some of the elements have below detection limit value in every sample. Methods to fill data in were developed, as elimination of most of the samples due to missing values does not make sense. However, artificially generated data is not as good as actually measured data. In PMF, contribution of each datum to model fit can be controlled by varying the uncertainty of that point. Thus, by increasing the uncertainty of missing data point to a very large value one can eliminate its contribution to fit without excluding whole sample from FA. Due to these advantages, PMF found very wide application in the field of source apportionment and became the most widely used receptor modeling tool in recent years.

EPA PMF 5.0 is used in this study. To prepare the data for PMF, 2 files should become ready, first the daily concentrations for each specie, and second the corresponding uncertainty for each data. Since PMF does not accept blank data, the missing data was replaced by arithmetic mean, median, or geometric mean value of that specie and the corresponding uncertainty for that data should be 4 times of the new value, as explained by Reff et al. (2007). If the concentration of the specie in some days, was below detection limit (DL), it can be replaced with half of the detection limit value (DL/2) and corresponding uncertainties can be assigned as five sixths of the detection limit values (5/6*DL). Figure 2- 2 shows the main screen of the software, in which the data and uncertainty files should be uploaded.



Model input data in tab-delimited (.txt), comma-separated value (.csv), or Excel workbook (.xls) format.
Species names in first row, units in second row (optional), and date/times in first column (optional).

Date Format: Automatic

Concentration Data File: C:\Users\SaBa User\Dropbox\pmf\AU\AU data.xlsx

Concentration data table with parameter names in the first row. Optionally, the second row may contain units and the first column may contain date/time.

Concentration Worksheet: matrix data

Uncertainty Data File: C:\Users\SaBa User\Dropbox\pmf\AU\AU data.xlsx

Observation-based or equation-based uncertainty values for each sample. Must match concentration data format.

Uncertainty Worksheet: UNC

Date/Time Column:

ID/Site Column: date

Unselect/Select All ☑

☑ 7.10.2014
☑ 7.11.2014
☑ 7.12.2014
☑ 7.23.2014

Display Site ID Lines ☑

Missing Value Indicator: -999

● Exclude Entire Sample ○ Replace Missing Values with Species Median

Output Folder: C:\Users\SaBa User\Documents\EPA PMF\Output\model1

Specify a destination folder for all model run output files.

Output File Prefix: model1

Output File Type: ○ Tab-Delimited Text (*.txt) ○ Comma-Delimited Text (*.csv) ○ Excel 97-03 Workbook (*.xls) ● Excel 07-10 Workbook (*.xlsx)

☑ Output Only Selected Run ☑ Display Overwrite Warning

Configuration may have changed.

Help | HAVE Concentration Data | HAVE Uncertainty Data | NO Base Results | NO DISP Results | NO Bootstrap Results | NO BS-DISP Results

Figure 2- 2 Interface of PMF 5.0

2.1.8 National and International Ambient Air Quality Standards

National and international air quality standards are provided to maintain and protect the environment and public health. Logically, the regulatory standards and limits vary according to the region, exposure time, and average value (daily and annually). We used Air Quality Assessment and Monitoring Regulation of Turkey (AQAMR) and EU standards in this study.

AQAMR has been revised 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

PM is not divided to PM10 and PM2.5 in AQAMR, and only the daily and annual average of total PM has been given. 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).

Table 2- 5 Air Quality Standards of EU

Pollutant	Concentration	Averaging Period	Permitted exceedances for each year
PM 2.5	25 µg/m3	1 year	n/a
PM 10	50 µg/m3	24 hours	35
	40 µg/m3	1 year	n/a
Pb	0.5 µg/m3	1 year	n/a
As	6 ng/ m3	1 year	n/a
Cd	5 ng/ m3	1 year	n/a
Ni	20 ng/ m3	1 year	n/a

The most noticeable difference between these standards and AQAMR is PM2.5. These standards include PM2.5 separately, as it given in Table 2-6.

Table 2- 6 Comparison of PM2.5 standard of WHO, EU and EPA

PM2.5	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

Ankara is the capital and second populous city in Turkey with 5,346,518 residents based on the results of 2016 census (Turkish Statistical Institute, 2016). The city is located at 32.53 E longitude and 39.57 N latitude, has a surface area of 26.897 km^2 and is 890 m above sea level. Ankara is under the effect of continental climate and average temperature of the city is 11.9 C (MGM, 2014). In this study, atmospheric aerosol samples were collected at two different stations in Ankara.

First station was at Middle East Technical University campus, behind the Environmental Engineering department. The station was far from the populated and polluted areas of the city and classified as a “suburban station”. The closest road to the sampling location is Anadolu Boulevard, which is 1.29 km to the east of the station. Other sources of traffic emissions, namely, Eskişehir Highway and Bilkent Boulevard are located at 2.42 km to the north and 1.49 km to the west of METU station, respectively. Location of the METU station and traffic sources affecting pollutant concentrations in the station is shown in Figure 3-1.a.

METU Campus is approximately 10 km away from the city center. Population in the campus is 15,000 during daytime. The main source of atmospheric particles, during daytime is traffic emissions. Population decreases to 2,000-3,000 at night. During that time emissions from heating facilities, both in and around the campus dominating source of atmospheric levels of pollutants in the campus. A picture of the station is depicted in Figure 3-1.b.

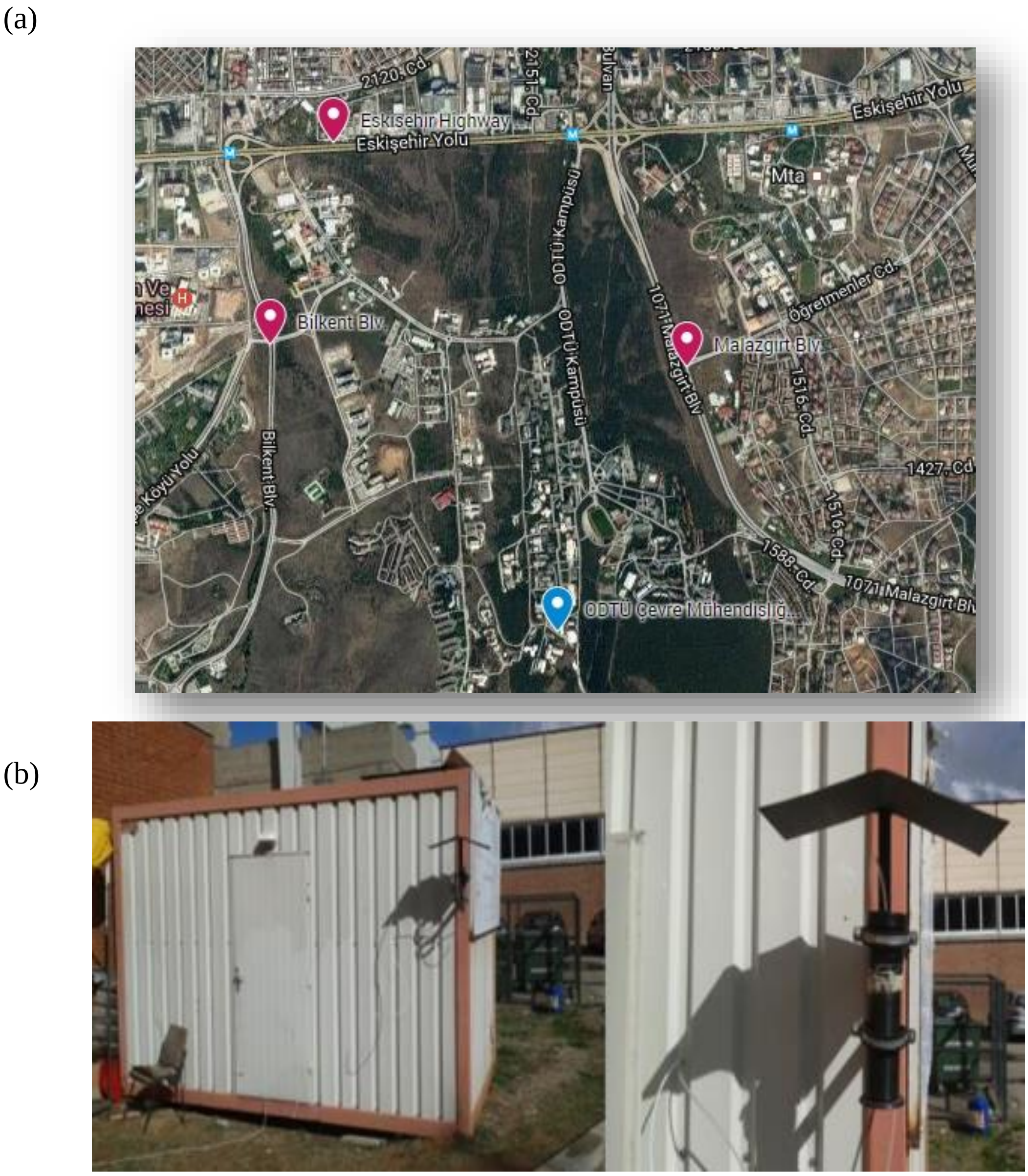


Figure 3- 1 METU Sampling Site

Second station was located at research fields of the Ankara University, Agriculture department, which is located close to the city center (sampling point is approximately 4 km to the West of Kızılay district, which is considered to be the center of the city). The sampling point is surrounded by residential areas and busy roads. The university has approximately 64,500 students and the pollution sources are mostly due to traffic and houses. AU Campus is surrounded by 4 roads with high traffic density. The closest road to the sampling location is İrfan Baştuğ Cd. at 50 meter east of it. Other roads are Fatih road (150 meter from the sampling point), and Turgut Özal Blv. which is 276 meter away from the station. With these characteristics, the station is classified as urban station. The map that shows the AU station and a picture of the station are given in **Error! Reference source not found.** Fihure 3-2. a and b.

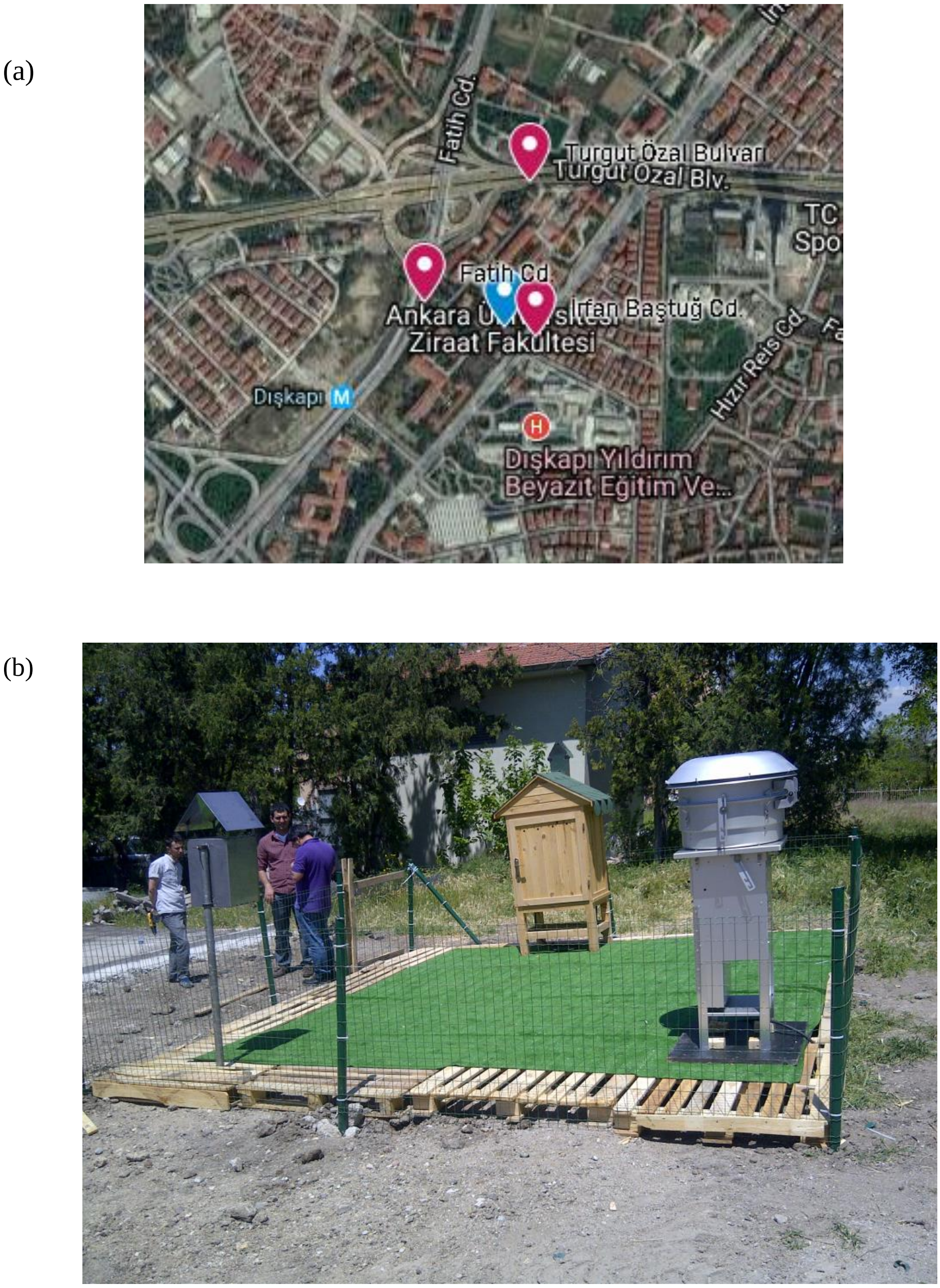


Figure 3- 2. AU Sampling Site

3.1.2 Sampling

Daily fine fraction ($PM_{2.5}$) samples were collected between July 8, 2014 and August 18, 2015 at Suburban station (METU), and from July 10, 2014 to August 30, 2015 at the Urban station (AU). A total of 248 and 263 $PM_{2.5}$ samples were collected at suburban and urban stations, respectively. The sampling was daily and the only interruption was for changing the filters each day.

Aerosol samples were collected using a 'GENT' stacked filter unit (SFU). Schematic diagram of the SFU are given in Figure 3- 3, (Vienna, Atomic and Agency, 1994).

The components of the sampler is depicted in Figure 3-4. The unit consists of a pre-impactor, which has a 50% collection efficiency at 10 µm equivalent aerodynamic diameter (EAD) at a flow rate of 16.7 L min^{-1}, a stacked filter cassette, which is fitted to the end of the pre-impactor, and finally a pump, which is fitted with mass flow controller, and electronics that show the flow rate, total volume of the air that is passed and sampling duration (in minutes or hours).

The filter holder is a 47 mm diameter, open face, two-stage, stacked filter cassette, which can hold two filters in series, without touching each other (NILU, model 9634). The first stage is loaded with alpha etched polycarbonate filter with pore size of 8 µm. The second stage is also loaded with polycarbonate filter, but with pore size of 0.4 µm. It is demonstrated in the literature, that if air pulled through the system with a flow rate of 16.7 L min^{-1}, particles smaller than 2.5 µm ($PM_{2.5}$) are not captured in the first filter and held on the second filter. However, particles with diameter > 2.5 µm are stopped in the first filter.

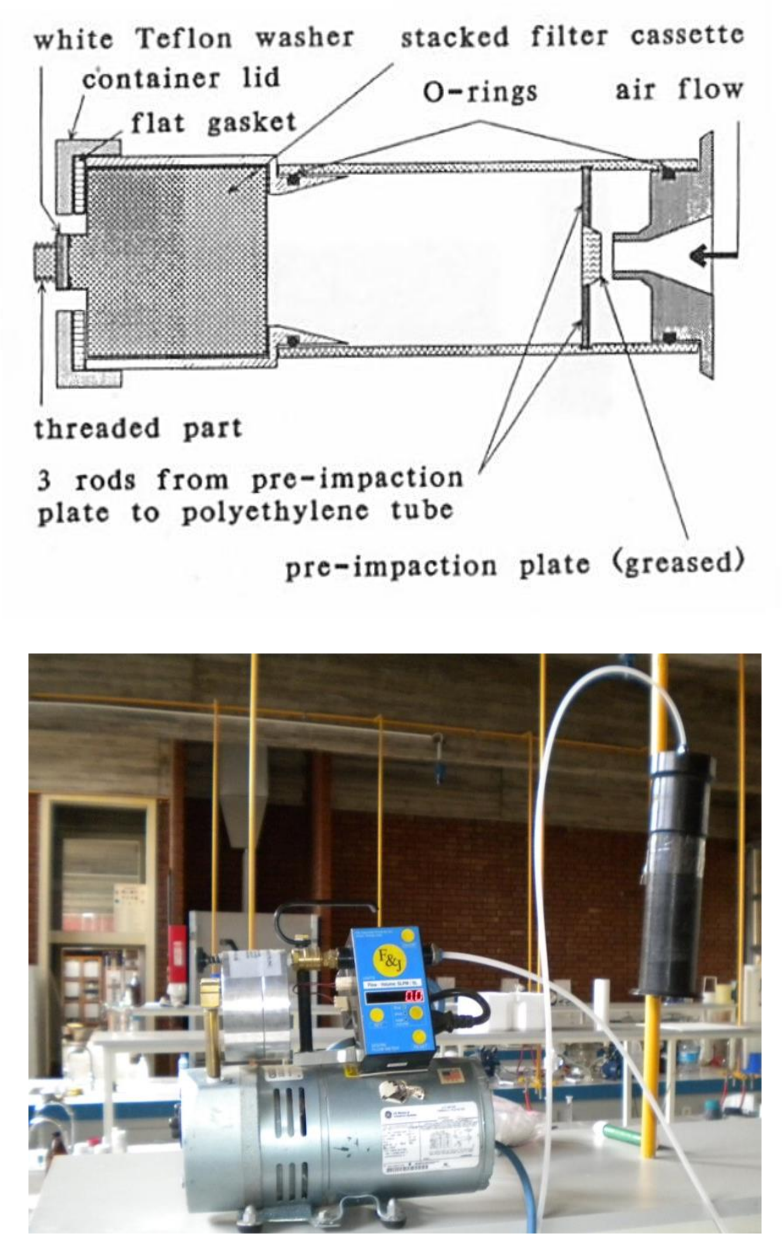


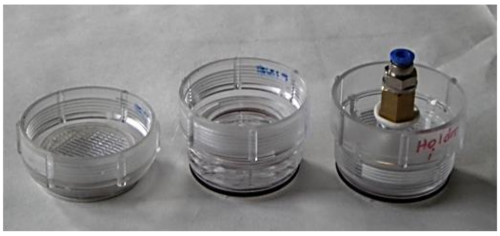
Figure 3- 3 Schematic view and a picture of the SFU Unit used in this study

Preimpactor
(bottom view)

Preimpactor
(filter cassette loaded)

Filter cassette
(ready to use)

Nuclepore filters



Filter cassette
(components)

Figure 3- 4 components of SFU

In SFU, this filter cassette is installed directly to pre-impactor and air is pulled at a flow rate of 16.7 L min^{-1}. During its regular operation at 16.7 L min^{-1} particles larger than 10 µm in dieter is stopped by the pre-impactor and cannot reach to filters. Among the ones that is allowed by the pre-impactor, the ones with diameter > 2.5 µm is held on the first filter and the ones with diameters smaller than 2.5 µm are held on the second filter. In this way, it is possible to collect both $PM_{2.5}$ and PM_{10} particles with SFU (please note that when particle masses collected on the first and second filters are summed result is the PM_{10} particle mass). Dimensions of the intake unit, which includes pre-impactor and filter cassette is 40 cm in length and 10 cm in diameter.

Filters used in SFU are made of polycarbonate and etched with bombardment of alpha particles. These etched points on the filters are then converted into pores by a chemical treatment. A view of a Nuclepore filter under electron microscope is depicted in Figure 3-5.

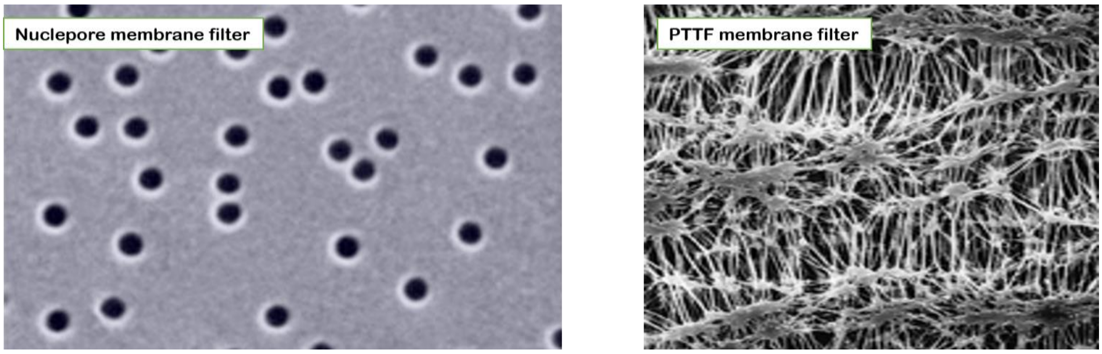


Figure 3- 5 Electron microscope pictures of a Nuclepore and Teflon filters

As can be seen in the figure, these filters are characterized by relatively uniform distribution of pores having exactly the same diameter. In all other membrane filters, pore size refers to an average diameter of pores, but in Nuclepore filters, it indicates the diameter of every single pore on the filter. With this characteristic, Nuclepore filters can separate particles into two size groups, but other membrane filters cannot perform this (Vienna, Atomic and Agency, 1994). A picture of the Nuclepore filters is depicted in Figure 3-6.

Figure 3- 6 Whatman Nuclepore track-etched polycarbonate filters

SFU, due to its low cost and high collection efficiency, is widely used to collect atmospheric particles in two size groups (Munzur, 2008, Yatin *et al.*, 2000, Godoy *et al.*, 2009, Godoy *et al.*, 2009). Extensive studies on size separation characteristics of the SFU demonstrated that actual cut point for coarse and fine particles is 2.2 µm, rather than 2.5 µm ((Hopke et al., 2017, Viana M. et al., 2008). In this work, we analyzed only fine fraction samples. Only few coarse samples (particles with diameter > 2.2 µm) were analyzed to get a feeling of the composition of coarse particles. High cost of the ICPMS analysis was the main reason for not analyzing coarse fraction filters. Coarse fraction samples dominated by soil particles in Ankara and soil and sea salt particles in coastal regions. It does not include any information about anthropogenic particles and their sources. Since the objective of this study was to generate information about sources of pollution-derived particles, it was decided that knowing how much soil particles exists in atmosphere does not worth the money that would be spent for digestion and analysis of coarse fraction samples.

3.2 Local Meteorology

3.2.1 Temporal variation of Temperature, wind speed and Rainfall

Meteorological features of the study area have profound influence on temporal and spatial variation in concentrations of trace elements and other pollutants, because it determines horizontal and vertical ventilation mechanisms in the air shed. General meteorological features of Ankara will be briefly discussed in this section. Variation of meteorological parameters, such as, temperature, wind speed relative humidity and mixing height, during our sampling period are also be compared with long term variations in those parameters. Meteorological data during sampling period was obtained from Etimesgut meteorological station. However, long-term meteorological data was generated in Keçiören meteorological station. The General directorate of Meteorology operates both stations. Long-term data for temperature, wind speed, wind direction, relative humidity and rainfall cover a period between 1950 and 2015, whereas data for mixing height covers a period between 1995 and 2015.

The climate in Ankara is classified as "Cold Semi-Arid" climate in Koppen – Geiger classification (Peel, Finlayson and McMahon, 2006). Summer in Ankara is mild. Temperatures do not climb to extreme levels frequently. As in all locations with semi-arid climate, temperature difference between daytime and night-time is fairly large. Annual average summer temperatures between 1950 and 2015 varied between 15°C and 19°C with a mean value of 16.8°C. The highest temperature recorded in the city is +41°C (recorded in July 27, 2012).

With its typical semi-arid climate, Ankara can be extremely cold in winter. Temperatures below 10°C are frequently observed in this season. As can be seen in Figure 3- 7.a , Winter temperatures, in 1950 – 2015 period, varied between 4.9°C and 10.3°C with an average value of 7.3°C. The coldest temperature recorded since 1926 is -25°C (recorded in January 5, 1942). Seasonal variation of temperature in Ankara between 1950 and 2015 and during our sampling are given in the Figure 3- 7.b.

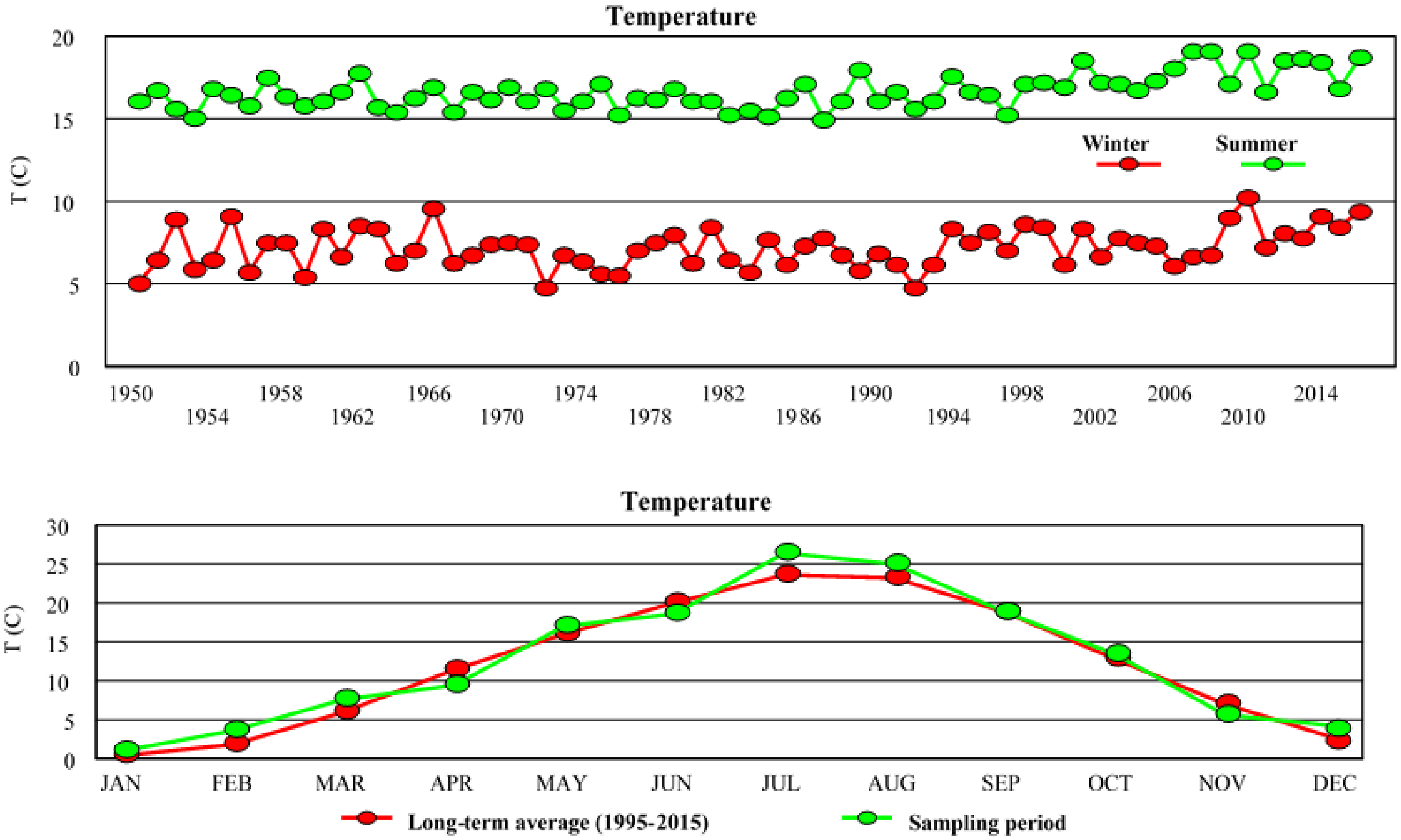


Figure 3- 7 Temporal variation of temperature in Ankara (a) Long term trends between 1950 and 2015, (b) seasonal variation

Monthly average temperatures, between 1950 and 2015 vary between 2.2 °C in January and 24.4 °C in July. Monthly average temperatures calculated for our sampling period is not significantly different from long-term monthly average temperatures. Annual average temperatures, both in summer and winter seasons, show a gradual increase after 1994. There may be several reasons for this trend. However, discussion of long-term trends in temperature and other meteorological parameters is beyond the scope of this manuscript.

Long-term and monthly average variations in wind speed, which is the key parameter for horizontal ventilation of the air shed, is depicted in Figure 3-8. Annual average wind speed showed interesting variation over years. It decreased from 3.6 in 1954 to 1.5 in 1984 and then increased to approximately 3.0 in 2004. Demographic changes around meteorological stations can generate statistically significant variations in meteorological parameters, particularly the wind speed. We do not know and did not investigate the reason, because, as pointed before long-term variation in meteorological parameters is beyond the scope of this work. Nevertheless, the variation is interesting and must be investigated.

Ankara is characterized by low wind speed. Average WS between 1950 and 2016 is 2.1 m s^{-1} in winter and 2.4 m s^{-1} in summer. These values are not significantly different from average wind speed calculated during our sampling period which is 2.3 m s^{-1}. It is noteworthy that wind speed values shown in the figure are close to meteorological “CALM” conditions, which represent WS values lower than 1.0 m s^{-1}. Such low WS indicates limited horizontal ventilation in Ankara atmosphere and strong potential for accumulation of pollutants over the city. Similarity in WS measured during sampling period with that measured between 1950 – 2015 periods can also be seen in Figure 3-8, where monthly average WS is plotted using both long term and sampling-period data. From the figure, it is also clear that WS does not show a substantial variation from one month to another.

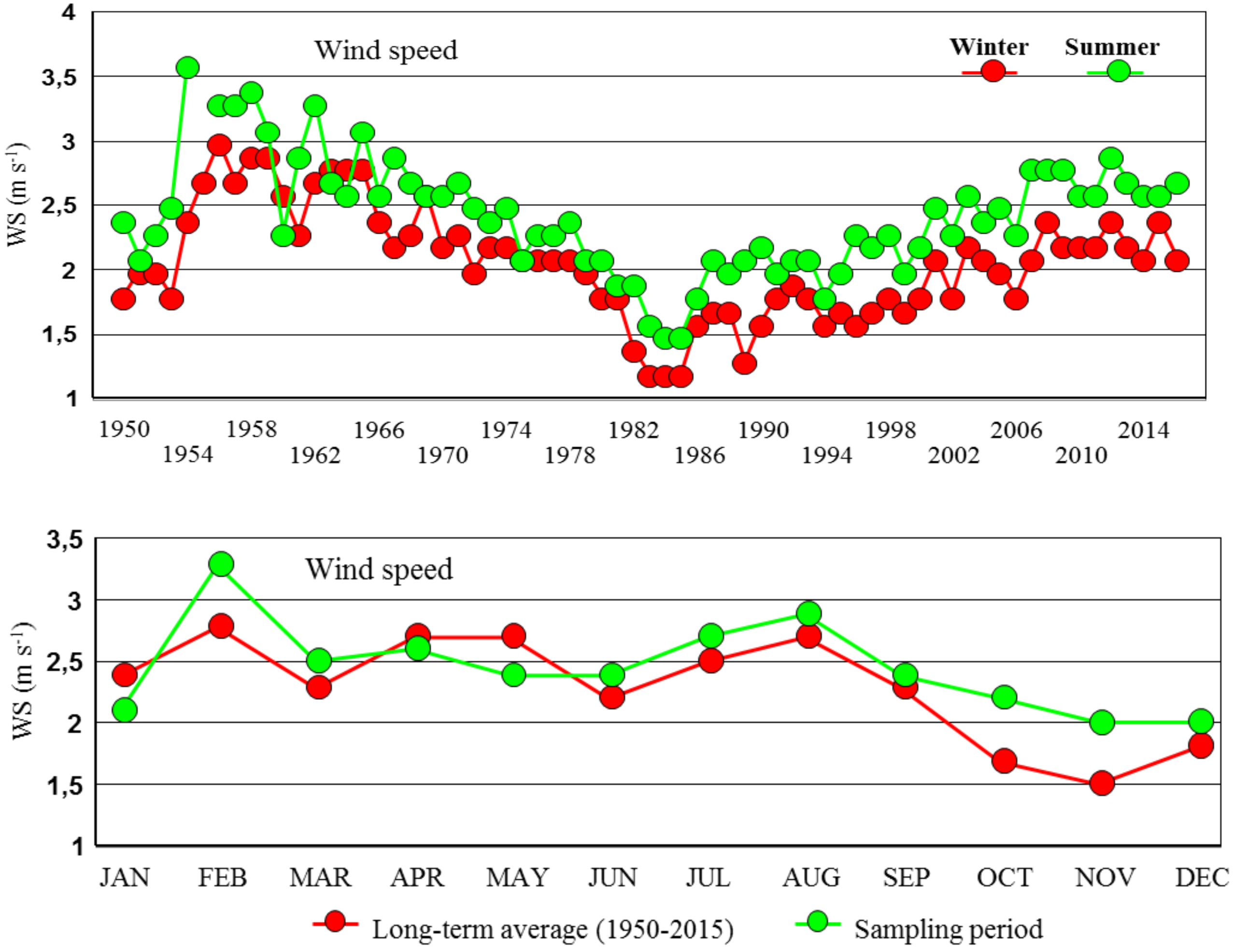


Figure 3- 8 Temporal variation of wind speed in Ankara. (a) Long term annual variation between 1950 and 2015, (b) seasonal variation

Monthly average rainfall and relative humidity are given in Figure 3-9 for both Long-term (1950 – 2015) and sampling period.

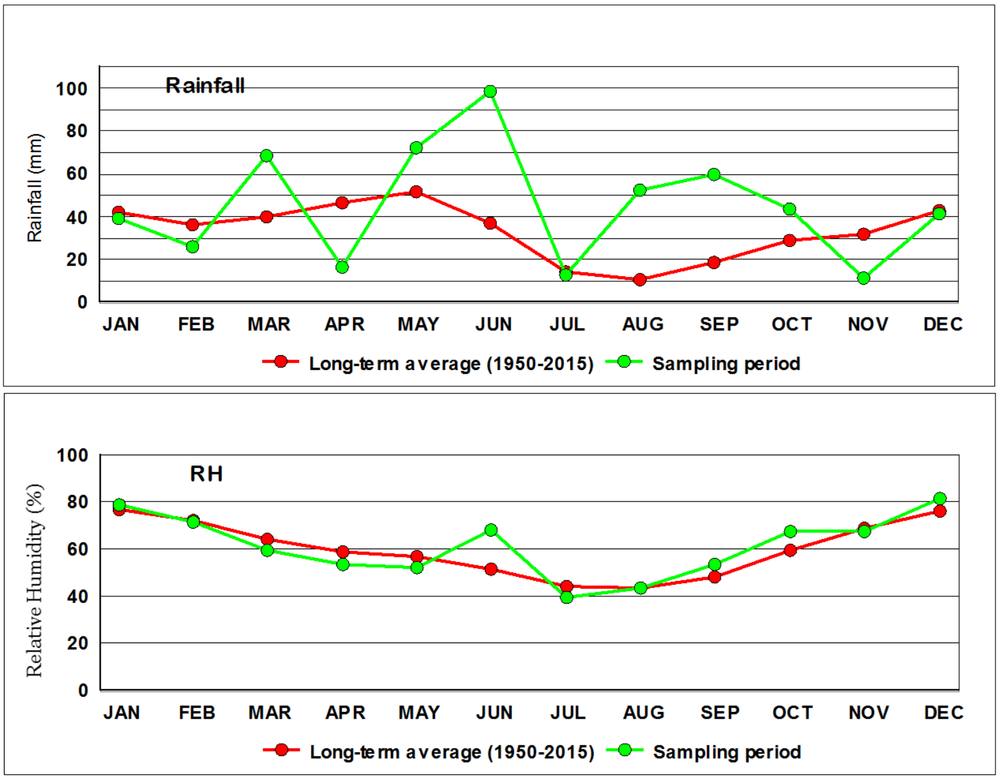


Figure 3- 9 Seasonal variation of rainfall and relative humidity in Ankara's atmosphere

Relative humidity measured during our sampling period is similar to long-term humidity data, except for the June, in which we observe higher humidity in our sampling period than usual. Relative humidity in Ankara changes between 80% in January and 40% in July. Relatively low humidity, particularly during summer months is one of the reasons why summers are pleasant in semi-arid climate.

Ankara is one of the driest regions in Anatolia. Long term average (1950 – 2015) rainfall is only 402 mm. Anatolia is surrounded by the Pontic Mountains at north and Toros Mountains at south, which prevents humid air coming from Black Sea and Mediterranean to penetrate central Anatolia. This is the main reason for small annual rainfall in most cities located in the central Anatolia. Long term monthly rainfall varies between 40 mm in May and approximately 10 mm in August.

Annual rainfall measured during our sampling period is 527 mm, which is higher than long-term annual rainfall between 1950 and 2015, (402 mm). Monthly average rainfall during sampling period, which is depicted in Figure 3-9 is similar to long term averages in January, February, May, July, October and December. However, monthly averages for sampling period are higher than long term averages for March, June, August, September and November and lower than long-term average for April. The figure suggests that our sampling period is not a typical year in terms of rainfall.

The wind rose in Ankara prepared by using wind data between 1995 and 2015 is given in

Figure 3- 10 3-10. Wind rose is overlaid onto the map of Ankara to highlight districts that can affect concentrations of elements in both stations. Dominant wind direction is from NE and ENE. These two sectors accounts for approximately 45% of the flow frequency. The third sector, which also contributes to the wind pattern is the WSW sector. Winds in this sector accounts for approximately 15% of total wind flow.

The wind frequency distribution suggests that Balgat, Dikmen and Çankaya districts are the regions that can potentially contribute to trace element concentrations measured in the METU station. Areas to the WSW of the METU station, including Umitköy, Bilkent can also contribute to elemental concentrations measured at the METU station, but these source areas are not as densely populates as the source areas located to the NE of the station.

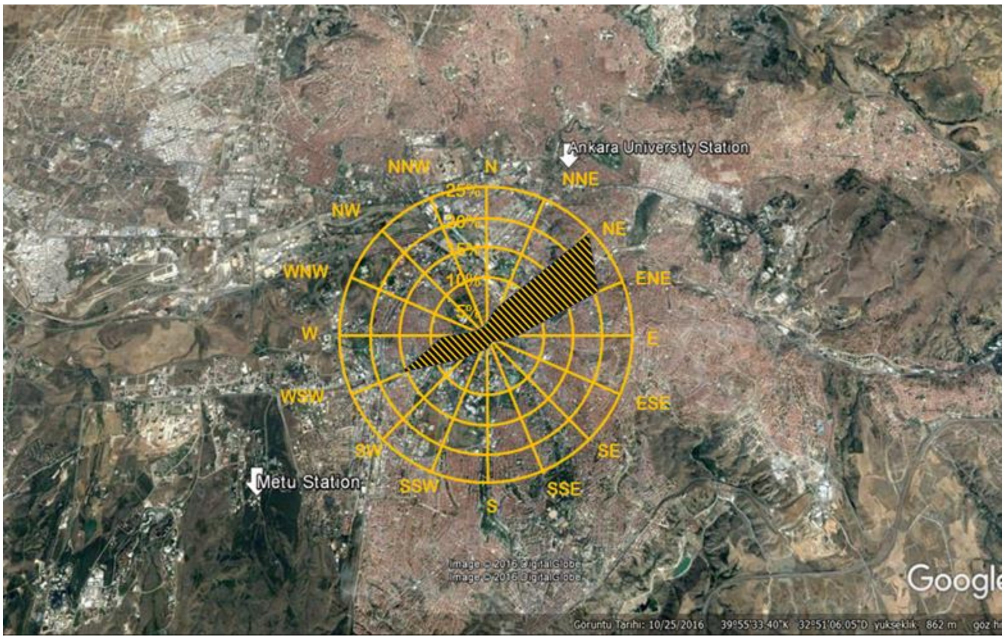


Figure 3- 10 Wind rose for Ankara prepeared using wind data between 1994 and 2015

Main source area located to NE of the AU station is the Keçiören district. Keçiören is an important source area because (1) it is densely populated and (2) it is a district with high pollutant emissions due to burning poor quality coal for space heating at least in some parts of the district. Most crowded parts of the city, including Ulus, Sıhhıye and Tandoğan are all located in the WSW sector. These regions, with their high emissions and high frequency of wind flow from WSW sector can significantly contribute to measured element concentrations at AU station. The highest insolation in Ankara is observed in May (1228 Wm-2), while the lowest is observed in January (614 Wm-2).

3.2.2 Temporal variation of Mixing Height and Ventilation Coefficient

Mixing height is a measure of vertical ventilation of the air shed. It defines the volume in which pollutants are dispersed. High mixing heights indicate large dilution volume and hence, lower concentrations of pollutants whereas low mixing height indicate a small volume in which pollutants can be dispersed which results in high concentrations of pollutants. However, it should be noted that mixing height is an important, but one of the parameters involved in ventilation process. Other parameters like wind speed and emission intensity also plays role in levels of pollutants in urban atmosphere.

Long-term annual average and monthly average variations in mixing height are given in Figure 3-11.a and b, respectively. Summer average mixing heights between 1995 and 2015 vary between 1224 m and 1660 m with an average value of 1462 m. winter mixing heights are consistently lower than summer mixing heights, as expected. In winter, mixing height in Ankara changes between 675 m and 1288 m with an average of 938 m. This clearly demonstrate that concentrations of pollutants with equal emission intensity in summer and winter seasons is expected to be higher in winter. Monthly average mixing heights, which were calculated for sampling period and for the period between 1995 and 2015, are shown in Figure 3-11.b. Mixing height is the highest in August and September and the lowest in January.

The difference is approximately a factor of three. The mixing heights calculated for the study period is not significantly different from monthly variation of mixing height between 1995 and 2015.

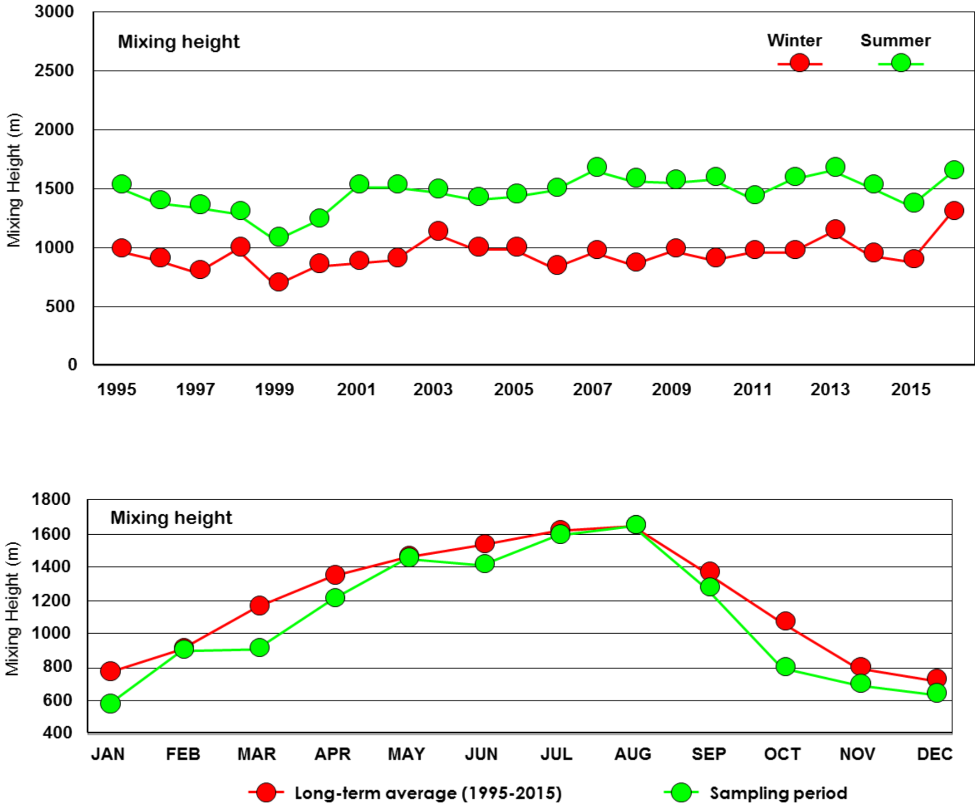


Figure 3- 11 Temporal variation of mixing height at Ankara. (a) Long term, annual variation from 1995to 2015, (b) Seasonal variation between 1995, 2015 and during our sampling period

Diurnal variation in mixing height in Ankara was studied by Genc et al (2010) and given in Figure 3-12 for summer and winter seasons between 1995 and 2005. The pattern depicted in this figure is typical for diurnal variation of mixing height, not only in Ankara, but also anywhere around the world. Mixing height is deeper during noontime and shallow at night.

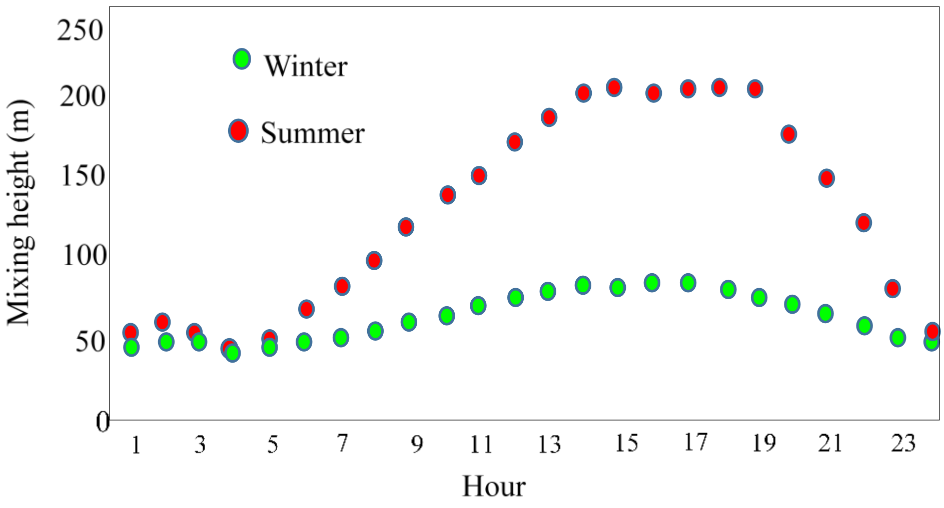


Figure 3- 12 Diurnal variation of mixing height at Ankara (Genc *et al*, 2010)

Nighttime mixing height (between 23:00 and 06:00) is the same in summer and winter seasons (approximately 500 m), but daytime mixing heights are different. During summer noontime, mixing height can go up to 2000 m, but it is approximately but it is only 800 m in the winter period.

In conclusion, a summary of the data obtained from General Directorate of Meteorology on meteorological parameters discussed in this chapter for Ankara during our studying period are presented in Table 3- 1.

Table 3- 1 Summary of Meteorological parameters during sampling period

Parameters		Summer	Winter	Annual
Temperature (ºC)	Mean	20.8	8.4	14.3
	min	2.1	-8.8	-8.8
	Max	29.9	27.9	29.9
Wind speed (m/s)	Mean	2.6	2.1	2.3
	min	1.2	0.5	0.5
	Max	4.8	7.2	7.2
Mixing Height (m)	Mean	2108.0	1069.2	1563.5
	min	508.9	81.9	152.7
	Max	3232.3	3603.5	2543.6
Ventilation coefficient (m2/s)	Mean	5391.4	2325.6	3784.3
	min	1379.9	212.4	224.3
	Max	14934.3	12767.3	12380.4
Relative Humidity (%)	Mean	55.7	78.1	67.4
	min	34.1	34.6	34.1
	Max	89.6	98.8	98.8

3.3 Analytical Procedure

3.3.1 Gravimetric Analysis

Before sampling, the filters needed to go through a conditioning process. First, all coarse and fine filters were kept in the Clean Room of the Department of Environmental Engineering, METU, to lose their humidity. For this purpose, filters were conditioned in a constant temperature (25 ± 5)ºC and constant humidity (26 ± 4)% chamber for at least 24 hours. After conditioning, they were weighted using a Sartorius model MC-5 microbalance, which has a 0.001 mg sensitivity. Nuclepore filters with their polycarbonate structure are easily charged with static electricity, which can cause difficulty in weighting procedure (the balance does not stabilize and reach to a constant weight easily). Static electricity is avoided using a deionizer consisting an alpha source. An alpha source after sampling, exposed filters were brought to the clean room again, they were conditioned one more time in order to remove humidity that formed during sampling and re-weighted. Particle mass was determined from the difference between weights before and after sampling.

All sample processing was performed in a homemade clean area under twice HEPA filtered air. The clean area consisted of two rooms without any windows, namely the inner and outer rooms. The two rooms are connected with a door. There are four clean-room HEPA filter units in the inner clean room. The air is pulled from outside the room by one of the clean room units. It is passed through the HEPA filter (with 0.000000001% removal efficiency for particles with diameters 0.1 μm and larger) and sent into the room. In the clean room this once heap-filtered air is passed through the HEPA filters (with the same particle removal efficiency) one more time by the other three clean room units. All sample processing was performed under small clean room units where the air is twice HEPA-filtered.

Since there is no window or any other outlet in the inner clean room, the air, which is pulled from outside by the large clean room unit can only leak out to the outer room from under the door. Since this mechanism generates a pressure difference with higher p in the inner room and lower p in the outer room. No unfiltered air can penetrate to inner room. Similarly, the air that enters to outer room from the inner room can only leaks out from under the door to corridor outside the the clean area. This ΔP also prevents the leakage of air from outside the clean area to outer room. We measure particle number concentrations at different locations in the clean area for several days. When all the clean area units are operated particle number concentration under inner clean room units (in twice HEPA-filtered air) was 1.7 ± 1.3 particles per liter. When all clean room units were shut down (and after letting the air in the room to reach a steady state for 24 hours), particle number concentration was 44 particles per liter of air. A picture of the inner clean room is depicted in Figure 3-13.

Figure 3- 13 Inner clean area and some of the clean room units.

3.3.2 Trace Element Analysis

Trace elements were measured by inductively coupled plasma emission spectrometry with a mass spectrometric detector (ICPMS) at Anadolu University, department of Environmental Engineering, after sample dissolution in a microwave digestion system (Milestone 900, ETHOS D, US) with a mixture of HNO_3 – HF.

The instrument was calibrated for measurement of approximately 65 elements, including Na, Mg, Al, K, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, P, S, Ca, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th and U. However, all of them were not routinely detected in all samples. Number of missing points for each element are discussed later in the manuscript.

3.3.2.1 Sample dissolution

Closed vessel microwave oven, including ten PTFE (polytetrafluoroethylene) digestion vessels (Milestone 900, ETHOS D, US), was used to digest collected samples for subsequent ICP-MS analysis. For this, filters were first put in the PTFE vessels and 5.0 mL ultra-pure HNO3 (Merc-suprapure) and 1.1 ml HF (Merc-suprapure) were added. Since the microwave consists of ten vessels, nine samples and one reagent blank filters were digested in each batch. The program used in this study for digestion of Polycarbonate has been developed by our Air Research Group and used to digest aerosol samples since 1993 (Tokgöz, 2013). It consists of 3 steps and takes 29 minutes to get completed. The features of the digestion program are given in Table 3- 2.

Table 3- 2 Program used in ETHOS 900 MW

Step	Temperature (ºC)	Time (min)	Power (%)
1	100	10	40%
2	150	10	80%
3	190	9	90%

After 29 minutes the microwave rotor along with the 10 vessels were taken and placed into the tap water for at least 45 minutes to cool down to the room temperature, because opening them immediately after the microwave digestion may lead to loss of some species and acid, and also there is a possibility of blowout due to the high pressure and temperature. After the cooling time, vessels were opened under the fume hood and the mixture was transferred to the PTFE beakers. The HF component should be removed in this step since injecting HF to ICP can etch the silica-based sampling tube of ICP torch and corrode the Ni cone interface (Tokgöz, 2013). In order to evaporate the HF, the beakers were placed on the hot plate at 80ºC under the fume hood, till the white smoke from the sample turned to yellow, and just one drop of the analyte remained in the container. At that point, 5 ml of pure Nitric Acid was added to the beaker and evaporation was repeated. After the second evaporation step, PTFE vessels was removed from the hot plate and kept in the room with closed lid to cool down to the room temperature. Then the residue in the beaker was diluted to 50 ml, with a 1% ultrapure HNO3 solution. Finally, the solutions were decanted to 15 ml falcons tubes and sent for ICP-MS analysis.

3.3.2.2 ICPMS analysis

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- 3. (Celik, 2014).

Table 3- 3 The operating conditions of ICP MS

a) Instrumental Parameters	
RF power (kW)	1350 watts
Argon gas flow (L/min)	
• Plasma	12
• Auxilary	1.2
• Nebulizer	0.99
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 standard
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)

3.4 Quality Assurance and Quality Control

3.4.1 Blanks

In aerosol studies, normally two type of blanks are getting used, namely laboratory blank and field blank. Since the previous studies done by our group (Celik 2014, Tokgöz 2013, Ozturk, 2009) show approximately no considerable difference between the concentration of elements measured in laboratory and field blanks, in this study only laboratory blanks are used. In each digestion set of filters, which contains 10 filters, one laboratory blank has been digested along with each nine samples. The preparation of the blank filters and their digestion were done in the exact same way as the sample filters. The results for the blanks show similar values, as expected.

In this study, quality assurance was obtained by controlling the flow rate for pump every week. As stated before, the required flow rate for low volume air sampling studies is 16.7 L/min. 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 3-14. Here, 2 pumps that used in sampling at both stations are given.

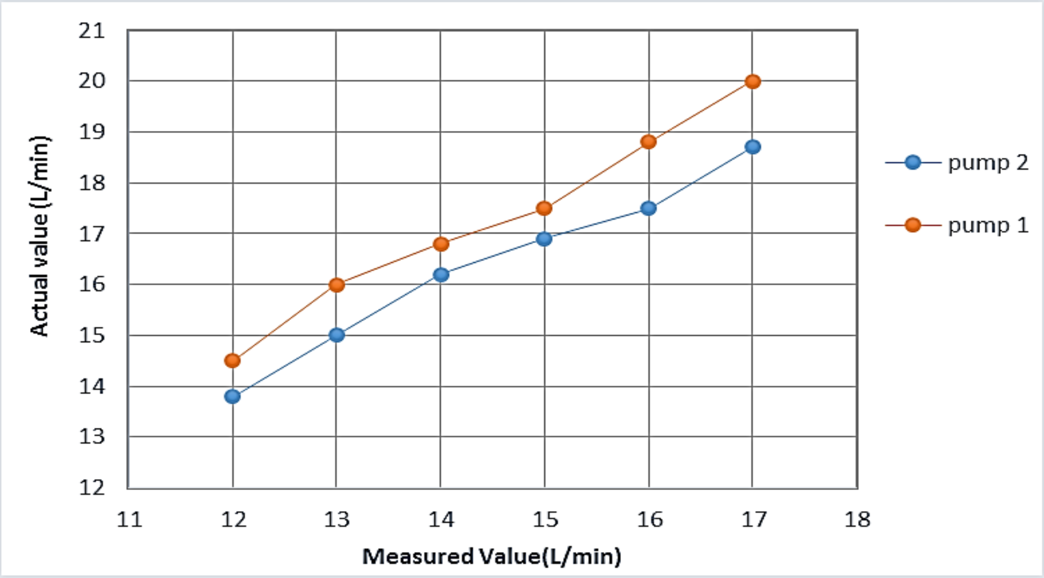


Figure 3- 14 The calibration graphs of Pump 1 and Pump 2

3.4.2 Detection limits

For calculating the detection limits since all the procedures, elements, and devices were the same as the recent study performed in our air group by Celik, 2014, same produced data have been used. In that study, detection limits of each species were calculated by having 3x of 10 replicates of the field blank concentrations. The calculated values are summarized in Table 3- 4.

Table 3- 4 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	Lu	<0.001
Co	0.013	Ta	0.006
Ni	0.215	W	0.014
Cu	0.039	Pt	0.003
Zn	1.336	Au	0.039
Ge	0.019	Hg	0.094
As	0.027	Tl	<0.001
Se	<0.001	Pb	0.032
Rb	0.007	Bi	0.002
Sr	0.099	U	0.002
Mo	0.016	Sn	0.018
Cd	0.010		

CHAPTER 4

RESULTS AND DISCUSSION

4.1 General Features of Data Set

4.1.1 Data

Sixty-five major, minor and trace elements were measured in fine fraction of the filters were collected at two stations in Ankara. Summary statistics of data generated in both stations are given in Table 4- 1 and Table 4- , respectively.

These statistical data include number of concentration values, mean, standard deviation, median, and geometric mean, minimum, maximum and number of missing days for each element measured in $PM_{2.5}$ fraction samples. It is observable that most of the data are distributed log normally or follow other right skewed distribution, as it will be discussed in more detail in the following sections of the thesis. Therefore, data is best represented by geometric median and median values of elemental concentrations, and arithmetic mean value is not a proper representation of measured concentrations. It is noticeable that geometric mean and median values are not very different from each other for most of elements; however, arithmetic mean value is approximately factor of two higher than these two values. Arithmetic mean values are included in the table to facilitate comparison of these values with corresponding data reported in literature, because arithmetic mean is still commonly used mode of data reporting in literature. Moreover, the minimum and maximum values are presented to demonstrate the variation range for each measured element.

4.1.1.1 Ankara University Station

In the first station, which is located at Ankara University, representing the urban air pollution, the mean value for each elements concentration measured in fine fraction of the particles ranges from 0.022 ng m^{-3} for Rh to 1795 ng m^{-3} for S. As it is expected from set of data, which is following log normal or any other right skewed distributions, the standard deviation values are mostly high, higher than the mean concentrations.

This observation is expected, because in such right-skewed distributions few abnormally high concentration values of elements, which highly affect both standard deviation and mean concentration values, are real and not outliers and thus cannot be excluded from data sets. Moreover, most of elements has positive right skew, having the higher mean concentration then the median value, which is going to be discussed further in this manuscript in next sections.

Frequency of detected concentrations varied between 20% for Nb and 99% for S. Thirty-six elements including Hg, Nb, Hf, Gd, Rh, Tb, Dy, Tm, Ho, W, Th, Ir, Sm, Tl, Eu, Lu, Nd, Yb, Er, U, Au, Re, Pt, La, V, Bi, Os, Pb, Ce, Mo, Ge, Se, Zn, Sr, In, Ta were detected in less than 60% of the samples, twenty-six species including Ni, Sc, Ba, Pr, Co, As, Cr, Ti, Ga, Cd, Na, Ag, Zr, Rb, P, K, Te, Sn, Ru, Pd, Al, Y, Mn, Cu, Mg, Fe have been detected in 60% to 90% of the samples, and three elements Ca, Sb, S were observed in more than 90% of the samples.

Table 4- 1 Statistical summary of PM, and concentration of elements in fine fraction aerosols in Ankara University station (ng/m^3)

Parameter	Na	Mean	STD	Median	Geometric Mean	Min	Max
PM 2.5	190	9978	9257	7502	7290	935	66830
Ag	188	0.926	1.818	0.305	0.298	0.003	12.500
Al	204	324.4	642.4	100.3		0.920	4690.6
As	174	0.554	0.607	0.373	0.299	0.005	3.465
Au	96	1.013	1.527	0.451	0.395	0.003	6.860
Ba	166	11.594	21.256	1.732	2.217	0.003	110.3
Bi	106	2.141	3.037	0.935	0.794	0.011	17.437
Ca	243	441.7	510.9	304.1		1.333	4154.8
Cd	183	0.061	0.134	0.037	0.032	0.000	1.208
Ce	121	0.079	0.102	0.054	0.047	0.001	0.694
Co	169	0.491	0.561	0.294	0.250	0.002	3.923
Cr	175	22.404	42.028	8.888	6.188	0.002	207.83
Cu	222	28.742	38.008	15.973	13.835	0.018	262.16
Dy	72	0.040	0.030	0.037	0.025	0.000	0.126
Er	92	0.035	0.028	0.025	0.021	0.000	0.100
Eu	86	0.076	0.046	0.072	0.056	0.002	0.197
Fe	229	534.5	619.7	324.6		8.374	4390.7
Ga	178	7.342	10.684	2.944	2.566	0.023	52.632
Gd	65	0.046	0.034	0.048	0.030	0.002	0.159
Ge	129	0.095	0.120	0.045	0.047	0.001	0.642
Hf	63	0.033	0.026	0.021	0.026	0.009	0.111
Hg	0	0.000	0.000	0.000		0.000	0.000
Ho	76	0.057	0.035	0.055	0.043	0.002	0.136
In	156	0.146	0.230	0.075	0.079	0.003	1.570
Ir	82	0.117	0.280	0.045	0.047	0.003	1.945
K	191	251.3	243.5	186.8		1.7	1876.6
La	102	0.061	0.061	0.051	0.040	0.000	0.509
Lu	88	0.030	0.023	0.027	0.018	0.000	0.097
Mg	223	124.4	157.5	78.3		0.4	1048.9
Mn	218	8.353	10.230	4.835	4.232	0.012	67.325
Mo	125	2.071	3.047	1.097	0.982	0.023	16.839
Na	185	227.8	251.5	152.8		0.0	1406.0
Nb	52	1.198	1.921	0.465	0.428	0.002	9.122
Nd	89	0.057	0.050	0.051	0.040	0.000	0.340

Table 4- 2 (Continued) Statistical summary of PM, and concentration of elements in fine fraction aerosols in Ankara University station (ng/m^3)

Ni	157	26.85	26.78	18.97	16.61	0.15	138.00
Os	107	0.042	0.044	0.033	0.023	0.000	0.335
P	189	13.416	12.704	8.721	7.334	0.268	52.770
Pb	107	1.926	1.429	1.656	1.407	0.020	9.506
Pd	201	0.172	0.287	0.084	0.088	0.000	2.302
Pr	167	0.281	0.181	0.361	0.150	0.000	0.600
Pt	100	0.068	0.045	0.060	0.053	0.001	0.295
Rb	189	0.585	0.782	0.366	0.303	0.004	6.405
Re	99	0.035	0.022	0.031	0.026	0.001	0.087
Rh	70	0.022	0.012	0.021	0.017	0.001	0.058
Ru	199	0.076	0.055	0.082	0.052	0.001	0.444
S	261	1794.6	1509.0	1313.6		42.1	11431.3
Sb	253	1.571	1.524	1.137	1.040	0.019	9.614
Sc	162	0.089	0.088	0.062	0.050	0.002	0.453
Se	130	0.292	0.227	0.264	0.203	0.002	1.820
Sm	83	0.050	0.036	0.042	0.034	0.001	0.177
Sn	198	0.892	1.101	0.618	0.587	0.010	10.84
Sr	155	5.770	7.636	2.800	2.472	0.038	46.87
Ta	156	0.264	0.440	0.134	0.148	0.003	3.343
Tb	71	0.044	0.029	0.040	0.034	0.004	0.133
Te	193	0.368	0.618	0.243	0.188	0.010	4.891
Th	80	0.125	0.082	0.110	0.101	0.023	0.405
Ti	176	32.34	46.12	15.49	12.969	0.301	274.3
Tl	85	0.133	0.244	0.068	0.067	0.001	1.585
Tm	76	0.036	0.023	0.035	0.027	0.000	0.104
U	92	0.074	0.040	0.076	0.057	0.001	0.174
V	105	4.444	7.290	1.242	1.227	0.008	37.53
W	77	7.420	10.095	3.031	3.090	0.160	44.63
Y	217	0.082	0.083	0.052	0.051	0.000	0.504
Yb	91	0.055	0.040	0.054	0.034	0.000	0.175
Zn	134	50.89	59.18	30.67	26.033	0.796	438.9
Zr	188	2.264	2.560	1.386	1.155	0.020	15.186

4.1.1.2 Middle East Technical University Station

In this station, which is located at METU, representing the suburban air pollution, the mean value for each elements concentration measured in fine fraction of the particles ranges from 0.095 ng m^{-3} for Y to 1901 ng m^{-3} for S. Frequency of detected concentrations in this station varied between 10.3% for Se and 99% for S.

Forty-three elements including Se, Sc, Ag, Mo, W, Cd, Pr, Ho, Tm, Er, Lu, Dy, Tb, Gd, Sm, Yb, Eu, Rh, Pt, Ge, In, Nd, U, Re, Nb, La, Tl, V, Ce, Te, Ni, Hg, Pb, Hf, Au, Ta, Ir, Th, Bi, Sn, Ru, Os, Pd, have been observed in less than 60% of the samples, twenty species including Y, As, Cu, Ga, Zn, Zr, K, Sr, Ti, Rb, Fe, Co, Al, Mn, Cr, Na, P, Mg, Sb, Ca, have been detected in 60% to 90% of the samples, and two elements, Ba and S were observed in more than 90% of the samples. In both stations 20 – 30 elements which are detected in >60% of samples are used in most of the statistical tests. However, some of the elements, like Se, Cd, Mo, Pb, Sn, which are detected in < 60% of the samples are either important due to their toxicity, or because they are good tracers for certain source types. These elements were included in statistical data treatment.

Table 4- 2 Statistical summary of PM, and concentration of elements in fine fraction aerosols in METU station (ng/m^3)

Parameter	Na	Mean	STD	Median	Geometric Mean	Min	Max
PM 2.5	179	8322	7397	5871	5987	223	59240
Ag	42	1.459	2.539	0.435	0.407	0.003	13.32
Al	197	253.9	586.1	74.2		0.004	4749.3
As	162	0.578	0.737	0.348	0.280	0.000	4.329
Au	138	23.860	23.413	9.246	6.100	0.003	65.74
Ba	244	12.926	15.236	8.207	7.646	0.199	99.69
Bi	140	2.506	3.744	1.162	1.361	0.073	28.100
Ca	239	547.1	567.1	375.3		14.043	4521.6
Cd	59	0.991	1.305	0.224	0.289	0.004	4.139
Ce	118	0.583	0.403	0.623	0.380	0.002	2.109
Co	197	0.378	0.526	0.181	0.174	0.001	2.507
Cr	209	8.52	9.45	4.59	4.457	0.022	54.79
Cu	169	18.47	31.84	7.97	7.694	0.030	217.46
Dy	68	0.508	0.119	0.527	0.491	0.218	0.757
Er	68	0.495	0.110	0.515	0.481	0.217	0.720
Eu	68	0.812	0.178	0.829	0.790	0.372	1.242
Fe	190	564.0	852.5	311.8		0.416	5512.6
Ga	176	4.780	5.777	2.636	2.303	0.005	28.303
Gd	68	0.534	0.126	0.548	0.517	0.218	0.824
Ge	73	0.182	0.267	0.074	0.062	0.001	1.320
Hf	136	0.285	0.239	0.262	0.172	0.011	1.417
Hg	122	8.016	10.720	0.217	0.761	0.007	37.97
Ho	67	0.741	0.159	0.758	0.721	0.324	1.102
In	73	0.254	0.348	0.114	0.123	0.011	1.747
Ir	140	0.410	0.368	0.354	0.214	0.002	1.985
K	185	250.6	327.0	92.8		2.337	1603.2
La	83	0.717	0.356	0.821	0.483	0.001	1.519
Lu	68	0.500	0.116	0.506	0.485	0.215	0.764
Mg	220	127.8	160.8	73.8		0.197	1278.0
Mn	206	7.582	9.649	4.118	3.623	0.037	67.128
Mo	50	2.231	3.270	1.125	0.875	0.009	16.271
Na	210	194.8	260.4	110.2		2.255	1697.3
Nb	77	1.452	1.910	0.828	0.640	0.011	10.281
Nd	73	0.558	0.187	0.588	0.486	0.024	0.864

Table 4- 2 (Continued) Statistical summary of PM, and concentration of elements in fine fraction aerosols in METU station (ng/m^3)

Ni	121	17.950	25.643	9.933	8.842	0.255	225.1
Os	146	0.416	0.356	0.211	0.253	0.019	1.304
P	219	18.15	17.17	12.51	10.91	0.140	99.63
Pb	128	20.54	16.83	21.83	10.09	0.103	56.31
Pd	146	1.337	1.111	1.134	0.931	0.121	5.552
Pr	67	0.499	0.105	0.508	0.486	0.218	0.697
Pt	69	0.409	0.122	0.423	0.387	0.094	0.713
Rb	189	0.623	0.786	0.294	0.299	0.005	4.176
Re	77	0.277	0.116	0.304	0.196	0.002	0.468
Rh	69	0.245	0.059	0.254	0.231	0.009	0.362
Ru	146	0.356	0.254	0.262	0.272	0.047	1.336
S	247	1901.0	1796.4	1326.0		164.2	12756.8
Sb	236	1.029	1.407	0.629	0.482	0.001	10.977
Sc	42	0.113	0.166	0.059	0.050	0.002	0.813
Se	12	0.594	0.542	0.405	0.400	0.103	1.859
Sm	68	0.570	0.131	0.577	0.553	0.244	0.862
Sn	142	5.354	2.504	4.826	4.871	1.290	15.52
Sr	186	7.978	9.718	4.092	3.884	0.018	56.78
Ta	139	0.853	0.998	0.555	0.525	0.043	6.00
Tb	68	0.530	0.122	0.541	0.515	0.236	0.818
Te	119	0.500	0.712	0.330	0.227	0.000	4.57
Th	140	0.793	0.601	0.677	0.506	0.017	3.27
Ti	188	47.7	70.9	23.9	18.3	0.071	459.7
Tl	113	0.338	0.328	0.268	0.180	0.000	1.992
Tm	68	0.494	0.116	0.508	0.479	0.211	0.746
U	73	0.841	0.261	0.862	0.751	0.024	1.328
V	117	3.60	7.54	1.02	0.962	0.017	44.4
W	53	8.07	10.27	3.79	3.598	0.083	45.4
Y	152	0.095	0.114	0.056	0.045	0.000	0.836
Yb	68	0.776	0.176	0.787	0.753	0.329	1.177
Zn	177	76.95	87.77	48.25	38.79	0.042	510.2
Zr	181	2.148	2.635	1.400	1.073	0.015	18.5

Frequency distributions of selected elements at AU and METU stations are given in Figure 4- 1 and Figure 4- 2 , respectively. Frequency distributions of all elements in our data set, without any exception, are right-skewed. Although log-normal distribution is the most frequently observed distribution in atmospheric data sets, there are other distributions which are also right skewed.

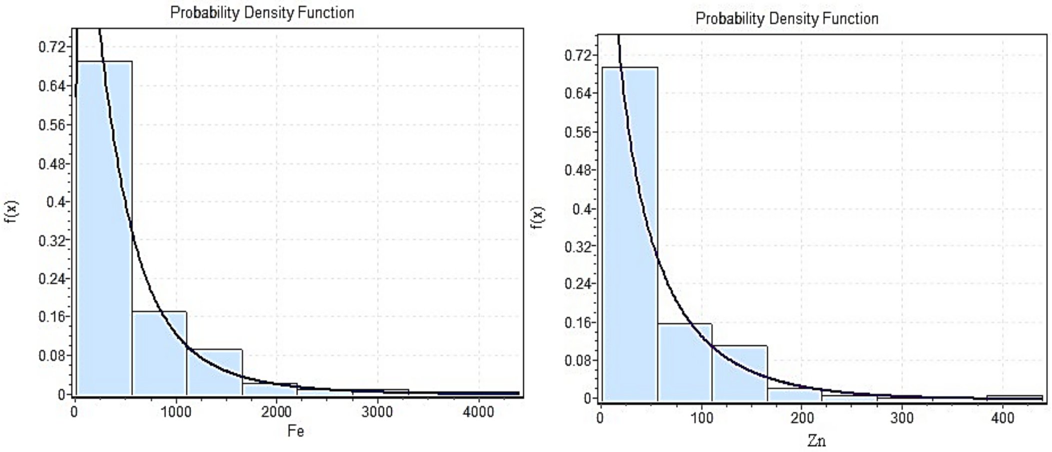


Figure 4- 1 Frequency distributions of selected elements in AU station

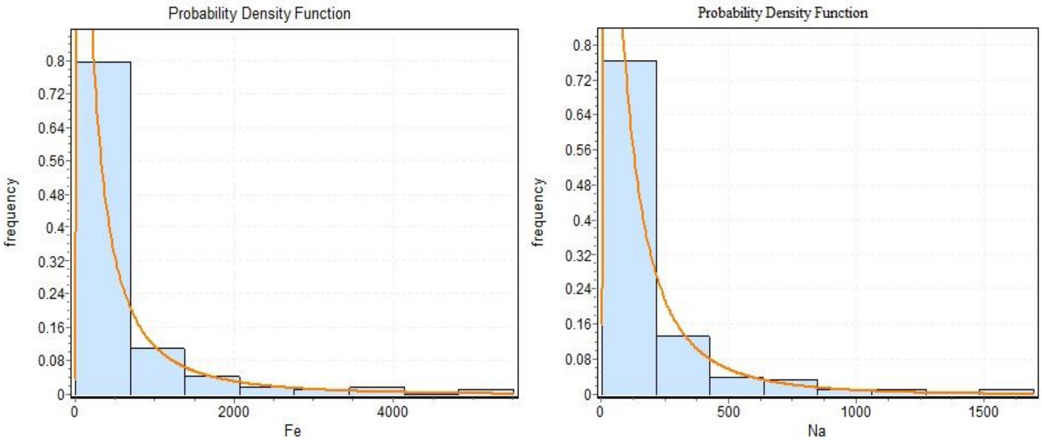


Figure 4- 2 Frequency distributions of selected elements in METU stations

In this study, we initially assumed that all elements are log-normally distributed. Then, for each element, we tested this assumption using chi-square test. The ones that are not log-normally distributed with 95% statistical significance were tested using 26 other right skewed distributions using Statgraphics software.

4.2 Comparison of concentrations of elements measured in this work with values reported for other urban areas around the world

Comparison of measured pollutant concentrations with comparable data reported in literature is useful to understand level of pollution in the air shed. In this study we performed a four-step comparison of trace element concentrations with comparable data from other studies. In the first step, the elemental concentrations data obtained from two stations in this study will be compared with each other, knowing that one station represents the urban area of Ankara and the other one suburban area. This provided very valuable information about similarities and differences of data sets generated in the city and in METU. Then data generated were compared with data obtained in previous studies in Ankara. Third step, discusses the comparison of our data and selected trace element concentrations obtained from the various studies performed in different parts of Turkey. Finally, concentrations were compared with data from other cities around the world.

Because in this study the elemental concentrations were measured in the fine aerosol fractions, therefore in this section the comparison with data available in the literature contains data about PM2.5 in different urban and suburban locations worldwide, except for Ankara comparison in which PM10 data has been considered as well, because there are few studies conducted in the Ankara. In each comparison part, the elements are divided into three groups of anthropogenic elements, elements with mixed origin and crustal elements, based on their sources.

Although data comparison is useful to put generated concentrations into a perspective, one should not overweight its importance, as concentrations of trace elements and other pollutants in an urban air shed depend on a number of factors, such as, closeness of the sampling point to sources, effectiveness of ventilation mechanisms at the sampling point, etc. Due to these factors, concentrations reported for any city do not necessarily represent average concentration of elements in that city. Since it is almost impossible to find data sets generated at two exactly similar geography, topography and meteorology, results of comparison generally provide crude, but useful, information on the state of pollution in that particular sampling point.

4.2.1 Comparison of trace element concentrations measured at suburban and urban stations

In the first step, concentration of elements measured in Urban and Suburban stations in this study is compared with each other. Data is presented in the Figure 4-3 and Table 4- 3. As it can be seen in the following table and graph, crustal elements show interesting values. Major crustal elements like Al, Fe, etc. are not much different in both stations; however, all the rare earthy elements such as La, Ce, Pr, Nd, Sm, etc. have an order of magnitude lower concentration at AU station as an urban location.

Table 4- 3 Comparison of trace element concentrations measured at suburban and urban stations (ng/m^3)

	Elements	**AU**	**METU**	**Elements**	**AU**	**METU**
	PM 2.5 (µg/m3)	9.98	8.32			
Anthropogenic Elements	S	1794.6	1901	Sb	1.57	1.03
	Cu	28.74	18.47	Te	0.37	0.50
	Zn	50.89	76.95	W	7.42	8.07
	As	0.55	0.58	Pt	0.07	0.41
	Se	0.29	0.59	Au	1.01	23.86
	Mo	2.07	2.23	Tl	0.13	0.34
	Ag	0.93	1.46	Sn	0.89	5.35
	Cd	0.06	0.99	Pb	1.93	20.54
	In	0.15	0.25	Ge	0.09	0.18
Mixed Origin	V	4.44	3.60	Ni	26.85	17.95
	Cr	22.40	8.52	Ti	32.34	47.68
	Mn	8.35	7.58			
Crustal Elements	Na	227.76	194.78	Ce	0.08	0.58
	Mg	124.37	127.81	Pr	0.28	0.50
	Al	324.40	253.86	Nd	0.06	0.56
	K	251.30	250.65	Sm	0.05	0.57
	Sc	0.09	0.11	Eu	0.08	0.81
	Fe	534.46	564.04	Gd	0.05	0.53
	Co	0.49	0.38	Tb	0.04	0.53
	Ca	441.66	547.11	Dy	0.04	0.51
	Rb	0.59	0.62	Ho	0.06	0.74
	Sr	5.77	7.98	Er	0.03	0.50
	Y	0.08	0.09	Tm	0.04	0.49
	Zr	2.26	2.15	Yb	0.05	0.78
	Nb	1.20	1.45	Lu	0.03	0.50
	Ru	0.08	0.36	Hf	0.03	0.28
	Rh	0.02	0.25	Ta	0.26	0.85
	Pd	0.17	1.34	Re	0.04	0.28
	Ba	11.59	12.93	Bi	2.14	2.51
	La	0.06	0.72	Th	0.13	0.79

The reason for this pattern of crustal elements, is not straightforward, but observed difference can be due to chemical composition of soil particles affecting two stations. Concentrations of major lithospheric elements like Al, Fe etc. do not change significantly from one mineral type to another, but concentrations of trace lithospheric elements (like rare earth elements) are variable. Observed difference in these elements, but lack of significant difference in major crustal ones (like Al, Ca, Fe etc.) implies that different mineral types influences the two stations. Yay OD 2008, demonstrated strong variability in concentrations of trace elements in Ankara Soil as well. Among anthropogenic elements, few (S, Cu, Sb) have higher concentrations at AU station. This is what we expect to see, because urban station is under stronger influence of anthropogenic emissions.

Most of the elements have comparable concentrations in both stations (As, Se, Mo, Ag, In, Te, W, and Ge). Similar pattern can be seen in earlier studies in Ankara which attributed it with very slow wind speed in Ankara and relatively homogeneous distribution of pollutants in atmosphere of whole city due to such slow winds (Yatin, Tuncel, Namik K Aras, *et al.*, 2000).

Interestingly, some of the elements have higher concentrations at Suburban station (Zn, Cd, Sn, Pt, Au, Tl, Pb). Why concentrations of these pieces are higher at METU station can be due the following facts. One reason might be having too many missing values. These are the elements with high missing data. However, differences are statistically significant that means they should be real and not an analytical artifact. Concentrations of anthropogenic elements measured in 1993 were higher in urban station compared to corresponding concentrations measured at METU. This implies that in time METU became more influenced by anthropogenic emissions. OSTIM industrial zone, which became 3 – 4 times larger in last 20 years and expansion of residential areas around METU, can be the reason for the observed pattern.

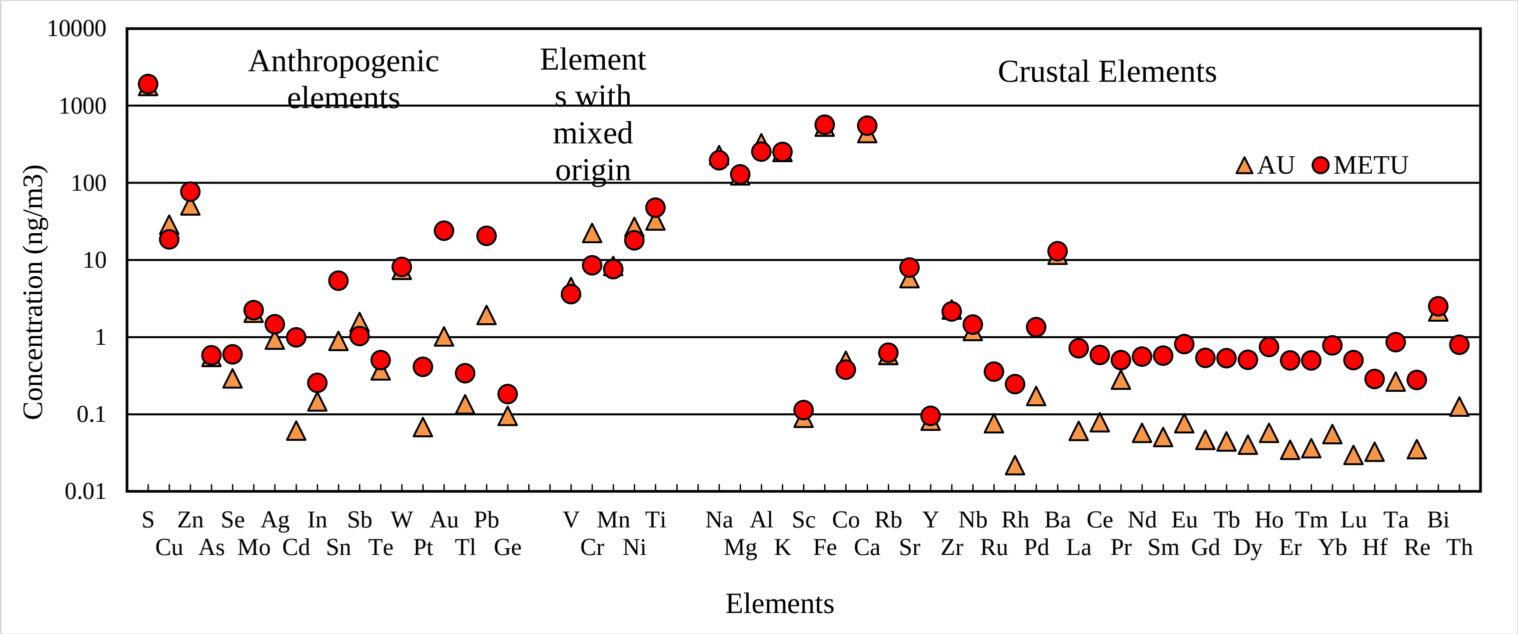


Figure 4- 3 Comparison of trace element concentrations measured at suburban and urban stations

4.2.2 Comparison of trace elements concentrations with data from other studies conducted in Ankara

In the second step, studies performed in Ankara have been considered and concentrations of elements in urban and suburban area of the city have been compared with our results separately. Because there are few researches conducted in Ankara, we have few references for this part which are relatively old without sampling PM2.5 and PM10 separately and just reporting and analyzing the total PM. Trace element concentrations in Ankara were measured in three different studies (other than this work) in 1975, 1989 and 1993. In Ölmez and Aras, 1977 study PM_{10} samples were collected at METU in 1975 and analyzed by Instrumental Neutron Activation Analysis (INAA).

After this 1975 study aerosol sampling were performed at Sıhhıye and METU, first in 1989 and then in 1993. Sampling in 1989 was short term. PM10 Samples were collected few weeks in summer and few weeks in winter. Results were published in Yatin 1994, a similar sampling was repeated in 1993, but this time samples were collected for six months covering parts of the summer and winter seasons and not only PM10, but also PM2.5 samples were collected (Yatin, Tuncel, Namik K Aras, et al., 2000). Since sampling in this work was PM2.5, we have used results of PM2.5 samples in Yatin, et al., 2000 for this comparison. Finally, this work was performed 21 years after 1993, in Yatın et al (2000) study. Results of this comparison between data sets generated in Ankara are given in Table 4- 4 and Figure 4-4. We used only METU data in comparison, because inter-station differences in concentrations measured elements are significantly smaller than differences between concentrations measured in different studies.

Table 4- 4 Comparison of trace elements concentrations with data from other studies conducted in Ankara (ng/m^3)

Parameters	This study METU (2014) PM2.5	METU (1975) PM 10	Urban (1989) PM 10	METU (1989) PM 10	METU (1993) PM2.5
Ag	1.46		0.15	0.03	
Al	253.86	3413	6900	780	110
As	0.58	14	31	11	1.5
Ca	547.11	8171	9600		95
Co	0.38	1.3	2.7	2.2	3.3
Cr	8.52	20.8	1	5	3.2
Fe	564.04	2074	2100	540	100
K	250.65		590	180	140
La	0.72	2	3	0.3	0.14
Mn	7.58	11.5	19	5	4.9
Na	194.78	913	1900	360	61
Ni	17.95	9.4			3.1
Pb	20.54	66			71
S	1901.00				
Sb	1.03	1.7	0.37	0.24	1.3
Se	0.59	116	2.1	0.9	0.48
Ti	47.68	157	1000		
V	3.60	9.6	130	5.5	3.9
Zn	76.95	90	90	24	16

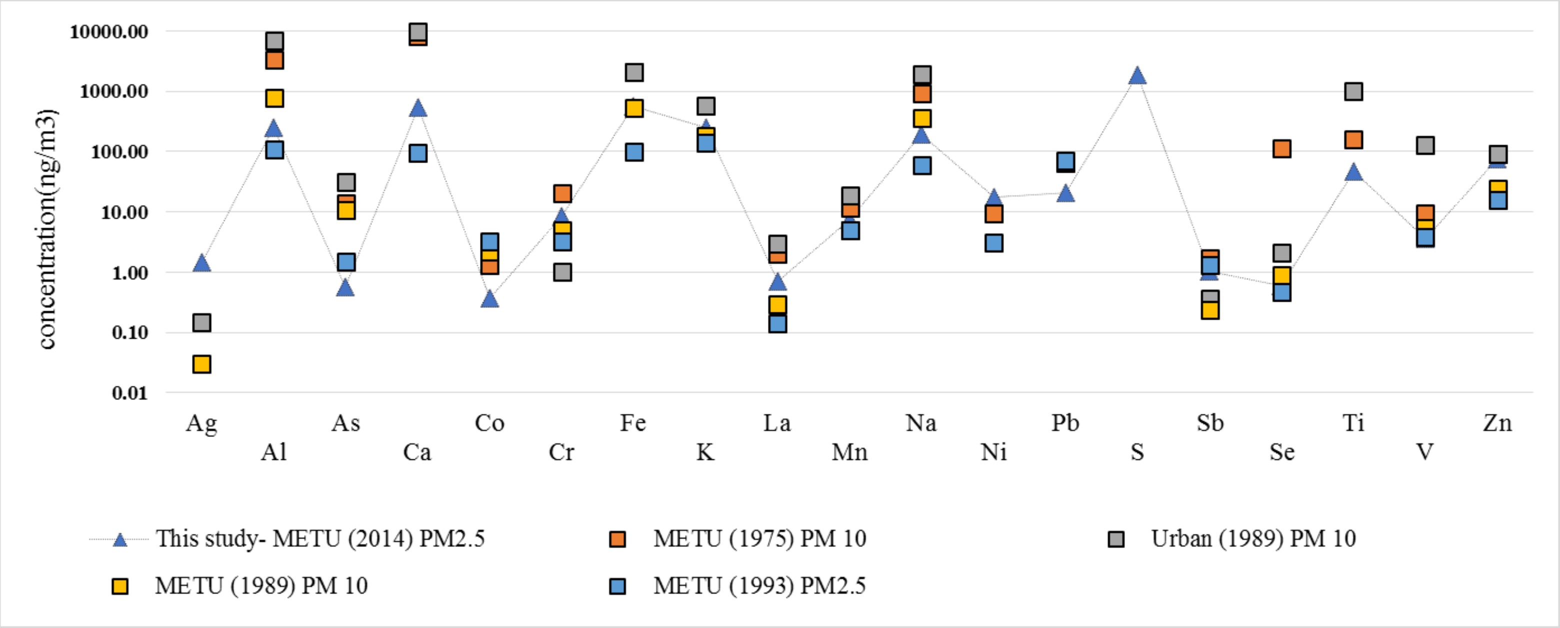


Figure 4- 4 Comparison of the elemental concentrations measured in this work with comparable data from earlier studies in Ankara

With few exceptions, the highest concentration of all elements were reported for 1975 sampling and samples collected at urban station in 1989, which are followed by data generated in 1989 at METU, $PM_{2.5}$ data generated at METU in 1993 and data generated in this work. This difference is partly due the PM_{10} sampling in 1975 and in 1989 and $PM_{2.5}$ sampling at 1993 and 2014 (this work). PM_{10} vs. $PM_{2.5}$ sampling is determining factor in concentrations of soil related elements, which are associated with coarse particles. However, trends observed in anthropogenic cannot be explained by sampling methodology, because no matter which type of samples were collected, these elements are in fine fraction ($PM_{2.5}$), Lower concentrations of pollution derived elements (Eg; As, Pb, Sb, Se, V and Zn) in 1993 and 2014 is the result of improved air quality in the city.

Concentrations of anthropogenic elements also decreased in time. However, this is more understandable, because in 70’s Ankara was under very heavy air pollution due to coal combustion, so very high concentrations measured in 1975 is because of this. Combustion related air pollution started to decrease in mid-80’s when coal with <1% S started to be used. Air quality further improved when mode of heating was switched to natural gas in early 90’s. Variation in concentrations of anthropogenic elements clearly reflects these changes.

It is noteworthy that the highest decrease between 1975 and 2014 was observed in Pb concentrations. In 70’s Pb was added to gasoline as anti-knocking agent and in those days Pb concentration was high everywhere around the globe. Later Pb was phased out from gasoline. This happened in 2000 in Turkey and we do not have Pb in gasoline after 2000. Therefore, this is the main reason for dramatic decrease in Pb concentration between 1975 and 2014. Pb concentrations in 1993 are higher than Pb levels in 1975. This is because (1) unleaded gasoline was not in use in 1993 and (2) number of cars in the traffic were higher in 1993, than in 1975. The other two elements that also depicted significant decrease between 1975 and 2014 are As and Se, both of which are good markers for coal combustion. Decrease in concentrations of these two elements is a result of reduction in coal combustion for space heating.

4.2.3 Comparison of trace elements concentrations with data from other cities in Turkey

Concentrations of trace elements measured in this work are also compared with corresponding concentrations of elements measured in other urban and rural sites in Turkey. Data used in comparison are given in Figure 4- 5 and Table 4- . We used METU data only, because difference in concentrations of elements measured at AU and METU stations are compared to differences between concentrations of elements in different data sets. Summary of the researches presented in this section is as follows:

a) Eastern Black Sea coast – Suburban

Fine and Coarse aerosol samples collection was conducted from 2011 to 2013 by using a “stacked filter unit”. The station is located at a suburban area close to Black Sea coast. Elemental analysis has been performed on the collected samples to identify and measure the concentrations of the trace elements on the filters by Energy dispersive x-ray fluorescence technique (EDXRF). (Balcilar *et al.*, 2014)

b) Izmir – Suburban and Urban

PM2.5 and PM10 fraction of the aerosols have been sampled at two stations in Izmir, from June 2004 to May 2005. The first sampling location was situated at the Dokuz Eylul University Tinaztepe Campus, representing the suburban area. The second one was located in the city center to measure urban pollution. The elemental composition analysis was performed using inductively coupled plasma-optical emission spectrometer. (Yatkin and Bayram, 2008)

c) Northeastern Mediterranean – Suburban

Fine and coarse fractions of the particulate matter have been sampled at a coastal suburban area in the northeastern Mediterranean from April 2001 to 2002. In total 562 collected filters have been analyzed for measuring the trace elements and water soluble ions in them. (Koçak, et al 2007)

d) Istanbul – Urban

PM2.5 fraction of the atmospheric aerosols have been collected in two urban station in Budapest (Hungary) and Istanbul (Turkey) using high-volume sampler between June 2010 and May 2011. Trace elements concentrations, major anions, and total and water soluble carbon have been determined for these samples. (Szigeti *et al.*, 2013)

e) Southern Black Sea – Urban

Daily fine and coarse samples from 25 December 2004 until 9 October 2005 were collected by dichotomous sampler in the urban area of the Zonguldak city which is located at the middle of the Black Sea coasts of Turkey. These 216 samples were analyzed for determination of their metallic composition, using X-ray fluorescence. (Tecer *et al.*, 2012)

Table 4- 5 Comparison of trace elements concentrations with data from other cities in Turkey

Elements	This study METU suburban	Black Sea coast suburban	Izmir suburban	Mersin suburban	Izmir urban	Istanbul urban	Zonguldak urban
S	1901	-	-	1122	-	-	-
Cu	18.5	14.6	15.5	-	35.8	14	61
Zn	77.0	28.4	113.3	4.9	176.9	72	58
Cd	0.99	-	0.6	-	1.2	0.56	-
Sn	5.35	-	-	-	-	3.4	-
Sb	1.03	-	-	-	-	3	-
Pb	20.5	13.1	32.9	-	92.3	13	11.9
V	3.6	4.4	7.1	4.5	12.3	10	-
Cr	8.5	39.4	9.6	1.8	24	2.8	3.8
Mn	7.6	14.5	9.7	1.8	16.1	12	8
Ni	18.0	8.6	7.8	1.6	15.7	4	3
Na	194.8	36.7	672.9	-	899.8	-	-
Al	253.9	337.3	531.8	-	834.2	-	94
K	250.6	123.5	195.9	116	473.9	-	208
Ca	547.1	550.9	902	158	1660	-	197
Fe	564.0	1126	268.6	53.3	393.4	460	130
Mg	127.8	69.9	63.6	-	101.2	-	66
Ti	47.7	96.6	-	4.1	-	-	12
Ba	12.9	-	4.9	-	11.4	-	-

For pollution-derived elements, concentrations measured in this work are comparable to the concentrations measured in other studies. Pollution derived elements have lower concentrations at rural stations, as expected. Concentrations of anthropogenic elements in urban studies in Turkey are not very different. The only exception to this is relatively low concentrations of pollution-derived elements at the İzmir suburban site. Discussion on reasons of this behavior is beyond the scope of this discussion.

The similar pattern prevails in crustal elements and elements with mixed origin. For all element groups, elemental concentrations measured in this work are comparable with corresponding concentration reported for other cities in Turkey.

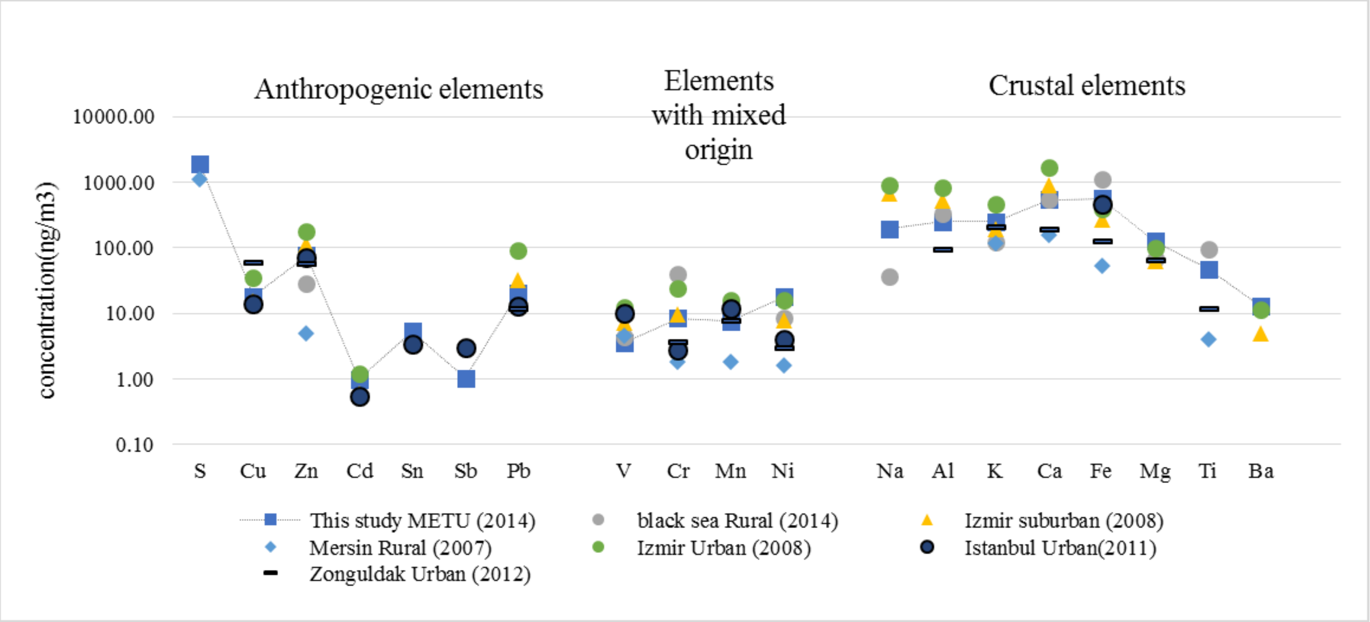


Figure 4- 5 Comparison of trace elements concentrations with data from other cities in Turkey

4.2.4 Comparison of trace elements concentrations measured in this study with data from other cities around the world

In the last step, different elements concentration related to the fine fraction aerosol in different stations in urban and suburban parts of the world is compared with the values observed in this study. Summary of researches included in this part are given below:

a) Mira Loma, California – Suburban

Fine samples have been collected for the duration of 20 weeks from September 2001 to January 2002and concentrations of thirty-five trace in ambient fine particulate matter (PM2.5) were measured in Mira Loma, a suburban area in southern California. (Na and Cocker, 2009)

b) New Jersey, New York – Suburban

Using low-volume PM2.5, trace elements associated with PM2.5 particulate matter were sampled at three stations around the NY–NJ Harbor-Bight from January 1998 to January 1999 and analyzed by inductively coupled plasma mass spectrometry. New Brunswick station is located in an inland suburban site away from the industrial or urban pollution. (Gao *et al.*, 2002)

c) Basel, Bern, Switzerland – Suburban and urban

Daily samples have been collected in two stations from April 1998 to March 1999 on pre conditioned quartz fiber filters using high-volume samplers Digital DA80 and PM2.5, PM10 and trace elements concentration have been measured by using destructive acid digestion followed with Ion chromatography. One station is placed at urban kerbside, near-city, and another one is located at rural sites in Switzerland. (Hueglin *et al.*, 2005)

d) Jiading, Shanghai – Suburban

One 24 hour PM2.5 sample has been taken each month from April 2004 to April 2005 in Shanghai at four stations. Jiading site represents suburban location covered with evergreen trees and is about 40 km away from the down-town. The ambient mass concentration and elemental composition were determined in the samples. (Chen *et al.*, 2008)

e) Mount Gongga, china - Suburban

From January to December 2006, once per week PM2.5 and PM10 and in total, 98 samples were collected on cellulosic filters using high-volume air sampler in the Mount Gongga station representing suburban area. The concentrations of fifteen trace elements were detected such as Na, Mg, Al, K, Ca, V, Fe, Ni, Cu, Zn, As, Ag, Ba, Tl, and Pb by using Inductively Coupled Plasma Mass Spectrometer (ICP-MS). (Yongjie *et al.*, 2009)

f) Milan, Italy – Urban

Using automatic low volume air-samplers, 24-h samples of PM10 and PM2.5 were collected from December 1997 to September 1998 in the urban location placed at central area of Milan. Elemental composition have been measured in both fractions using energy dispersive Xray fluorescence technique. (Marcazzan *et al.*, 2001)

g) Barcelona, Spain – Urban

PM10, PM2.5 and PM1 collection were conducted from June 1999 to June 2000, at an urban area in the Metropolitan part of Barcelona. MCV high volume samplers with DIGITEL PM10 and PM2.5 inlets was used for sampling and filters have been digested and analyzed in order to identify trace elements concentrations. (Querol *et al.*, 2001)

The values measured in the above mentioned studies around the globe and the results obtained in this study are compared in the Table 4- and Figure 4-

6. Concentration of some selected elements have been presented because there is not available data in the literature for all of our elements. In addition, the mean concentration of the elements is used because average value has been considered mostly in the literature.

For crustal elements, concentrations measured at Ankara and particularly at METU are higher than concentrations reported for other cities around the world, probably because Ankara is in the middle of an arid Anatolian plateau, which does not have much vegetation cover. Therefore, resuspension of dust is easy in this area, particularly during summer months when soil is dry.

Table 4- 6 Comparison of trace elements concentrations with data from other cities around the world (ng/m^3)

Species	*This study METU*	*This study AU*	Mira - CA	New Jersey - NY	Basel - switzerland	Jiading – Shanghai	Mount China	Milan - Italy	Bern - Sw	Barcelona - Spain
	sub urban	*urban*	suburban	sub urban	Sub urban	Sub urban	sub urban	urban	urban	urban
S	*1901*	*1794.6*	19.4	-	-	-	-	2630	-	-
Cu	*18.47*	*28.74*	1.7	7.3	6	26	2.2	17.5	8.7	52
Zn	*76.95*	*50.89*	2.1	18	-	300	154.6	110	-	178
As	*0.58*	*0.55*	0.4	-	0.4	27	4.3	-	0.21	-
Se	*0.59*	*0.29*	0.7	-	0.4	1.6	-	-	0.21	-
Mo	*2.23*	*2.07*	0.4	-	0.39	-	-	-	0.72	-
Pd	*1.34*	*0.17*	1.5	-	-	-	-	-	-	-
Ag	*1.46*	*0.93*	0.6	-	-	0.18	0.1	-	-	-
Cd	*0.99*	*0.06*	2.4	0.015	0.48	1.6	-	-	0.21	-
Sn	*5.35*	*0.89*	11.1	-	-	-	-	-	-	-

Table 4- 6. (Continued) Comparison of trace elements concentrations with data from other cities around the world (ng/m^3)

Sb	*1.03*	*1.57*	2.9	0.88	0.41	22	-	-	0.95	-
Au	*23.86*	*1.01*	1.7	-	-	-	-	-	-	-
Tl	*0.34*	*0.13*	1.9	-	0.03	-	0.3	-	0.05	-
Pb	*20.54*	*1.93*	2	6.6	19	67	39.4	138	30	130
Ni	*17.9*	*26.8*	0.4	4	1.7	6	0.9	7	1.3	6
V	*3.6*	*4.44*	1.4	3.6	1.2	4	0.7	7	1.6	9
Cr	*8.52*	*22.4*	5.6	1.4	-	17	-	5	-	6
Mn	*7.58*	*8.35*	5	-	3.1	29	-	13	4.4	14
Na	*194.8*	*227.7*	-	-	117	-	211.5	-	84	230
Al	*253.9*	*324.4*	47.2	27	37	-	295.8	210	26	-
K	*250.6*	*251.3*	41.7	-	224	-	498.2	263	186	480
Ca	*547.1*	*441.7*	4.2	-	64	-	372.8	90	106	510
Fe	*564.04*	*534.5*	2.8	83	66	666	224	190	204	260
Co	*0.38*	*0.49*	0.4	-	-	0.5	-	-	-	-
Mg	*127.81*	*124.4*	5.9	-	16	139	167.8	-	13	80
Ti	*47.7*	*32.3*	9.9	-	-	32	-	11	-	20
Ga	*4.8*	*7.34*	0.7	-	0.07	-	-	-	0.03	-
Sr	*7.98*	*5.77*	0.8	-	-	-	-	-	-	4
Y	*0.09*	*0.08*	0.5	-	0.01	-	-	-	0.01	-
Rb	*0.62*	*0.59*	0.4	-	0.58	-	-	-	0.44	-
Ba	*12.93*	*11.59*	52.8	-	-	10	6	-	-	23
La	*0.72*	*0.06*	3.7	-	0.05	0.5	-	-	0.09	-

Concentrations of elements with mixed sources (crustal + anthropogenic) are also high in our stations, which can be due to the reason that crustal component dominates this group of elements (Ni, V, Cr, Mn). As it is expected, concentrations of anthropogenic elements are not particularly high in Ankara, because Ankara is not an industrial city and concentration of pollution derived elements are highly related to the anthropogenic emissions in the sampling location. In addition, year by year the concentration of these elements are reducing in the developed countries due to the environmental steps they take. In our comparison the data has been presented from studies performed after 2001, however, they are not all from the same year. Therefore, different dates is also another factor affecting the results.

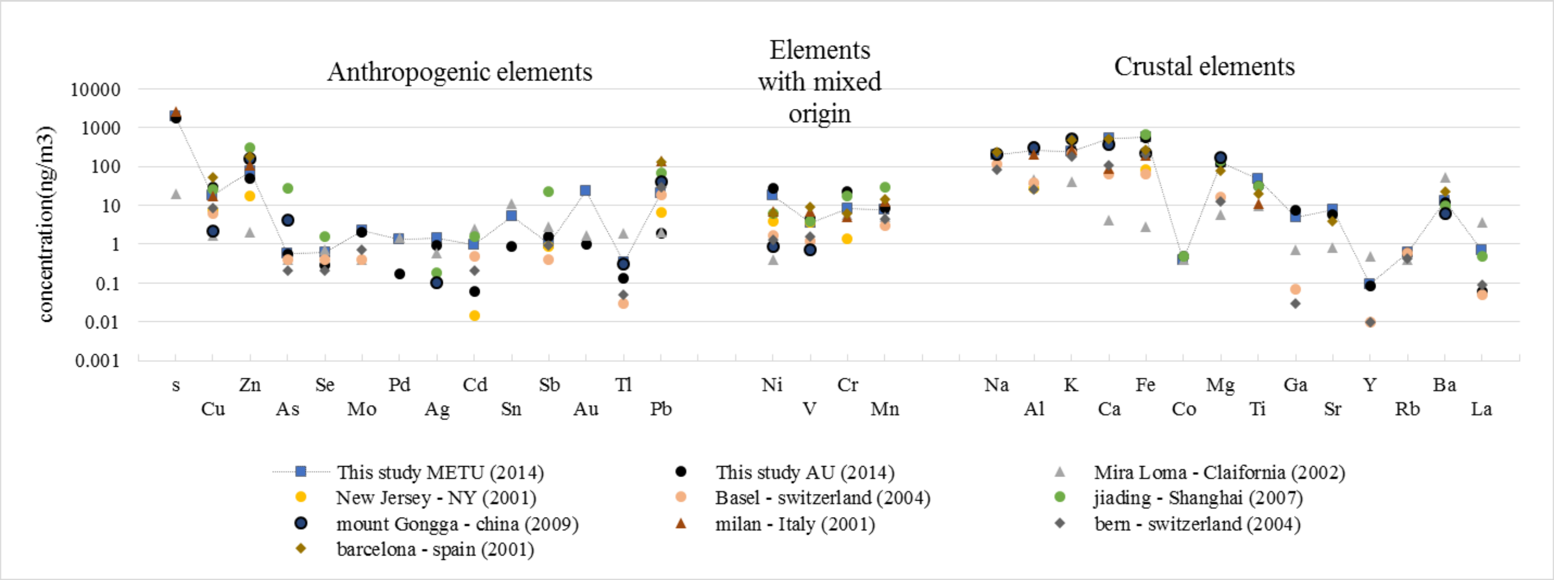


Figure 4- 6 Comparison of the elemental concentrations measured in this work with comparable data from other urban areas around the world

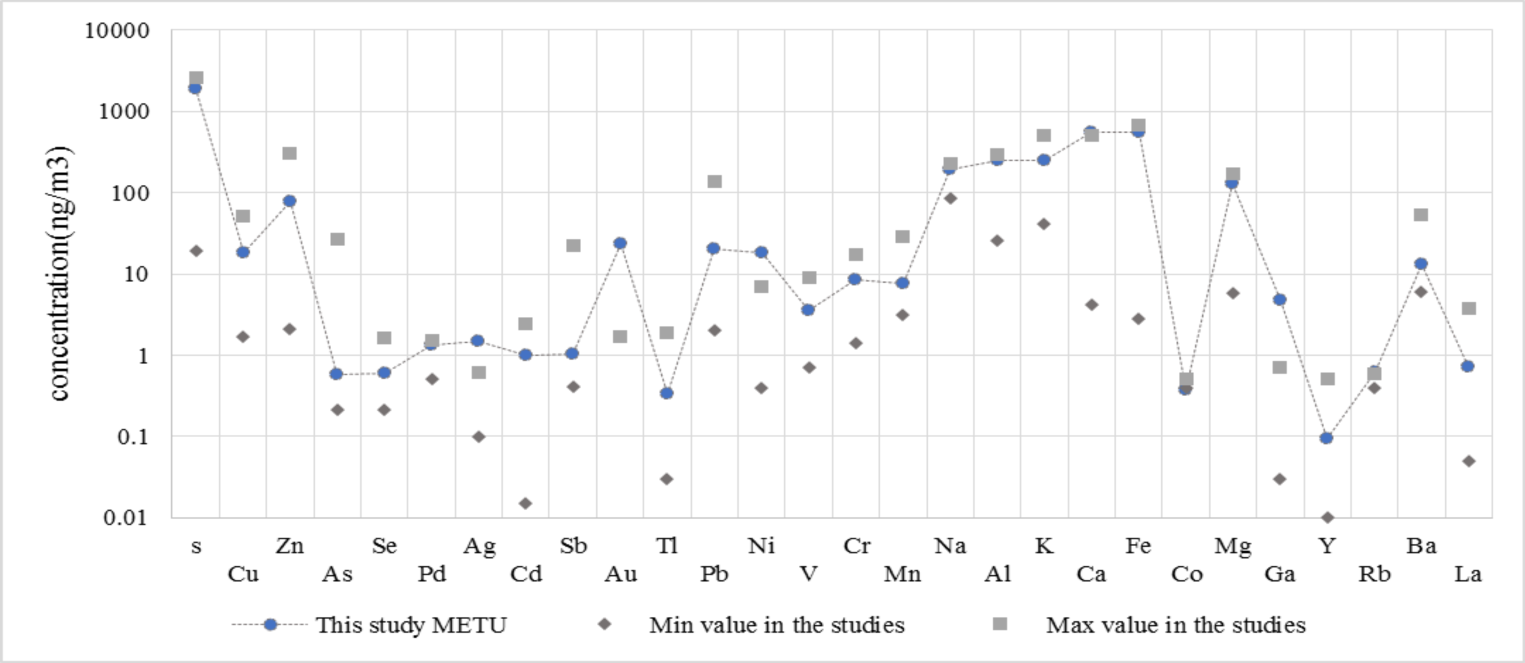


Figure 4- 7 Range of the concentrations in other studies worldwide and the concentrations in Ankara obtained in this study

4.3 Temporal variation in concentrations of measured elements at urban and suburban stations

Concentrations of particles in atmosphere and elements associated with them show short- and long-term variations due to several reasons. Short-term variations are generally quick changes in meteorology or emissions. Variability in wind speed and direction, rain events and start – stop of a certain industrial activity are the main reasons for episodic changes in concentrations of particles and pollutants in general.

Long-term variations include diurnal variations, weekday-weekend differences, and seasonal variations in pollutant concentrations. Long-term variations in meteorology, such as annual variation in wind speed and direction, seasonal variation in precipitation patterns, seasonal variation in mixing height and long-term variation in emissions, such as seasonal variation in pollutants emitted from heating sources are sources of long-term variability in pollutant concentrations. Long-term trends are variations in pollutant concentrations over long years. Since meteorology does not change over the years, trends in pollutant concentrations are due to variations in emissions. Because of this statistically significant trends in levels of pollutants are frequently used to assess consequences of actions taken to improve air quality both in local (urban) and regional scale.

In this study, we cannot evaluate long-term trends, because such variations require at least 10 years of time series. Diurnal variations are also not discussed, because sampling was daily. Episodic changes, weekday-to-weekend ratios and seasonal variations in concentrations of measured elements are briefly discussed in this section of the manuscript. Short-term variations (or episodic changes) in concentrations of selected elements in urban and suburban stations are depicted in Figure 4-8. The patterns observed for all elements can be characterized by rapid increase and sudden decrease in concentrations, which are named as episodes.

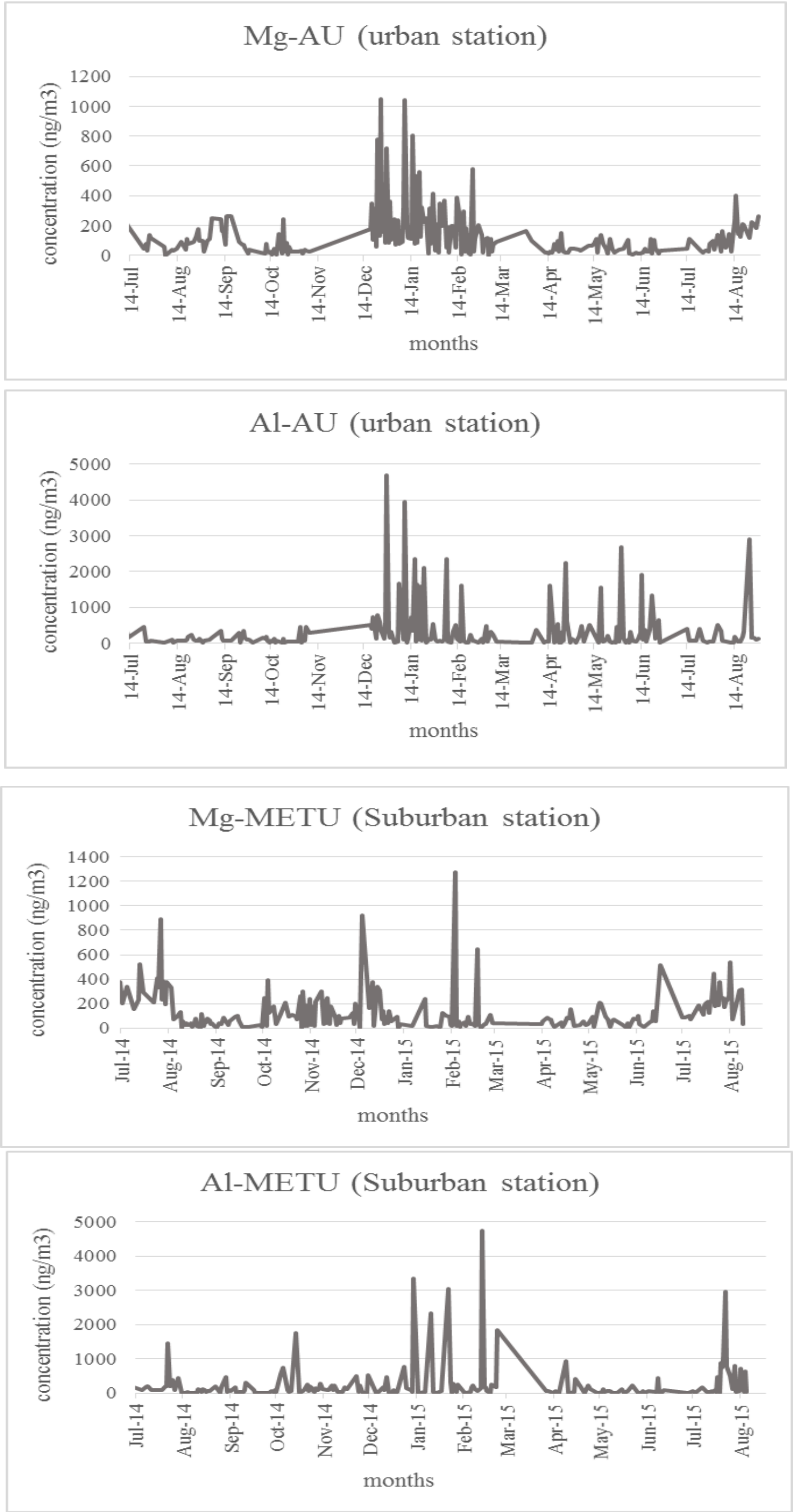


Figure 4- 8 Short-term variations in concentrations of selected elements in urban and suburban

The patterns in the figures indicate that there are episodic variations in concentrations of all elements in our urban and rural data sets. Such episodic variations of pollutants in atmosphere is very typical for atmospheric concentrations of pollutants and observed in every study. There are several reasons for episodes in trace element data sets. One of the reasons is variations in wind speed. Increase in wind speed results in decrease in concentrations of elements and decrease in wind speed results in an increase, as will be discussed in more detail later in the manuscript.

Since wind speed is variable in short time-scales, it can be at least one of the reasons for observed episodes. Another reason is the variations in wind direction. As in wind speed, wind direction also changes in short-time scales which results in rapid increase and decrease in concentrations of elements. If the wind blows from direction of a strong anthropogenic or natural source, concentrations of particles and elements emitted from that source will be high, but when wind changes direction and blow from a sector where there is no source, concentrations quickly drop to low levels, generating an episode. The relation between wind direction and concentrations of elements are discussed later in the manuscript.

Rain is the most important meteorological parameter that affects pollutant concentrations in the short term. Since rain washes particles from atmosphere, concentrations of trace elements, which are bound to particles decrease during and after rain. It is demonstrated that reloading time of the atmosphere is different for crustal and anthropogenic species and changes between 2 – 10 days (Güllü *et al.*, 1998, 2005). Concentrations of trace elements measured in Urban and suburban stations are affected from rain evens. Number of rain events that occurred during our sampling period (June 2014 and August 2015) is 137 with total rainfall of 585.2 mm. Seventy-nine of these events, with a total rainfall of 331 mm, matched with samples collected at the suburban station. Ninety-one of the events, with 372 mm rainfall matched with samples collected at urban station. Two data sets (urban and suburban) were combined to improve statistical significance of results. This approach is warranted, because rain data is common and the effect of rain on elemental concentrations cannot be different at two stations. Separate average and median concentrations of elements were calculated for the days without rain and with rain. The ratio of rain-to-no rain concentrations were calculated for each element. Ratios varied between 1.0 for Cd and 1.7 for Ga. The average ratio is 1.25 ± 0.21, indicating that the impact of rain scavenging on concentrations of elements is approximately 25%. It should be noted that samples collected in both stations were fine fraction only. Since coarse particles are scavenged more effectively by rain, impact of rain scavenging on coarse fraction concentrations of elements is expected to be higher than 25%.

Seasonal variations in concentrations of elements can provide useful preliminary information about sources of elements. Since expected seasonal variations in concentrations of elements due to meteorology is well known, deviations from expected behavior can be attributed to seasonal variations in emissions. Elements measured in this work are separated into three groups as crustal (litophilic), anthropogenic (chalchophilic) elements and elements that have mixed anthropogenic and crustal sources. Since many elements were measured in each group, some representative elements were selected and included in figures. Monthly median concentrations of selected soil related elements at Suburban and urban stations are depicted in Figure 4- 9 and Figure 4- 10, respectively. Interestingly, same crustal elements showed two different monthly pattern in urban and suburban stations. In suburban station, Concentrations of crustal elements are high in summer season and decreases in winter. This is typical pattern expected from crustal elements based on meteorology. Concentrations of soil related elements are low in winter, because soil is mud or ice covered in that period. However, soil is dry in summer and soil particles can be easily suspended by wind action, increasing concentrations of crustal aerosol in atmosphere.

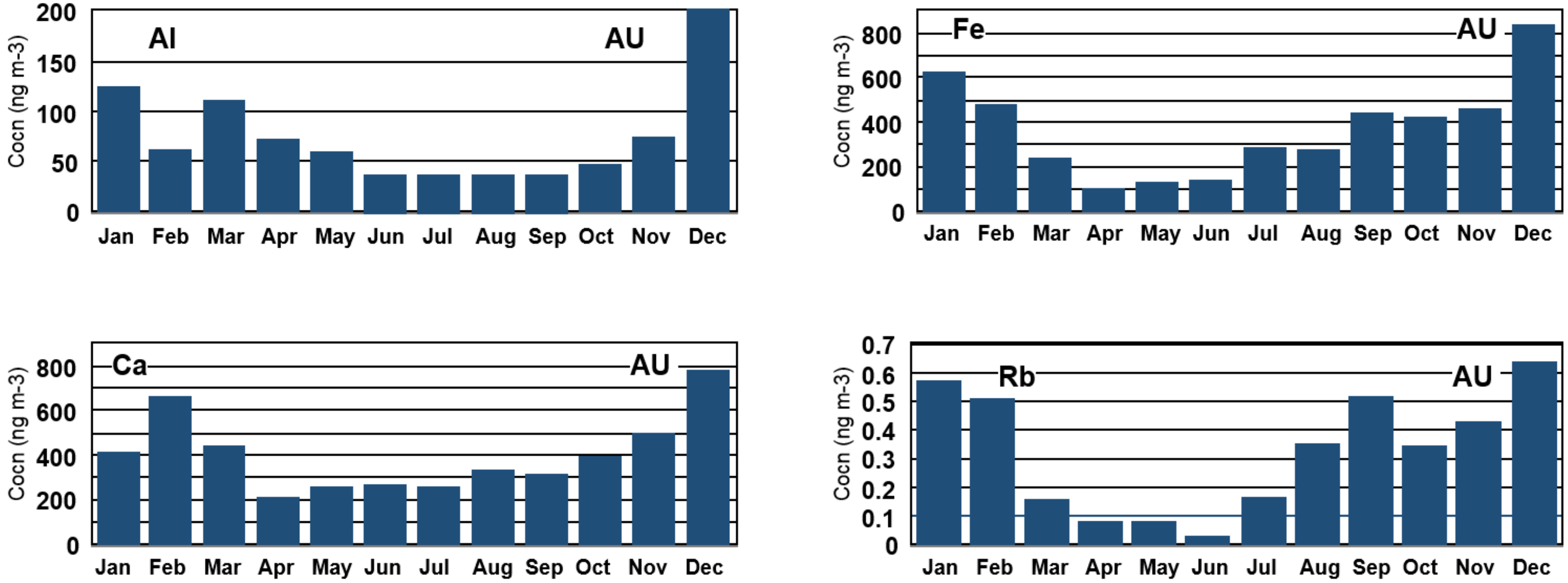


Figure 4- 9 Monthly median concentrations of selected crustal elements at urban (AU) station

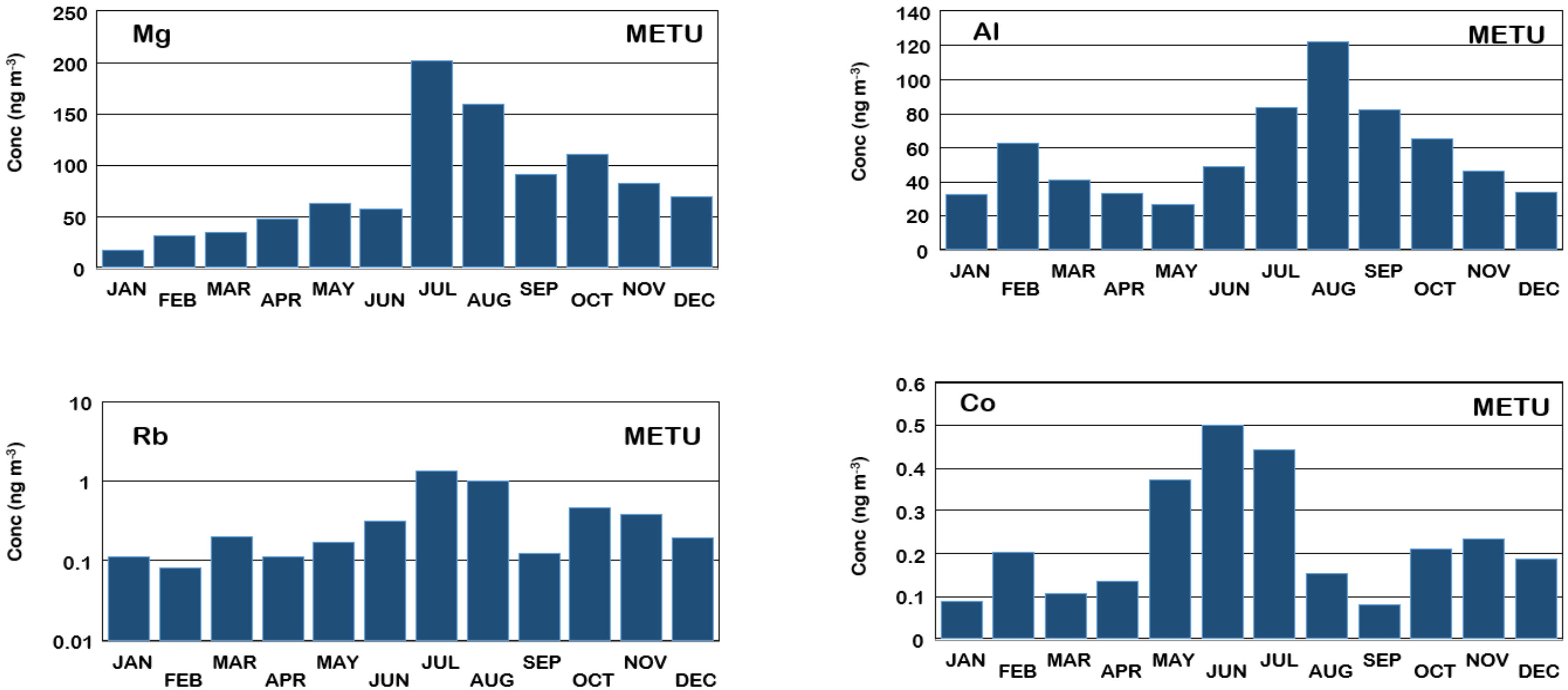


Figure 4- 10 Monthly median concentrations of selected crustal elements at suburban (METU) station

Concentrations of crustal elements do not follow a similar pattern in urban station. There, concentrations are high in winter months and decrease, by approximately a factor of two, during summer. This pattern is opposite to the monthly variation of same elements at METU station. Higher concentrations of litophilic elements in winter does not necessarily mean more extensive resuspension of soil particles in winter. If resuspension does not change in summer and winter, concentrations of these elements would be higher owing to lower mixing height and less effective ventilation process in winter. The difference in seasonal variations of crustal elements observed in two stations is probably due to different demographic conditions around these stations. Suburban station, which is located at METU campus, is surrounded by unexposed soil in all directions. Urban station, which located at Ankara University campus, on the other hand, is surrounded by residential areas. Exposed soil surface around urban station is not much, because soil is covered by buildings. Because of this resuspension of soil particles is limited in both summer and winter. Obviously enhanced resuspension of crustal particles in summer does not work at the urban station due to lack of exposed soil surface from where resuspension occurs.

Monthly variation of selected elements with anthropogenic sources are depicted in Figure 4-11 and Figure 4- 12 for urban and suburban stations, respectively. The monthly variations observed in concentrations of anthropogenic elements are similar to variations in concentrations of crustal elements. In urban station on the other hand, their concentrations are high in winter and decrease by approximately a factor of two in summer. This monthly pattern observed at urban station is understandable and expected. Since there is not much industry in Ankara sources of anthropogenic elements are either traffic emissions or emissions from coal combustion for space heating. Mode of heating had changed from coal and oil combustion to natural gas in early 90s. More than 15 years after that transition, approximately 25% of households in the city is still being heated by coal combustion (MoEUP, 2013).

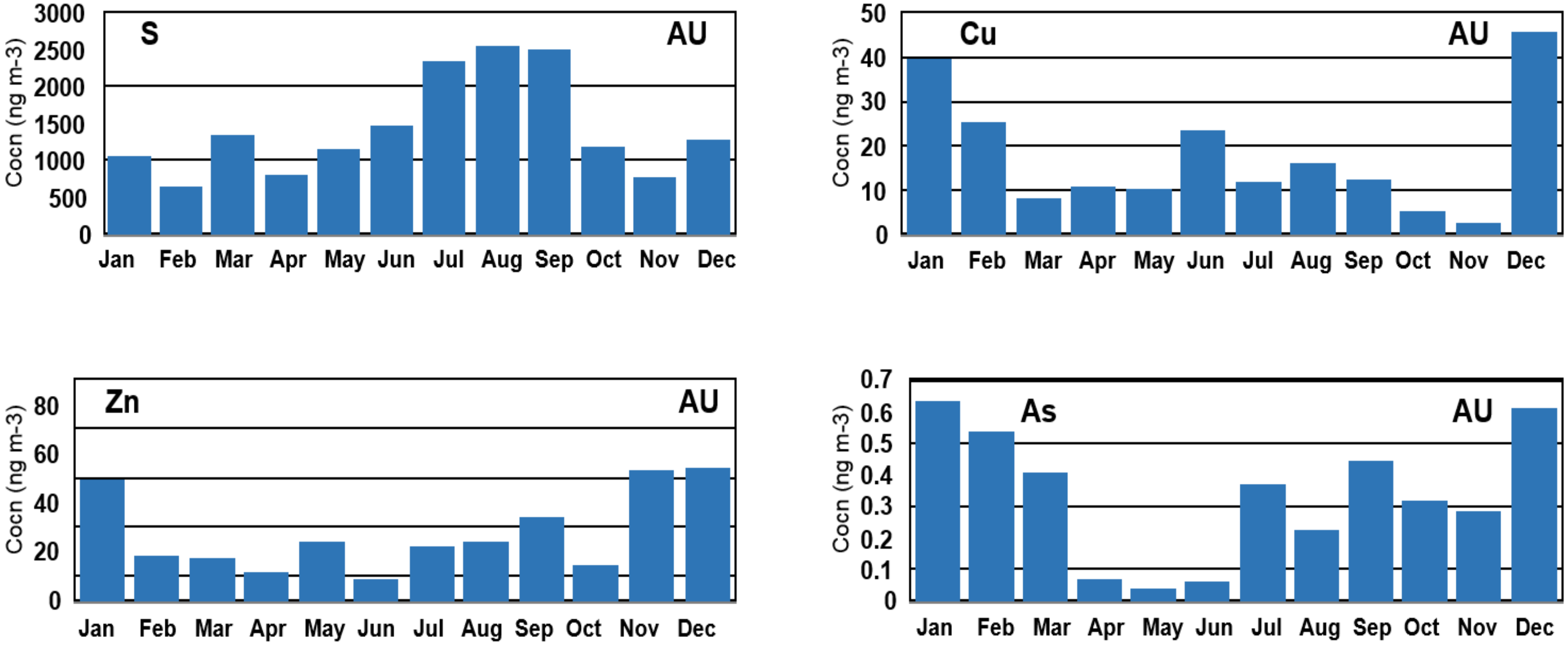


Figure 4- 11 Monthly median concentrations of selected anthropogenic elements at urban(AU) station

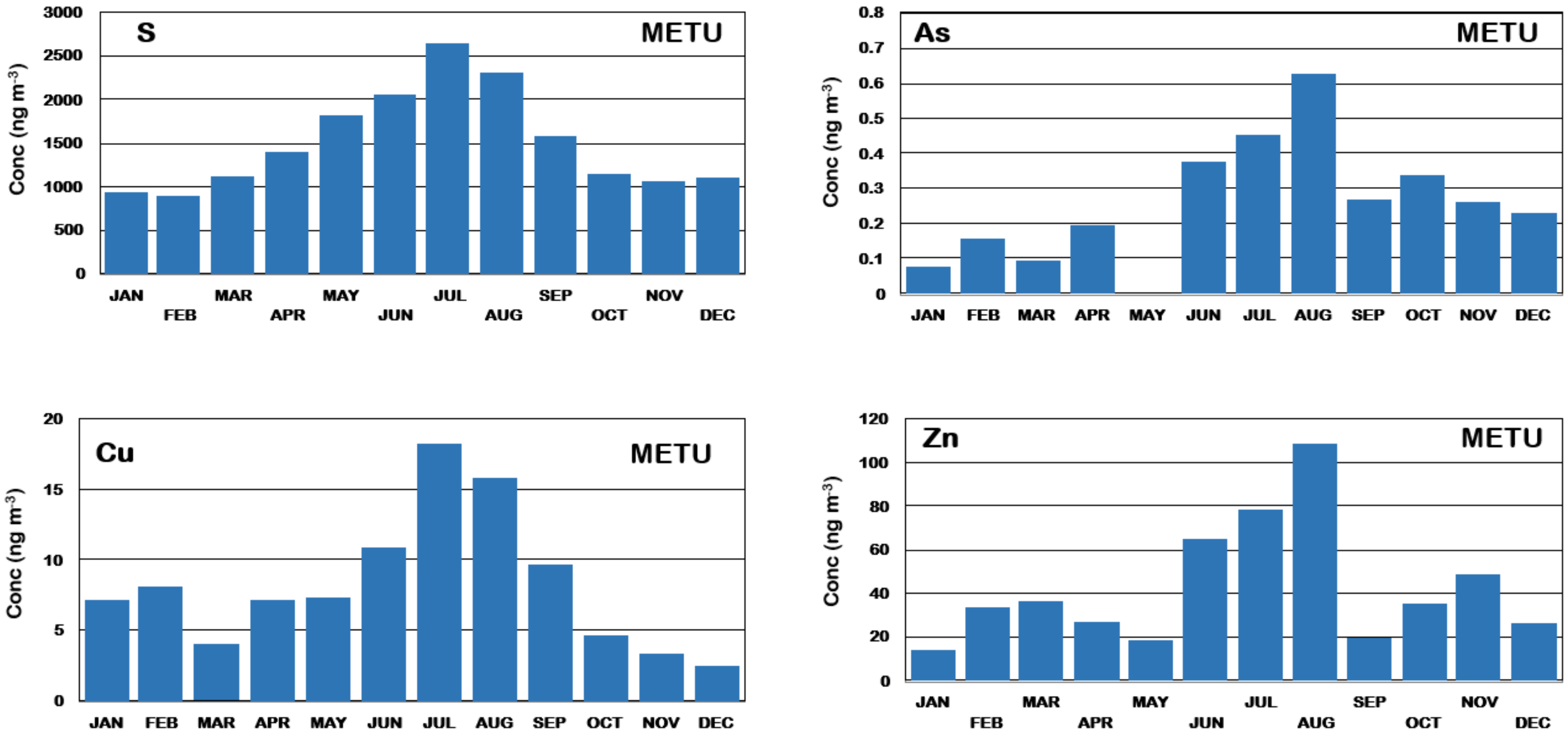


Figure 4- 12 Monthly median concentrations of elements with anthropogenic sources at suburban (METU) station

A very large fraction of PM10 emissions in Ankara is still from coal combustion. A recent (2013) emission inventory for PM10 and other pollutants demonstrated that total of 5800 tons of PM10 is emitted in the city. Fifty-eight percent of those emissions is from space heating, 33% from traffic and approximately 9% is from industrial activities (MoEUP, 2013). Since 98% of PM10 emissions from space heating originates from coal combustion, it will not be wrong to state that 58% of PM10 emissions in Ankara comes from coal combustion for residential heating. Since most of the households that are heated by coal are located at low income districts at the peripherals of the city and since our urban station is close to those areas, it will be reasonable to believe that urban station is affected from coal burning emissions in the city. This explains higher concentrations of pollution-derived elements observed during winter season.

At the Suburban station, concentrations of anthropogenic elements (not only the ones shown in the figure) are high during summer months and gradually decrease towards winter. This monthly pattern is unexpected. Sources of anthropogenic species are either combustion, for which emissions are higher in winter or traffic for which emissions do not change seasonally, as discussed in previous paragraphs. Even if emissions from traffic do not change seasonally, concentrations of pollutants emitted from traffic is expected to be higher due to lower mixing height and inefficient ventilation of the city during winter season. However, what was observed at suburban station is just the opposite, with higher concentrations of anthropogenic elements in summer. Observed pattern does not also agree with the earlier study. In 1993, fine aerosol samples were collected at the METU, Environmental Engineering department and collected samples were analyzed by instrumental neutron activation analysis for approximately 40 trace elements (Yatın et al., 2000). Although sampling duration was not as long as the sampling duration in this work, data provided information on summer and winter concentrations of elements. Winter-to-summer concentration ratios of elements was 5.3 for S, 3.5 for As and 2.1 for Zn. Copper was not measured at that time.

These ratios indicate that in 1993 concentrations of anthropogenic elements was higher in winter at our suburban station. A very different seasonal pattern observed in 2015 suggests that something affecting concentrations of anthropogenic elements have changed in last 22 years.

During previous study (in 1993), coal and residual oil combustion were the only means of residential heating in Ankara. Winter-to-summer concentration ratios for most of the pollution-derived elements is a clear indication of that. In 2015, on the other hand, most of the areas around our suburban station are heated by natural gas. Anthropogenic particle emissions from coal combustion occurs at peripheral of the city like Keçiören, Mamak etc, which are far away from our suburban station (for example Keçiören and Mamak are both approximately 15 km from our station. This denotes that combustion elements measured at suburban station comes from margins of Ankara. This may explain higher concentrations of pollution-derived elements in summer, because transport is limited in winter due to low mixing height, which enhances dry deposition and more frequent wet scavenging.

Modification of seasonal variations in concentrations of anthropogenic elements at METU in last 22 years is due to elimination of combustion sources in suburbs of the city and the difference between seasonal patterns of anthropogenic elements in two stations is due to close proximity of urban station to peripherals of Ankara where coal combustion for space heating continues. This is an important finding because we reach this conclusion by using some elements that are good markers for anthropogenic activity, but other pollutants that were not measured in our study are also expected to show similar variations and these patterns and differences with earlier studies demonstrate how general air quality in Ankara changed in time.

Monthly variation in concentrations of elements with mixed sources are depicted in Figure 4- 13 for urban and in Figure 4- 14 for suburban stations, respectively.

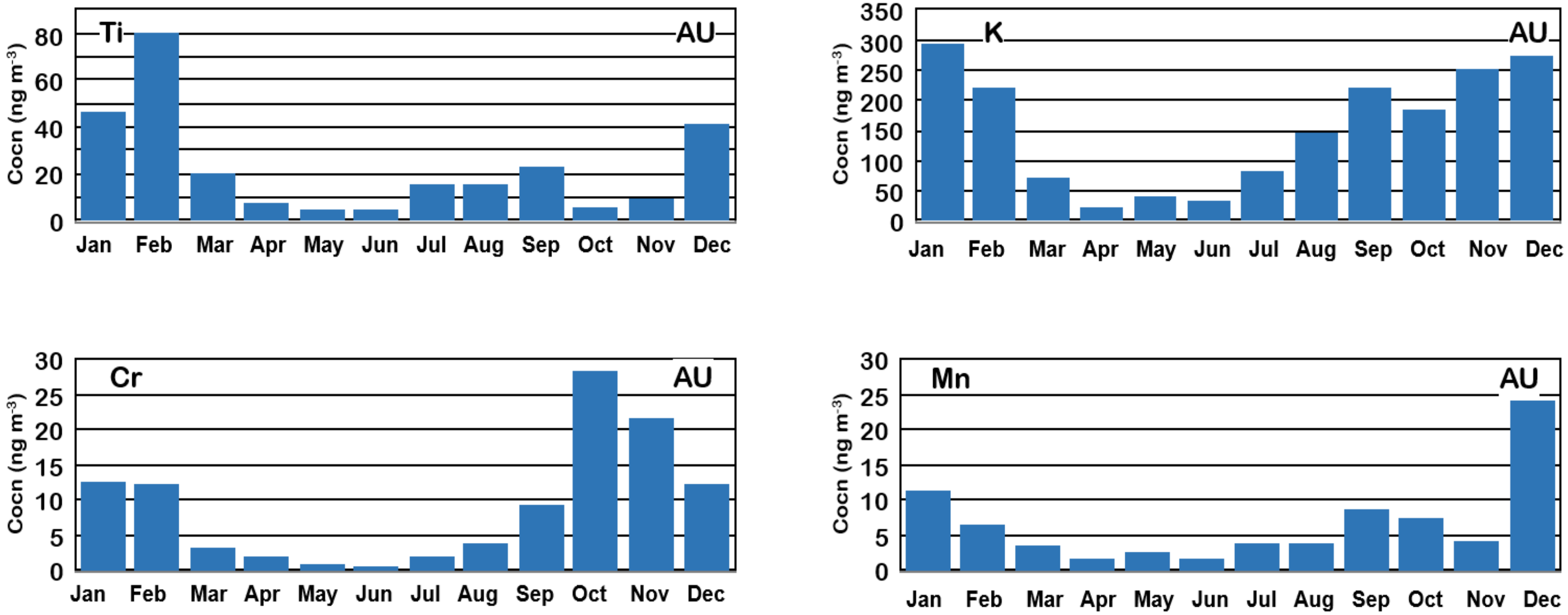


Figure 4- 13 Monthly median concentrations of elements with mixed sources for urban (AU) station

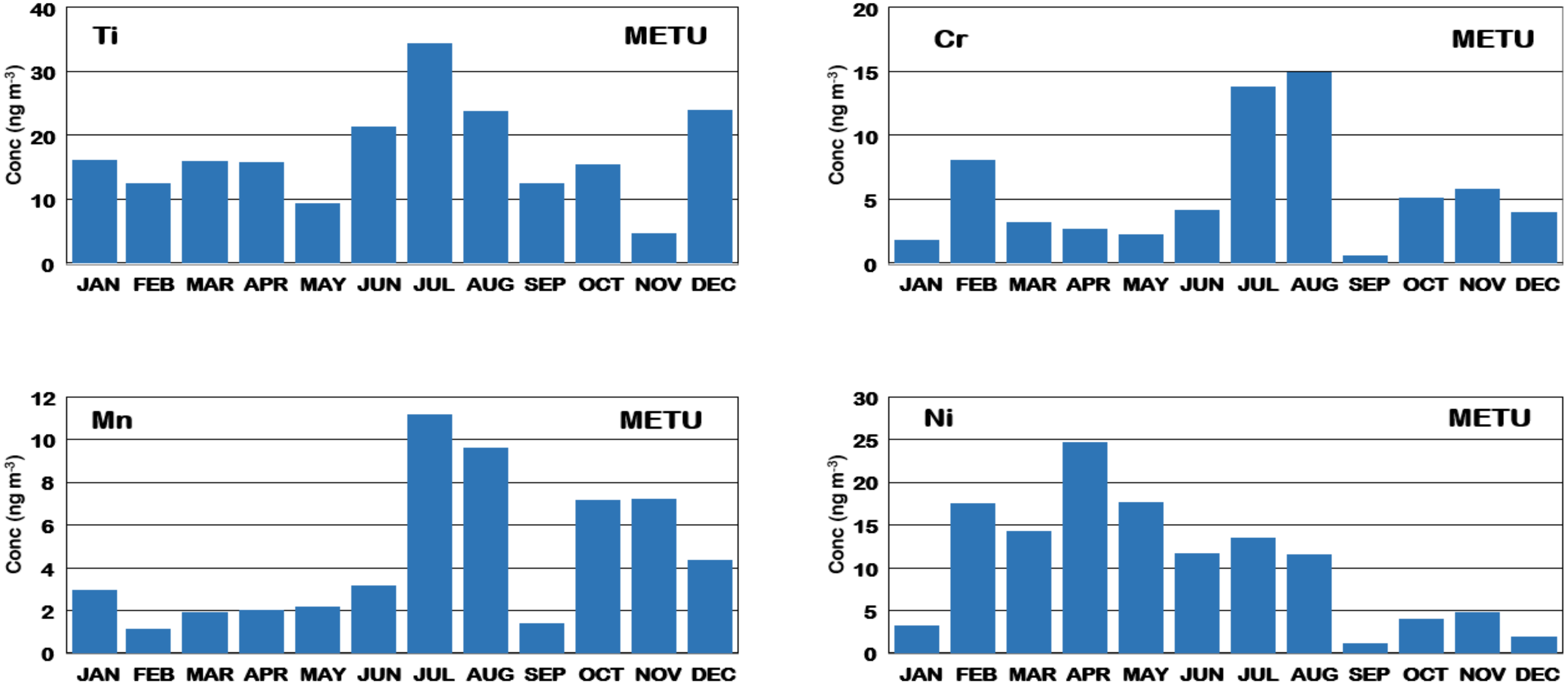


Figure 4- 14 Monthly median concentrations of elements with mixed sources at suburban (METU) station

Ti, Cr, Mn, K and Ni have relatively high concentrations in soil and because of that in remote areas, where contribution of anthropogenic sources does not exist or limited, they behave like crustal elements. However, they also have anthropogenic sources and in places, which are under influence of combustion, traffic or industrial sources, their concentrations can be dominated by anthropogenic emissions. At our suburban station concentrations of this group of elements are high in summer months and low in winter. In urban station on the other hand their concentrations are high in winter and low in summer. The difference in monthly variation in concentrations of these elements at urban and suburban stations shows that their concentrations is determined by anthropogenic (primarily combustion) sources at urban site, but determined by crustal material at suburban site.

Moreover, due to the change of human activities during the weekdays and weekends, the concentration of atmospheric particles and their elemental content in the city are different during the weekdays and weekends (Almeida et al., 2006; Morawska et al., 2002). For example, some anthropogenic elements which are emitted by the traffic activities are expected to be higher during the weekdays due to the more intense traffic in those days (Almeida et al., 2006). However, the concentration of elements related to the activities which are more intense during the weekends, are expected to be higher on those days, such as elements related to the combustion. Because space heating by fossil fuel combustion is more on weekend, the tracers of combustion emissions are expected to be higher during these days. (Thurston et al., 2011).

Weekend and weekday concentrations of selected elements and their weekday to weekend concentration ratio for AU and METU stations are given in Figure 4- 15. 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.

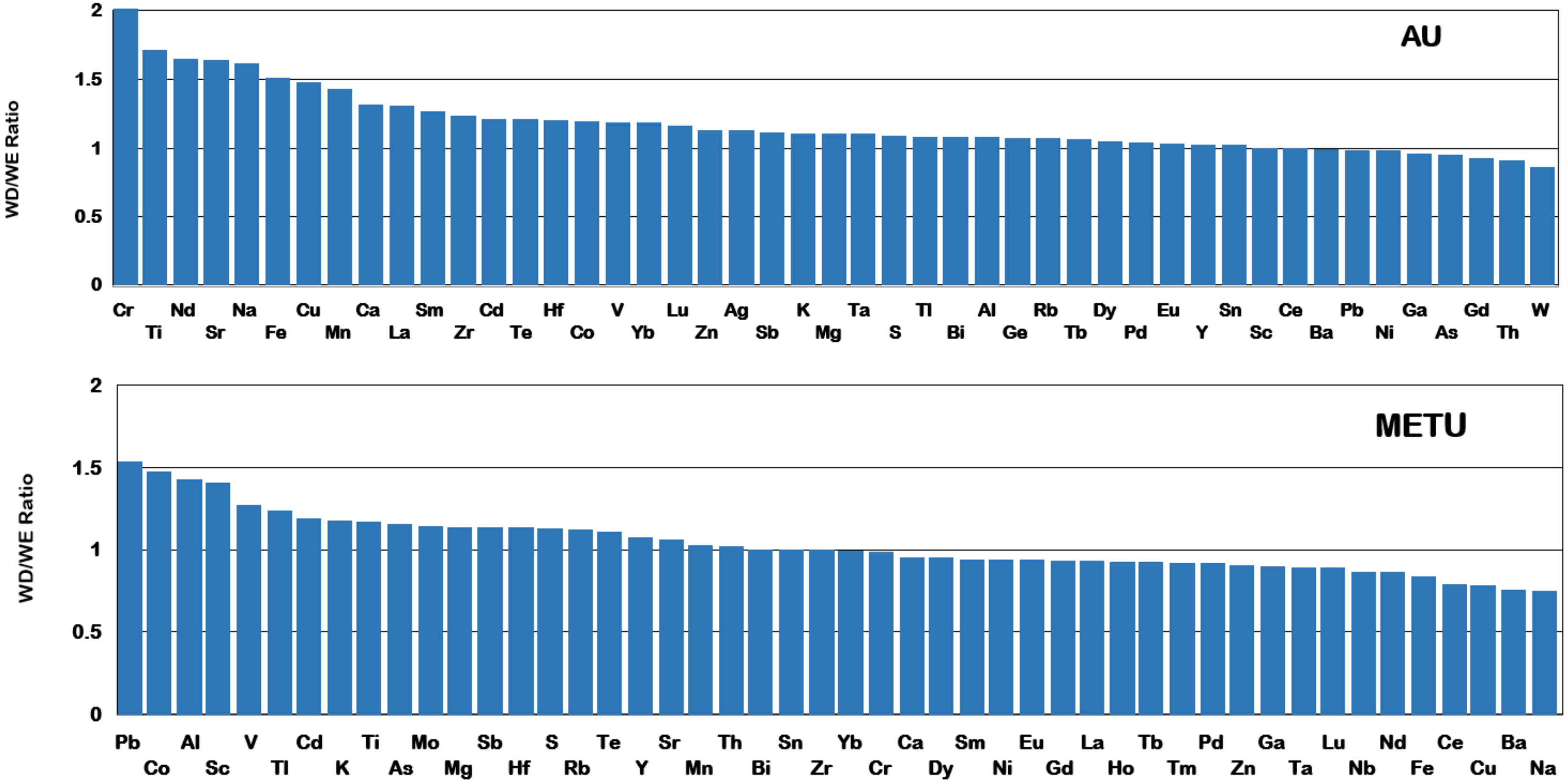


Figure 4- 15 Weekday to Weekend concentration ratios of elements for both urban and suburban stations

For both stations, most of the crustal and anthropogenic elements do not show much difference between their weekday and weekend concentrations. The observable thing in two stations is that in METU station, most elements are having very similar concentrations during weekday and weekends and the Weekday/Weekend ratio vary between 1.0 ± 0.5. In this station, most anthropogenic and crustal elements are higher during the weekends, which can be due to the fact that lots of students and their families come to METU for picnic on weekends and the fossil fuel combustion heating for dormitories is not changing during different days. However, in Ankara station, as an urban location, most of element show higher concentration during the weekdays, probably because of the higher traffic and human activities, as expected.

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. Variations in emission strength, transport pathways and local meteorological conditions are reported to cause episodes in trace element data set. 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, especially in METU station, there does not seem to be sufficiently different activities at weekdays and weekend days to generate weekday-to-weekend ratios significantly different from unity.

4.4 Dependence of measured concentrations of elements on local meteorology

There are two important factors affecting variations and levels of the concentrations of elements in both temporal and spatial aspects. One of them is their emission strength, and the other is meteorology of the region. Therefore, understanding and analyzing the meteorology of the city and stations has a great significance in our study.

For the METU station, as a suburban area, meteorological data was obtained from the Etimesgut meteorology station, which is the closest meteorological station to the sampling site. For AU station, as an urban station, meteorology data measured in Kecioren station has been used, due to the similarity of this station to our AU station. It is noteworthy that only the days with samples were included in averages in this chapter, as mentioned previously, months between May and October are considered as summer, and months between November and April are considered as winter season. The division was done by considering temporal and precipitation changes during these months. In part 3.2, the meteorology of the Ankara was mentioned, and in this section the relation of those parameters with the observed concentrations will be discussed. The summary of the data obtained from General Directorate of Meteorology on meteorological parameters discussed in the chapter 3,2, for both stations during our studying period are presented in Table 4- 7 and Table 4- 8.

Table 4- 7 Summary of Meteorological parameters during sampling period at Etimesgut representing our METU station

Parameters		Summer	Winter	Annual
Temperature (ºC)	Mean	20.8	8.4	14.3
	min	2.1	-8.8	-8.8
	Max	29.9	27.9	29.9
Wind speed (m/s)	Mean	2.6	2.1	2.3
	min	1.2	0.5	0.5
	Max	4.8	7.2	7.2
Mixing Height (m)	Mean	2108.0	1069.2	1563.5
	min	508.9	81.9	152.7
	Max	3232.3	3603.5	2543.6
Ventilation coefficient (m^2/s)	Mean	5391.4	2325.6	3784.3
	min	1379.9	212.4	224.3
	Max	14934.3	12767.3	12380.4
Relative Humidity (%)	Mean	55.7	78.1	67.4
	min	34.1	34.6	34.1
	Max	89.6	98.8	98.8
Rainfall (mm)	Mean	211.7	102.4	314.1

In METU station, the temperature has varied from -8.8 ºC in January, to 29.9 ºC in July, during our sampling period. The mean temperature in winter is 8.4 ºC and 20.8 ºC during the summer, giving the annual mean temperature equal to 14.3 ºC.

Table 4- 8 Summary of Meteorological parameters during sampling period at Kecioren representing our AU station

Parameters		Summer	Winter	Annual
Temperature (ºC)	Mean	18.8	7.5	14.0
	min	2.1	-10.3	-10.3
	Max	29.1	27.9	29.1
Wind speed (m/s)	Mean	2.6	2.4	2.5
	min	1.0	1.1	1.0
	Max	7.7	6.9	7.7
Mixing Height (m)	Mean	1436.2	818.0	1177.6
	min	238.6	128.2	128.2
	Max	3218.9	2264.9	3218.9
Ventilation coefficient (m^2/s)	Mean	3806.9	2145.0	3111.8
	min	449.5	374.0	374.0
	Max	12964.3	12106.6	12964.3
Relative Humidity (%)	Mean	48.3	71.0	57.8
	min	0.0	27.0	0.0
	Max	88.1	97.3	97.3
Rainfall (mm)	Mean	253.3	100	353.3

4.4.1 Dependence on wind speed

Wind speed is an indication of effectiveness of horizontal ventilation process in urban atmosphere. When emissions do not change, concentrations of pollutants are expected to decreases with increasing wind speed due to enhanced horizontal ventilation over the city. Variation in concentrations of selected crustal elements with wind speed in both urban and suburban stations are given in Figure 4- 16 and Figure 4- 17, respectively.

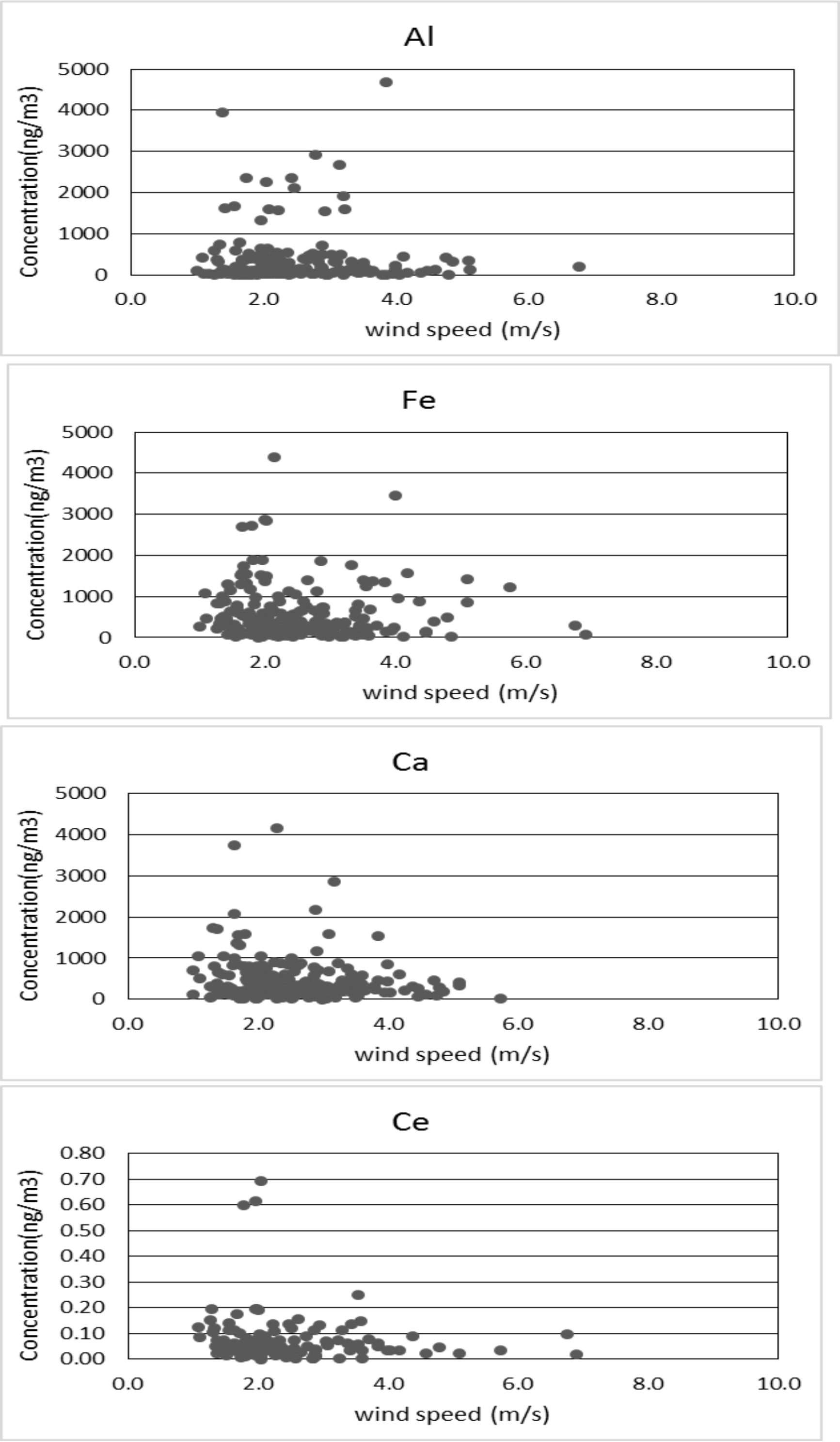


Figure 4- 16 Variation in concentrations of selected crustal elements with wind speed at urban station

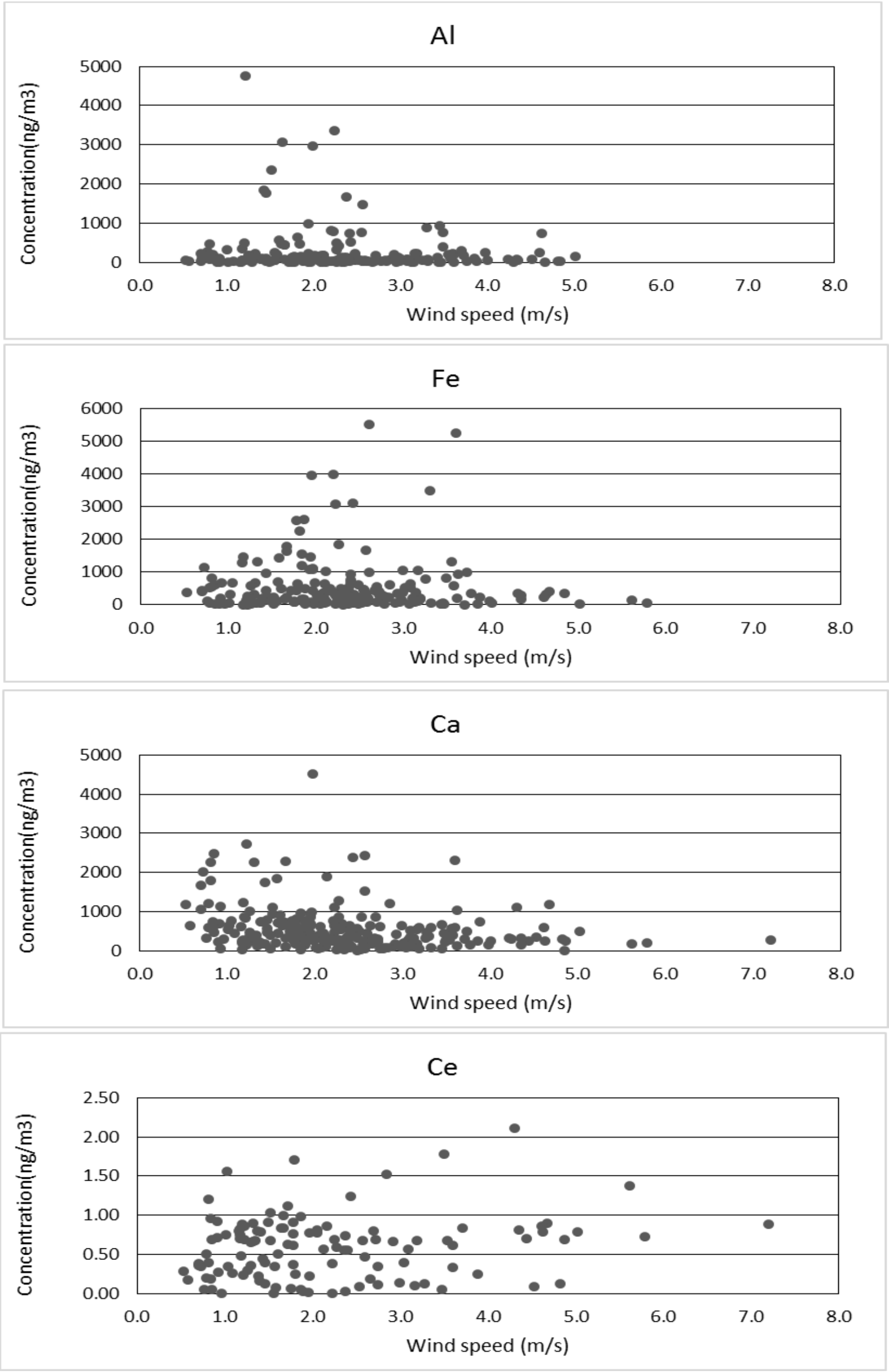


Figure 4- 17 Variation in concentrations of selected crustal elements with wind speed at METU station

In both stations, crustal elements did not show a well-defined decreasing pattern with wind speed. Please note that concentrations of atmospheric constituents decrease with increasing wind speed if emissions remain constant. However, concentrations of crustal elements depends strongly on wind speed. More soil aerosol is generated when wind speed is high. Also they are diluted more at high wind speed as ventilation coefficient (assimilative capacity of atmosphere) will be high. With these two factors, concentrations of crustal elements did not show a definable, consistent variation with wind speed.

Variations in concentrations of anthropogenic elements with wind speed are depicted in Figure 4-18 and Figure 4-19 at urban and suburban stations, respectively. Patterns observed in the two stations were similar for most pollution-derived elements. Concentrations of chalchophilic elements decreased with increasing wind speed. This was an expected behavior for pollutants that are emitted with same emission rate throughout the year. Thirty years ago, when combustion was the main source of chalchophilic elements, their emissions were higher in winter. However now, emissions from coal combustion for residential heating decreased approximately 70% and traffic and industrial activities became their dominating source. Since both traffic and industrial activities emits them throughout the year, the decrease in their concentrations with wind speed is not surprising. There is a third group of elements, which are contributed by both anthropogenic and crustal sources. This group includes elements Na, Mg, K, Ti, V, Cr, Mg, Mn, and Ni. Among these Na and Mg have both crustal and marine sources. However, since there is no sea-salt emissions around stations, both Na and Mg have only crustal sources in this study. Potassium have three sources, it is emitted from marine emissions (which does not exist in this work), it is emitted from biomass burning (wood combustion) and it has high concentration in crustal aerosol. Remaining elements, in this group, have both crustal and anthropogenic sources.

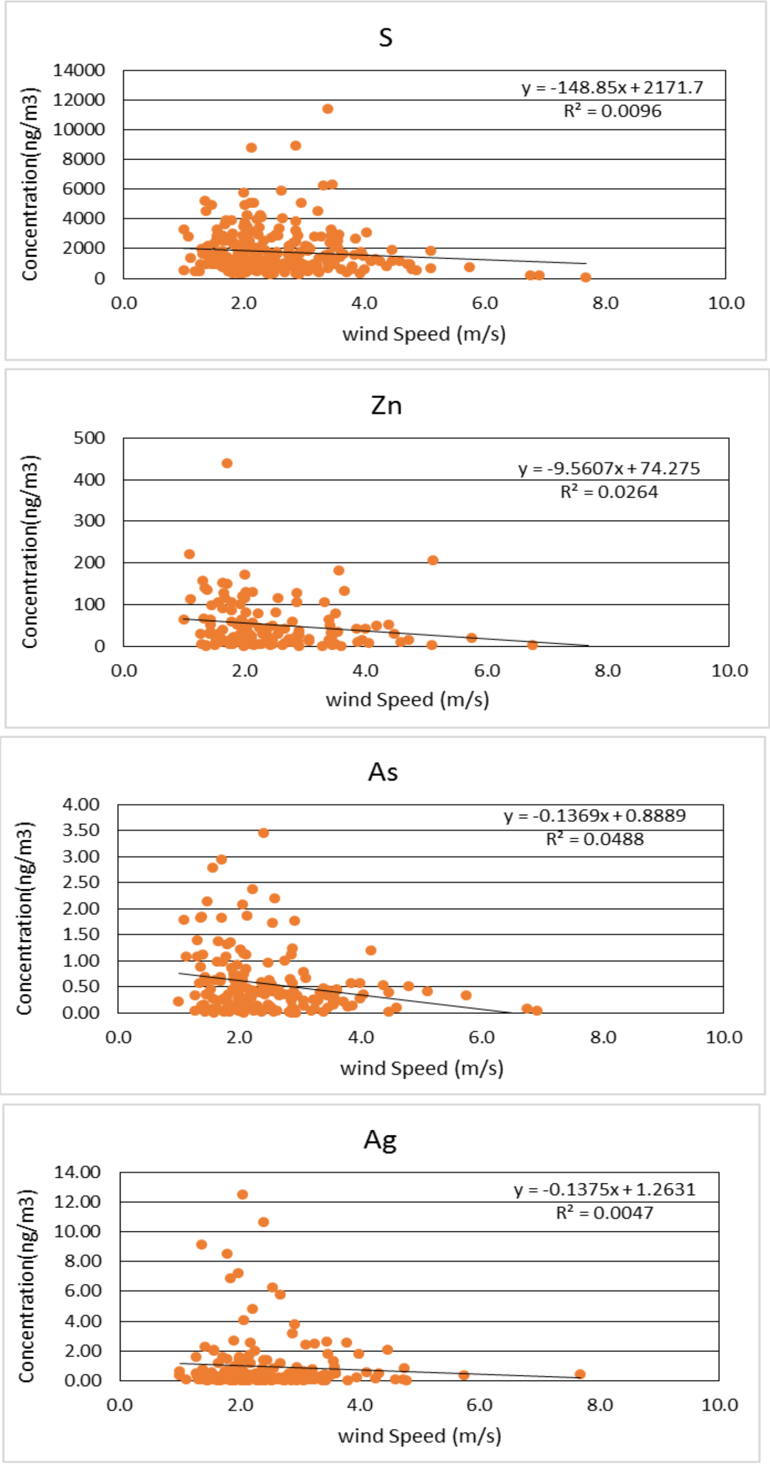


Figure 4- 18 Variation in concentrations of selected pollution-derived elements with wind speed at urban station

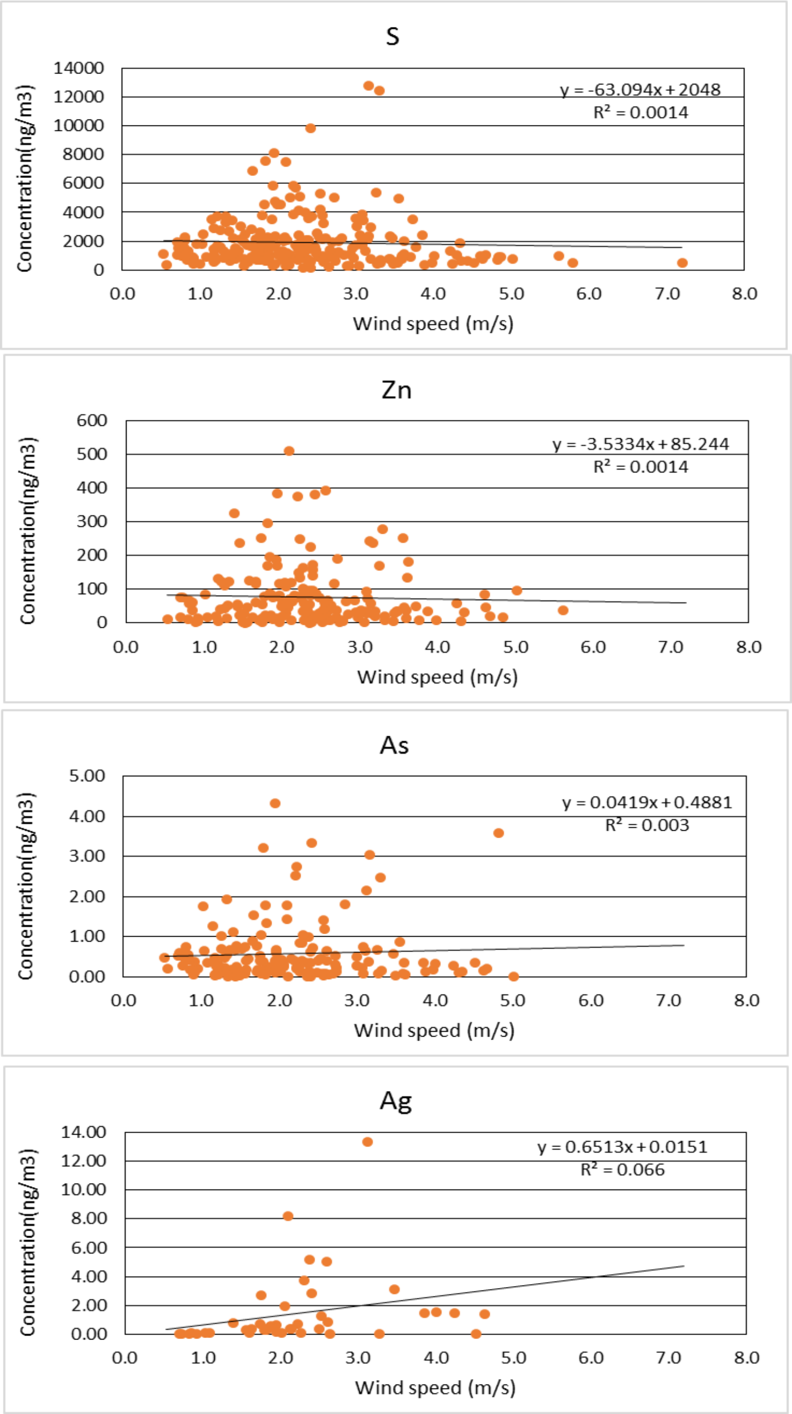


Figure 4- 19 Variation in concentrations of selected pollution-derived elements with wind speed at METU station

Variation in concentrations of selected elements with mixed anthropogenic and crustal sources are given in Figure 4-20 for urban and in Figure 4-21 in suburban station. Interestingly this group of elements depicted two different patterns in urban and suburban stations. At suburban satiation, they did not show a clear variation with wind speed and behaved like crustal elements, but at urban station, their concentrations decreased with wind speed and in this sense, they behaved like an anthropogenic element. The same difference was also observed in ventilation coefficient and will be discussed later in that section. This difference in behaviors of elements with mixed sources in the two stations is due to difference in contributions of anthropogenic and crustal source on their concentrations in urban and suburban stations. At urban station, contribution of anthropogenic sources on their concentrations is higher because the station is in the middle of residential and traffic activities. However, contribution of crustal source is limited, because there is not much exposed surface in the city (as surface is covered by buildings and roads). This explains why their concentrations decrease with wind speed at urban station. The suburban station is in METU campus. Although there are residential areas developing around the campus, there are still fair amount of uncovered ground. Consequently, contribution of soil-resuspension on concentrations of elements with mixed sources is expected to be higher at suburban station.

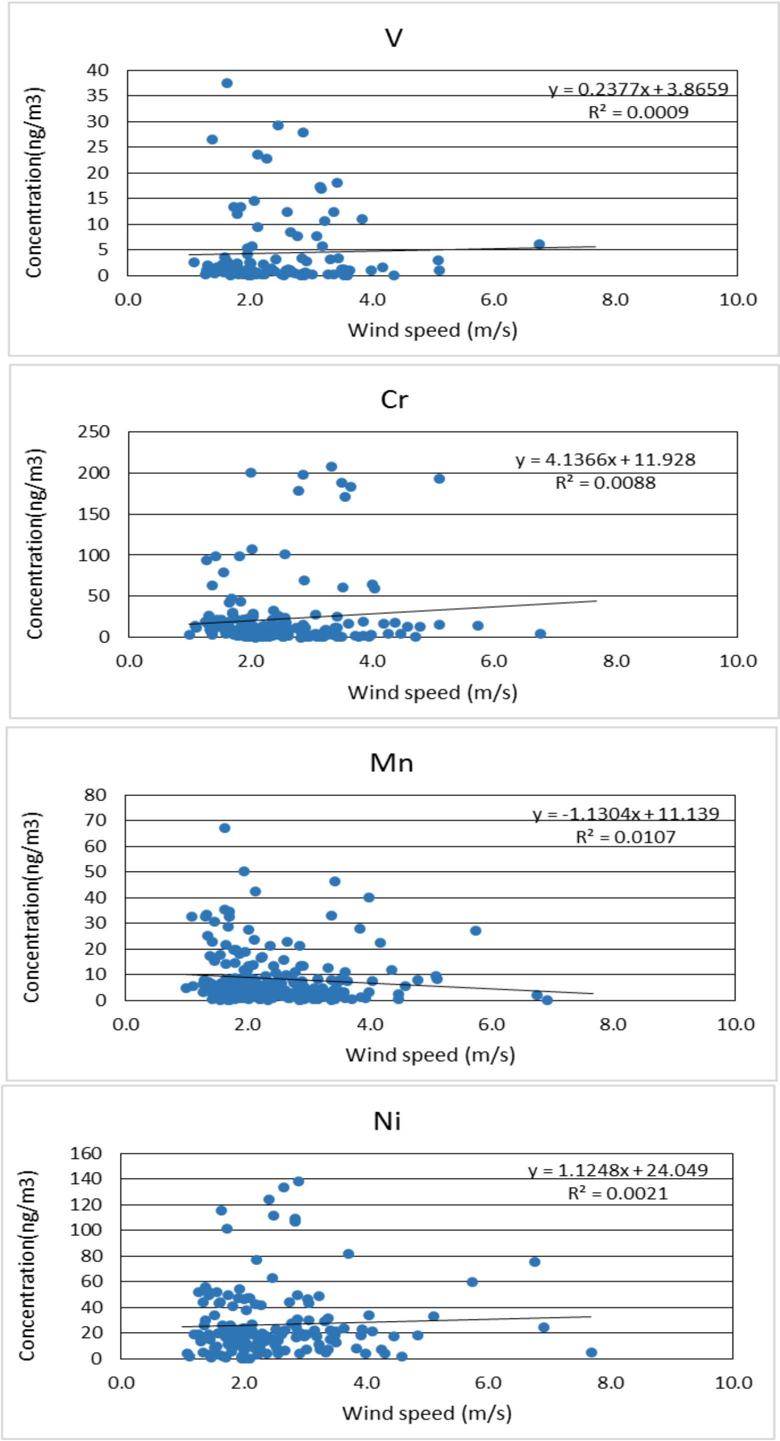


Figure 4- 20 Variation in concentrations of selected elements with mixed sources with WS at urban station

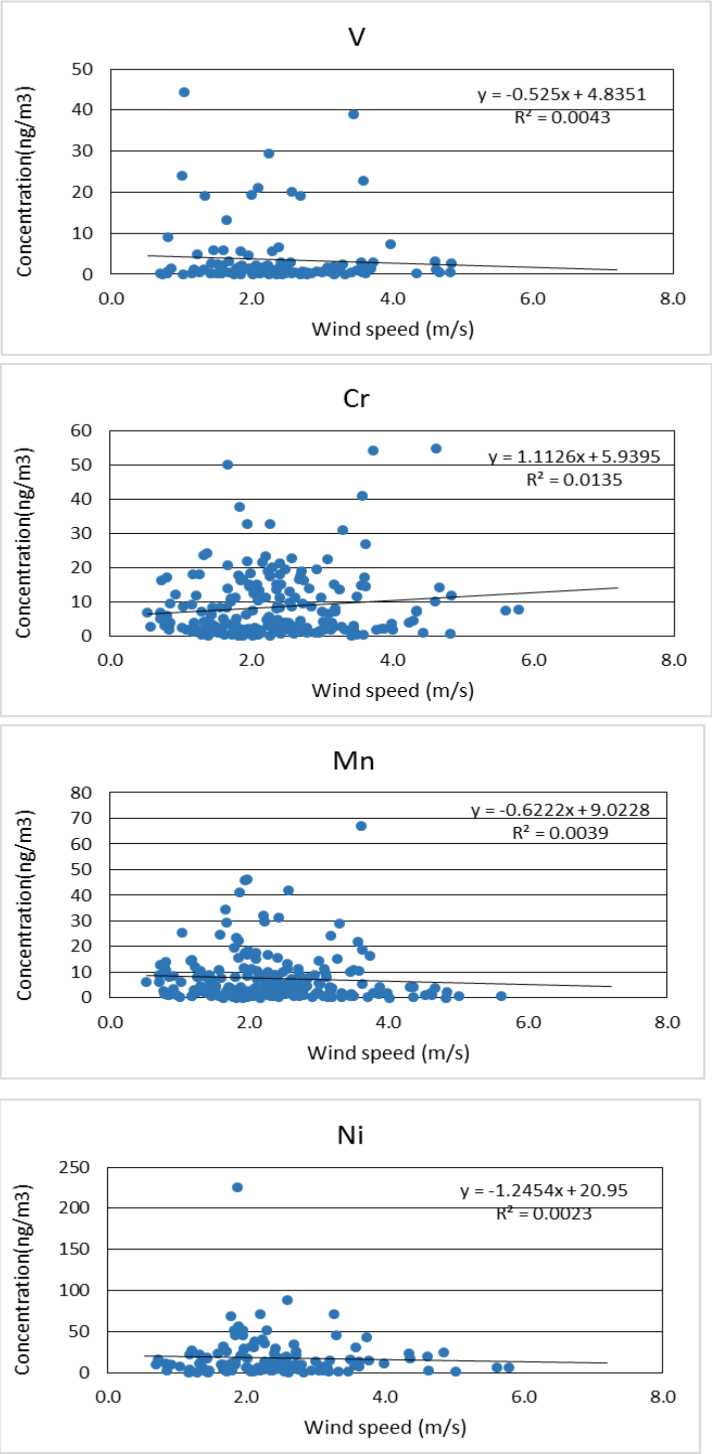


Figure 4- 21 Variation in concentrations of selected elements with mixed sources with wind speed at METU station

4.4.2 Dependence on temperature

Relation between concentrations of elements and temperature is indirect. Since temperature is high in summer, concentrations of elements, which have higher source strength in summer season appears as increasing with temperature. On the other hand, concentrations of those elements with higher source strength in winter appears as inversely related with temperature. In this work, different groups of elements behaved differently. Variation in concentrations of crustal elements with temperature is depicted in Figure 4- 22 for urban station and in Figure 4- 23 in suburban station. Soil related elements depicted increasing concentrations with temperature in both stations. This pattern is due to higher source strength of litophilic elements in summer season, when temperature is high. During summer, surface soil is dry and resuspension of soil particles with wind is easier. Because of these concentrations of crustal aerosol and elements associated with crustal particles is high in summer. Since temperature is also high in summer this generates temperature dependence shown in the below mentioned figures.

Variation in concentrations of pollution-derived elements are given in Figure 4- 24 and Figure 4- 25 for urban and suburban stations, respectively. Unlike crustal elements, concentrations of this element group decrease with increasing temperature. This pattern is again due to higher concentrations of anthropogenic species in winter season. Conventionally, since there is not much industrial activity in the city, coal combustion for space heating was the main source of anthropogenic species in Ankara atmosphere. However, with the use of natural gas for heating this pattern has changed. Now traffic is the main source of pollutants that are markers for residential heating emissions.

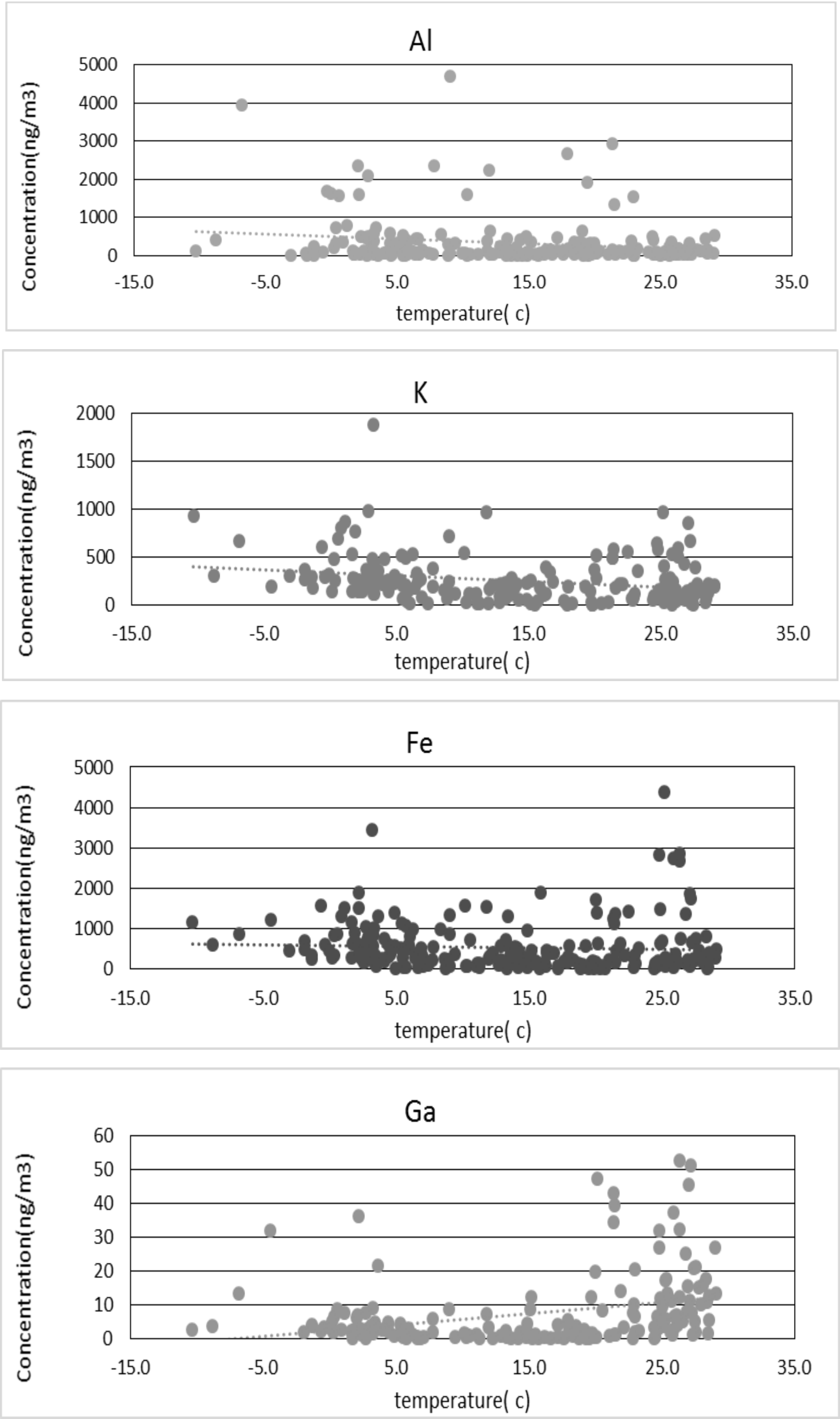


Figure 4- 22 Variation of concentrations of selected crustal elements with temperature at urban station

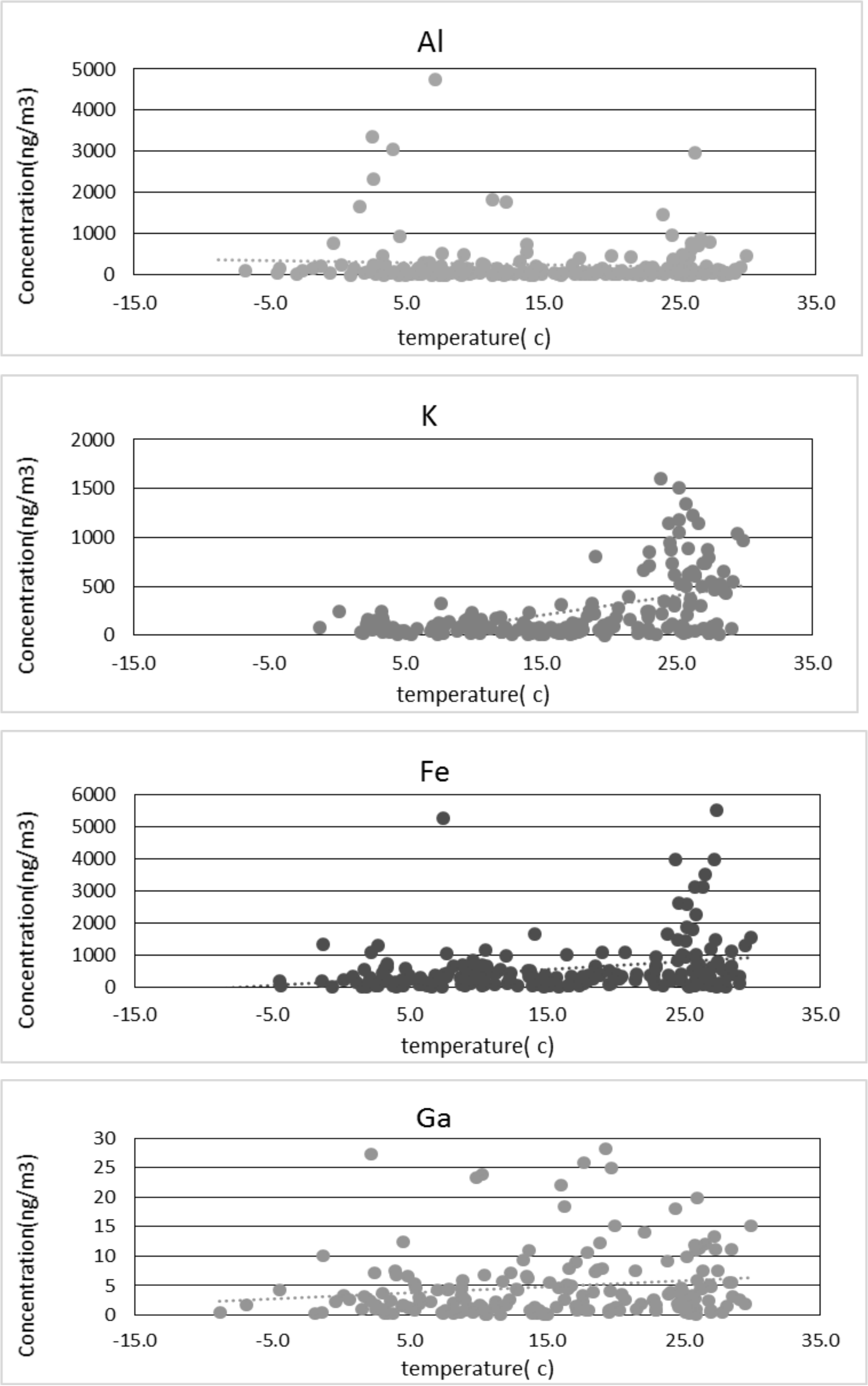


Figure 4- 23 Variation of concentrations of selected crustal elements with temperature at suburban station

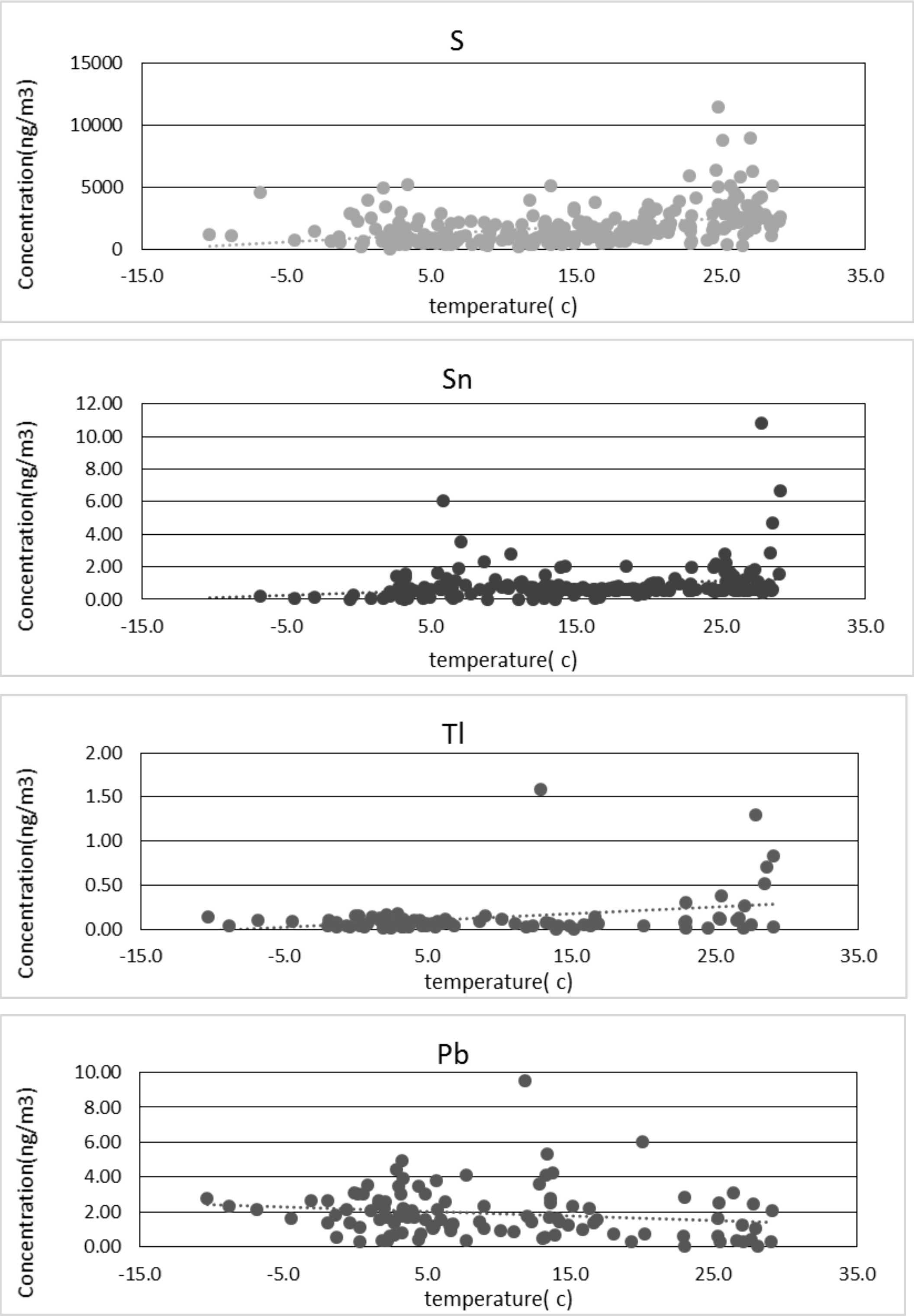


Figure 4- 24 Variation of concentrations of selected pollution-derived elements with temperature at urban station

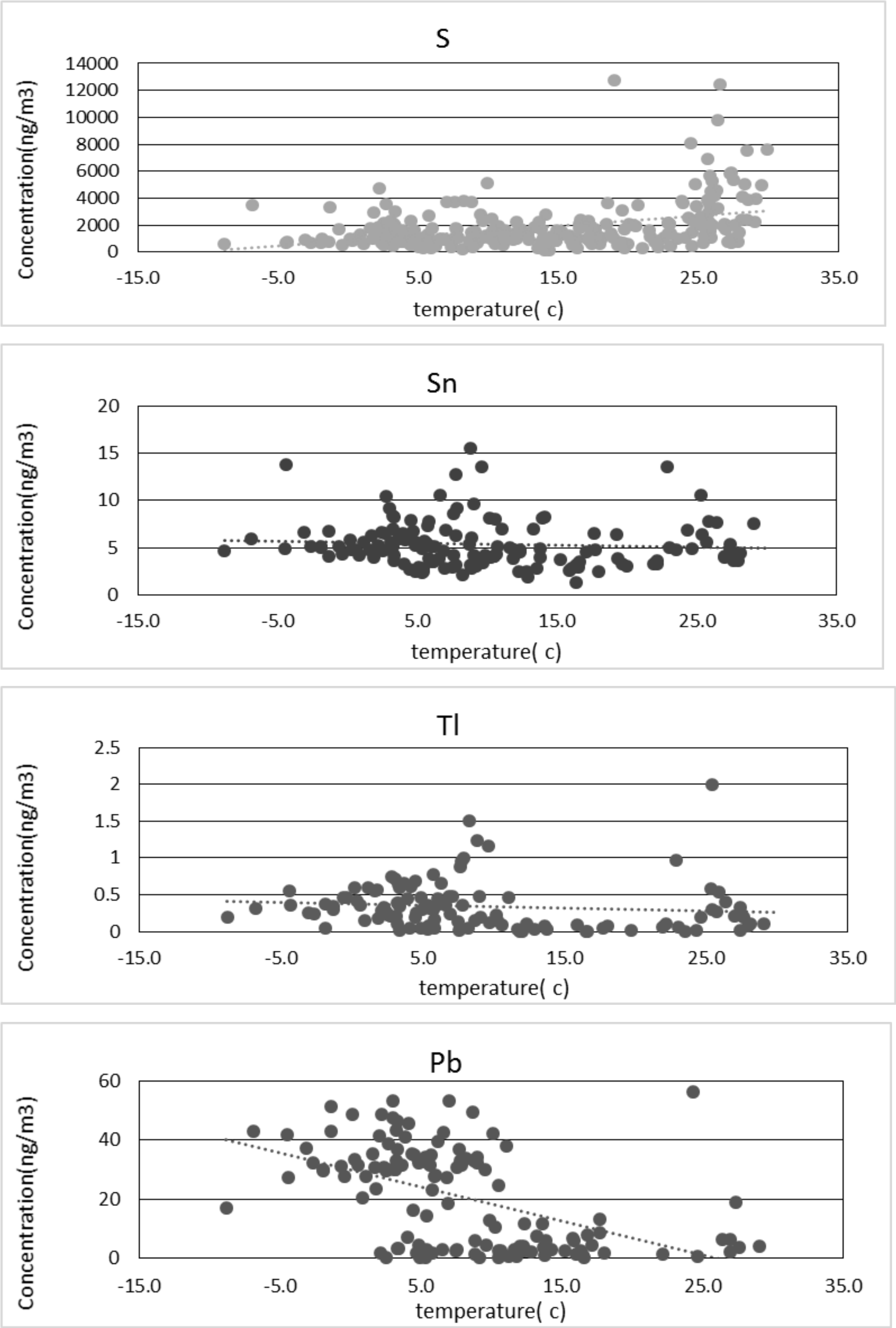


Figure 4- 25 Variation of concentrations of selected pollution-derived elements with temperature at suburban station

In a recent study in our group, it was demonstrated that diurnal variation in SO_2 concentrations in Ankara, which is well-known marker for coal-combustion, is similar to diurnal variation in CO concentration, which is known to be emitted from traffic (Genc, *et al*, 2010). The transition from coal combustion to natural gas for space heating is not complete. Even today 40% of the residences in Ankara is heated by coal. This is partly due to the lack of infrastructure to use gas at outskirts of the city and partly due to high gas prices. In any case, approximately 30% of the households in Ankara, particularly at the low income districts at the peripherals of the city are heated by coal and thus coal emissions are not entirely eliminated. Higher emissions of coal combustion related elements in winter could result in decreasing concentrations of these elements with increasing temperature. Emissions from traffic do not change significantly from one season to another. When emission of an element is equal in summer and winter its concentration is expected to be higher during winter months owing to lower mixing height in winter (Zhao *et al.*, 2017, Tang *et al.*, 2016). Higher concentrations in winter, whether it is due to higher emissions in winter or due to lower height in winter appears as decreasing concentrations of elements with increasing temperature. This explains why concentrations of anthropogenic elements decrease with increasing temperature in both urban and suburban stations at Ankara. The only exception to this pattern was observed in S concentration. Concentration of S increase with increasing temperature in both station. This is due to faster photochemical oxidation of SO_2 to SO_4^{2-}during summer, which appears as stronger SO_4^{2-}source strength. Higher concentrations in summer reflects as increasing concentration with temperature, as discussed previously in the manuscript.

Concentrations of elements with mixed sources showed different patterns in urban and suburban stations as shown in Figure 4- 26 and Figure 4- 27 for AU and METU stations, respectively.

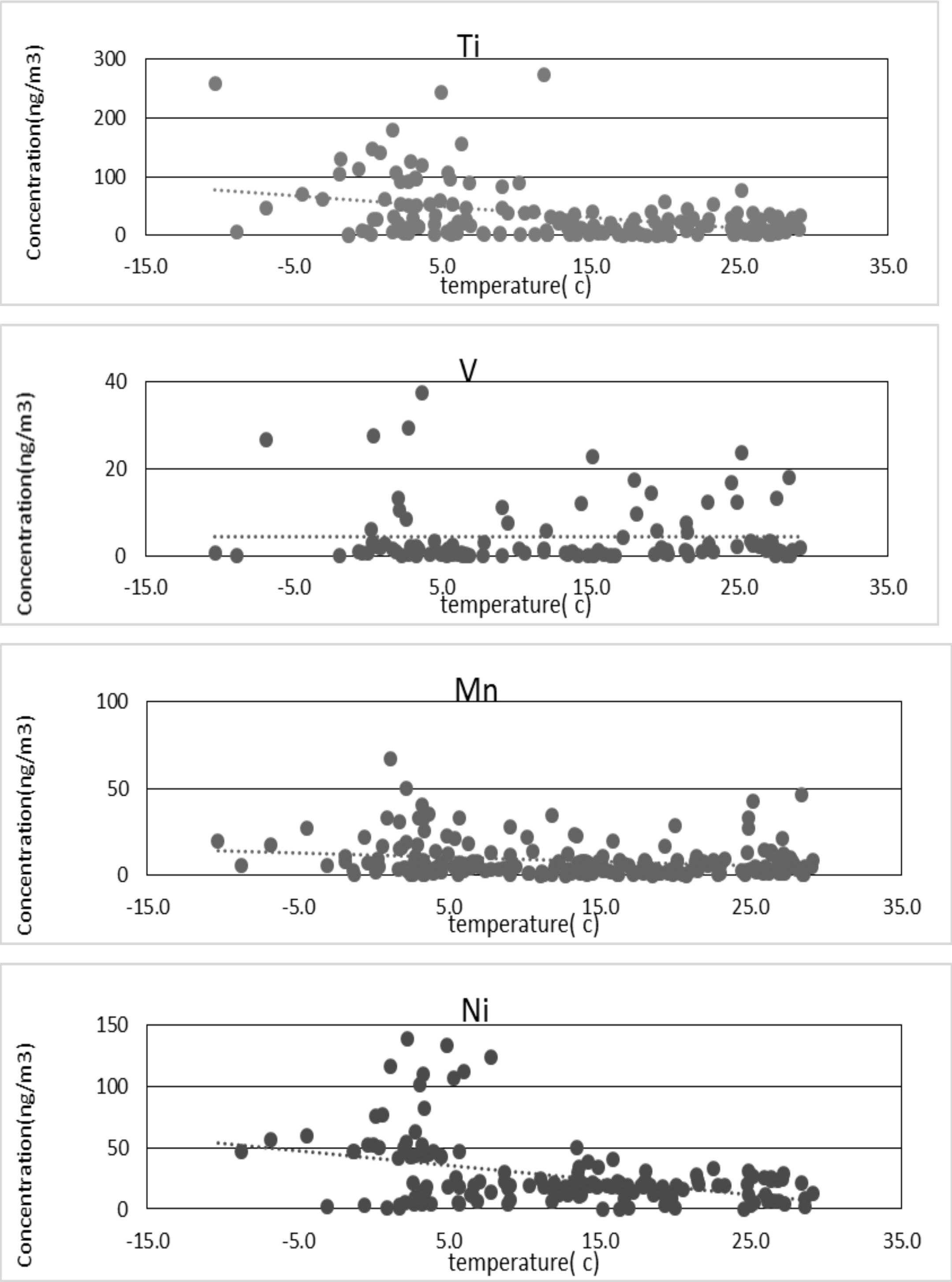


Figure 4- 26 Variation of concentrations of selected elements with mixed sources with temperature at urban station

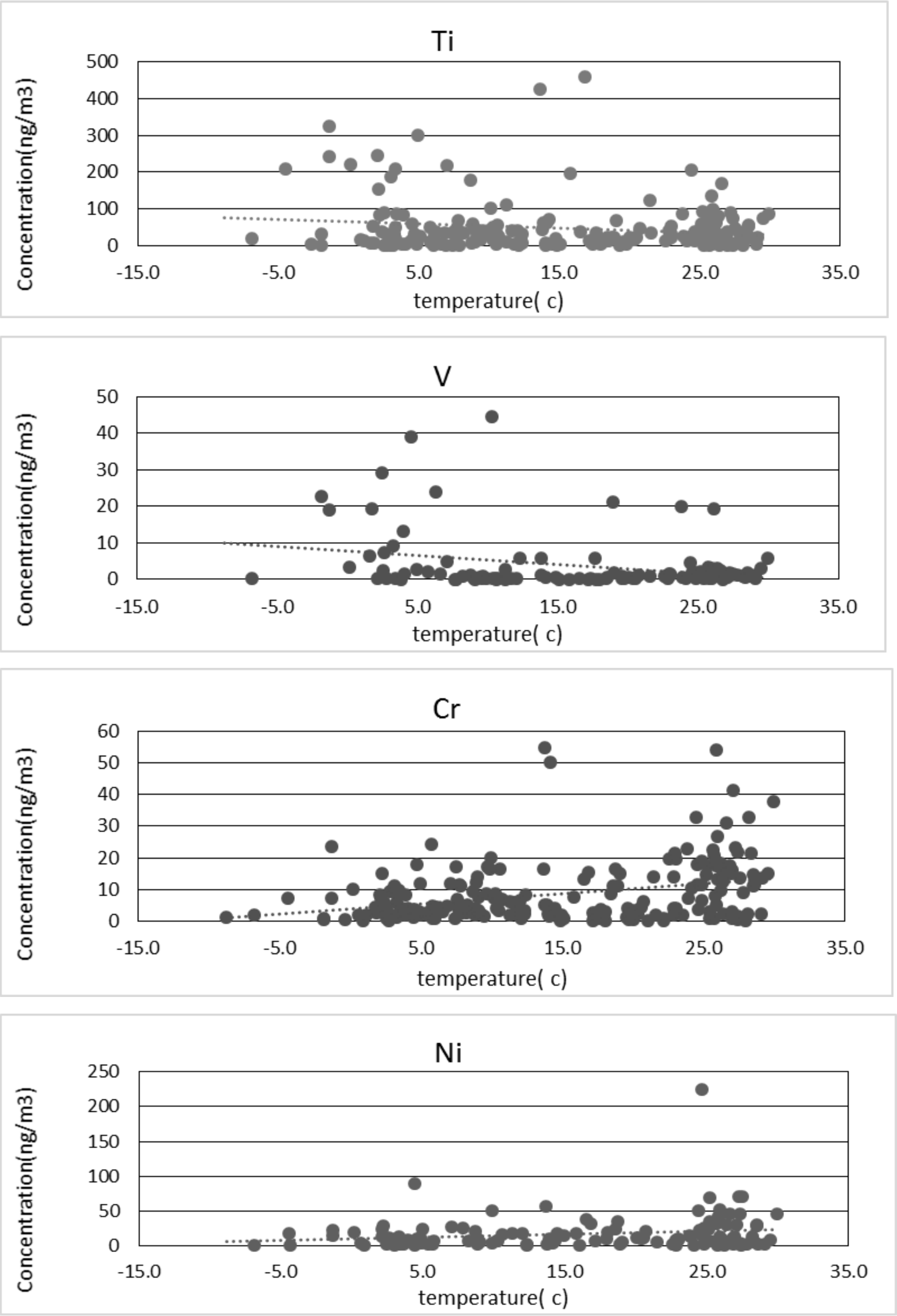


Figure 4- 27 Variation of concentrations of selected elements with mixed sources with temperature at suburban station

At suburban station concentration of mixed source elements do not show a consistent increasing or decreasing pattern. At the urban station, on the other hand, their concentrations decrease with increasing temperature. The reason for these two different patterns in two stations is the same with the reason discussed in previous section on dependence of concentrations of these elements on wind speed. Concentrations of this group of elements is contributed more by anthropogenic sources at the urban station and contributed by earth’s crust at suburban station. That is why these elements behave like anthropogenic elements at urban station and like crustal elements at suburban station.

4.4.3 Dependence on mixing height

Mixing height is the height of the atmosphere in which pollutants are distributed homogeneously. This also means that it is the volume in which emitted pollutants are distributed. High mixing height means lower concentrations of elements and other pollutants as it means larger volume in which these species are distributed. Consequently, having low mixing height results in high measured pollutants concentrations. If a pollutant emitted equally in summer and winter its concentration is expected to be higher in winter, because mixing height is lower in winter. Dependence of pollutant concentrations on mixing height is reported frequently in literature (Tang *et al.*, 2016, Li et al., 2015; Schafer et al., 2013)

Relation between Al and Fe concentrations, which are well documented crustal markers, and mixing height is given in Figure 4- 28 for both urban and suburban stations. Crustal elements do not show a consistent increasing or decreasing trend with mixing height. Concentrations of litophilic elements are higher during summer months, when mixing height is deep, due to easier resuspension from dry surface, as discussed previously in the manuscript. However, increased source strength in summer is compensated by distribution in a larger atmospheric volume in summer owing to deeper mixing height. Because of these contradicting factors, concentrations of soil-related elements do not change consistently with mixing height.

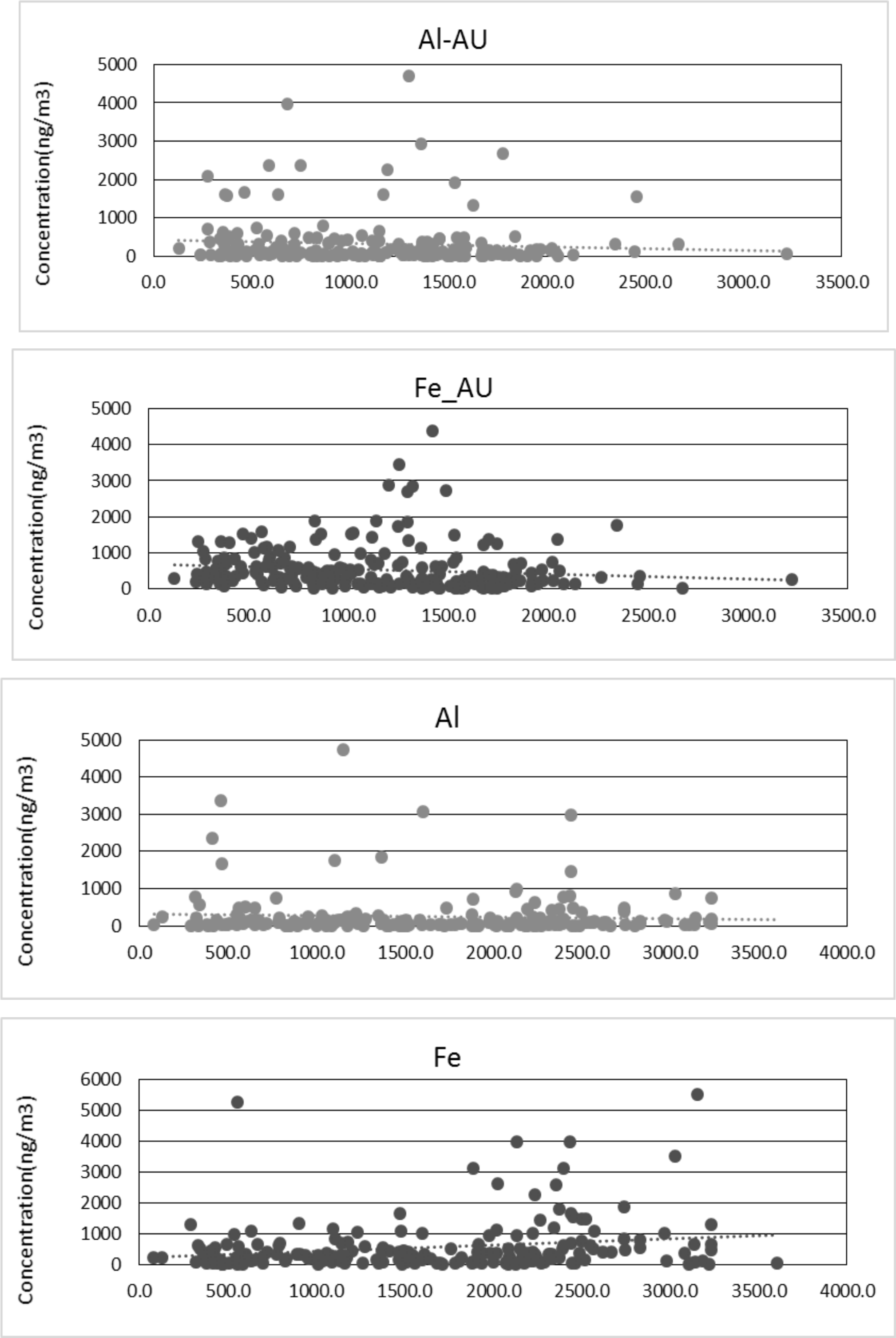


Figure 4- 28 Variations in concentrations of crustal elements with mixing height at urban and suburban stations

Variation in concentrations of anthropogenic elements with mixing height is depicted in Figure 4- 29, and Figure 4- 27 for METU and AU station, respectively. Concentrations of all anthropogenic elements in both stations decrease with increasing mixing height. This the expected behavior for elements that have stronger source strength in winter or hat have equal source strengths throughout the entire year. Traffic emissions that is the main source of pollution-derived elements in Ankara do not change during the year and coal combustion source, which is another possible source of chalchophilic elements, have higher source strength in winter. Both of these sources suggest decreasing concentrations of anthropogenic elements with mixing height as shown in the figure. The only exception to this pattern is SO_4^{2-}. Concentration of SO_4^{2-} increase with mixing height in both stations, because of higher source strength of these elements in summer due to faster photochemical oxidation rate of SO_2 to SO_4^{2-} in summer, is discussed previously in the manuscript.

Variation in concentrations of V and Mn, which are examples of element with mixed anthropogenic and crustal sources, in both stations are given in Figure 4-31. Behaviors of other elements in this group with mixing height was not any different. In AU station their concentrations decrease with increasing mixing height, but they do not show a significant variation with mixing height at METU station. This pattern is due to their different sources in different stations, as discussed previously. At AU station, they behave like pollution-derived elements, but at METU station, they behave like crustal elements.

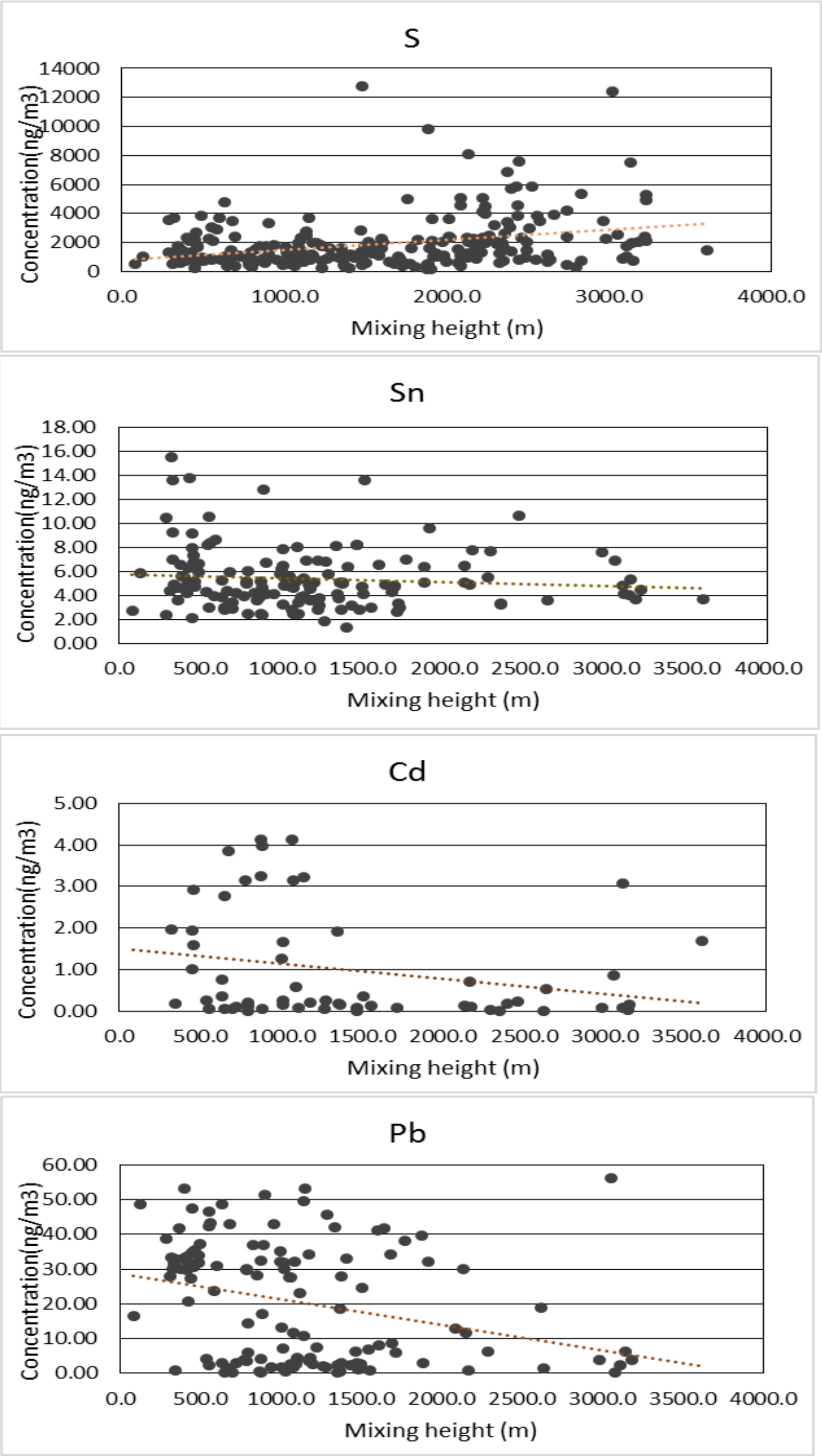


Figure 4- 29 Variation in concentrations of anthropogenic elements with mixing height suburban (METU) station

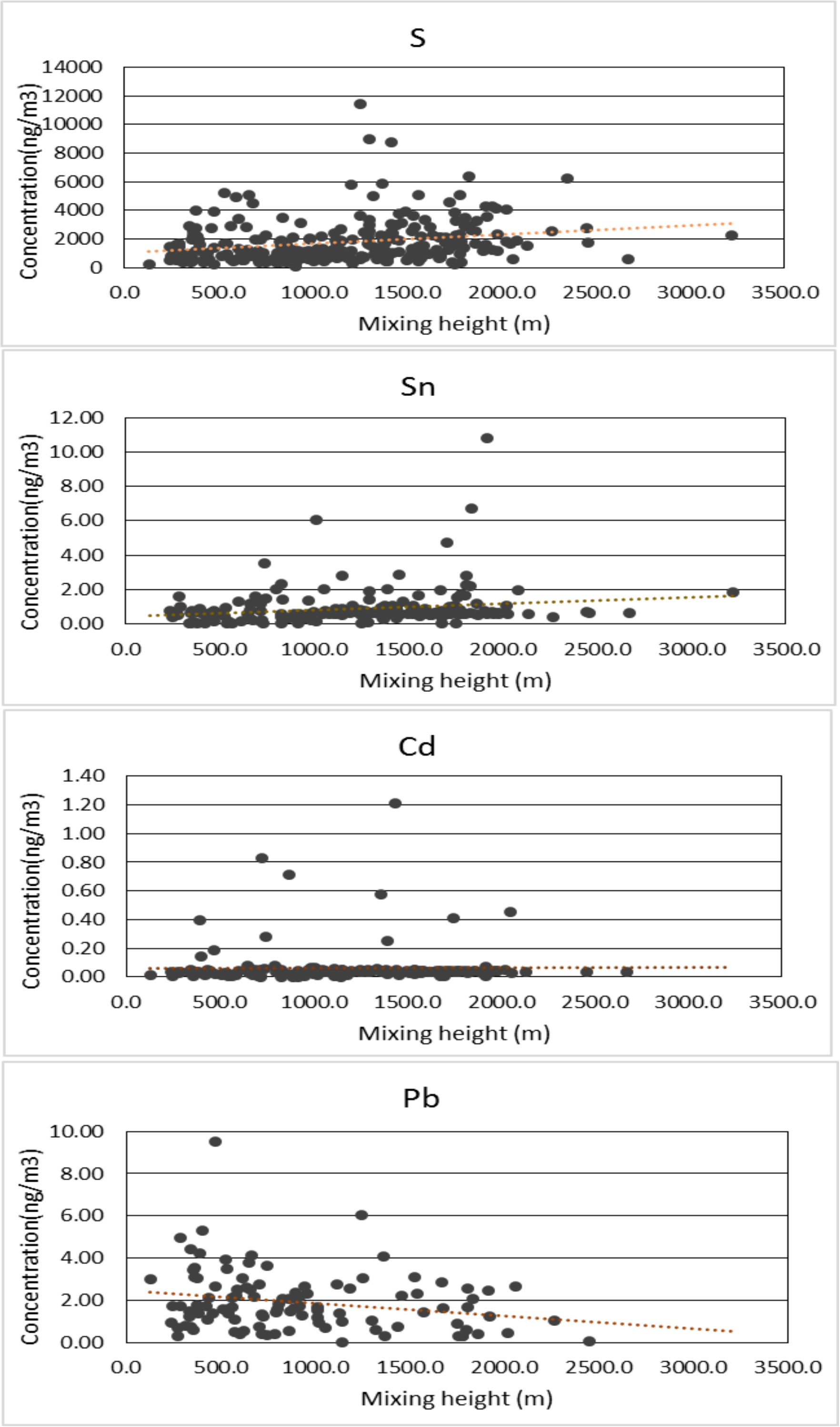


Figure 4- 30 Variation in concentrations of anthropogenic elements with mixing height at urban (AU) station

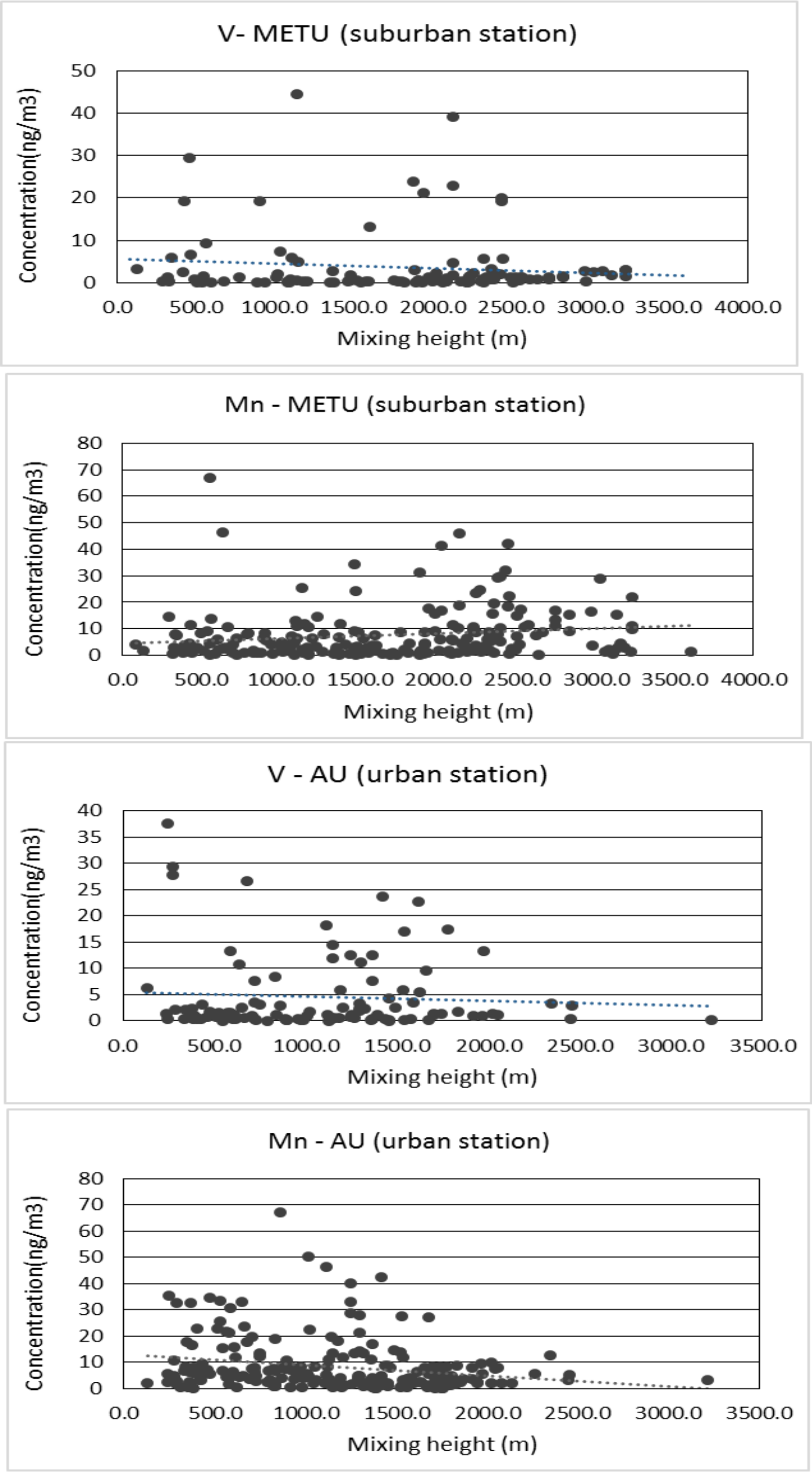


Figure 4- 31 Variations in concentrations of elements that have mixed origin with mixing height at urban and suburban stations

4.4.4 Dependence on ventilation coefficient

Ventilation coefficient is the product of mixing height and wind speed. Please note that mixing height is a measure of vertical ventilation and wind speed is a measure of horizontal ventilation in an urban airshed. Ventilation coefficient is a good indicator of dependence of pollutant concentrations on meteorology, as it accounts for both horizontal and vertical ventilation processes. Ventilation coefficient also referred to as "assimilative capacity" of the atmosphere. Variations in concentrations of crustal elements Al and Fe at suburban and urban stations are given in Figure 4- 32. Neither Al, nor Fe concentrations depict well defined decreasing or increasing trends with ventilation coefficient. This lack of a specific trend is also valid for most of the litophilic elements measured in this study.

If a pollutant is emitted in equal amounts in summer and winter its concentration is expected to decrease with increasing ventilation coefficient, as concentration of that particular pollutant will be high in winter when ventilation coefficient is low (when horizontal and vertical ventilation mechanisms are not very effective and its concentration is expected to be low in summer, when VC is high (when horizontal and vertical ventilation processes are highly effective). The lack of a specific relation between concentrations of crustal elements with ventilation coefficient is due to their high source strength during summer months when VC is high. Source strength of soil-related elements are high in summer, because, as pointed before, soil is dry in summer months and hence resuspension of surface soil is easier.

Variation in concentrations of selected pollution derived elements with ventilation coefficient is depicted in Figure 4- 33 and Figure 4- 34 for AU and METU station, respectively. As pointed in previous sections wind speed, which indicates effectiveness of horizontal ventilation in the study area, is not a determining factor in temporal variation in concentrations of elements because it is low and do not change substantially from one season to another. Hence, variability in ventilation coefficient is primarily determined by variations in mixing height in Ankara. Because of this variation in concentrations of all elements with mixing height is similar to their variation with mixing height.

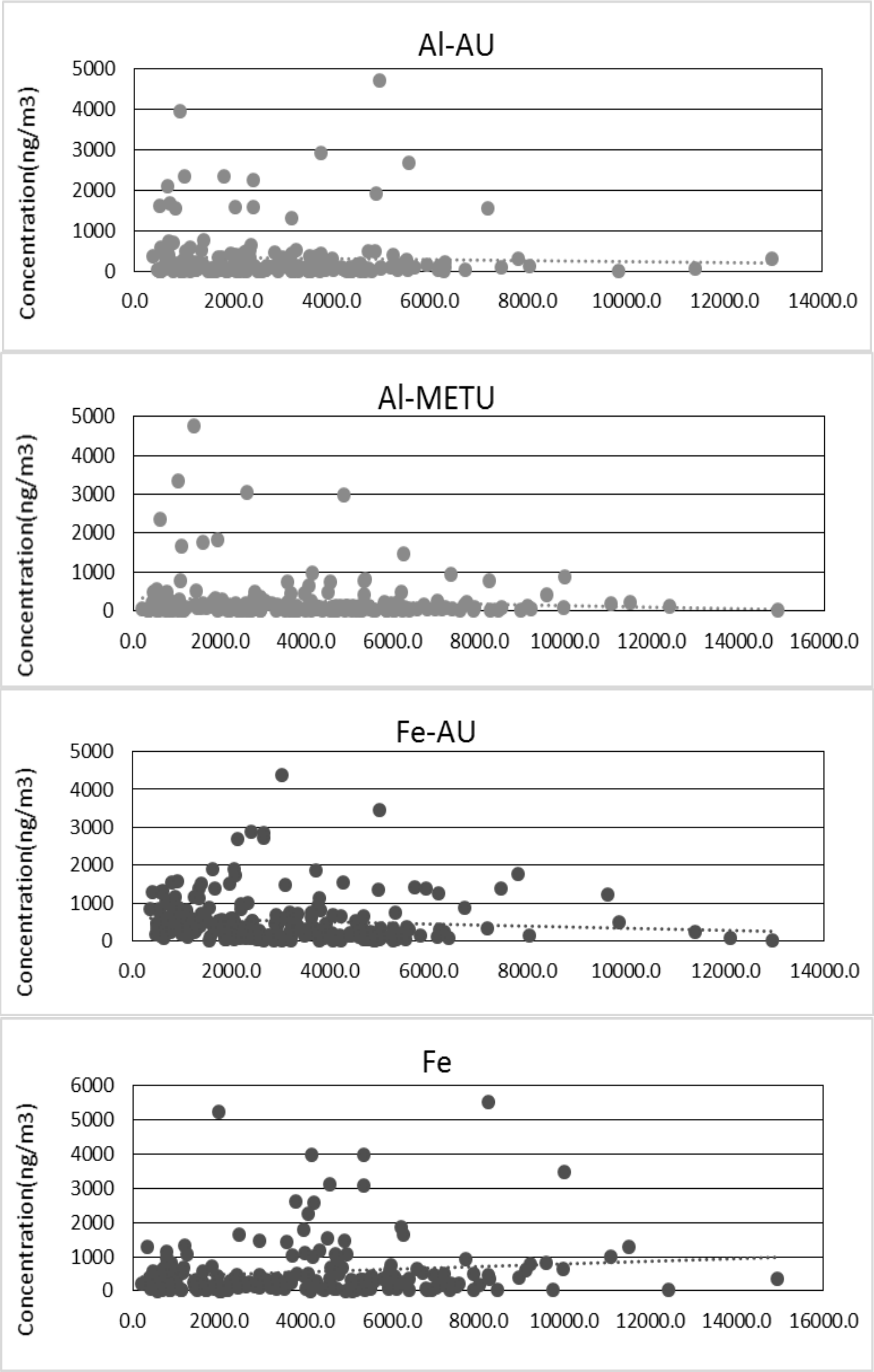


Figure 4- 32. Variation of concentrations of selected crustal elements with ventilation coefficient at urban and suburban stations

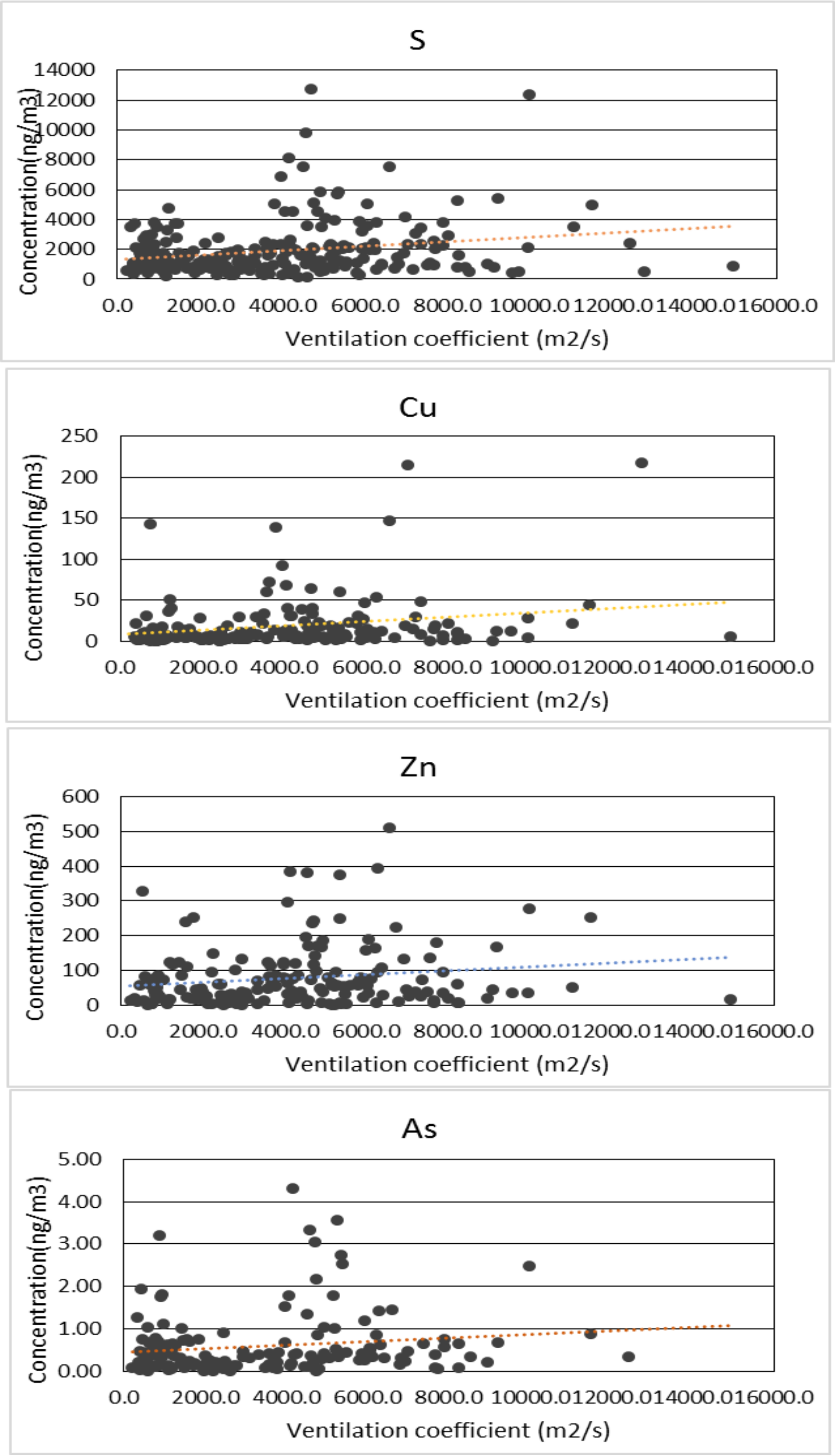


Figure 4- 33 Variation of concentrations of selected anthropogenic elements with ventilation coefficient at suburban (METU) station

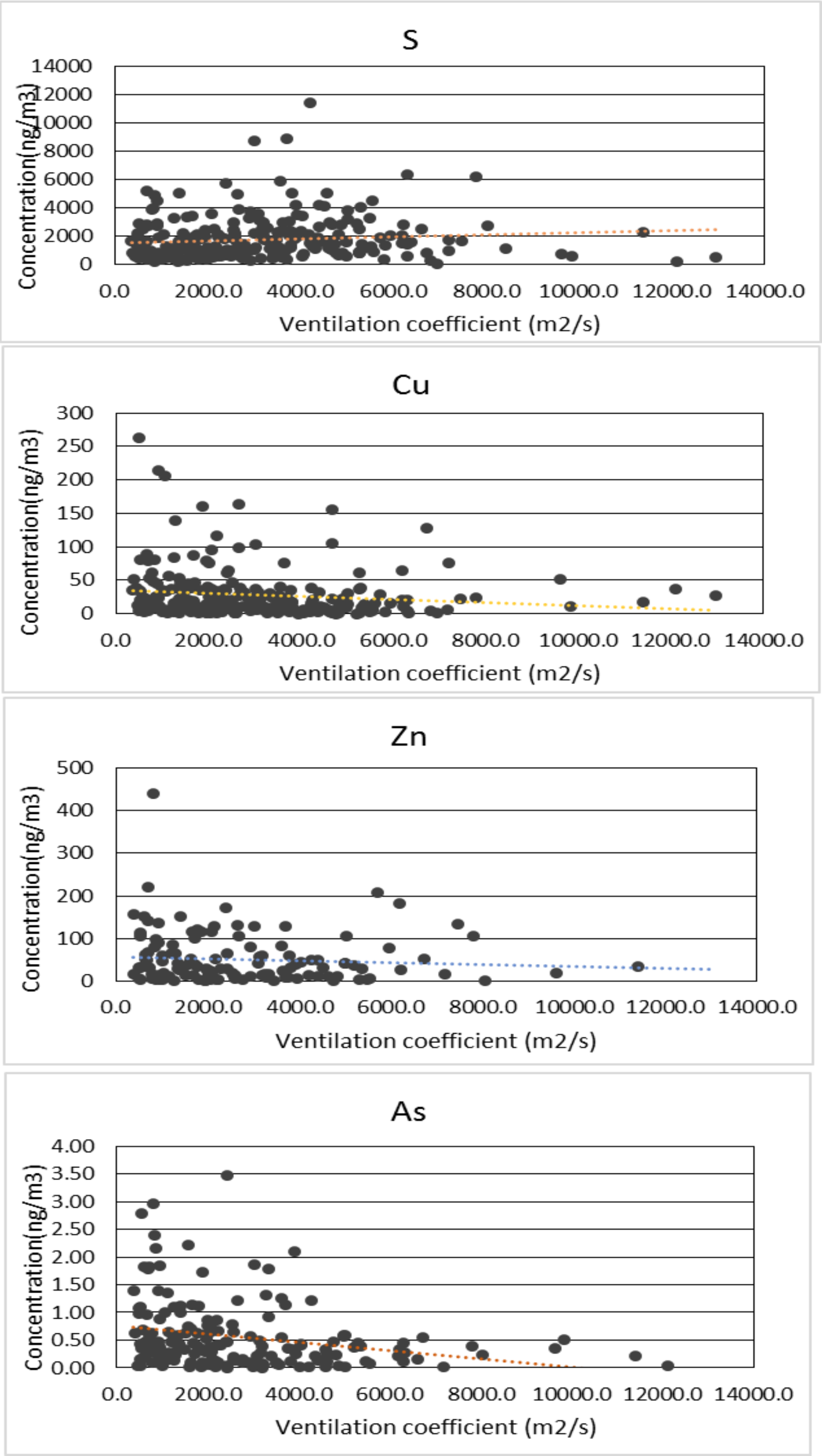


Figure 4- 34 Variation of concentrations of selected anthropogenic elements with ventilation coefficient at urban (AU) station

Concentrations of anthropogenic elements depicted clear decreasing trend with increasing ventilation coefficient due to more effective ventilation, particularly vertical ventilation at high VC's. The only exception to this is variation of S concentration, which did not show any significant variation with VC. This pattern observed in S concentration is similar to the pattern observed in variation of S concentration with mixing height and can be explained by faster photochemical oxidation of SO_2 to SO_4 during summer season when both ventilation coefficient and mixing height are high. Variation in concentrations of Ti and Mn, which are both elements that are emitted from both anthropogenic and crustal sources, at urban and suburban stations are given in Figure 4- 35. Interestingly, these elements showed different variations with ventilation coefficient at urban and suburban stations. They did not show a clear variation with VC at METU (suburban) station, but their concentrations clearly decreased with increasing VC at AU (urban) station. This pattern is also observed in concentrations of other elements with mixed sources, such as Cr, Ni, V. Such lack of a substantial pattern at suburban station and decreasing trend in urban station is probably due to different demography around these two stations, as explained, previously during the discussion of dependence of elemental concentrations on mixing height. Anthropogenic and crustal sources have different contributions to concentrations of this group of elements at suburban and urban stations. At urban station, resuspension of surface soil is not as important source as it is in the suburban station, because there is not much exposed soil surface due to intensive urbanization. On the other hand, anthropogenic emissions is higher around the urban station due to much higher population density and more intense traffic activity around the station. Soil is more important source of these elements with mixed sources owing to larger areas of exposed soil surface. With such polarity of sources, these elements that are contributed by both crustal and anthropogenic sources are expected to behave like crustal elements at suburban station and like anthropogenic elements at the urban station.

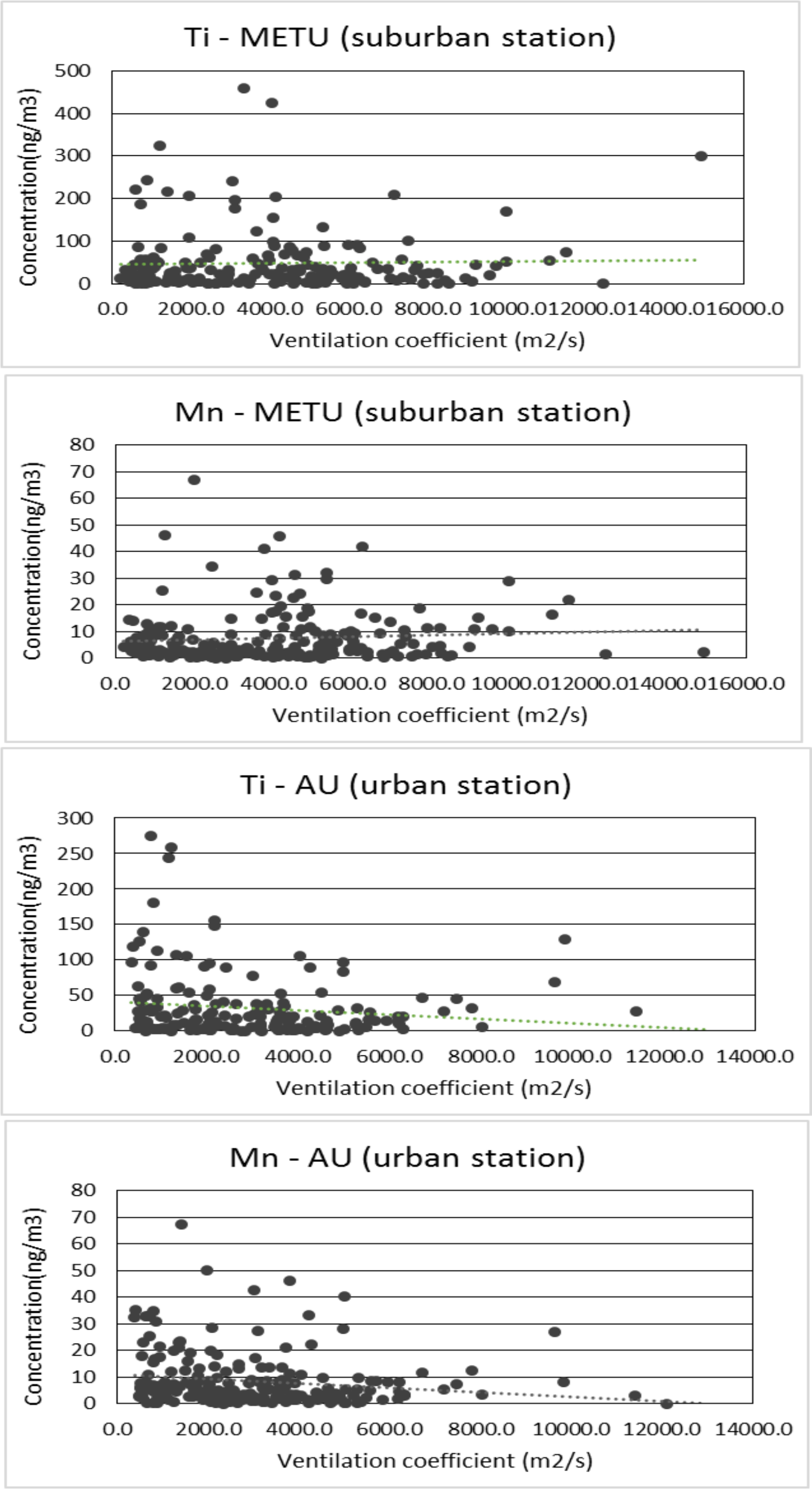


Figure 4- 35 Variation of concentrations of selected elements emitted from mixed sources with ventilation coefficient at urban and suburban stations

4.4.5 Dependence of elemental concentrations on wind direction: Conditional probability function approach

Wind direction is an important meteorological parameter that strongly affect measured concentrations of elements and other pollutants at any receptor. Since pollution, sources are not distributed uniformly around receptors, high concentrations of pollutants are measured when winds blow from the direction of sources and concentrations can be very low when wind blows from sectors where there is no source for that pollutant. Because of such polar nature of source impacts, investigation of wind direction dependence of pollutant concentrations can provide information on sources of measured pollutants (elements in our case).

There are two commonly used approaches to determine wind direction dependence of elemental concentrations. One of these approaches is to determine average or median concentrations of elements in each wind sector. Naturally, high average concentrations will be obtained for sectors including sources and low average concentrations would be obtained for sectors without any source. Although this is a reasonable way of assessing relation between wind direction and concentrations of elements, there is one problem. If there is one single data with a very high value in a sector, sector average of that pollutant will be very high in that sector, which will give an impression that particular wind sector is very important for measured concentration of that pollutant at the receptor, but it is not true. One datum cannot be very influential on average concentration of pollutants. Wind sector average approach provides information about presence or absence of source or sources in wind sectors. However, results can be entirely misleading in terms of contribution of that source to average concentration of pollutants at the receptor, because contribution is not determined by concentration level alone, but also influenced from number of times wind blows from that sector.

An approach that avoids this drawback, which is the one we used in this work, is conditional probability function (CPF). The CPF estimates the probability that a given source contribution from a given wind direction will exceed a predetermined threshold criterion. The CPF is defined as:

$$CPF = \frac{m_{\Delta\theta}}{n_{\Delta\theta}} \qquad \text{Equation 4-1}$$

$m_{\Delta\theta}$ is the number of occurrences from wind sector Δθ that exceeded the threshold criterion, and $n_{\Delta\theta}$ is the total number of hourly wind occurrences from the same wind sector. In this study, 8 wind sectors were used (Δθ=45 degrees). Calm winds (<1 m/s) were excluded. The threshold was set as the highest 40% of the source contribution concentrations (Ashbaugh et al., 1985; Xie and Berkowitz, 2006).

Distribution of conditional probability function values of selected anthropogenic elements at suburban station are depicted in Figure 4- 36. CPFs were not calculated for crustal elements, because their sources are all around the station and because of that their concentrations do not show a directional preference. Concentrations of pollution derived elements show strong directional preferences at suburban station. This is partly because anthropogenic PM sources are not uniformly distributed around the station.

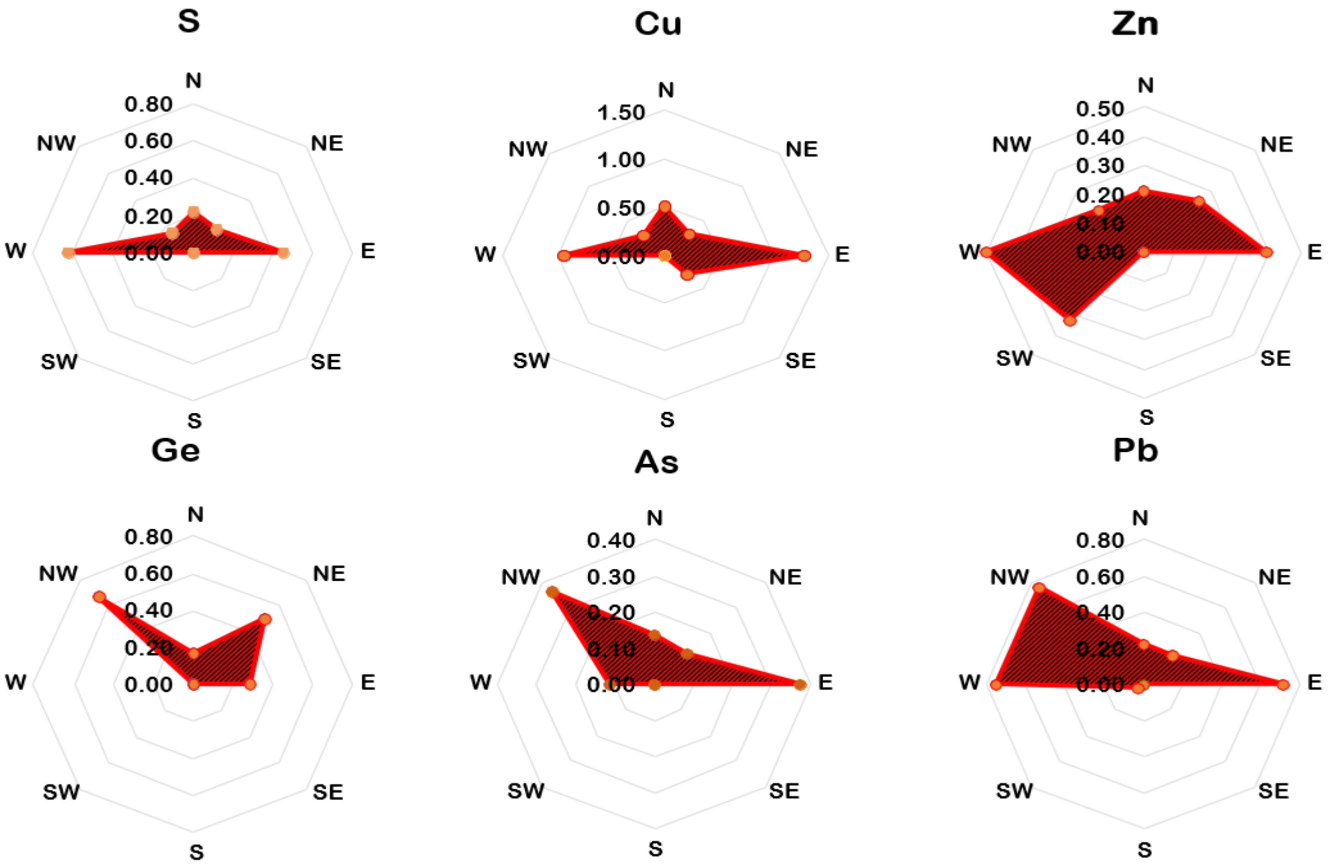


Figure 4- 36 Distributions of conditional probability function values of anthropogenic elements among wind sectors at suburban station

Potential high PM emitting areas at Ankara are given in Figure 4- 37. Mamak, which lies to the East of our suburban station, Altındağ and Keçiören, which are in North and Northeast wind sectors relative to our station are main PM source regions, because (1) population is high in these districts and (2) they are the districts where natural gas is not available due to lack of necessary infrastructure. Coal combustion is common mode of space heating in some, if not all, parts of these residential areas. Gecekondu regions at Altındağ and Keçiören are relatively far from METU, but they are very close to our urban station at Keçiören. Please note that all of Keçiören is not gecekondu region. Parts of it at the outer-skirts of the city consists of gecekondu. Among these, Mamak is closest to our suburban station and thus, expected to be the most influential source area on concentrations of pollution-derived elements measured at METU. Another potential source area, particularly for elements measured at suburban station is the OSTIM, which is approximately 7 km to METU and 11 km to our urban station.

Another reason for strong directional preferences in CPF plots is non-uniform distribution of wind occurrence frequency in different wind sectors. During our sampling period East was the dominant wind direction. Wind blew from East for 63% of the time. When this is combined by the presence of Mamak, which is one of the high emitting areas, in this wind sector, it makes East wind sector the most important source sector for suburban station. This is clearly reflected in distributions of CPF values of anthropogenic elements given in the figure. For all anthropogenic elements, without any exception, CPF are high in the east sector. High CPF values for most elements in the East sector is due to combination of presence of high-emitting sectors in that sector and frequent winds from East.

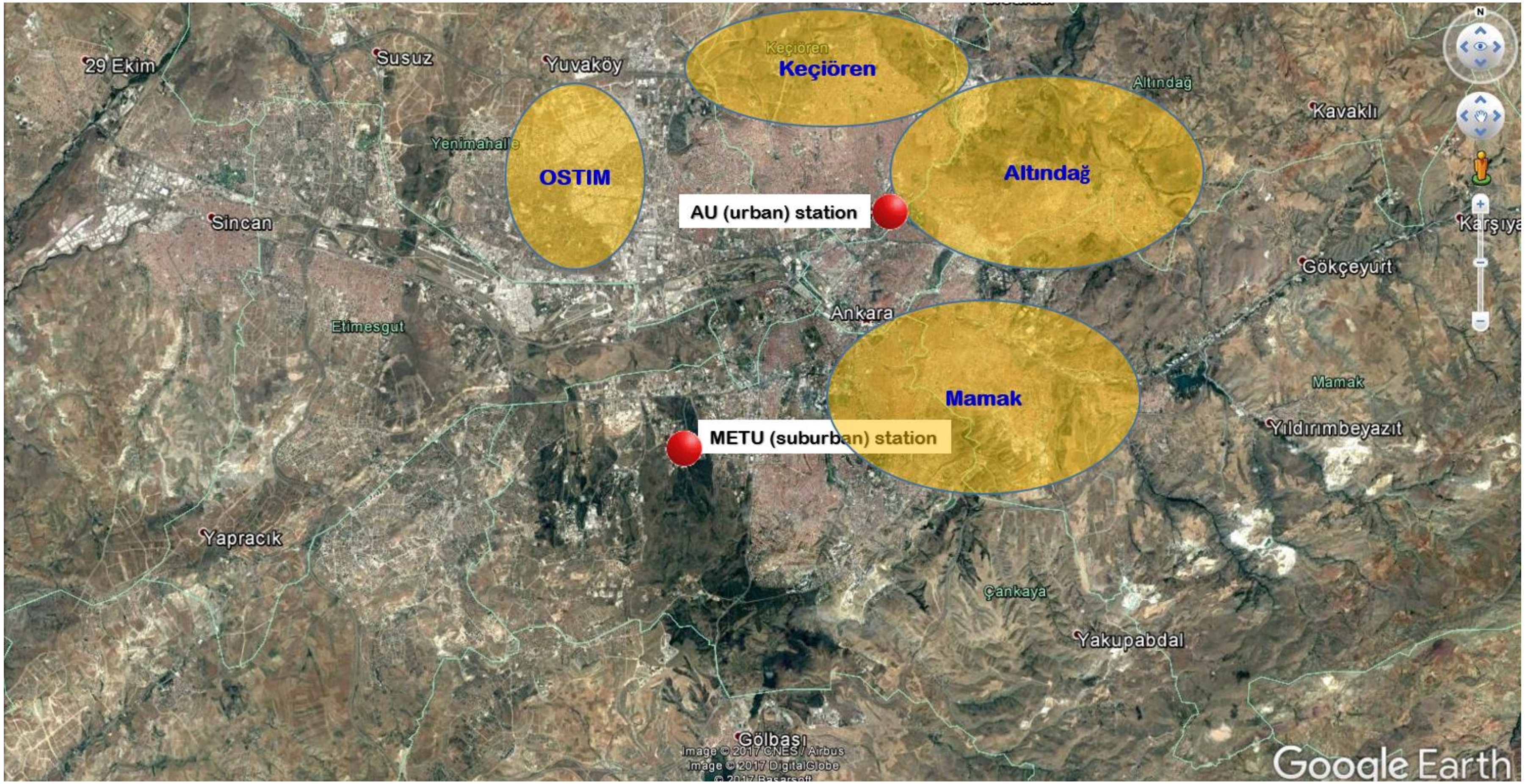


Figure 4- 37 Regions with high PM emissions around urban and suburban stations

For most of the elements shown in the figure there are relatively high CPF values in N and NE sectors this is probably due to presence of OSTIM (Organized industrial district), which hosts large number of small scale industrial facilities. Since it is approximately 7 km from our suburban station, its impact on concentrations of anthropogenic elements measured at METU is not surprising, when the wind blows from N and NE. Observed distributions of CPF values clearly demonstrated that Mamak area with high emissions from residential coal combustion and OSTIM with emissions from industrial activities have the strongest contribution on measured concentrations of pollution-derived elements at METU.

Understanding sources affecting urban station for CPF distributions is more difficult, because there are PM sources all around the station. Urban station is very close to high emitting districts Altındağ and Keçiören, which are located to the North and Northeast to station. However, there is one point to note in discussing relation between pollutant concentrations and wind direction; minor sources that are very close to station will have equal CPF value with a stronger source that is further away. There are two roads with high traffic density, which are very close to urban station. These are Irfan Baştuğ caddesi, which passes from approximately 50 m to the east of station and Fatih caddesi, which is approximately 400 m to the west of the AU site. Since these are very close the station they should have impact on the chemical composition of sampled particles at AU site.

Effect of these roads can be seen in distribution of CPF values for anthropogenic elements at urban station, which is given in Figure 4- 38. For all elements, CPF value at East sector is high pointing to strong effect of the Irfan Baştuğ Caddesi on these elements with anthropogenic sources. For most of the elements shown in the figure CPF values are also high in W sector pointing to the contribution of Fatih Caddesi. Other than these two sectors, which are strongly influenced from traffic emissions, distribution of CPF values of elements show uniform distribution around the station as expected.

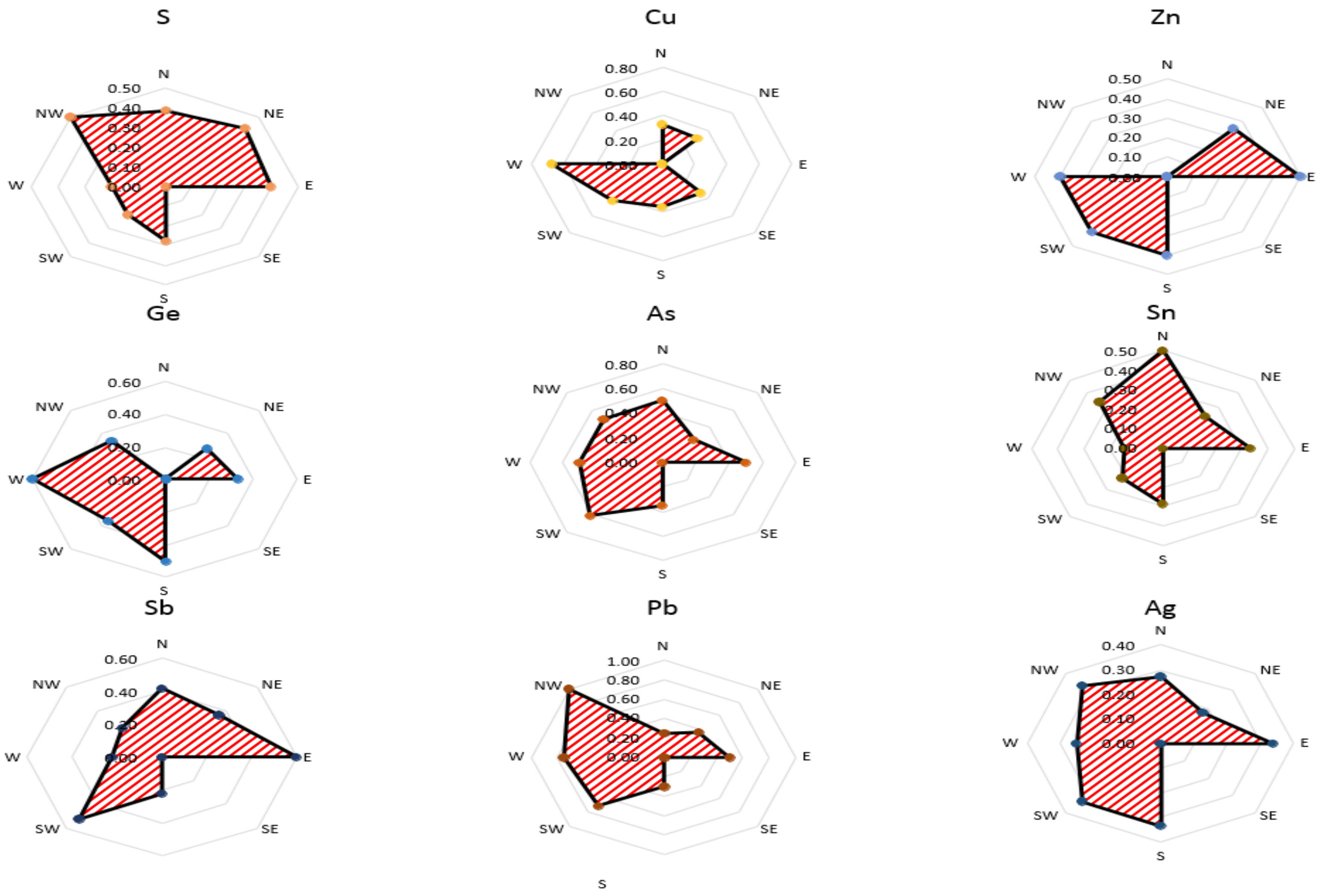


Figure 4- 38 Distributions of conditional probability function values of anthropogenic elements among wind sectors at urban station

Please note that zero CPF values in some sectors for elements like Zn, Ge, Cu are not due to non-uniform distribution of sources, but rather due to small number of data in those sectors. For example there were four concentration values for Cu at E sector and none of them were high (among highest 40% of available Cu data), resulting in CPF = 0. Similarly, there were three data in NW for the same element. Again, none of them was high. All CPF = 0 sectors in Ge (N sector), Zn (N and NE) are due to small number of data in those sectors. The value of CPF is zero at SE sector for all elements, because there were no wind from SE sector during our sampling period. The wind data obtained from Keçiören station operated by the General Directorate of Meteorology was hourly and given in degrees. This data was converted to 8 wind sectors. Since concentration data was daily, the most frequent wind sector in 24 hours was taken as the wind direction for that day. This approach probably increased the uncertainty in our estimations, but unfortunately, there is no good way of converting hourly wind direction data to daily. For most other meteorological parameters, we were able to take average values of 24 period as the daily value of that particular parameter. However, this cannot be done for WD, as it is in degrees.

4.5 Source Apportionments

4.5.1 Source apportionment using positive matrix factorization

Source apportionment can be described as identification of sources that contribute to measured concentrations of pollutants at a receptor. It is a very important tool to take regulatory actions to improve air quality. Source apportionment can be performed either using "source oriented" approach or using "receptor oriented approaches. Source oriented approach includes numerical modeling, which is totally different methodology and will not be discussed here. Receptor oriented approach, which is known as receptor modeling" refers to methods where statistical tools are applied to concentration data generated at the receptor. There are variety of receptor modeling tools that can be used to apportion sources of atmospheric particles. Factor analysis, principal component analysis, and target transformation principal component analysis chemical mass balances are well known examples of the multivariate tools.

In this work, positive matrix factorization (PMF) is used to determine sources of trace elements and particles measured at urban and suburban stations in Ankara. PMF is one of the latest receptor modeling techniques, which is used very frequently in last 15 years. It is developed in late 1990's by Pentti Paatero, 1997 as an alternative to earlier versions of multivariate statistical tools, such as factor analysis (FA), principal component analysis (PCA),

The PMF, its execution, the method for preparing data and uncertainty files for it, are discussed in detail in Section 2.1.7 and will not be discussed here. There are some quality control parameters to find out the optimum result with PMF, they will be briefly discussed in this section.

In total, 21 species are taken into account for the PMF for both station, which are Na, Mg, Al, K, Ti, V, Cr, Mn, Fe, Co, S, Ca, Cu, Zn, Ge, As, Rb, Sr, Cd, Sb, and Pb. At the beginning, there were 263 samples for urban (AU) station, and 248 samples for suburban (METU) station. After dismissing the outliners, which were causing high residual values, we ended up with 245 samples for AU and 224 samples for METU.

PMF provides Signal-to-noise ratio (S/N) for all elements after entering the data, which indicates whether the variability in the measurements is real or within the noise of the data. To conservatively use the S/N ratios to categorize species, the species with S/N ratio less than 0.5 should be labeled “Bad”, and “Weak” if the S/N ratio is greater than 0.5 but less than 1. However, detailed knowledge of the sources, sampling, and analytical uncertainties is the best way to decide on the species category. Finally, twelve of these elements were categorized as “strong”, and other nine were labeled “weak”, using 4, 5, 6, and 7 factors, to be able to find the most logical iteration.

Solution with 6-factors was selected as optimum based on the closeness to the performance criteria in PMF analysis. Unlike in factor analysis, the approach that can be used to select optimum number of factors in PMF is not well defined and not easy. The approach commonly used is to compare the model outputs against some predefined performance criteria. These criteria includes closeness of theoretical Q values ($\mathrm{Q_{true}}$) and model generated Q values ($\mathrm{Q_{Robust}}$), number of observations that are beyond the 0 ± 3.0 limit in distribution of scaled residuals, closeness of the observed and predicted concentrations of elements, investigation of correlations between factor scores (or G-scores) and the proven robustness of generated factors in bootstrapping test.

The first quality assessment control parameter is the ratio of $\mathrm{Q_{Robust}}$ to $\mathrm{Q_{true}}$. Determination of factor numbers, which is a significant step in PMF analysis (Yurdakul, 2014) can be determined based on goodness of fit of this parameter.

PMF gives the value of $\mathrm{Q_{Robust}}$ in each run. The value is compared with$\mathrm{Q_{true}}$, which is theoretical value, and can be calculated based on the number of samples, species and factors, using the below equation.

$$Q_{true} = nm - p(n + m) \qquad \text{Equation 4-1}$$

In which n is the number of species, m is number of samples, and p is number of factors. Therefore, this value can be calculated for each set of data and factor numbers. Finally, the ration of $\mathrm{Q_{Robust}}$ to $\mathrm{Q_{true}}$ should be less than 1.5. For METU and AU station Qtheoretical/Qrobust is 1.38, 1.17 and Qrob/Qtrue ratio of 1.12, 1.17, respectively. Both of these ratios are reasonably good and indicate that model fitted data properly and peak events may do not influence the model significantly

In addition, Bootstrapping is a tool to test the stability of factors generated in PMF. In this study, bootstrapping was executed using 100 iterations to test the stability of PMF results. The threshold value of 0.6 was used as coefficient of determination value for assigning bootstrap factor to base run factor. As it can be seen in Table 4- 9 and Table 4- 10, for both stations, number of unmapped bootstraps are very small, and perfectly acceptable.

Table 4- 9 Bootstrap factors mapped to base factors for METU station

	Base F1	**Base F2**	**Base F3**	**Base F4**	**Base F5**	**Base F6**	**Unmapped**
Bootstrap F1.	97	0	0	0	0	0	3
Bootstrap F2.	0	98	0	2	0	0	4
Bootstrap F3.	0	0	98	0	0	0	2
Bootstrap F4.	2	0	0	98	0	0	0
Bootstrap F5.	0	0	0	0	100	0	0
Bootstrap F6.	0	0	0	0	2	97	1

Table 4- 10 Bootstrap factors mapped to base factors for AU station

	Base F1	**Base F2**	**Base F3**	**Base F4**	**Base F5**	**Base F6**	**Unmapped**
Bootstrap F1.	97	0	1	0	0	0	2
Bootstrap F2.	0	98	0	0	0	2	0
Bootstrap F3.	0	0	97	0	0	0	3
Bootstrap F4.	0	0	0	98	0	2	0
Bootstrap F5.	0	0	0	0	99	0	1
Bootstrap F6.	0	3	0	0	0	97	5

4.5.2 Apportionment of sources at suburban station

At suburban (METU) station, PMF solution with six factors was adopted. Factor loadings, which corresponds to concentrations of elements in that source, or in emissions from that particular source, fractions of concentrations of elements accounted for by that source, are standard outputs of PMF. Another standard PMF output is the G-scores, which are the weight of factors in each sample. We calculated monthly median values of G-scores for each factor, to determine seasonal variation in significance of factors.

We also calculated crustal enrichment factor for each element in each factor as it has been discussed in part 2.1.6 using the factor loadings for each elements contribution to each factor. As discussed, Al is being used normally as reference element for crustal material, but since Al is not available in all factors, Fe has been used as the reference element. Using these information the factors have been identified as follows.

Factor 1, shown in Figure 4- 39, explains 85% of Cu concentration. This is a Cu factor. It accounts for smaller fractions of other anthropogenic elements Zn, Ge, Cd, and Pb. G-scores are higher during summer season. This pattern is similar to monthly average variation in concentrations of most anthropogenic elements at our suburban station and attributed to enhanced transport of pollution-derived elements from high emission areas in the city, particularly from Mamak area. Crustal enrichment factors calculated using Factor 1 loadings and demonstrated that Cr, S, Cu, Zn, Ge, As and Cd are enriched in this factor. The factor appears as a traffic factor, because it includes elements that are good traffic markers, such as Cr, Zn, Cd and Pb. Identifying traffic related factors without using organic markers, became difficult after Pb and Br was phased out from gasoline. However, these elements were suggested as traffic markers in the literature, because they are emitted from wearing tires and brake linings (Krudysz et al., 2008; Querol et al., 2007; Molnar et al., 2007; Suzuki et al., 2006).

Factor 2 accounts for 75% of the Pb concentration and 60% of concentrations of Sb and Cr, as shown in Figure 4- 40. The factor also accounts for significant fractions of concentrations of crustal elements, including K (45%), Fe (40%), and Co (65%). Sb and S are highly enriched (EFc > 100), but the others are only moderately enriched (EFc >10). Crustal elements are not enriched as expected. Factor 2 is identified as "contaminated soil". In a similar work done in 1993 Yatın et al (2000) identified three different soil components in Ankara aerosol population. One of the factors authors identified was contaminated surface soil. Surface soil in Ankara became contaminated, by settling of combustion particles and particles emitted from traffic over the years. Later this proposal was supported by Yay et al. (2008) who analyzed surface soil samples for trace elements at 100 points in Ankara. This factor which contains both crustal and pollution-derived elements is similar in composition to polluted surface soil component in Ankara aerosol population found by Yatın et al. (2000).

Factor 3, does not explain large fraction of the concentrations of any elements. However, it explains approximately 30% of the concentrations of Cr and Zn and approximately 20% of the concentrations of As and Pb. Sulphur, Zn, As and Pb are enriched in this factor relative to soil indicating that the factor represents an anthropogenic component in aerosol population. G-scores of factor 3, as depicted in Figure 4- 41, are high in summer months, which is similar to monthly variation in concentrations of anthropogenic elements as discussed earlier in the manuscript. Higher G-scores during summer can be attributed to suppression of pollution transport from high emitting areas in the city during winter, owing to meteorological conditions.

Elements that has EFc > 10 in this factor, namely S, Zn, As and Pb are good markers for coal combustion. Please note that this factor does not account for large fractions of S, Zn, As and Pb, suggesting that combustion is not as important as other sources in determining concentrations of these elements, which is not surprising, because residents are heated by natural gas in the proximity of our suburban station and there is no strong coal combustion sources in and around METU. Consequently, Factor 3 was identified as coal combustion factor.

Factor 1
Traffic

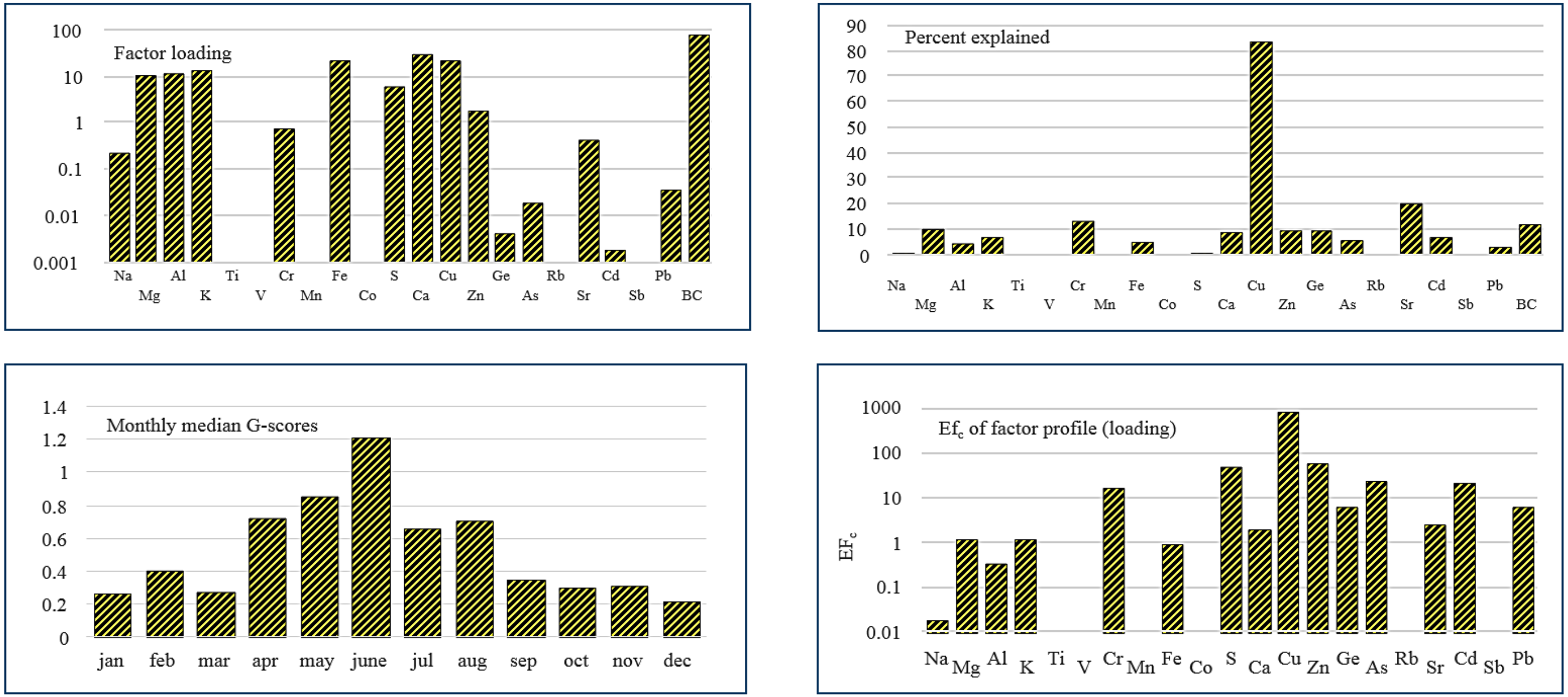


Figure 4- 39 Factor 1 parameters, Factor loadings (a), Percentage of concentrations explained by each factor (b) monthly median G-scores (c), crustal enrichment factor calculated using factor profiles (loadings) (d)

Factor 2

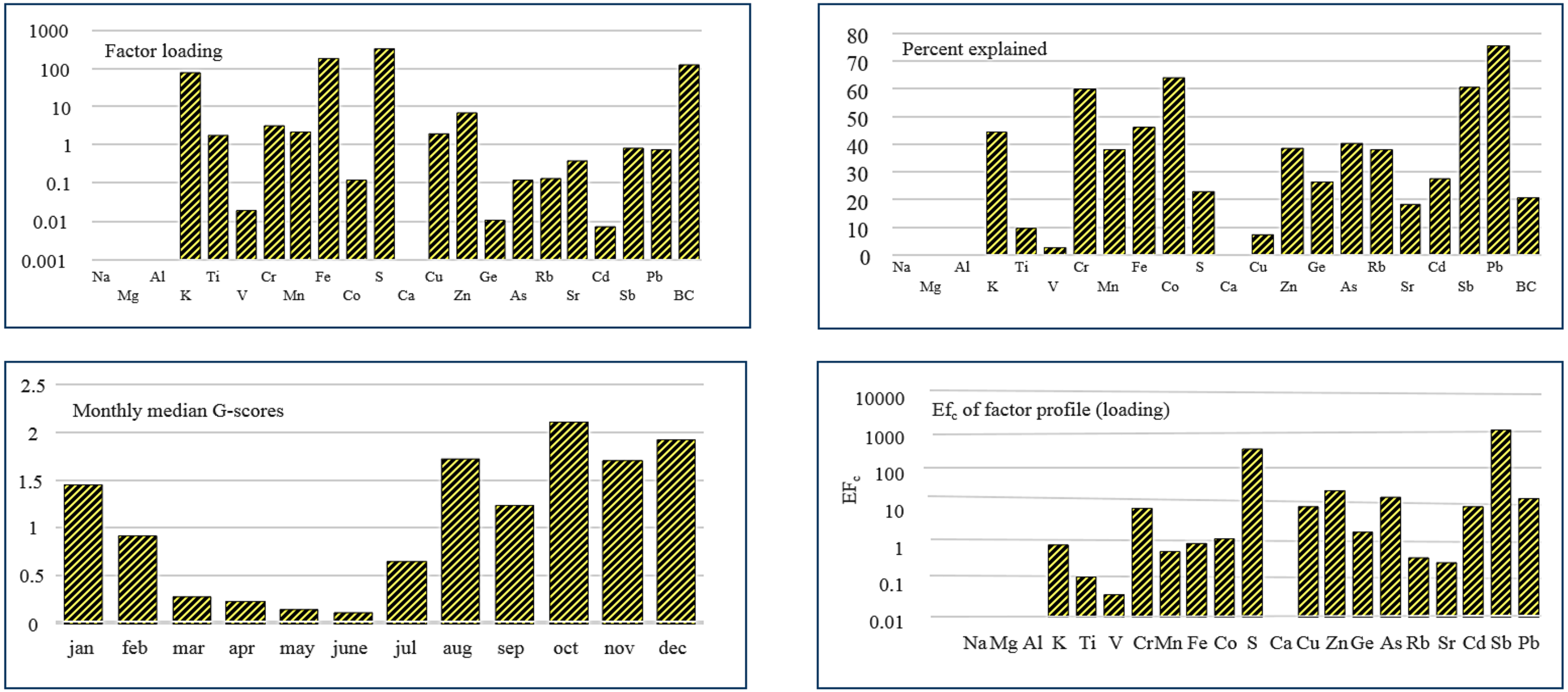


Figure 4- 40 Factor 2 parameters, Factor loadings (a), Percentage of concentrations explained by each factor (b) monthly median G-scores (c), crustal enrichment factor calculated using factor profiles (loadings) (d)

Factor 3

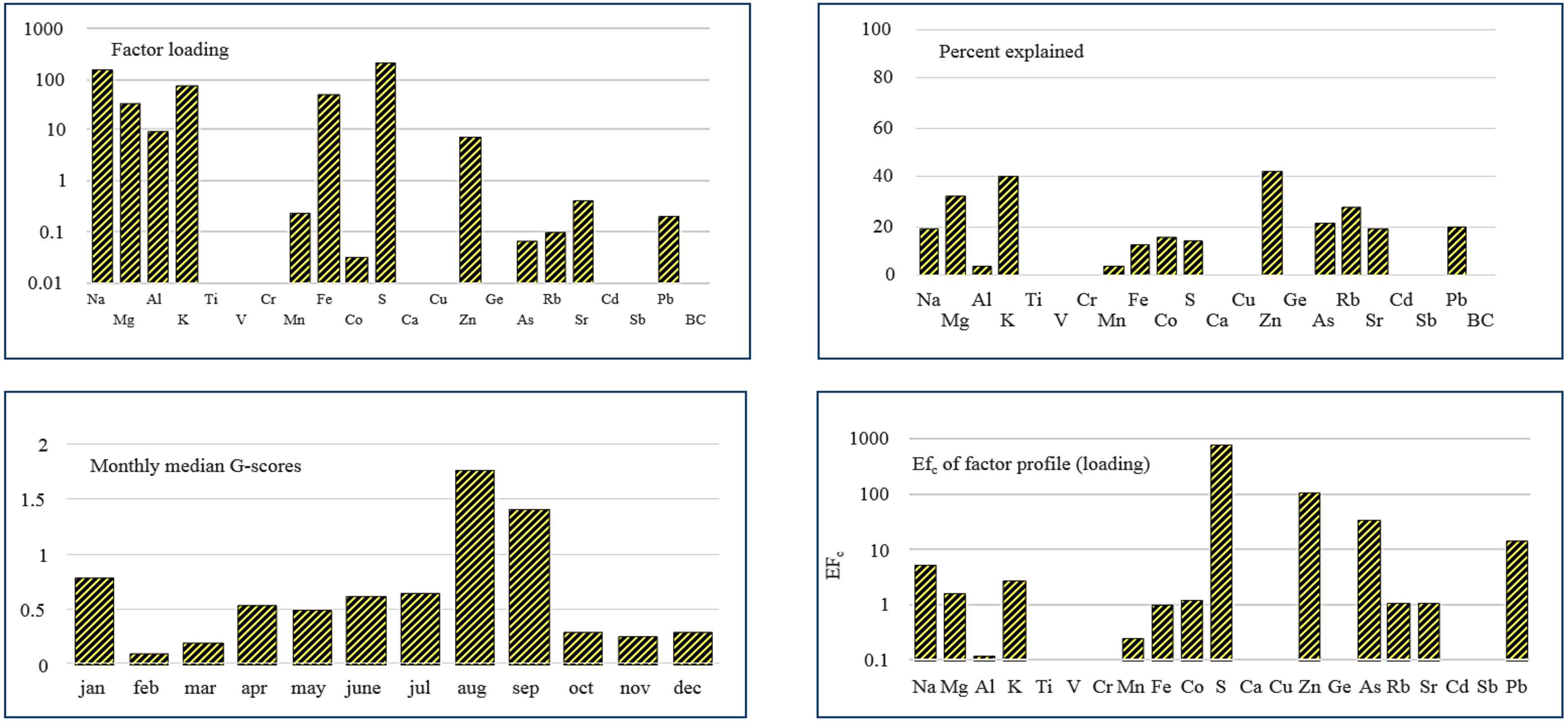


Figure 4- 41 Factor 3 parameters, Factor loadings (a), Percentage of concentrations explained by each factor (b) monthly median G-scores (c), crustal enrichment factor calculated using factor profiles (loadings) (d)

Factor 4 accounts for approximately 60% of the concentrations of S and Cd, 40% of the Sb concentration and approximately 20% of the concentrations of Ge. EFc calculations demonstrated that among these elements S, Cd, Sb highly and Cu, Ge, As are moderately enriched relative to soil. These elements are emitted from very different anthropogenic activities including combustion traffic etc. However, one interesting point about factor 4, is that it accounts for approximately 40% of black carbon concentration. Diesel emissions is the unique source of black carbon in urban atmosphere. Factor 4, G-scores are higher in summer season. This is probably due to lack of heavy vehicle traffic, which is the main source of BC emissions in the campus. Black carbon we measured at METU is probably transported from city, which is enhanced in summer, or suppressed in winter as discussed previously in the text. Thus this factor is identified as Diesel factor representing particles emitted from diesel engine in the atmosphere.

Factor 5 is a clear crustal factor. It explains >80% of the concentrations of Al and Ti and >20 of the concentrations of Na, Mg, Cr, Mn, Fe, Co, Ca, Sr and Rb. All of which are crustal elements. The factor also accounts for 20 -40% of the concentrations of some anthropogenic elements, including Ge, and As. However, none of these elements are significantly enriched relative to soil. Please note that most of these chalcophile elements do occur in earth crust but in small quantities. Consequently, fractions of concentrations of these elements accounted for by Factor 5 are their crustal fractions. None of the elements associated with factor 5 are highly or moderately enriched relative to soil composition. Small enrichments of these elements (up to 10 or so) can be due to different composition of crustal material impacting our station and Mason's global soil compilation, which was used in our EFc calculations. Factor 5 scores are low in winter and high in summer due to easier resuspension of soil aerosol during summer months.

Factor 6 accounts for 80% of V concentration and smaller fractions of other anthropogenic parameters and black carbon. Enrichment factor calculations demonstrated that that V, S, Cu and Cd are highly enriched in Factor 6. G-scores do not depict a clear seasonal pattern.This factor was identified as oil-combustion factor, because V is an excellent tracer for oil combustion emissions. Oil combustion can also account for other elements enriched in factor 6.

Factor 4

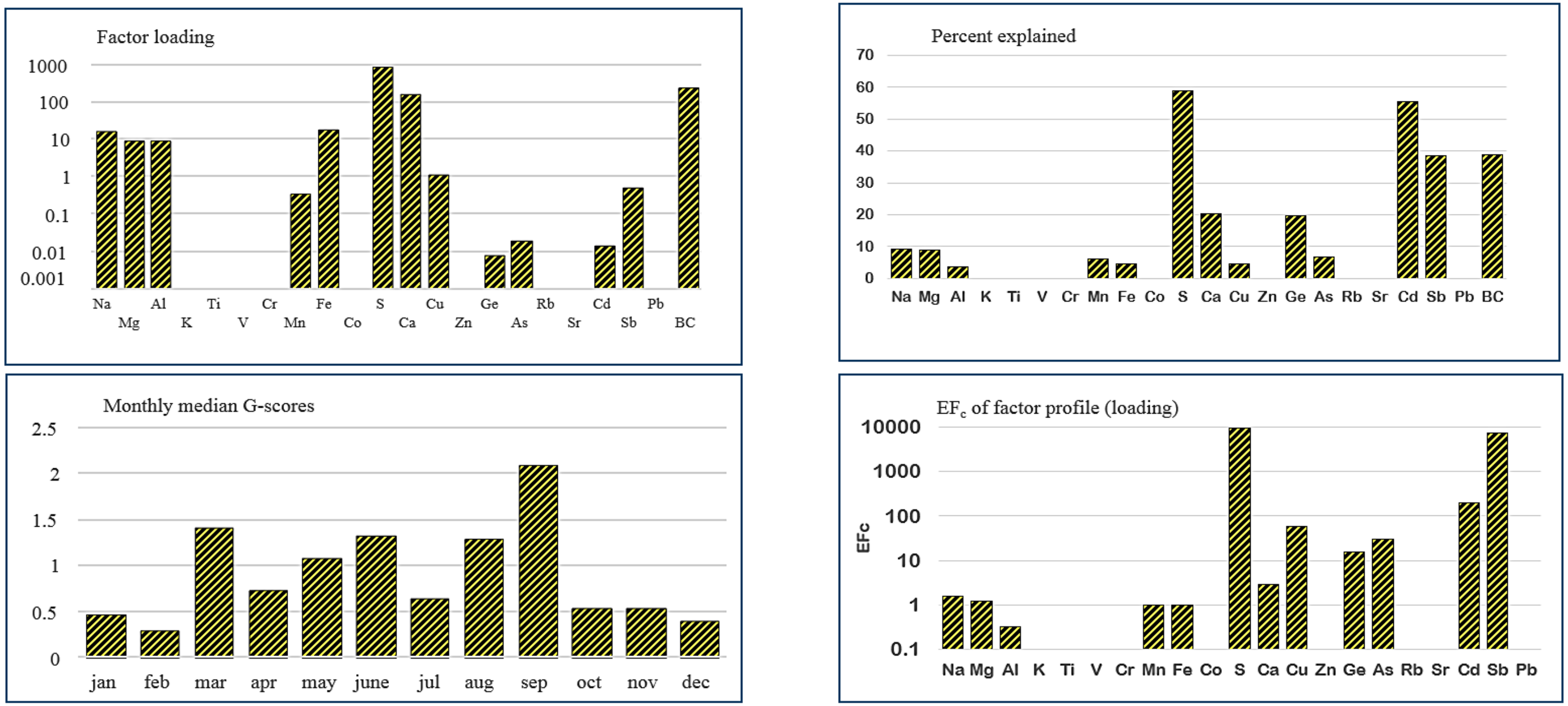


Figure 4- 42 Factor 4 parameters, Factor loadings (a), Percentage of concentrations explained by each factor (b) monthly median G-scores (c), crustal enrichment factor calculated using factor profiles (loadings) (d)

Factor 5

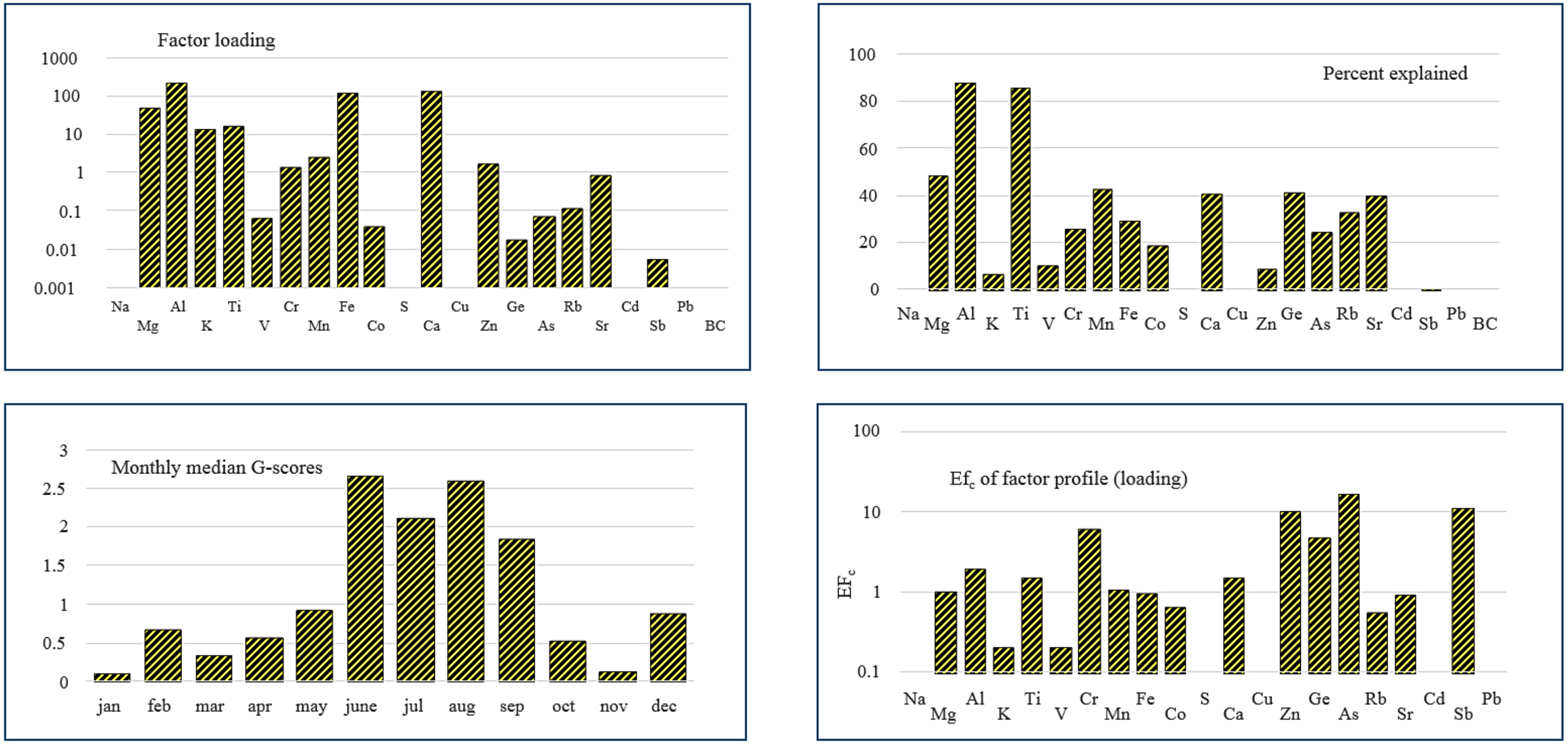


Figure 4- 43 Factor 5 parameters, Factor loadings (a), Percentage of concentrations explained by each factor (b) monthly median G-scores (c), crustal enrichment factor calculated using factor profiles (loadings) (d)

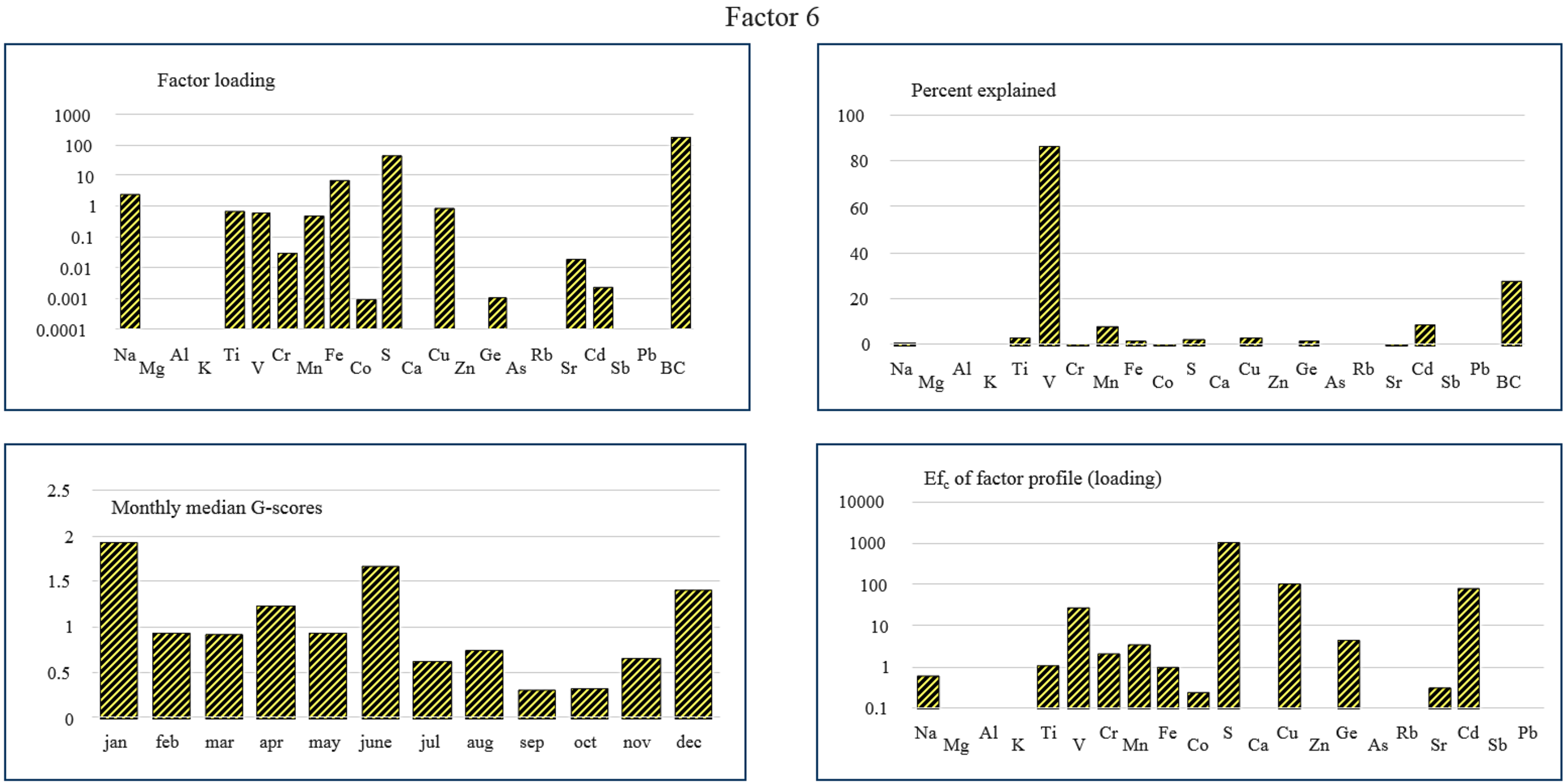


Figure 4- 44 Factor 6 parameters, Factor loadings (a), Percentage of concentrations explained by each factor (b) monthly median G-scores (c), crustal enrichment factor calculated using factor profiles (loadings) (d)

Contribution of factors to total elemental concentrations at METU station is depicted in Figure 4- 45. Contaminated surface soil (Factor 2) is the largest contributor to total element concentrations. It accounts for approximately 29% of the concentrations of elements, containing both crustal and pollution-derived elements. It is followed by Factor 5, which represents clearly a crustal factor, containing high percentage of important crustal markers elements. This source accounts for 21% of the total element concentrations. Factor 3, which represents coal combustion source, contributes as 16% of total elemental concentration. Other anthropogenic sources are diesel source (Factor 4), oil combustion (Factor 6), and traffic (factor 1). They account for approximately 14%, 11%, and 9% of total concentrations of elements, respectively.

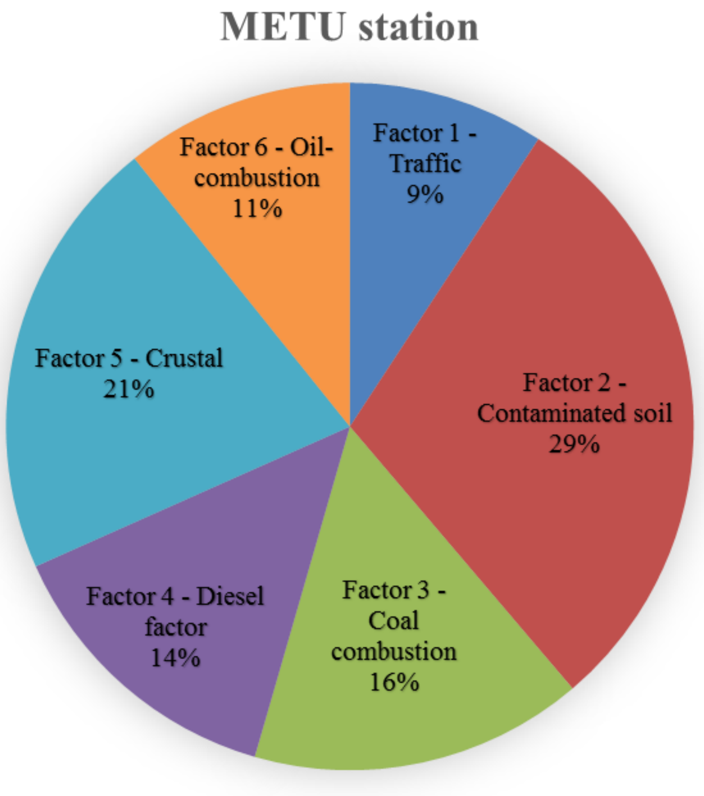


Figure 4- 45 Contribution of factors on total element concentration for METU station

4.5.3 Apportionment of sources at urban station

Positive matrix factorization tool was also optimized for the data set generated at our urban station. Since optimization process was discussed in previous section it will not be discussed here. Six-factor solution resulted in Qtheoretical/Qrobust of 1.45 and Qrob/Qtrue ratio of 1.17. Some of the six factors found at urban station have quite similar profiles with corresponding factors found at suburban station. Other factors represent similar sources, but their profiles are not entirely similar with corresponding profiles found at METU.

Factor 1 accounts for > 50% of the concentrations of Na, Mg, Ti, Rb and Sr, as it can be seen in Figure 4- 46. Crustal enrichment factors shows that none of the elements are significantly enriched relative to soil, except for Zn and As for which EFc's are slightly higher than 10 indicating a weak enrichment. Please note that EFc's of elements that are < 10 can be due to differences in soil composition and does not indicate enrichment due to non-crustal sources. Based on these arguments Factor 1 is identified as crustal component of aerosol population.

Factor 2 profile and fractions of elements accounted by this factor are, with small modifications, similar to Factor 1 in METU station, which was identified as traffic factor and it can be observed in Figure 4- 47. The factor explains > 70% of the concentrations of V and Cu and smaller fractions of other anthropogenic elements Zn, Ge, As and Pb. As discussed previously in relation to factor one of the METU, PMF study, these elements are shown to be associated with traffic emissions through exhaust emissions, wearing of tires and brake linings (Budai and Clement 2011; Kummer et al., 2009; Świetlik et al., 2013).

Factor 1

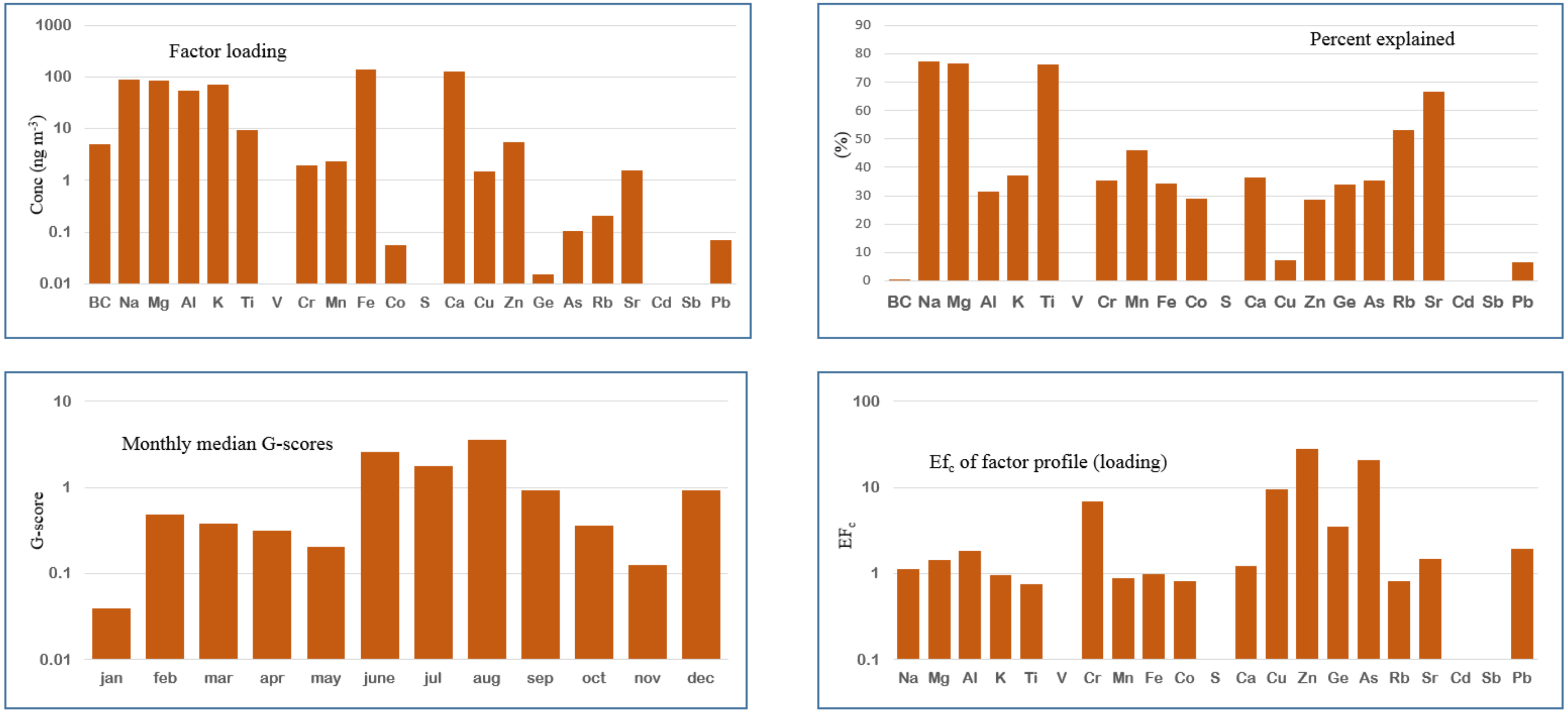


Figure 4- 46 Factor 1 parameters, Factor loadings (a), Percentage of concentrations explained by each factor (b) monthly median G-scores (c), crustal enrichment factor calculated using factor profiles (loadings) (d)

Factor 2

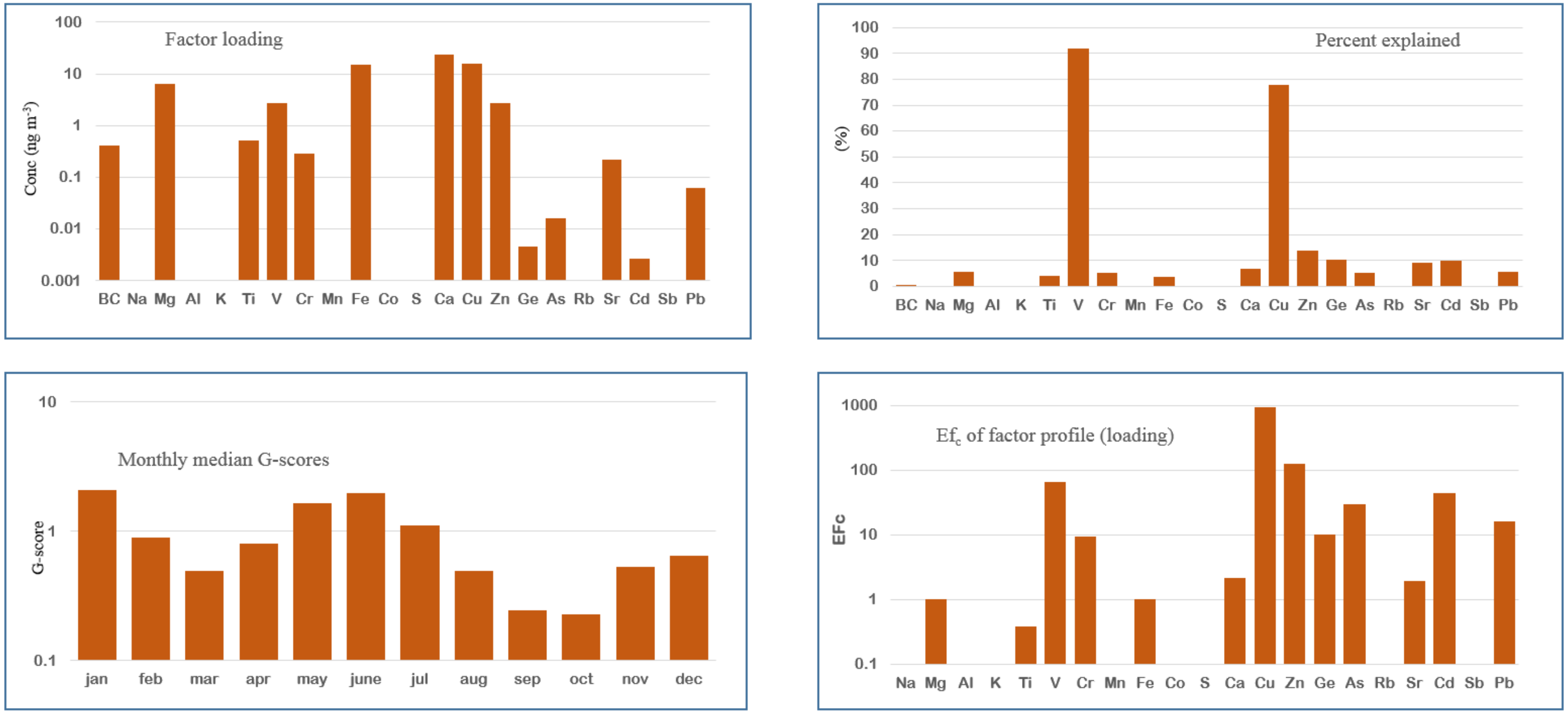


Figure 4- 47 Factor 2 parameters, Factor loadings (a), Percentage of concentrations explained by each factor (b) monthly median G-scores (c), crustal enrichment factor calculated using factor profiles (loadings) (d)

Factor 3, shown in , accounts for 85% of Al concentration and smaller fractions of other crustal elements, such as Cr, Mn, K, Fe, Co and Sr. Enrichment factors of these elements are all <1, indicating that this is crustal factor. However, S moderately enriched, relative to crustal composition. Suggesting that Factor 3 does not represent a clean subsurface soil, but it rather represents surface soil, which is contaminated from long years of deposition of anthropogenic particles. In this sense, Factor 3 in our urban station corresponds to Factor 2 at METU, which was also identified as contaminated soil.

Factor 4, is a unique factor and explains approximately 90% of EC concentration. S, Cu, Cr, As and Cd are enriched in the factor. As pointed previously in discussing results of PMF at METU station, EC is a very good indicator for diesel emissions. Enrichment of S in diesel emissions is expected, because S can occur in relatively high concentrations in diesel fuel. Genç et al., (2010) demonstrated that diurnal variation of gaseous SO2, which was a very good tracer of coal combustion for space heating followed traffic pattern with two well-defined rush hour maxima in recent years. Consequently, appearance of S in diesel factor should be expected. Moderate enrichment of Cu, Cr, As and Cd are due to wearing tires, engine components and brake linings (Budai and Clement 2011; Kummer et al., 2009; Świetlik et al., 2013).

Factor 5 Accounts for > 40% of concentrations of anthropogenic elements S, Zn, Ge, As, Sb and Pb. Among these S, Ge, As and Sb are highly enriched relative to soil. These highly enriched elements (Ge, As, and Sb) are well-known tracers for coal combustion. So this factor is clear coal combustion factor, which corresponds to Factor 3 in suburban PMF. There is two important points to note with this factor. Fractions of elemental concentrations accounted by factor 3 in suburban PMF exercise are significantly lower than fractions of their concentrations accounted by this factor. This indicates that contribution of coal combustion is significantly higher at urban station. This is how it should be, because urban site is very close to strong emission areas at Altındağ and outer edges of Keçiören. The second point worth noting that is higher g-scores of this factor in winter season. Monthly median G-score values in Factor 3 in METU PMF was higher during summer. The difference is due to the proximity of sources to stations. As discussed previously, combustion elements, which are intercepted at our suburban station comes from polluted areas in the city, most likely from Mamak area. This transport is favored in summer and suppressed in winter. However, combustion aerosol intercepted at AU station originates from source areas, which are very close to the sampling site. These heating emissions are high in winter.

Factor 6 is not very clear. It explains > 60 of the S concentration and smaller fractions of concentrations of other anthropogenic elements, namely, Ge, As, Cd and Sb. They are all enriched relative to soil. This is a factor representing an anthropogenic source, but what that source is not very clear. One possibility is road dust, because the factor explains small fractions in concentrations of crustal elements and Black carbon. Higher g-factors in summer months also supports this hypothesis, because road dust can be rersuspended more easily during dry summer season. This factor is tentatively assigned as road dust.

Factor 3

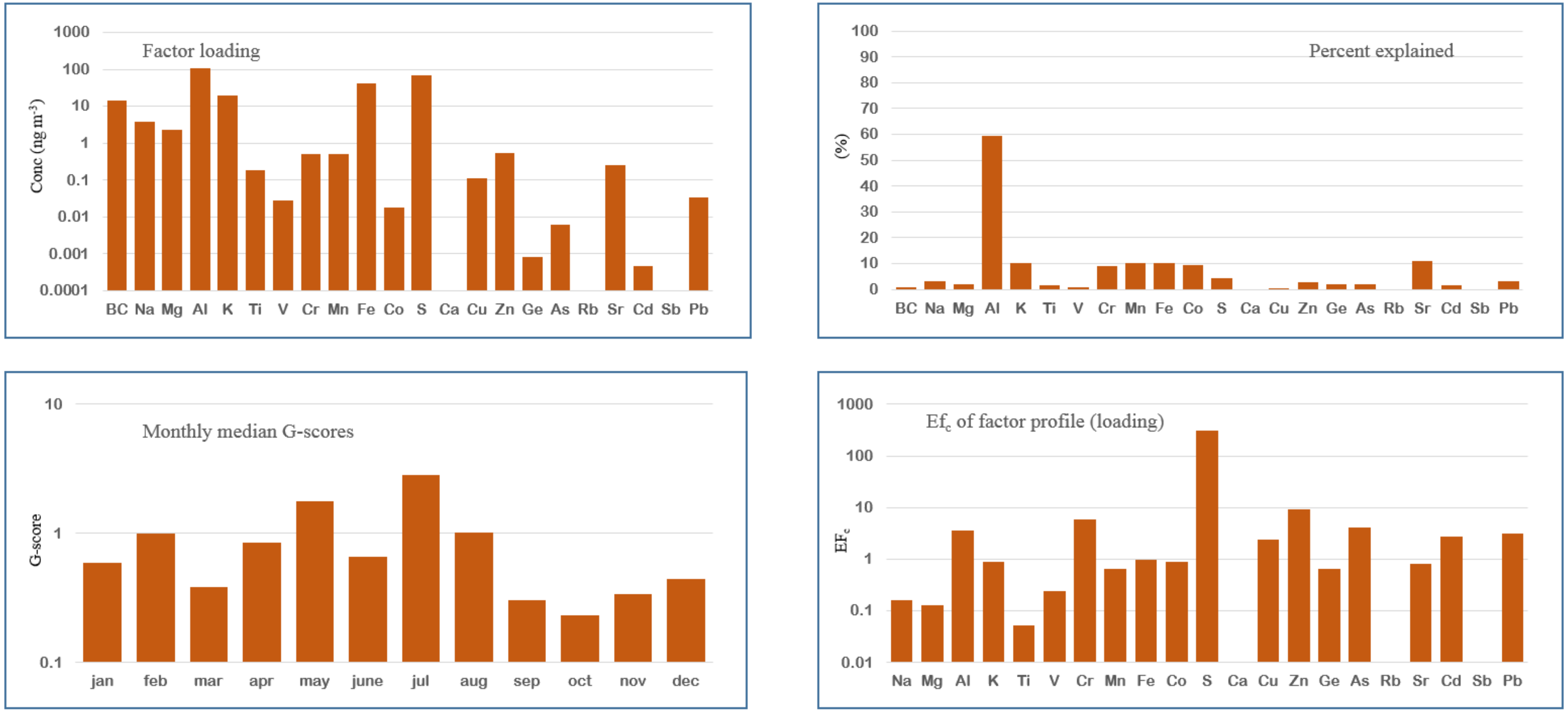


Figure 4- 48 Factor 3 parameters, Factor loadings (a), Percentage of concentrations explained by each factor (b) monthly median G-scores (c), crustal enrichment factor calculated using factor profiles (loadings) (d)

Factor 4

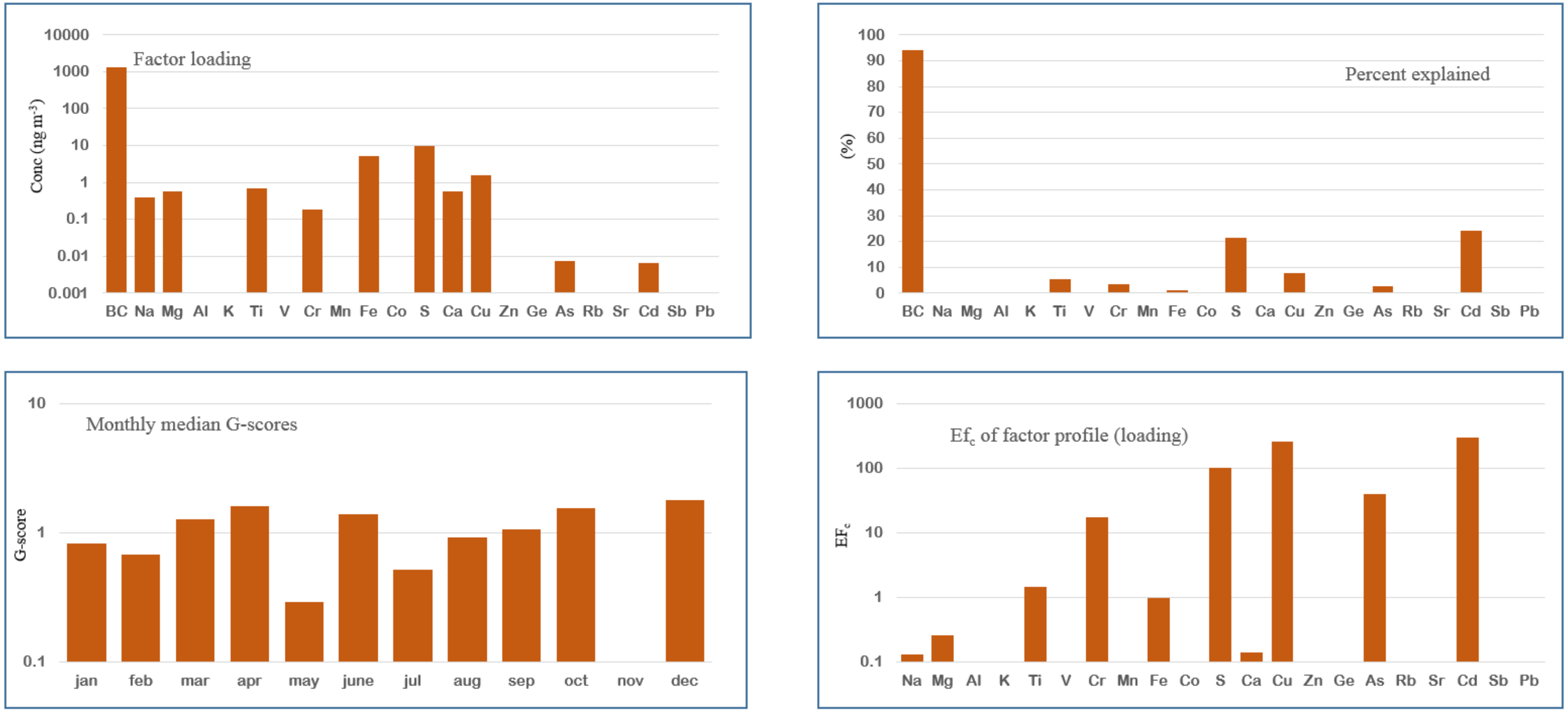


Figure 4- 49 Factor 4 parameters, Factor loadings (a), Percentage of concentrations explained by each factor (b) monthly median G-scores (c), crustal enrichment factor calculated using factor profiles (loadings) (d)

Factor 5

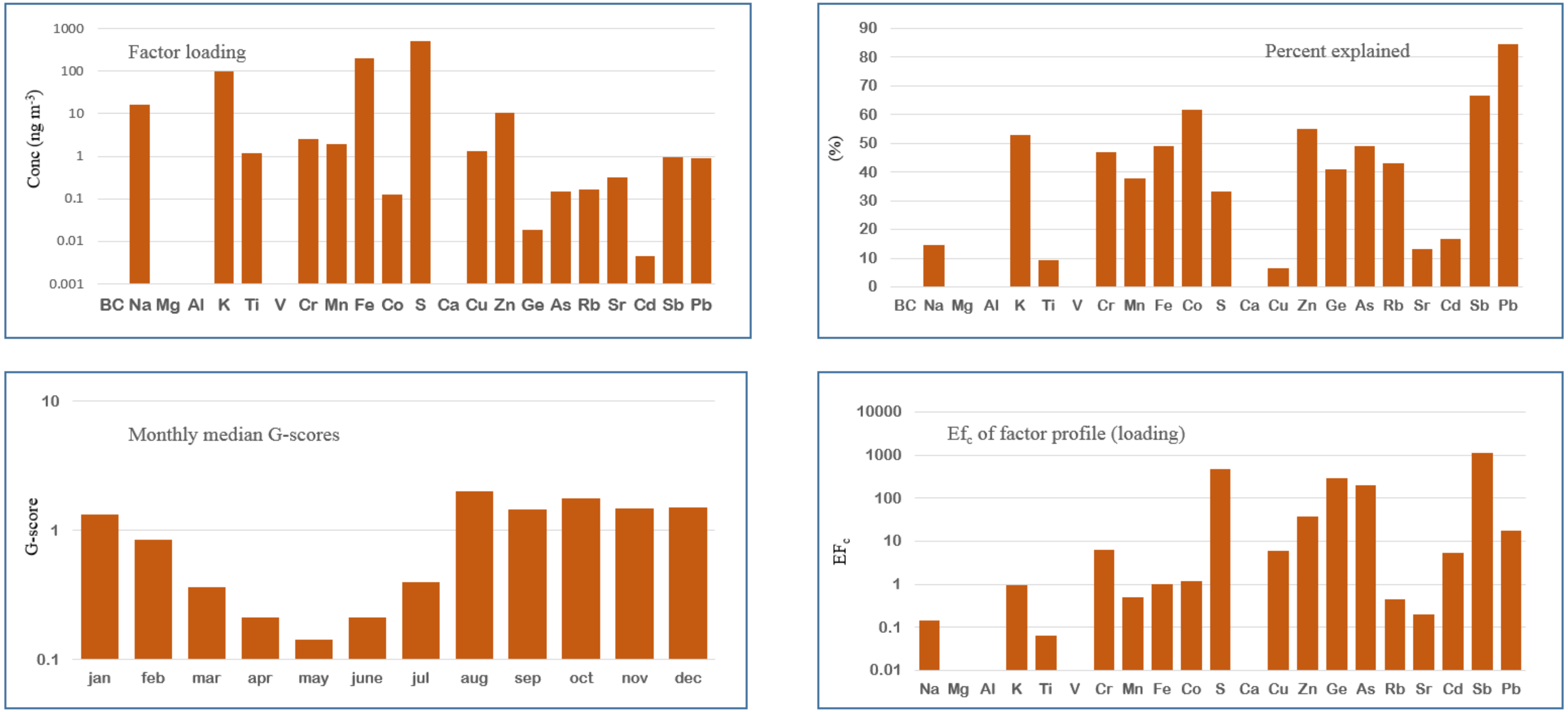


Figure 4- 50 Factor 5 parameters, Factor loadings (a), Percentage of concentrations explained by each factor (b) monthly median G-scores (c), crustal enrichment factor calculated using factor profiles (loadings) (d)

Factor 6

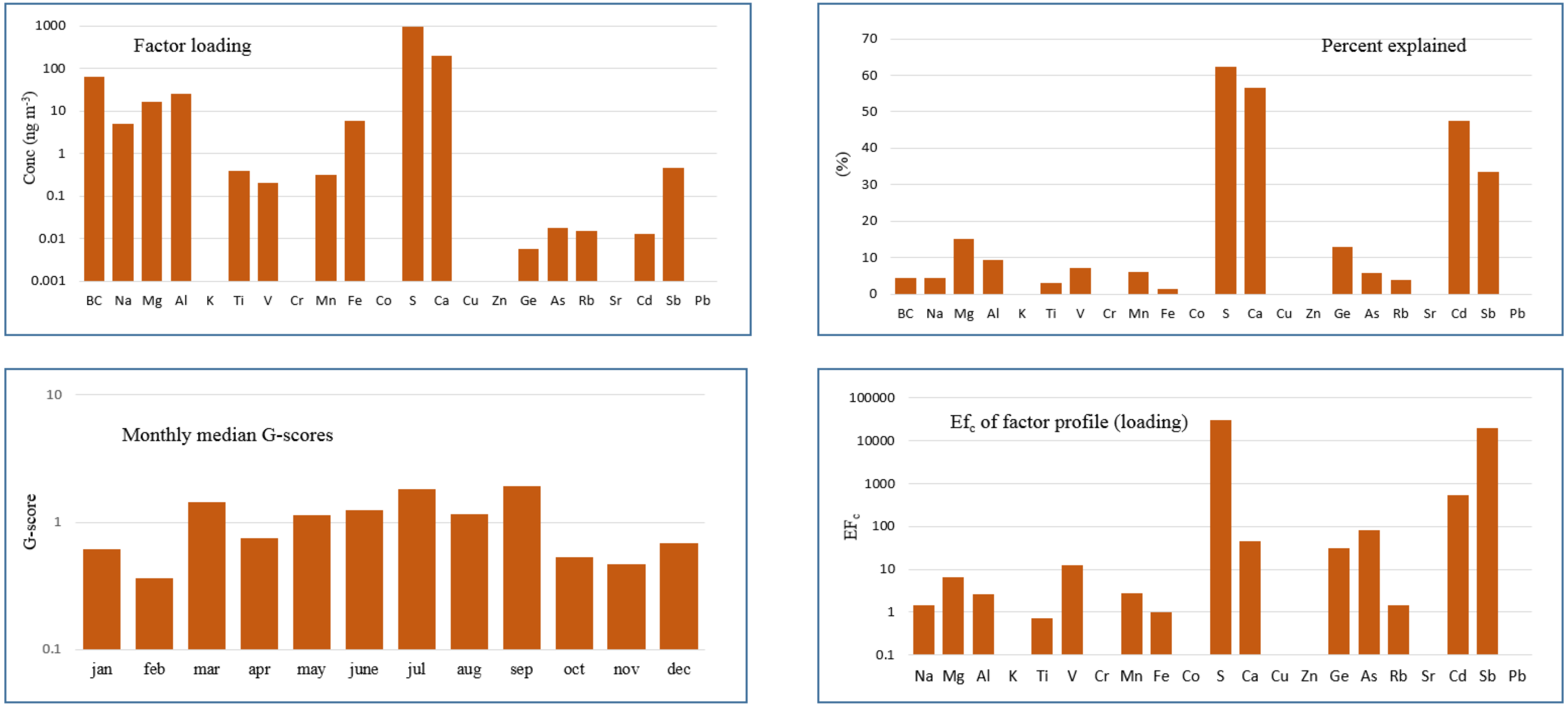


Figure 4- 51 Factor 6 parameters, Factor loadings (a), Percentage of concentrations explained by each factor (b) monthly median G-scores (c), crustal enrichment factor calculated using factor profiles (loadings) (d)

PMF exercises performed at our urban and suburban stations revealed six components of aerosol at Ankara atmosphere. Five of these factors were common. Common aerosol components observed in both stations are crustal, contaminated soil, light duty vehicle, coal combustion and diesel components. In addition to these, particles originated from oil combustion was detected at suburban station but not at not detected in urban site. Similarly, road dust was detected at urban station, but not at suburban station. Similarity of sources found at urban and suburban stations indicates homogeneity of the atmosphere over the city, which is due to low wind speed throughout the year. With low wind speed particles emitted at high emission areas at the borders of the city gradually diffuses to other parts of the city. Since such diffusion is more favored in summer we observed high concentrations of combustion-related elements and high g-scores of coal combustion factor during summer seasons at our suburban. Particles emitted from coal combustion affects particle composition at urban station more than they effect it at suburban station due to close proximity of urban station to Altındağ and Keçiören which are important coal-burning areas in the city. Sources of combustion related particles at suburban station is at Mamak area, which is another coal burning area in the city.

Another interesting finding in PMF exercise is three different soil components found. Two of these, namely crustal component and contaminated soil components were common in both stations. Road dust was identified (tentatively) at our urban stations, but it is not detected at suburban site. The difference between crustal material and contaminated soil is that contaminated soil represents surface soil, whereas crustal material represents subsurface soil, whose composition was not modified. Top soil in Ankara is contaminated due to deposition of anthropogenic particles over years. Maybe this may not sound as a strong source to change chemical composition of soil, but Ankara was very heavily polluted before the year 2000, and in those years deposition of particles from atmosphere was an important source that can modify trace element composition of soil. It is also interesting to note that same three soil-related source was identified in another source apportionment study performed by Yatın et al. (2000).

Contribution of factors to total elemental concentrations at AU station is depicted in Figure 4- 52. Crustal factor (Factor 1) is the largest contributor to total element concentrations. It accounts for approximately 31% of the concentrations of elements, containing more than 50% of Na, Mg, Ti, Rb and Sr. It is followed by Factor 5, which clearly represents coal combustion, containing highly enriched coal combustion markers, such as Ge, As and Sb. This source accounts for 31% of the total element concentrations. Factor 6, contributing as 13% in total concentrations, is not very clear and was tentatively assigned as road dust. Other sources are traffic source (Factor 2), contaminated soil (Factor 3), and diesel source (factor 4). They account for approximately 11%, 8%, and 6% of total concentrations of elements, respectively.

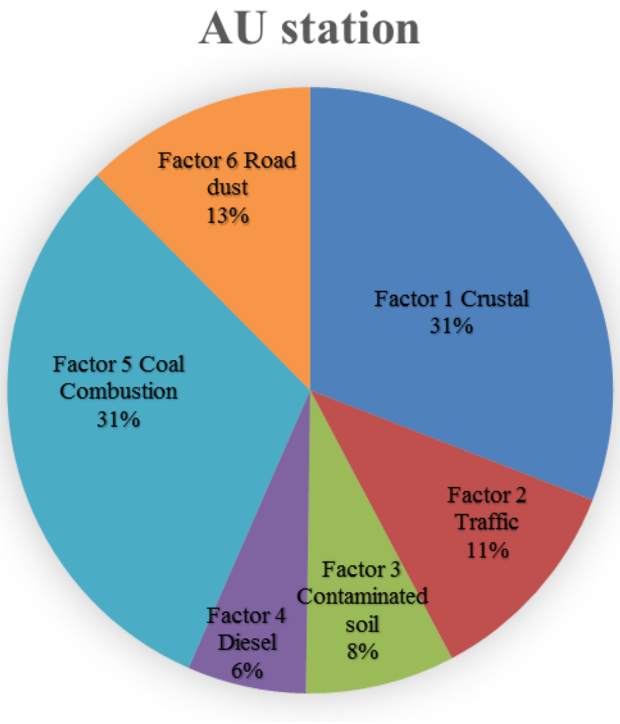


Figure 4- 52 Contribution of factors on total element concentration for AU station

CHAPTER 5

CONCLUSION

Daily fine aerosol samples are collected in Ankara at two stations. The first station located at Ankara University, close to the city center, is a representative of the urban area of the city, and the second one located at Middle East Technical University, far from the populated and polluted areas of the city, is classified as suburban station. Aerosol samples have been collected on a daily basis at both stations, from July 2014, to August 2015, using a ‘Stack Filter Unit’ on polycarbonate filters. Samples were digested by Microwave digestion method using Nitric and Hydrofluoric acid, and analyzed by ICP MS, to measure the concentration of 63 trace elements in them.

Firstly, concentration of elements in two station have been compared with each other. Most of elements have comparable values at both stations. Among anthropogenic elements, few (S, Cu, Sb) have higher concentrations at AU station, which is expected from an urban station, being under stronger influence of anthropogenic emissions. Major crustal elements like Al, Fe, etc. are not much different in both stations; however, all the rare earthy elements such as La, Ce, Pr, Nd, Sm, etc. have an order of magnitude lower concentration at AU station, which can be explained by the different mineral type’s influences on two stations, as it was also reported in the previous studies.

Comparing the data generated in this study, with the concentrations measured at Ankara in last 40 years, show a significant decrease in the concentrations of pollution-derived elements since 1975, due to actions taken to improve air quality. For crustal elements, concentrations measured at Ankara and particularly at METU are higher than concentrations reported for other cities around the world, probably because Ankara is in the middle of an arid Anatolian plateau, which does not have much vegetation cover, and due to the higher resuspension of the dry soil. Anthropogenic elements are not particularly high in Ankara, as expected, because it is not an industrial city.

Short-term and long-term variations were witnessed in concentrations of most of the measured elements. Variability in wind speed and direction, rain events and start–stop of a certain industrial activity are the main reasons for short-term (episodic) changes in concentrations of particles and pollutants in general.

Dependency of the measured elemental concentration on meteorological parameters are investigated in this study. Concentrations of crustal elements depends strongly on wind speed, since more soil aerosol is generated when wind speed is high. In addition, they are diluted more at high wind speed, as ventilation coefficient will be high. Considering these two factors, concentrations of crustal elements did not show a definable, consistent variation with wind speed. Concentrations of chalchophilic elements decreased with increasing wind speed, which was an expected behavior for pollutants, which are emitted with same emission rate throughout the year.

The conditional probability function(CPF) for anthropogenic elements show that Concentrations of pollution derived elements demonstrates strong directional preferences at suburban station, which is partly due to non-uniformly distribution of anthropogenic PM sources around the station, and non-uniform distribution of wind occurrence frequency in different wind sectors. During our sampling period, East was the dominant wind direction, and combined with the presence of Mamak, which is one of the high pollution mitting areas at the East of our METU station, it makes East wind sector the most important source sector for suburban station.

For most of the elements there are relatively high CPF values in N and NE sectors. This is probably due to presence of OSTIM (Organized industrial district), which hosts large number of small scale industrial facilities. Since it is approximately 7 km from our suburban station its impact on concentrations of anthropogenic elements measured at METU is not surprising, when the wind blows from N and NE. Observed distributions of CPF values clearly demonstrated that Mamak area with high emissions from residential coal combustion and OSTIM with emissions from industrial activities have the strongest contribution on measured concentrations of pollution-derived elements at METU.

For all elements at AU station, CPF value at East sector is high,pointing to strong effect of the Irfan Baştuğ Caddesi on these elements with anthropogenic sources. In addition, high CPF values in West sector points to the contribution of Fatih Caddesi. Other than these two sectors, which are strongly influenced from traffic emissions, distribution of CPF values of elements show uniform distribution around the AU station, as expected.

PMF model applied to data set, revealed six factors for both stations, indicating that aerosol population in these stations consists of six different components. For METU station, 2 factors are soil related, accounting for 50% of the total elemental concentration, with the highest contribution being from contaminated soil. For AU station, 3 factors are soil related, with approximately 75% contribution to the total concentration of measured elements.

These soil particles contain both crustal and pollution-derived elements. In a similar work done in 1993, Yatın et al (2000) identified three different soil components in Ankara aerosol population. One of them was contaminated surface soil. Surface soil in Ankara became contaminated by settling of combustion particles and particles emitted from traffic over the years. 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. Later this proposal was supported by Yay et al. (2008) who analyzed surface soil samples for trace elements at 100 points in Ankara. Similar factor was also identified in and Celik, (2014) study at METU station.

The coal combustion factor accounts for 16% of the total elemental concentration at METU, but 31% of it at AU. This indicates that contribution of coal combustion is significantly higher at urban station, as expected because urban site is very close to strong emission areas at Altındağ and outer edges of Keçiören.

The predicted concentration by PMF, are highly agreeable with the measured concentrations for strong species, which implies that 6 factor solution was adequate. In addition, $\mathrm{Q_{Robust}}$ to $\mathrm{Q_{true}}$ .ratio being lower than 1.5, having distribution of scaled residuals less than 0 ± 3.0 limit, having few number of unmapped data in bootstrapping, indicate that the modeling is accurate for both stations.

In this study, reliable information is generated on levels and temporal variations of crustal and anthropogenic aerosols in urban and suburban locations in Ankara. Moreover, the sources contributing in the measured concentrations and factors influencing chemical composition of aerosols were identified. This information can be useful for both Ministry of the Environment and Municipality and Ankara municipality, assisting them in their endeavors toward achieving a better air quality in Ankara. The results indicated that for both stations, contaminated surface soil is the highest contributing factor. Therefore, reducing the resuspension of soil is recommended in order to improve the air quality of the city, both in suburban and urban areas.

5.1 Recommendation for Future Research

Several useful analysis can be done on the data generated in this study or new data to be collected in the future studies, in order to gain better understanding of the atmospheric aerosol sources in Ankara, and their contribution, which were out of the scope of this study, such as:

1. Estimation of local dust contribution on PM2.5 concentrations at both stations
2. Estimation of desert dust contribution on PM2.5 concentrations at Ankara
3. Spatial correlations of elemental data at both stations to find the local sources

In addition, in this study, PM concentrations and source apportionment were performed on fine aerosol fractions. In order to evaluate coarse-to-fine ratios and temporal variations better, coarse fractions should also be analyzed.

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