CHEMICAL COMPOSITION OF PARTICLES AT A RURAL SITE AT NORTHWESTERN TURKEY: GATEWAY TO THE CENTRAL ANATOLIAN PLATEAU

by

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ABSTRACT

CHEMICAL COMPOSITION OF PARTICLES AT A RURAL SITE AT NORTHWESTERN TURKEY: GATEWAY TO THE CENTRAL ANATOLIAN PLATEAU

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In this study, the concentrations of 51 elements (Li, Be, Na, K, Mg, Al, P, S, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Se, Rb, Sr, Y, Mo, Cd, Sn, Sb, Cs, La, Ce, Pr, Nd, Eu, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, W, Pt, Au, Pb, Bi, Tl, Th, U), and the amounts of particulate matter ($PM_{2,5}$ ve $PM_{2,5-10}$) were determined in the atmosphere of Bolu which is located at the West Black Sea Region of Turkey. Aerosol samples were collected in the period of February 2011 and February 2012 at the Abant Izzet Baysal University Golkoy Campus with a semi-rural atmosphere.

Measured concentrations of trace elements at the Bolu station were compared with those measured at various sites around the world and as a result of comparison, concentrations of crustal elements (except for REE) in this study are found to be higher than those reported stations around the world. In addition, Cr concentration in fine mode and Cd concentration in coarse mode in Bolu station are higher than all the other sites.

Concentrations of elements measured at Bolu station showed seasonal variations. Such variations in concentrations are explained by variations in the source strengths and transport patterns.

Factor Analysis (FA) was applied to determine possible pollution sources. FA revealed six possible emission sources for fine fraction such as soil, coal and wood burning, iron-steel works, road dust, sea-salt and regional background. Also five possible pollution sources were determined for coarse fraction and these are soil, coal burning, road dust, sea-salt and long-range transportation. Lastly, possible pollution factor identification was supported with backtrajectories.

Key words: Fine fraction, coarse fraction**,** elements, receptor modelling, wind sector analysis, long range transport

ÖZET

KUZAYBATI TÜRKİYE KIRSALINDAKİ ATMOSFERİK PARTİKÜLER MADDENİN KİMYASAL KOMPOZİSYONU: ORTA ANADOLU PLATOSU'NA TAŞINIM

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Bu çalışmada, Türkiye'nin Batı Karadeniz Bölgesi'nde yer alan Bolu İli atmosferdeki 51 elementin (Li, Be, Na, K, Mg, Al, P, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Se, Rb, Sr, Y, Mo, Cd, Sn, Sb, Cs, La, Ce, Pr, Nd, Eu, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, W, Pt, Au, Pb, Bi, Tl, Th, U) konsantrasyonları ve $PM_{2,5}$ ve $PM_{2,5-10}$ partiküllerin miktarları belirlenmiştir. Aerosol örnekleri Şubat 2011 ve Şubat 2012 tarihleri arasında, yarı-kırsal bir atmosferi olan Abant İzzet Baysal Üniversitesi Gölköy Kampüsü'nde toplanmıştır.

Bolu'da ölçülen eser element konsantrasyonları, dünyanın çesitli yerlerinde ölçülen konsantrasyonlar ile karşılaştırılmıştır ve bu karşılaştırmanın sonucunda, bu çalışmadaki toprak elementlerinin konsantrasyonlarının (nadir toprak elementleri hariç) dünya genelindeki diğer bölgelerden daha fazla olduğu saptanmıştır. Bunu yanında, Bolu istasyonunda belirlenen ince moddaki Cr ve kaba moddaki Cd konsantrasyonunun diğer bölgelerden daha fazladır.

Bolu istasyonunda ölçülen elementlerin konsantrasyonlarının mevsimsel değişiklikler gösterdiği görülmüştür ve bu gibi değişiklikler, kaynakların emisyonlarındaki ve hava akımındaki değişikliklerle açıklanmıştır.

Olası kirlilik kaynaklarını belirlemek amacıyla Faktör Analizi (FA) uygulanmıştır. FA ince fraksiyon için toprak, odun ve kömür yanması, demir-çelik işletmeleri, yol tozu, deniz tuzu ve bölgesel geri plan gibi altı olası emisyon kaynağını işaret etmiştir. Ayrıca, kaba fraksiyon için de beş olası kirlilik kaynağı belirlenmiştir ve bunlar toprak, kömür yanması, yol tozu, deniz tuzu ve uzun mesafeli taşınımdır. Son olarak, olası kirlilik faktörleri backtrajektörler ile desteklenmiştir.

Anahtar Kelimeler: Faktör analizi, ince fraksiyon**,** kaba fraksiyon, elementler, alıcı ortam modellemesi, rüzgar sektörü analizi, uzun mesafe taşınım

Dedicated to my family

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1. INTRODUCTION

One of the most popular air pollution definition is “gases, dust, fumes or odour containing air in critical amounts which could be harmful to the health or comfort of humans and animals or which could cause damage to plants and materials with long residence times (Wark et al, 1981). Environmental Protection Agency (EPA) classified pollutants as -particle pollution (often referred to as particulate matter), ground-level ozone, carbon monoxide, sulfur oxides, nitrogen oxides, and lead- according to their content and property damage. EPA calls these pollutants "criteria" air pollutants because it regulates them by developing human health-based and/or environmentally-based criteria (science-based guidelines) for setting permissible levels.

While a large fraction of aerosols are remaining in the boundary layer of atmosphere, some of lifted into the troposphere and collected in an area after long range trasportations over countries. Long range trasportation of this pollutants could reach hundreds of kilometeres by wind and other potential impacts. This mechanism starts with emission of contaminants from the source and continues propagation in the atmosphere. This cycle completes with precipitation of pollutants on plants, surface water, soil and other materials.

Rural receptor regions remote from the sources are quite suitable to monitor the behavior of physical and chemical behaviours of aerosols, in order to correctly predict pollution inputs. Possible long range transport information and

meteorological conditions are aid in understanding the nature of pollution and developing control strategies. Air pollutants can be originated from natural sources such as sea spray and volcanic eruptions, they can be emitted from antropogenic factors such as industrial wastes, vehicles and domestic heating (Finlayson-Pitts and Pitts, 2000).

In this study, trace elements and pollutant concentrations were determined in $PM_{2.5}$ and $PM_{2.5-10}$ mode and then possible pollution sources were determined by various statistical methods and receptor modeling approach.

1.1. Aim of the Study

The main aims of this study are to determine chemical composition, in particular, the size differentiated composition of atmospheric particles and to identify sources and potential source locations of pollutants in the west Black Sea region. In order to assess atmospheric trace metal load and its relationship with the size of particulate matter (PM), daily fine and coarse aerosol samples were collected in Bolu. Contrary to the urban sites that remain under the stress of anthropogenic emissions, the sampling site was almost independent from local pollution effects confirming that this was a representative semi-rural background site. Therefore, it should be expected that the data generated from this site allow evaluating atmospheric pollution by long range transport.

In this study, the measured concentrations of elements were compared with those measured at vastly seperated parts around the world provided that selected sites should be representative for a reliable comparison. While comparing, the data obtained from different regions in Turkey were also included to demonstrate whether

the level and composition of elements observed in Bolu are a general feature of the country or specific to the location.

To examine the air current patterns of the West Black Sea region annual and seasonal wind roses were prepared by using surface wind data obtained at sampling site during the sampling period. Whereby it is aimed that, if there is a local pollution effect to sampling site, it is interpreted clearly to verify the validity of this study. Besides that, upper air data with combining different altitudes were used to investigate the transport of pollutants from different wind sectors. The paths of flow were obtained by backtrajectories which describe the path of air masses before it is reached at a receptor site. Also, temporal variations were investigated by long-term variations and episodic changes and their reasons were discussed.

Finally, various methods were applied to identify source types and regions. Firstly, correlations between species were used to indicate similarities of sources or transport pattern. Afterwards, chemical character of the aerosols was evaluated by enrichment factor calculation. In addition, factor analysis was applied to estimate the existing sources and apportion the particulate matter mass to each source.

1.2. Particulate Matter

Aerosol is described as the stable suspension of solid or liquid material in gaseous medium. It is also named as particulate matter in atmospheric studies. The particle diameter may vary approximately from 0.005 μm to 100 μm. Moreover, size distribution of suspended particles generally consist of a small diameter of 40 μm. Particulate matter contains substances such as elements and organic compounds,

silicon oxides, aluminum, iron, trace elements, sulfates, nitrates and ammonia (Finlayson-Pitts and Pitts, 1998).

Particles are clasified as primary and secondory based on formation mechanism. Primary particles are directly emitted into the atmosphere whereas secondary particles formed in the air by chemical transformations and reactions (Seinfeld and Pandis, 1998). Figure 1.1 illustrates the physical and chemical interactions of atmospheric particles.

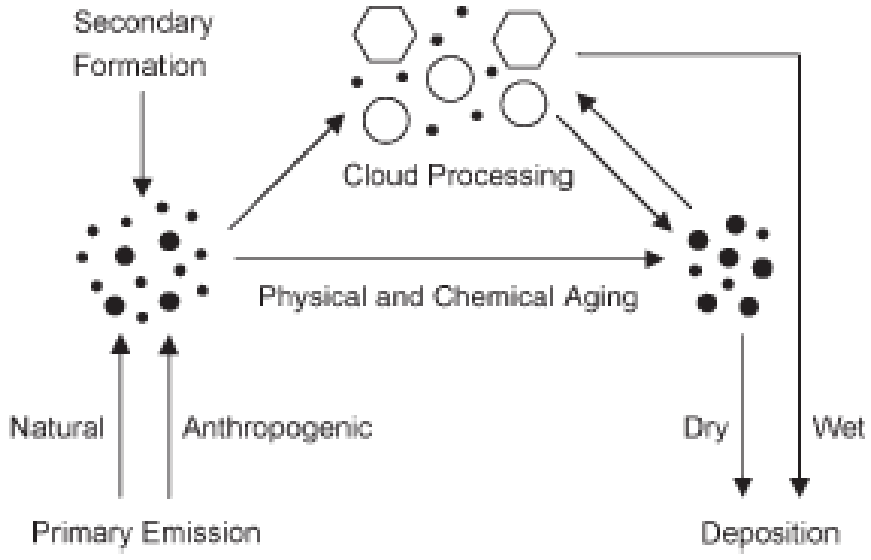


Figure 1.1 Atmospheric cycling of aerosols (Pöshl, 2005)

Some formation pathways and typical size distrubition of atmospheric particles range from 0.001 µm to 100 µm (Figure 1.2). Particles with diameter greater than 2.5 µm are referred to as coarse particles ($PM_{2.5-10}$), and particles with diameter less than 2.5 µm are referred to as fine particles ($PM_{2.5}$). Fine mode upward can be divided into two sub regions; nucleation (aitken) and accumulation range. While particles in nucleation range have diameters less than 0.08 µm, particles in accumulation range

have diameters betwen 0.08 µm to 2.5 µm. In literature, fine and coarse mode can be seen as two major modes of particles (EMEP, 1999; Lazaridis et al., 2002).

Coarse mode containing particles are produced by mechanical processes of large particles by crushing or grinding, the bubble-bursting process over the sea surface (sea spray) and dust resuspension (EPA, 2004). Additionally fly ash from combustion, oxides of crustral elements, pollen, fungal spores and animal-plant fragments are found in coarse fraction (Wilson and Suh, 1997). Coarse mode particles are removed from the atmosphere by gravitational settling. Because of being large in size and mass, they do not travel longer distances and can settle out rapidly from the atmosphere with short lifetimes of minutes to hours. Although most of the coarse particles are primary, some particles in this mode can be classified as secondary particles (Watson and Chow, 1994).

Accumulation mode particles are generally produced from combustion of low vapor pressure vapors from combustion processes and coagulation of small particles. This range is composed of ammonium, nitrate, sulphate and hydrogen ions, large variety of organic compounds, metals, and particlebound water (Wilson and Suh, 1997). Condensation usually occurs on smaller particles and the rate for coagulation of two particle decreases as particle size increases. That is why aitken particles grow into the accumulation fraction; but not grow into the coarse mode. Accumulation mode particles have long residence times in the atmosphere and they can be transported over long distances until they are removed by deposition mechanisms (EPA, 2005). Aitken mode particles are formed as a result of combustion and by gas to particle conversion in atmosphere. Although they have high concentration in atmosphere, their contribution to the total mass is small. These particles affect global climate by absorbing and scattering light and consequently may also cause haze formation, a

decrease in visibility and an increase in respiratory health problems in humans (Watson and Chow, 1994).

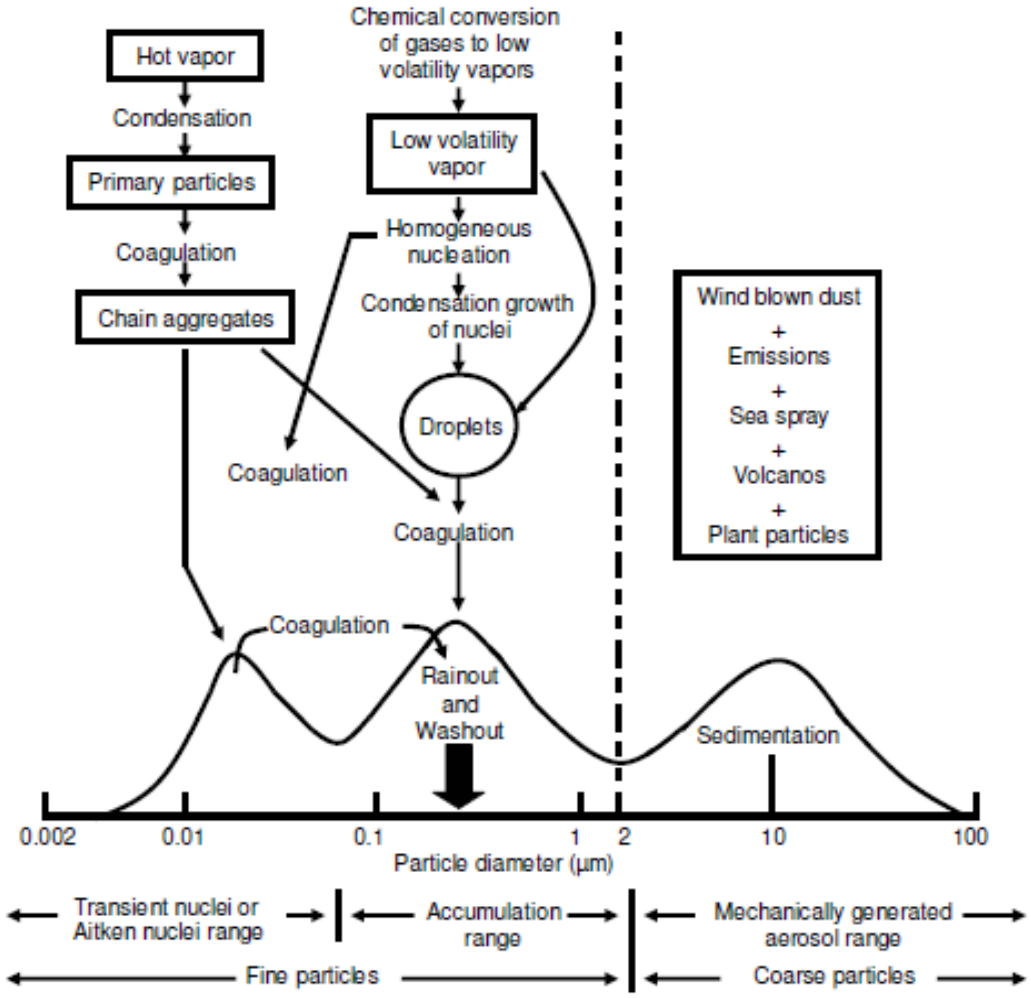


Figure 1.2 Schematic of atmospheric size distribution showing the tree mode, main sources of mass for each mode, and the principle processes involved in inserting mass into and removing mass from each mode (Finlayson-Pitts, 1986)

1.3. Sources of Particulate Matter

Atmospheric particles arise from both natural and antropogenic sources and contain organic, inorganic and biological components such as ammonium, sulfate, nitrate, carbon (organic and elemental), mineral dust and water, pollen, spore. The superioriy

of these components in particulate matter and their size distribution are closely related with their sources. Figure 1.3 illustrates the basic factors responsible for the composition of inorganic particulate matter.

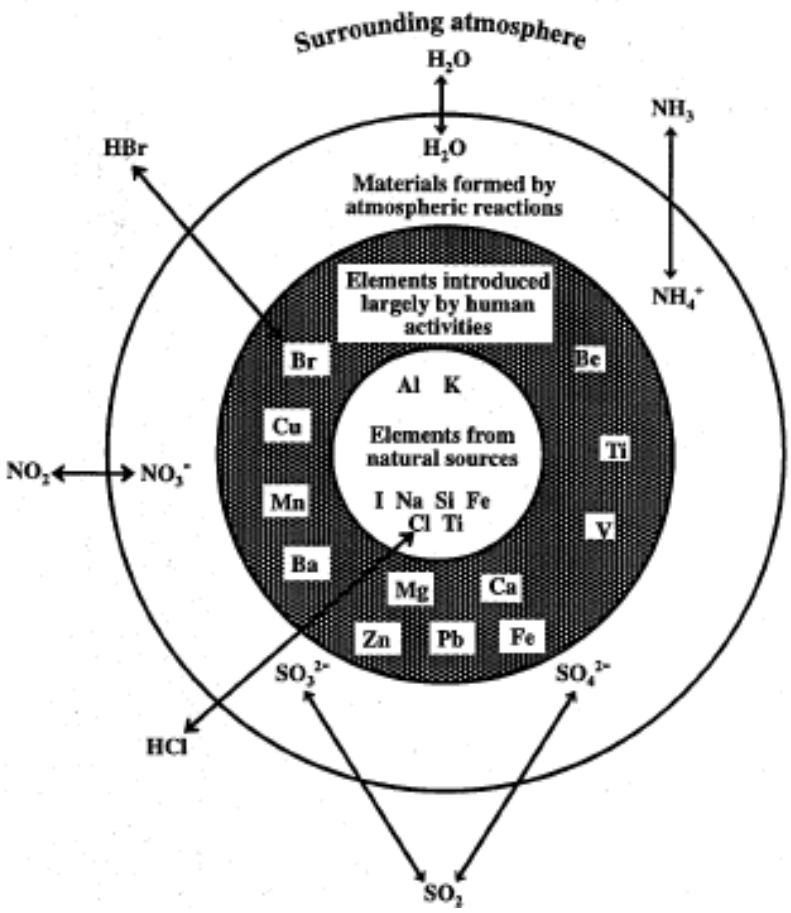


Figure 1.3 Some of the components of inorganic particulate matter and their origin (Manahan, 2000)

Natural sources are dominant on a global scale because of their emissions from large areas. On the other hand, antropogenic particles can be dominated in industrialized small regions (Mathys et al., 2001). Both natural and antropogenic sources give rise to primary and secondary fraction of particulate matter. Mineral particles originated from soil, volcanic emissions, sea spray, biogenic materials such as micro-organisms, pollen and spores are natural sources of primary particles (Seinfeld and Pandis,

1998). Sulfate, nitrate and organic aerosol compose the secondary fraction of natural source of secondary particles. Natural sulfate is formed by oxidation of reduced sulphur gases emitted from oceans and SO_2 and H_2S emitted by volcanoes. Nitrate is the final pruduct of the oxidation of nitrogen oxides. The main sources of NOx are the lightning (Priece et al., 1997) and soil perspiration (Roelle et al., 2001).

Antropogenic primary particles consist of mineral particles eroded by road traffic, fly ash particles, unburned fuel particles, motor vehicle exhaust and particles emitted by industrial activities. In addition, oxidation of SO_2 emitted from fossil fuel combustion, NOx emitted from fossil fuel combustion and hydrocarbons emitted from burning processes form the antropogenic secondary particles (EMEP, 1999).

1.4. Effects of Particulate Matter

1.4.1. Health

PM can alter the body's defense systems against foreign materials, damage lung tissues, aggravate existing respiratory and cardiovascular disease, and can lead to cancer. In some cases, PM exposure can even lead to premature death. Adverse health effects have been associated with exposures to PM over both short periods (such as a day) and longer periods (a year or more). The people who are most at risk are people with asthma, influenza, lung, heart, or cardiovascular disease, the elderly, and children.

Humans have developed a means of protecting themselves against the large particles (www.hcdoes.org/airquality/monitoring/pm.htm). Particles larger than 10 microns generally get caught in the nose and throat, never making it as far as the lungs. Unfortunately, more recent human activity has created many particles that are much

smaller, which can make it past our natural defenses, and can enter our systems. This is why particles smaller than 10 microns are often called "inhaleable particulates" and are regulated by the EPA. Particles that are smaller than 5 microns can get into the bronchial tubes and the top of the lungs. Particles smaller than 2.5 microns in diameter can get into the deepest portion of the lungs where the gas exchange occurs between the air and blood stream. These are the dangerous particles because the body has no efficient mechanisms for removing them.

New studies have shown that there is an 18% increase in deaths from heart disease among people with long term exposure to particulate matter. While exposure clearly impacts the lungs, "long-term, chronic exposure to air pollution seems to manifest more in cardiovascular disease than it does in respiratory disease" (Pope et al., 2007).

These studies show the biological mechanism by which long-term exposure to tiny-particle pollution can actually lead to ischemic heart disease, which causes heart attacks, as well as irregular heart rhythms, heart failure and cardiac arrest (www.hcdoes.org/airquality/monitoring/pm.htm). While strong bouts of pollution can make breathing hard and increase respiratory problems, they also provoke low-grade pulmonary inflammation, accelerating the development of atherosclerosis - a leading cause of heart disease - and altering heart function.

The Air Quality Index (AQI) for particulate matter provides information on the health effects of different levels of particulate in the air (EPA, 2004). AQI levels and cautionary statements are given in Table 1.1.

Table 1.1 Air Quality Index (AQI): Particulate Matter

Index Values	Levels of Health Concern	Cautionary Statements*	
		$PM_{2.5}$	PM_{10}
0 - 50	Good	None	None
51 - 100**	Moderate	None	None
101 - 150	Unhealthy for Sensitive Groups	People with respiratory or heart disease, the elderly, and children should limit prolonged exertion.	People with respiratory disease, such as asthma, should limit outdoor exertion.
151 - 200	Unhealthy	People with respiratory or heart disease, the elderly, and children should avoid prolonged exertion; everyone else should limit prolonged exertion.	People with respiratory disease, such as asthma, should avoid outdoor exertion; everyone else, especially the elderly and children, should limit prolonged outdoor exertion.
201 - 300	Very Unhealthy	People with respiratory or heart disease, the elderly, and children should avoid any outdoor activity; everyone else should avoid prolonged exertion.	People with respiratory disease, such as asthma, should avoid any outdoor activity; everyone else, especially the elderly and children, should limit outdoor exertion.
301 - 500	Hazardous	Everyone should avoid any outdoor exertion; people with respiratory or heart disease, the elderly, and children should remain indoors.	Everyone should avoid any outdoor exertion; people with respiratory disease, such as asthma, should remain indoors

* PM has two sets of cautionary statements, which correspond to the two sizes of PM that are measured:

•Particles up to 2.5 micrometers in diameter ($PM_{2.5}$)

• Particles up to 10 micrometers in diameter (PM_{10})

**• An AQI of 100 for $PM_{2.5}$ corresponds to a $PM_{2.5}$ level of 40 micrograms per cubic meter (averaged over 24 hours).

• An AQI of 100 for PM_{10} corresponds to a PM_{10} level of 150 micrograms per cubic meter (averaged over 24 hours).

1.4.2. Environment

Atmospheric particles have numerous effects on environment. The most obvious of these is reduction and distortion of visibility. The most visible effects of aerosol particles upon air quality result from their optical effects. Particles smaller than about 0.1 μm in diameter scatter light much like molecules, that is, Rayleigh scattering. Generally, such particles have an insignificant effect upon visibility in the atmosphere. The light-scattering and intercepting properties of particles larger than 1 μm are approximately proportional to the particles' cross-sectional areas (Manahan, 2000). Particles of 0.1 μm–1 μm cause interference phenomena because they are about the same dimensions as the wavelengths of visible light, so their light-scattering properties are especially significant (Manahan, 2000).

Particle pollution can stain and damage stone and other materials, including culturally important objects such as statues and monuments by acid rains. The fine particulate matter and acid deposition issues are closely linked and both share the same dominance of large sulfate fraction in the chemical composition of collected samples. Sulfates are a significant component of fine particles and have been directly linked to ecosystem damage. Both direct emissions of particulate matter and secondary particle formation caused by oxidation of sulfur dioxide, nitrogen dioxide and aerosol organic carbon species contribute to overall levels of airborne particles. In urban environments this greatly affects many construction materials and paints, while its effects on agricultural and natural ecosystems range from reduced productivity to disruption of nutrient cycles to the massive summer fish kills observed through the last decades (Bulgur et al., 1998).

PM also affects the environment by harming plant life. Particulate matter precipitate on soil and plants depends on their chemical and physical properties. These particles

affect plant growth by reducing their photosynthetic activities. Air suspended particles in Beijing atmosphere that cause a decrease in the rate of 5-30% of the country's agricultural crop production has been determined (Sun et al., 2003). This has an effect on the wildlife of the area, as many animals are dependent on the plants for food. This effect can be passed on up the food chain.

1.5. Trace Elements

Trace elements are used as tracers to determine the sources of aerosol. They are also known as potentially toxic elements, trace metals, heavy metals, micronutrients, and minor elements. The term “potentially toxic elements” describes that while some elements are toxic to humans and plants, not all elements are toxic at all concentrations. Indeed, some elements (e.g., Fe) are necessary for life in small amounts (Alloway, 1995).

Interest in trace elements has increased in recent years because of the widespread trace element emission formed by industrial processing. Some trace elements such as Fe, Al, Cu, Pb, Mn, Br, Cd, Ni, Hg, As, and Se are required for manufacturing products, so these elements become common in industrial wastes. The Resource Conservation and Recovery Act (RCRA), enforced by the United States Environmental Protection Agency (EPA), has set mandatory clean-up guidelines for the following trace elements which are known as the RCRA metals.: Ag, As, Ba, Cd, Cr, Hg, Pb, and Se (Albright, 2004).

Natural sources include sea, volcanic activities, lithosphere and biosphere. Particles emitted from these sources are generally have larger diameter than antropogenic particles and found in coarse mode.

Atmospheric antropogenic aerosols originate from various souces. In urban areas, the sources of antropogenic aerosols contribute about 70% of the total particulate air pollution. The heavy and transition metals form 10 to 20% of the atmospheric antropogenic aerosols. Table 1.2 indicates elements that can be correlated to specific emission sources.

Table 1.2 Indicator elements of each source type (Kasahara, 1992; Gone, 1999)

Source Type	**Indicator Elements**
Crustal material	Al, Sc, REE*, Ti, Sc, Mn
Marine (sea salt)	Na, Cl
Coal combustion	As, Se, Hg
Oil combustion	V, S, La, La/Sm
Refineries	La, La/Sm
Motor vehicles	Br, Zn, Sb
Automobile exhaust	Pb, Br
Diesel exhaust	C
Wood burning	K
Incinerators	Na, K, Cl, In, Hg
Paint	Ba, Ti
Aluminum plants	Al, Mg, Hg
Industrial urban areas	V, Zn, Se, Mo, Sb
Iron/steel works	Fe, Zn, Se, Mo, Sb
Zn, Cd, Pb smelters	In, As, As/Se, Co, Cd, Cr
Ni, Cu smelters	Hg, As, As/Se
Precious metals	Au, Cr, Mo
Cement, Limestone	Ca

REE*: rare earth elements like La, Ce, Sm etc.

At elevated levels, trace elements are harmful to humans. For example, Pb, which is added to gasoline to reduce automobile engine knock, has become widespread in soils. Other additions of Pb to the environment include contamination from Pb paint, smelters, and Pb arsenate, an insecticide. Lead is toxic to humans, especially

children, and damages the central nervous system, causing retardation and even death in extreme cases (Ewers and Schlipköter, 1991). Trace element levels are also important because of their potential to bioaccumulate in the food chain.

1.6. Longe Range Trasport of Aerosol Particles

Regional air pollution has been a significant concern in many parts of the world since the industrial revolution. While industrialized nations have been actively working to improve their air quality by reducing local emissions, many developing countries are now facing growing air pollution problems because of their rapid population and economic growth. Atmospheric transport between continents takes 1-2 weeks on average and, as a result, continental emissions of even short-lived species (lifetimes of weeks to months) can affect the atmosphere above other continents.

Long-range transport of particulate and gaseous air pollutants has been studied extensively over the last decades under the cooperation of the European Monitoring and Evaluation Program (EMEP) and several national and international efforts (Berdowski et al., 1998; EPA, 1996a,b; EU, 1996, 1997; Quality of Urban Air Review Group, 1996; Position Paper on Particles, 1998).

By the buoyancy effects, air pollutants emitted to atmosphere and disperse horizontally and vertical due to turbulence field and prevailing meteorological patterns. The last years there is an extensive research focus on particulate matter (PM) mainly because of serious public health risks for susceptible members of the population and risks to sensitive ecosystems. The transport of PM in the atmosphere is similar to that of gaseous pollutants for the fine particle fraction but deviates at larger sizes (coarse particles) due to deposition processes. Therefore, the long-range

transport of PM contributes significantly in the background particle mass and number size distribution. However, there is still considerable debate among the scientific community regarding the vertical exchange processes involved and the spatial and temporal scales of atmospheric particle transport (Lazaridis et al., 1999).

1.7. Receptor Modelling Studies

1.7.1. Enrichment Factor

Trace metals in aerosols are divided from a variety of sources which include the Earth's crust, the oceans, volcanic activity, the biosphere, and a number of anthropogenic processes (e.g. fossil fuel burning, waste incineration and the processing of ores.). The degree to which a trace metal in air aerosol is enriched, or depleted, relative to specific source can be assessed to a first approximation using an enrichment factor (EF_{crust}) (Chester et al., 1999).

It has been the practice to categorize trace metals in the marine aerosol on the basis of their crustal EFs, calculated according to an equation of the type:

$$EF_{crust} = \frac{\left(C_X / C_R\right)_{air}}{\left(C_X / C_R\right)_{reference}}$$

where, C_X is the concentration of element of interest in the sample and in the reference materials and C_R is the concentration of the reference element in the sample and reference materials. The selection of reference element is very important in EF_{crust} analysis to get correct results. The reference element to be used should be non-volatile lithophile element, which is abundant in crustal material, accurately measured with various analytical techniques, and to be measured in all samples. In

EF_{crust} calculations, generally Al is used as the reference element if measured as it is the only element which obeys all these criteria. When Al is not measured at the study area then other crustal elements like Fe, Ca, Si, and Sc can be used as a reference element, too.

By convention, an arbitrary average EF value of <10 is taken as an indication that a crust trace metal in an aerosol has a significant crustal source, and these are termed as the non-enriched elements (NEEs). In contrast, an EF value of >10 crust is considered to indicate that a significant proportion of an element has a non-crustal source, and these are referred to the anomalously enriched elements (AEEs); however, when sufficient crustal material is present in the air the AEEs can switch character and behave as NEEs. This is an essentially crude classification, but is useful in interpreting aerosol chemistry (Chester et al., 1999).

1.7.2. Factor Analysis

Factor analysis provides fundamental information about the possible sources that may influence the receptor area. Principally, it indicates groups of elements where concentrations behave together from one sample to another and separates these elements into factors (Henry et al., 1984).

The major aims of factor analysis are to determine the number of factors needed to describe the experimental data satisfactorily and to determine the matrix of factor loadings (A).

If a dataset of elemental concentrations is determined at *N* observations for a total of *n* elements, the concentration of the *j*-th element (*j*=1…n) at the *i*-th sampling duration (*i*=1…N) is denoted by x_{ji}. It is convenient to transform the data set to the standardized variables z_{ji} by

$$z_{ji} = \frac{x_{ji} - \overline{x}_j}{\sigma_j}$$

where $\overline{x}$, and σ are the mean and standard deviation of element *j*, respectively.

Normalized concentrations of elements give their equal weight in the factor analysis regardless of its average concentration. Normalized concentration z_{ji} has a mean value of 0 and a variance of 1.

As a result, the z_{ji} have a mean of zero and a variance of unity. In the factor model, the z_{ji} are assumed to be a linear sum of common factors with *m* and r_i which account for the correlations between the variables and a unique contribution which is specific for each individual sample.

$$z_{ji} = \left(\sum_{k=1}^{m} a_{jk} f_{ki} \right) + d_j u_{ji}$$

The coefficients a_{jk}, representing the correlation of element *j* with factor *k*, are indicative for the relative elemental composition of the factor *k*. These coefficients are often called the factor scores. They represent the contribution of factor *k* to sample *i*. The product $d_j u_{ji}$ represents the residual error for variable *j* in sample *i*, which is not accounted for by the m common factors. The total variance of each element *j* can be split into a fraction, which is accounted for by the factor model, and unexplained fraction given by the uniqueness d_j^2. This unexplained variance is reflected in observed variations on a local scale. Uniqueness is also referred to as

local variance. The coefficients u_{ji} indicate how sample *i* contribute to the uniqueness of element *j* (Kuik et al., 1993).

In factor analysis the number of factors *m* is described by the eigenvalue cutoff. As the cutoff value decreases, *m* increases. One of the serious drawbacks in factor analysis is the selection of this cutoff value which in turn governs the value of *m*. On the selection of the cutoff value, there is no universally applicable method for establishing *m* and it is necessary to discard a number of small eigenvalues. Generally, eigenvectors with eigenvalues greater than 1 are more signal than noise and should be kept in the model. Those eigenvectors with eigenvalues less than 0.5 have more than twice as much as noise as signal and should be eliminated from the model. For eigenvalues between 1 and 0.5, the associated eigenvectors are more noise than signal, but they may be important enough to kept in the model.

By definition, multivariate analysis requires several observations, the more the better. If there are a few samples, the results of a multivariate model are not likely to be reliable. Experience has shown that 100 samples or more is generally acceptable and that 20 or 30 is usually too few (Henry et al., 1984).

1.7.3. Back-trajectory Analysis

Trajectory is the time integration of an air parcel's position while it is transported by wind. Trajectory models, which describe the paths of air parcels take in the atmosphere, are useful tools for determination of source-receptor relationship of air pollutants. Various trajectory computation methods have been developed based on different assumptions.

In most of the trajectory models, observed or model analyzed winds are used to compute horizontal advection component. The vertical component of the trajectories, on the other hand, are computed based on one of the following assumptions:

- Isobaric
- Isentropic
- Kinematic

The isobaric trajectory models have been used in several studies in the past. However, it has been found that the significant vertical motions were ignored in isobaric assumption (Harris and Kahl, 1994). Nowadays, the isentropic trajectory models are widely used in trajectory calculations. Isentropic models are advantageous due to not requiring vertical motion data. The vertical motions occur implicitly as air parcels move along slopping isentropic surfaces (Fuelberg et al., 1996).

The isentropic assumption has been used widely in preparing three-dimensional trajectories (e.g., Merrill et al., 1986; Pickering et al., 1994). This method has the advantage of not requiring vertical motion data. Instead, vertical displacements occur implicitly as parcels move along the sloping isentropic surfaces. The isentropic assumption is appropriate for periods of several days when investigating cloud-free regions away from the Earth's surface. For longer periods, however, radiative processes cause the assumption to become suspect even in the clear, free atmosphere. The assumption certainly is unsuitable in areas of precipitation and in the boundary layer. Furthermore, isentropic trajectories are difficult to compute accurately in areas where the thermal lapse rate approaches neutral stability.

Three-dimensional trajectories can also be prepared by allowing parcels to be transported by the horizontal and vertical wind components (Krishnamurti et al., 1993; Garstang et al., 1996). Since wind data are used exclusively in the calculations, we will refer to this method as the kinematic approach. The technique makes no explicit assumptions about the flow; however, the vertical motion data that are needed are subject to considerable uncertainty (Belt and Fuelberg, 1982; Bluestein, 1992). These motions are most suspect when diagnosed from the horizontal winds, i.e., when they are not supplied by a numerical model or data assimilation scheme where they are constrained to be dynamically consistent with the other meteorological variables.

Backtrajectories in this study were calculated using Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) three dimensional isentropic model. Trajectories used in this study were 5 days long (gives the path of the air mass within 120 h before the sample collected) and at height levels 500, 1000, 1500 m.

2. EXPERIMENTAL STUDY

2.1. Field Studies

2.1.1. Sampling Site Description

In this study, daily particulate matters of fine ($PM_{2.5}$) and coarse (PM_{10}) fractions were sampled between 22 February 2011 and 22 February 2012 in Abant İzzet Baysal University Campus (AIBU) on the roof of Presidency Building (40^{o} 42.864' north latitude and 31^{o} 31.035' east longitude). Location of sampling area is shown in Figure 2.1. Bolu is one of the cities suffering from frequent air pollution episodes, particularly in the winter season, due to its peculiar geography and emissions releasing from domestic heating and motor vehicles. Also, Bolu is on the migration path of air masses coming from Europe and Russia and in this manner it is possible to monitor the long range pollutant at the gateway to Anatolia.

Bolu along with Kastamonu, Zonguldak and Düzce is located at the west site of Black Sea and it settles in the valley grooves of North Anatolian Mountains which is parallel to the coast. Gölköy is roughly 34 km away from the Black Sea and open to the influence from the sea. Approximately fifty percent of city is forest area and has an important part of the flora richness of Turkey. According to the data of 2008 Bolu Environment Report (Bolu Çevre Durum Raporu, 2008); 44 quarry reserves such as clay, limestone, gravel are available in Bolu city center and in its districts.

Figure 2.1 Location of the sampling site

In city center, the prevailing wind direction is usually west and southwest. Most of the industrial plants in city have emission permit and not affecting the air quality significantly. In 2008; 19,850 of the 69,813 motor vehicle emissions were measured (Bolu Çevre Durum Raporu, 2008). Although these numbers may seem bleak, D-100 and TEM highway -which is connecting the two big metropolis İstanbul and Ankara to each other- are causing the increase in traffic sourced air pollution. Natural gas utilization has gradually increased since 2010 but coal, wood and fuel-oil are still in use for heating.

Site selection is an important step in establishing reference stations where sampling is performed to study long-range transport. The sampling site should not be under the influence of any local point or area sources to be able to detect low levels of pollutants that are being advected from upper atmosphere. Site selection criteria are fairly well established and include factors such as minimum distance from settlement areas, from industrial point sources, from major and secondary roads.

A semi-rural station was chosen for sampling to monitor air pollution caused by long-distance transportation and there are no natural or man-made obstacles around the station to prevent the dominant wind direction. Also 500 meters away from the station there is no direct emission sources and the sampler located at a height of 15 meters above the ground level. The possible pollution sources around the station are; 1.5 km away from D-100 and TEM highway, 8 km away from city center, 2 km away from asphalt plant.

The Bolu station also consists of a platform and a field laboratory. The platform contains SFU aerosol sampler, dichotomus ($PM_{2.5}$ and PM_{10}) sampler and a wet/dry deposition collector. The field laboratory is a container with dimensions of 2.5 m x

1.5 m x 1.5 m and contains automated; sulfur dioxide, nitrogen oxides, ozone analyzers and two separate $PM_{2.5}$ and $PM_{2.5-10}$ aerosol sampler. The concentrations were related with the meteorological variables such as wind direction, wind speed, temperature, humidity and solar radiation obtained from the meteorological station set up in the sampling station (Figure 2.2).

Figure 2.2 General view of the Bolu station

2.1.2. Sampling Study

Aerosol samples were collected in the period of February 2011 to February 2012 at the AIBU Gölköy Campus. The sample collection period was 24 h for all collected samples and sampling were interrupted only to change filters. Particulate matter sampling and analysis method are illustrated in Figure 2.3.

2.1.2.1. GENT Stacked Filter Unit (SFU)

Samples were collected using a "GENT" stacked filter unit (SFU). The device has a PM10 pre-impactor and contains two filters, a coarse and a fine filter, placed in series. The air enters the unit through the pre-impactor designed to have a 50% collection efficiency at 10 μm equivalent aerodynamic diameter (EAD) and particles with diameters larger than 10 μm are removed in this stage. Air was then drawn through two polycarbonate sequential filters. The SFU was operated at a fixed flow rate of 16 L min^{-1}. The initial and second filter were 47 mm in diameter with pore sizes of 8 and 0.4 μm, respectively. Coarse and fine fractions of the aerosol were collected seperately on these filters. The flow through filters will result in the collection of the particles with diameters larger than 2.2 μm on the initial filter (coarse fraction). Those with diameters smaller than 2.2 μm pass through the initial filter and were held on the backup filter (fine fraction). The cut-point (d50-value) of 2.2 μm EAD between the coarse and fine size fractions in a SFU is less sharp than cut points in certain other types of aerosol collection devices, such as cascade impactors (Hopke et al., 1997). Although the cut size between fine and coarse is 2.2 μm, the data for the fine fraction are grouped with the PM2.5 filter data. SFU is a relatively low cost system with a simple flow controller. However, the total volume

of air sampled is directly measured by the dry test meter built into the system (Hopke et al., 1997; Maenhaut et al., 1993).

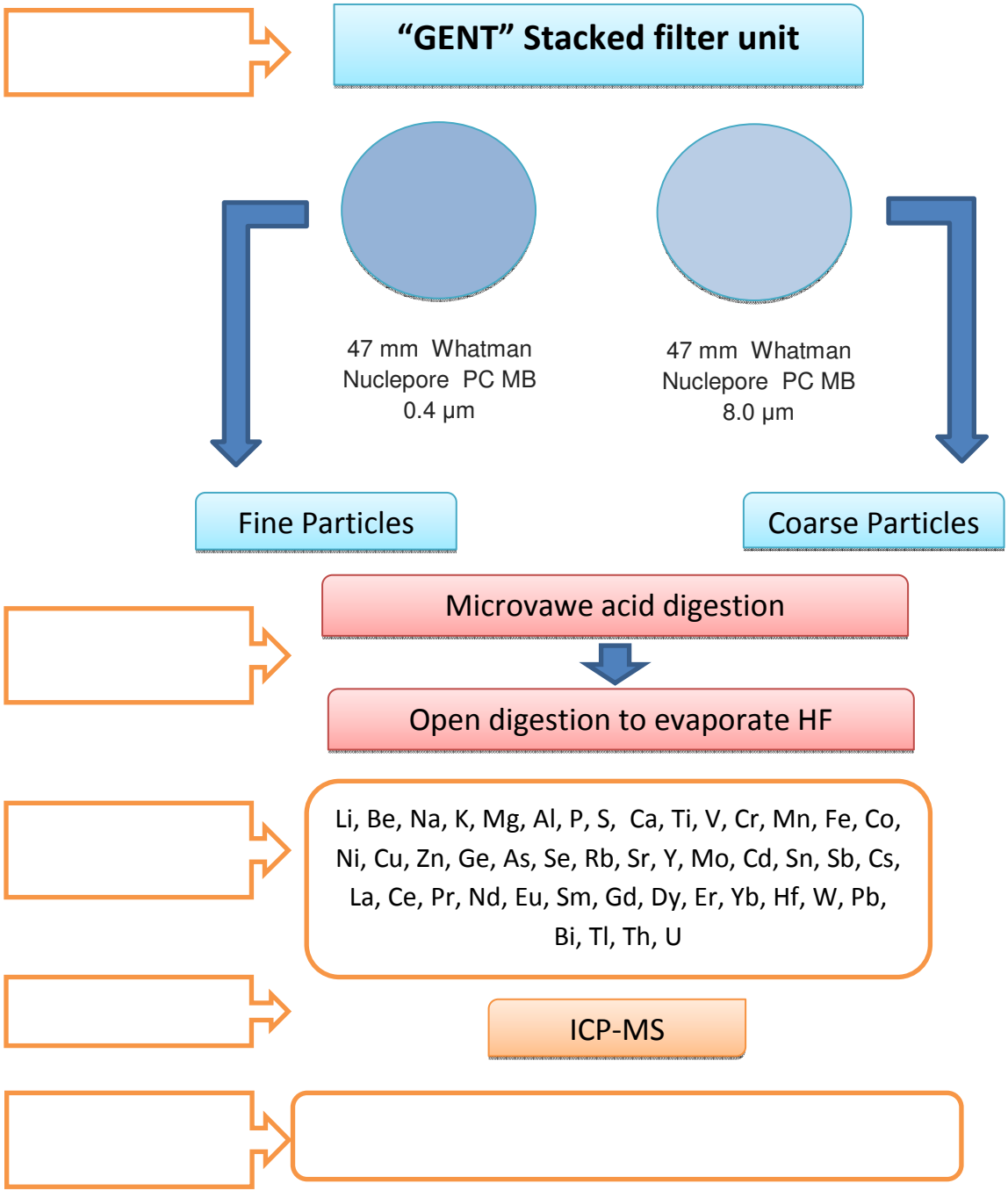


Figure 2.3 Particulate matter sampling and analysis method

In literature, there are various studies conducted with SFU for sample collection (Artaxo et al., 1999; Maenhaut et al., 2002; Al-Momani et al., 2005). The complete unit design of SFU is shown in Figure 2.4.

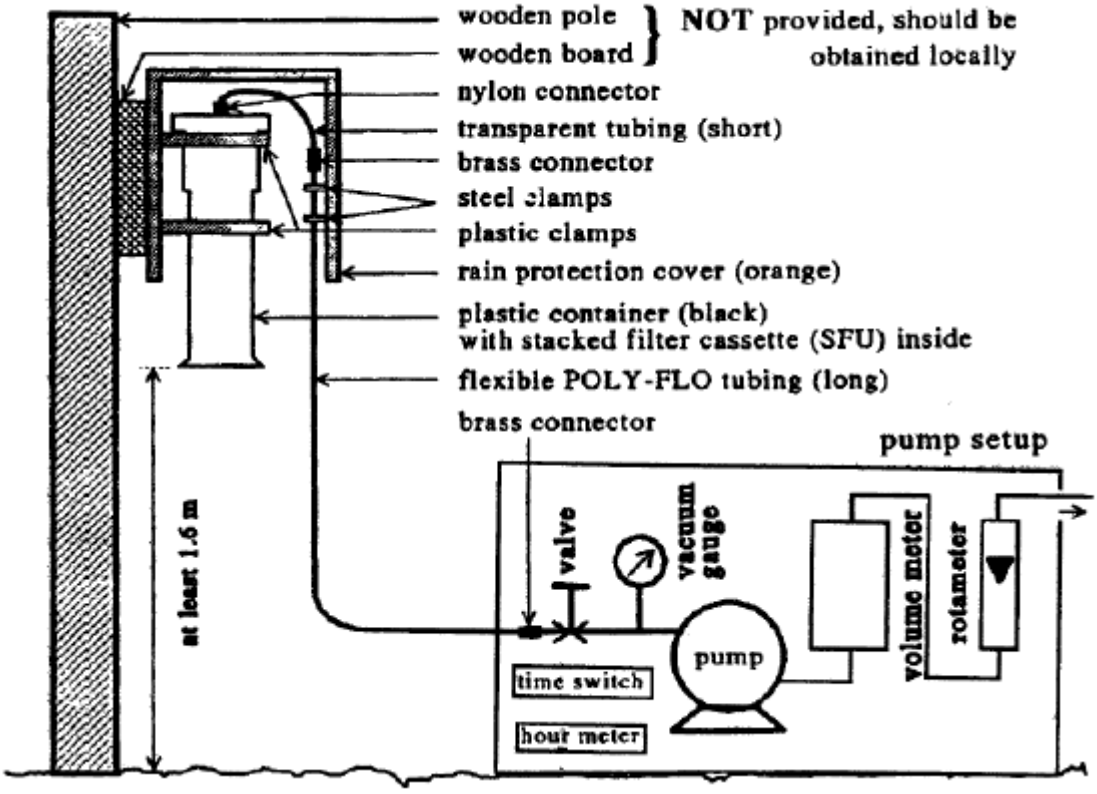


Figure 2.4 Schematic of the SPU as typically deployed in the field including the pump, flow control system and rain shield (Hopke et al., 1997)

Meteorology Station

WeatherLink meteorology station is operated with integrated sensors (including wind vane and and rain gauge) and control panel located in field laboratory. Aproximate 30 variables can be measured and saved hourly. Frequently used variables are given in Table 2.1.

Table 2.1 Some measured variables in meteorology station

1.	Barometric pressure
2.	Evapotranspiration
3.	Humidity - high and low
4.	Dew point
5.	Rain
6.	Rain rate
7.	Outside temperature - high and low
8.	Inside temperature - high and low
9.	Solar index
10.	Solar radiation - high
11.	Solar energy
12.	Heat index
13.	Wind speed - high
14.	Wind direction - high
15.	UV Radiation index
16.	UV Dose

2.2. Laboratory Studies

2.2.1. Gravimetric Analysis

Before sampling, the coarse and fine filters were placed into a constant humidity (25%-35%) chamber at room temperature (25°C), in open plastic Petri dishes, for at least 24 h, in the clean area to reach a constant humidity. Afterwards, they were

weighed with a microbalance in 0.001 mg sensitivity. After sampling, the filters were transferred to the laboratory. They were placed in the constant humidity chamber, again for 24 h, and then weighted under exactly the same conditions as the empty filters to determine coarse and fine particle mass.

2.2.2. Elemental Analysis of Samples

Filter samples are prepared for analysis by microwave acid digestion. Analysis of filters was performed using an inductively coupled plasma mass spectrometry (ICP-MS) in Kocaeli University, Geological Engineering Department. Samples were analyzed for a total of 51 elements (Li, Be, Na, K, Mg, Al, P, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Se, Rb, Sr, Y, Mo, Cd, Sn, Sb, Cs, La, Ce, Pr, Nd, Eu, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, W, Pt, Au, Pb, Bi, Tl, Th, U).

2.2.2.1. Microwave Digestion

All materials used for sample preparation and extraction were stored in 30% HNO_3 (65%-Merck) bath for one day. Filter samples were placed into teflon digestion vessel with a clean teflon forceps. 1 mL suprapure 40% HF (Merck) and 5 mL 65% ultrapure HNO_3 (distilled by subboiling) were added into the samples. Vessels were placed into the microwave (BERGHOF) and heated with the program shown in Table 2.2.

Microvawe oven has 10 vessels with a capacity of 15 milliliters. In each set, 9 filter samples and 1 acid blank were digested. After microwave digestion process, the vessels were cooled to room temperature and poured into open digestion teflon vessels by washing with deionized water (Millipore 18.1 MΩ Ultrapure Water). Samples were evaporated on hot plate until one drop remains and 3 mL ultrapure HNO_3 were added into the vessels two times. Then, vessels were washed with 1%

HNO_3 and diluted to 50 mL. Digested filter samples were analyzed by using Perkin Elmer-ICP-MS-DRC-e.

Table 2.2 Operating conditions for BERGHOF microwave

Step	T (°C)	P (bar)	Ramp (min)	Time (min)	Power (%)
1	120	30	6	5	75
2	160	30	1	10	85
3	180	35	1	15	90
4	75	25	1	2	0
5	75	25	1	2	0

2.2.2.2. General Information about ICP-MS

Several methods have been developed for elemental analysis of samples including proton induced X-ray emission (PIXE), neutron activation analysis (NAA), atomic absorption spectroscopy (AAS), inductively coupled plasma mass spectrometry (ICP-MS) and mainly X-ray fluorescence (XRF).

ICP-MS has many advantages over other elemental analysis techniques;

• Detection limits are 10-100 times superior to those of ICP/AES.

• Ability to provide elemental isotopic ratio information.

• Roughly 25 elements can be analyzed in duplicate and with good precision in 1-2 minutes.

• Large linear dynamic working range.

• The effective combination of differing types of ICP-MS instruments coupled with the many varied types of sample introduction allow for customization of techniques for a specific sample type or form of analyte.

ICP technology was built upon the same principles used in atomic emission spectrometry. Samples are decomposed to neutral elements in a high temperature argon plasma and analyzed based on their mass to charge ratios. An ICP-MS can be thought of as four main processes, including sample introduction and aerosol generation, ionization by an argon plasma source, mass discrimination, and the detection system (http://www.webapps.cee.vt.edu).

In this technique, sample –generally in liquid form- is introduced by way of a nebulizer which aspirates the sample with high velocity argon, forming a fine mist. The aerosol then passes into a spray chamber where larger droplets are removed via a drain. Typically, only 2% of the original mist passes through the spray chamber. This process is necessary to produce droplets small enough to be vaporized in the plasma torch. Once the sample passes through the nebulizer and is partially desolvated, the aerosol moves into the torch body and is mixed with more argon gas. A coupling coil is used to transmit radio frequency to the heated argon gas, producing an argon plasma "flame" located at the torch. The hot plasma removes any remaining solvent and causes sample atomization followed by ionization. In addition to being ionized, sample atoms are excited in the hot plasma, a phenomenon which is used in ICP-atomic emission spectroscopy. The aerosol moves into the bottom of the torch body. Because atomization/ionization occurs at atmospheric pressure, the interface between the ICP and MS components becomes crucial in creating a vacuum environment for the MS system. In the first stage of the mass spectrometer ions are removed from the plasma by a pumped extraction system. An ion beam is produced and focused further into the actual unit. Ions are separated based on their mass to charge ratio and measured by detector. Technical information and measuring conditions presented in Table 2.3.

Table 2.3 Operating conditions for the Perkin Elmer-ICP-MS- DRC-e

Parameter	**Value**
RF power (W)	1100
Plasma gas flow (L min^{-1})	15
Auxiliary gas flow (L min^{-1})	1.2
Nebulizer	Gemtip crossflow
Nebulizer gas flow (L min^{-1})	0.96
Sampling cone (orifice dia., mm)	Platinum (1.1)
Skimmer cone (orifice dia., mm)	Platinum (0.9)
Injector	Alumina
Peristaltic pump flow (rpm)	20
Spray chamber	Ryton Scott
Scanning mode	Both (analog and pulse)
Number of Scans (sweeps/reading) for each isotope	20
Ion lens setting	Adjusted to obtain maximum signal/noise ratio (CeO/Ce < %3, Ba^{++}/Ba < % 3), Background 220: 1.2, Background 8.5: 2.1
Auto sampler	CETAC ADX-500
Rinse time (s)	45
Sampe Uptake time (flush) (s)	35

2.2.3. Method Validation

Certified reference materials SRM 1648a-Urban Particulate Matter (NIST) was analyzed to check the accuracy of the anaysis method. Results of these analysis were given in Table 2.4.

Table 2.4 SRM NIST 1648a Urban Particulate Matter method accuracy results (number of analyses: 10)

	Results (Average conc ± STD) (mg kg^{-1})	**UPM Certificate value (mg kg^{-1}) (Average conc. ± expanded uncertainty) (k=2)**	**% Error**
Al	3.54% ± 0.74%	3.43% ± 0.13%	3.1
As	115.1 ± 4.2	115.5 ± 3.9	-0.3
Ca	5.56% ± 0.17%	5.84% ± 0.19%	-4.9
Cd	71.9 ± 1.9	73.7 ± 2.3	-2.4
Ce	46.4 ± 1.5	54.6 ± 2.2	-15
Co	17.62 ± 0.94	17.93 ± 0.68	-1.7
Cr	270 ± 21	402 ± 13	-33
Cu	570 ± 18	610 ± 70	-6.5
Fe	3.90% ± 0.20%	3.92% ± 0.21%	-0.6
K	1.05% ± 0.10%	1.06% ± 0.05%	-0.8
Mg	0.82% ± 0.09%	0.81% ± 0.01%	0.9
Mn	775 ± 33	790 ± 44	-1.8
Na	3455 ± 905	4240 ± 60	-19
Ni	81.0 ± 1.5	81.1 ± 6.8	-0.1
Pb	0.62 ± 0.006	0.66% ± 0.033	-5.9
Rb	50 ± 3.9	51 ± 1.5	-1.1
Sb	41.9 ± 0.7	45.4 ± 1.4	-7.7
Sr	215 ± 5	215 ± 17	-0.2
Ti	3678 ± 235	4021 ± 86	-8.5
V	125 ± 2	127 ± 11	-1.6
Zn	4647 ± 107	4800 ± 270	-3.2
Cs[b]	3.3 ± 0.1	3.4 ± 0.2	-4.3
La[b]	32 ± 1	39 ± 3	-18
Se[b]	28.3 ± 2.2	28.4 ± 1.1	-0.5
Sm[b]	3.9 ± 0.2	4.3 ± 0.3	-9.4
W[b]	4.6 ± 0.3	4.6 ± 0.3	-0.2
Hf[c]	5.1 ± 2.0	5.2	-2.2

[a] reference value, [b] information value

While measuring the concentrations by ICP-MS with external standard, fluctuations in the measurement of ionic currents occurring as a result of the electrical noise in the detector, instabilities in plasma discharge, instabilities of the electrical parameters of the analyzer, lead to uncertainties in the determination of the parameters of the calibration line. Possible errors in the preparation of the calibration solutions increase the uncertainties (Voica et al., 2012).

Detection limit (DL) or limit of detection (LOD) is defined as the lowest amount of analyte in a sample that can be detected and reported with 99% confidence that the analyte concentration is greater than zero. Various calculation methods of detection limit are available in literature (Javier del RioBocio et al., 2003; Gatari et al., 2005). In this study, calculation of LOD for each element was based on replicate analyses using blank samples and expressed as the "concentration value corresponding to 3 times the standard deviation of 10 replicate analysis of a blank filter" (Lopes et al., 2006) were used. The values of LOD for each element are given in Table 2.5.

Table 2.5 Validation table of analyzed elements by ICP-MS*

	Reproducibility % RSD (N)		Recovery (%)	Linear range (µg L^{-1})	R^2	LOD (µg L^{-1})	LOQ (µg L^{-1})
Al	21	(10)	103	0.01-200	0.9999	1	4
As	4	(10)	100	0.01-200	1.0000	0.01	0.04
Ca	3	(10)	95	0.01-2000	1.0000	6	19
Cd	3	(10)	98	0.01-200	1.0000	0.01	0.03
Ce	3	(10)	85	0.01-40	1.0000	0.01	0.04
Co	5	(10)	98	0.01-200	1.0000	0.001	0.002
Cr	8	(10)	67	0.01-200	1.0000	0.1	0.3
Cu	3	(10)	93	0.01-200	1.0000	0.02	0.07
Fe	5	(10)	99	0.01-2000	1.0000	0.1	0.4
K	10	(10)	99	0.01-2000	1.0000	0.3	1.2
Mg	10	(10)	101	0.01-2000	1.0000	0.1	0.5
Mn	4	(10)	98	0.01-200	0.9999	0.02	0.06
Na	26	(10)	81	0.01-2000	1.0000	1	3
Ni	2	(10)	100	0.01-200	1.0000	0.04	0.12
Pb	1	(10)	94	0.01-200	1.0000	0.1	0.2
Rb	8	(10)	99	0.01-200	1.0000	0.001	0.005
Sb	2	(10)	92	0.01-40	1.0000	0.001	0.004
Sr	2	(10)	100	0.01-200	1.0000	0.01	0.02
Ti	6	(10)	91	0.01-200	1.0000	0.1	0.3
V	1	(10)	98	0.01-200	1.0000	0.01	0.05
Zn	2	(10)	97	0.01-200	1.0000	0.02	0.07
Cs	3	(10)	96	0.01-200	1.0000	0.001	0.002
La	3	(10)	82	0.01-40	1.0000	0.002	0.006
Se	8	(10)	99	0.01-200	1.0000	0.01	0.03
Sm	6	(10)	91	0.01-40	1.0000	0.001	0.004
W	7	(10)	100	0.01-200	1.0000	0.02	0.07
Hf	38	(10)	98	0.01-40	1.0000	0.01	0.03

*SRM NIST 1648a Urban Particulate Matter is used. N: number of analyses

Table 2.5 Validation table of analyzed elements by ICP-MS* (continued)

	Reproducibility % RSD	**Recovery (%)**	**Linear range (µg L^{-1})**	**R^2**	**LOD (µg L^{-1})**	**LOQ (µg L^{-1})**
Li	-	-	0.01-2000	1.0000	0.01	0.04
Be	-	-	0.01-200	1.0000	$0.3x10^{-3}$	$1x10^{-3}$
P	-	-	0.01-200	1.0000	0.1	0.2
S	-	-	0.01-200	1.0000	0.1	0.4
Ge	-	-	0.01-200	1.0000	0.01	0.04
Y	-	-	0.01-40	1.0000	0.002	0.006
Mo	-	-	0.01-200	1.0000	0.01	0.03
Sn	-	-	0.01-40	1.0000	0.01	0.02
Pr	-	-	0.01-40	1.0000	0.001	0.003
Nd	-	-	0.01-40	1.0000	0.002	0.006
Eu	-	-	0.01-40	1.0000	0.001	0.002
Gd	-	-	0.01-40	1.0000	0.001	0.005
Dy	-	-	0.01-200	1.0000	0.001	0.003
Er	-	-	0.01-40	1.0000	0.01	0.03
Yb	-	-	0.01-40	1.0000	$0.4x10^{-3}$	$1x10^{-3}$
Au	-	-	0.01-1	0.9991	0.2	0.5
Bi	-	-	0.01-200	1.0000	0.01	0.02
Tl	-	-	0.01-200	1.0000	0.001	0.002
Th	-	-	0.01-200	1.0000	0.002	0.007
U	-	-	0.01-200	1.0000	0.002	0.006

*SRM NIST 1648a Urban Particulate Matter is used. N: 10

The reproducibility of the digestion and analytical procedure was assessed by ten replicate analysis of SRM 1648a and the analytical recovery of each element is then calculated. The percent recovery values of these elements are higher than 85% except for Cr, Na and La.

3. RESULT AND DISCUSSION

3.1. General Characteristics of Data

$PM_{2.5}$ and $PM_{2.5-10}$ mode particles are sampled by "GENT" stacked filter unit between 22 February 2011 and 22 February 2012 at Bolu station during one year. Generally every other day samples were selected and anayzed for 51 elements (Li, Be, Na, K, Mg, Al, P, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Se, Rb, Sr, Y, Mo, Cd, Sn, Sb, Cs, La, Ce, Pr, Nd, Eu, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, W, Pt, Au, Pb, Bi, Tl, Th, U) with ICP-MS. Totally 276 $PM_{2.5}$ and 267 $PM_{2.5-10}$ filter samples were analyzed.

Statistical summaries for all measured species in fine and coarse fraction are given in Tables 3.1 and 3.2, respectively which include number of observations (*N*), arithmetic mean, standard deviation, geometric mean values, median values, mode and detection limit values (DL). High standard deviations are not unusual in environmental data sets and not necessarily due to sampling and analysis procedures. The observed high standard deviations are due to large variability of the atmospheric concentrations of the elements over short periods of time, which are caused by the variations in the meteorological conditions, physical and chemical transformations, air mass transport patterns and the variations in emissions affecting the receptor site.

Table 3.1 Summary statistics of elemental concentrations in fine fraction aerosols (ng m^{-3})

	N	Arithmetic mean	Standard deviation	Geometric mean	Median	Mode	DL
Li	269	0.2	0.4	0.1	0.1	0.2	0.03
Be	154	0.01	$5x10^{-3}$	$5x10^{-3}$	0.01	0.01	$7x10^{-5}$
Na	274	217	275	120	104	69	2
K	272	184	111	149	163	125	1
Mg	267	73	89	44	44	14	0.3
Al	270	1342	3301	315	218	125	3
P	276	8	9	6	6	6	0.2
Ca	271	756	1035	467	465	308	13
Ti	276	11	10	8	8	11	0.2
V	276	1	1	1	1	1	0.03
Cr	276	20	21	15	15	12	0.2
Mn	276	4	3	3	4	2	0.04
Fe	276	199	646	123	136	129	0.3
Co	265	2	7	0.2	0.1	0.1	$2x10^{-3}$
Ni	275	6	14	3	3	2	0.1
Cu	273	6	8	4	4	3	0.05
Zn	272	27	27	19	18	16	0.05
Ge	224	0.1	0.1	0.1	0.1	0.1	0.02
As	275	1	1	1	1	1	0.03
Se	252	0.4	0.2	0.3	0.3	0.1	0.02
Rb	274	1	0.3	0.4	0.5	0.3	$3x10^{-3}$
Sr	272	4	14	2	2	2	0.02
Y	273	0.05	0.05	0.04	0.04	0.03	$4x10^{-3}$
Mo	272	0.3	0.3	0.2	0.2	0.1	0.02
Cd	276	5	35	1	0.4	0.1	0.02
Sn	273	1	1	0.5	0.5	1	0.01
Sb	272	1	0.5	0.5	1	0.5	$3x10^{-3}$
Cs	273	0.1	0.1	0.1	0.1	0.1	$2x10^{-3}$
La	275	0.1	0.2	0.1	0.1	0.1	$4x10^{-3}$
Ce	276	0.3	1	0.2	0.2	0.1	0.03
Pr	270	0.02	0.02	0.01	0.01	0.01	$2x10^{-3}$
Nd	275	0.1	0.1	0.05	0.05	0.1	$4x10^{-3}$

N: number of observations

Table 3.1 Summary statistics of elemental concentrations in fine fraction aerosols (ng m^{-3}) (continued)

	N	Arithmetic mean	Standard deviation	Geometric mean	Median	Mode	DL
Eu	162	0.01	0.02	$5x10^{-3}$	$5x10^{-3}$	0.01	$8x10^{-4}$
Sm	253	0.01	0.01	0.01	0.01	0.01	$3x10^{-3}$
Gd	264	0.01	0.01	0.01	0.01	0.01	$3x10^{-3}$
Tb	52	$4x10^{-3}$	$2x10^{-3}$	$3x10^{-3}$	$3x10^{-3}$	$3x10^{-3}$	$1x10^{-3}$
Dy	248	0.01	0.01	0.01	0.01	0.01	$2x10^{-3}$
Ho	59	$4x10^{-3}$	$2x10^{-3}$	$3x10^{-3}$	$3x10^{-3}$	$2x10^{-3}$	$1x10^{-3}$
Er	243	0.1	0.4	0.01	0.01	0.01	$1x10^{-4}$
Tm	10	$4x10^{-3}$	$1x10^{-3}$	$3x10^{-3}$	$4x10^{-3}$		$1x10^{-3}$
Yb	214	0.01	0.01	$4x10^{-3}$	$4x10^{-3}$	0.01	$9x10^{-4}$
Lu	18	$3x10^{-3}$	$1x10^{-3}$	$3x10^{-3}$	$3x10^{-3}$	0.02	$1x10^{-3}$
Hf	229	0.03	0.04	0.02	0.02	0.01	$9x10^{-3}$
W	268	0.2	0.3	0.1	0.1	0.2	0.05
Pt	19	0.01	0.01	$3x10^{-3}$	$4x10^{-3}$		$1x10^{-3}$
Au	33	0.2	0.3	0.1	0.1		$1x10^{-3}$
Pb	270	12	29	6	6	5	0.1
Bi	255	0.1	0.1	0.05	0.05	0.05	0.01
Tl	254	0.1	0.1	0.04	0.04	0.02	$2x10^{-3}$
Th	261	0.03	0.04	0.02	0.02	0.02	$5x10^{-3}$
U	210	0.1	0.1	0.02	0.01	0.01	$4x10^{-3}$
$PM_{2.5}$	266	17782	16305	12845	16247		

N: number of observations

While soil originated elements Al, Ca, K, Fe and Mg have highest concentrations, subsequent elements Zn, Cr, Pb, Ni, Eu, Be, Yb, Ho, Tb and Cu are antropogenic in $PM_{2.5}$ mode. The lowest concentrations were seen in Tm, Lu and Pt.

Elements measured with the highest frequency are P, Cd, Ti, V, Cr, Mn, Cd, Fe, Ce, Ni, As, Ca, Na, K, Al, Cu, Zn, Nd, Pb, Sn, Sb, Cs, La Rb and Y which are measured in almost all samples. As can be seen from Tables, standard deviations are higher

than the mean values for most of the data. Such high standard deviations are not unusual for aerosol data and are attributed to the lognormal distribution of data.

Arithmetic mean concentrations of elements in the fine fraction vary between 1342 ng m^{-3} for Al and $4x10^{-3}$ ng m^{-3} for Tm, Ho, Tb. However, concentration range in the coarse fraction is between 1494 ng m^{-3} for Ca and $3x10^{-3}$ng m^{-3} for Pt. The results indicated that concentrations of Al in fine fraction, Ca and Al in coarse fraction are high compared to concentrations of other elements.

Table 3.2 Summary statistics of elemental concentrations in coarse fraction aerosols (ng m^{-3})

	N	Arithmetic mean	Standard deviation	Geometric mean	Median	Mode	DL
Li	265	0.4	0.4	0.3	0.3	0.2	0.03
Be	175	0.01	0.01	0.01	0.01	$1x10^{-3}$	$7x10^{-5}$
Na	265	310	351	164	156	60	2
K	263	135	113	96	103	188	1
Mg	266	128	106	97	97	125	0.3
Al	260	1393	4270	514	419	394	3
P	267	17	14	13	13	15	0.2
Ca	267	1494	1145	1098	1203	1380	13
Ti	267	22	17	17	18	13	0.2
V	264	1	1	1	1	1	0.03
Cr	267	11	11	9	9	11	0.2
Mn	267	5	4	4	5	11	0.04
Fe	267	237	198	170	183	175	0.3
Co	258	2	12	0.3	0.2	0.2	$2x10^{-3}$
Ni	265	3	5	1	2	1	0.1
Cu	261	5	22	3	2	2	0.05
Zn	265	28	56	13	13	36	0.05
Ge	197	0.1	0.1	0.1	0.1	0.1	0.02
As	267	1	1	0.3	0.3	0.2	0.03
Se	188	0.3	0.4	0.1	0.1	0.1	0.02
Rb	263	0.4	0.4	0.3	0.3	0.3	$3x10^{-3}$
Sr	265	6	6	4	4	1	0.02
Y	265	0.1	0.1	0.1	0.1	0.1	$4x10^{-3}$
Mo	256	0.2	0.2	0.1	0.1	0.1	0.02
Cd	264	13	31	2	2	18	0.02
Sn	260	0.5	2	0.2	0.2	0.1	0.01
Sb	265	0.4	0.3	0.3	0.3	0.3	$3x10^{-3}$
Cs	265	0.1	0.05	0.04	0.04	0.03	$2x10^{-3}$
La	266	0.2	0.2	0.1	0.1	0.1	$4x10^{-3}$
Ce	266	1	2	0.3	0.3	0.1	0.03
Pr	266	0.03	0.03	0.02	0.03	0.03	$2x10^{-3}$
Nd	266	0.1	0.1	0.1	0.1	0.1	$4x10^{-3}$
Eu	236	0.01	0.02	0.01	0.01	0.01	$8x10^{-4}$

N: number of observations

Table 3.2 Summary statistics of elemental concentrations in coarse fraction aerosols (ng m^{-3}) (continued

	N	Arithmetic mean	Standard deviation	Geometric mean	Median	Mode	DL
Sm	263	0.02	0.02	0.02	0.02	0.02	$3x10^{-3}$
Gd	261	0.02	0.02	0.02	0.02	0.03	$3x10^{-3}$
Tb	90	$5x10^{-3}$	$2x10^{-3}$	$4x10^{-3}$	$4x10^{-3}$	$4x10^{-3}$	$1x10^{-3}$
Dy	262	0.02	0.01	0.01	0.02	0.01	$2x10^{-3}$
Ho	92	0.01	$3x10^{-3}$	$5x10^{-3}$	$5x10^{-3}$	$4x10^{-3}$	$1x10^{-4}$
Er	251	0.3	2	0.01	0.01	0.02	$1x10^{-4}$
Tm	55	$4x10^{-3}$	$2x10^{-3}$	$3x10^{-3}$	$3x10^{-3}$	$3x10^{-3}$	$1x10^{-3}$
Yb	261	0.01	0.01	0.01	0.01	0.01	$9x10^{-4}$
Lu	63	$4x10^{-3}$	$2x10^{-3}$	$3x10^{-3}$	$3x10^{-3}$	$2x10^{-3}$	$1x10^{-3}$
Hf	238	0.04	0.1	0.03	0.03	0.1	$9x10^{-3}$
W	251	0.4	1	0.1	0.1	0.2	$1x10^{-2}$
Pt	18	$3x10^{-3}$	$2x10^{-3}$	$2x10^{-3}$	$3x10^{-3}$		$1x10^{-3}$
Au	28	0.2	0.3	0.1	0.1		$1x10^{-3}$
Pb	256	11	45	2	2	1	0.1
Bi	220	0.04	0.05	0.02	0.02	0.02	0.01
Tl	235	0.04	0.04	0.02	0.02	0.01	$2x10^{-3}$
Th	266	0.1	0.05	0.03	0.04	0.02	$5x10^{-3}$
U	222	0.1	0.1	0.02	0.02	0.02	$4x10^{-3}$
$PM_{2.5-10}$	220	15476	20512	8245	9622		

N: number of observations

Although Au was quantified in 33 samples for fine fraction and 28 samples for coarse fraction out of 276 samples, measured concentrations were found to be unreasonably high. It could be arised from erroneous calibration of the instrument or from an error while applying measurement conditions. As a result, average values of Au in Tables are affected by samples reported with extremely high concentrations. Therefore, concentrations determined for Au is excluded in this study.

A first step in identifying natural and anthropogenic sources of particles is to evaluate coarse to fine concentration ratios (C/F). Elements show different characteristics of existence between two fractions that constitute PM_{10}. Coarse to fine ratios of median values, illustrated in Figure 3.1, vary between approximately 3.5 for Cd and 0.3 for Pb. Crustal elements, such as Ca, Sr, Ti, Gd, Y, Be, Mg, Th, P, Dy, Yb, Nd, Li, Sm, Al, Pr, U, La, Er, Ho, Ce, Th, Eu, Na, Hf, Mn and Lu are mostly found in the coarse fraction, with coarse to fine ratios varying between 1.1 and 3.5. This observation is not surprising as particles bearing these elements are known to be coarse (Albright, 2004). Besides that anthropogenic species, Cd dominates in the coarse fraction (ratio 3.7). Cadmium makes up about 0.1 ppm of the Earth's crust rarely (Wedepohl, 1995). Cadmium is produced mainly as a byproduct from mining, smelting, and refining sulfidic ores of zinc, and, to a lesser degree, lead and copper. Small amounts of cadmium, about 10 % of consumption, are produced from secondary sources, mainly from dust generated by recycling iron and steel scrap (Ayres et al., 2003). On the other hand, anthropogenic species, Pb dominates in the fine fraction as reported in previous studies (Chan et al., 1999; Koçak et al., 2004; Salvador et al., 2007).

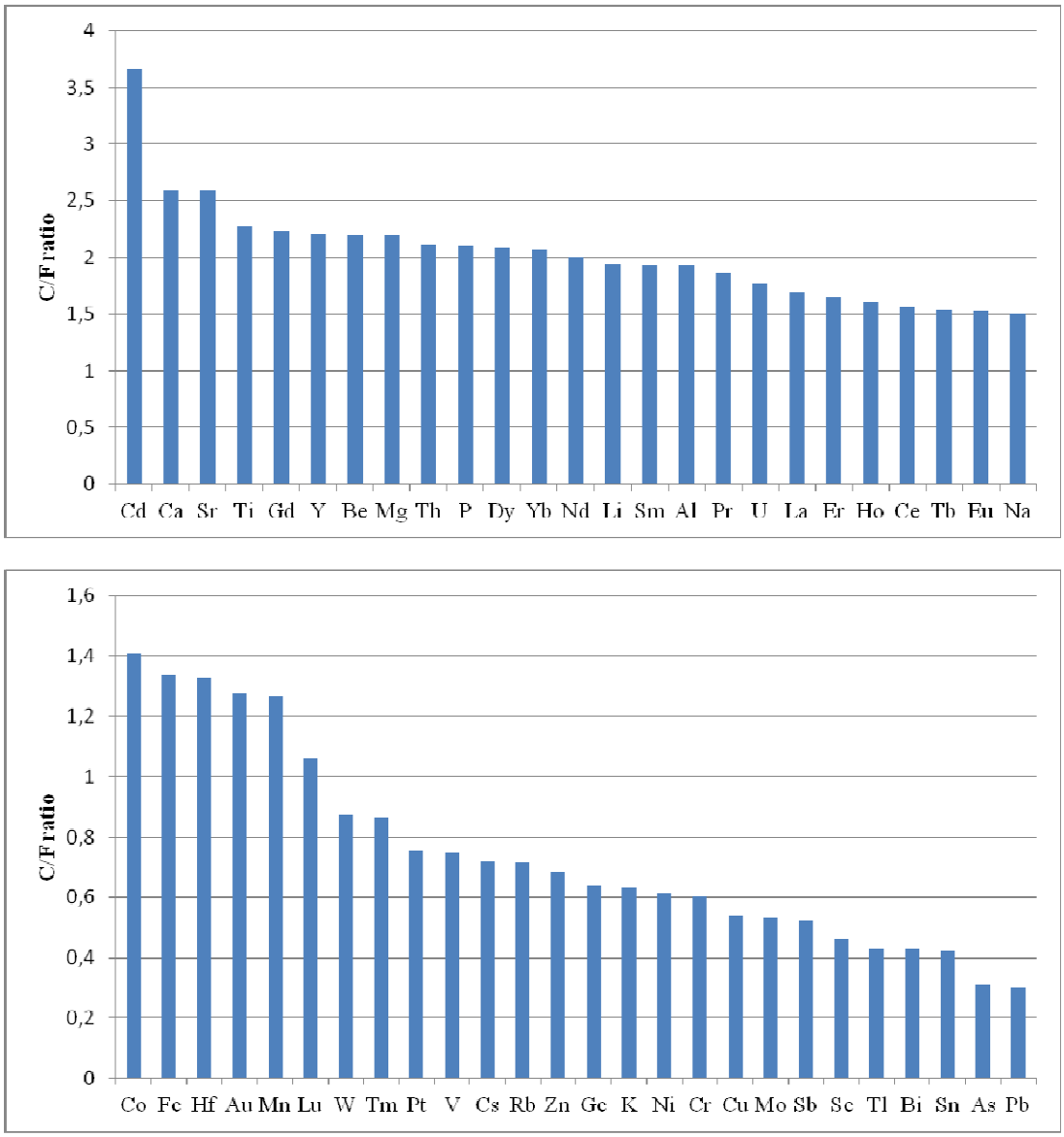


Figure 3.1 Coarse-to-fine median concentration ratios (C/F) of elements

Atmospheric Co concentrations are contributed by anthropogenic sources, it is mostly observed in coarse fraction. It is indicated that high contribution of atmospheric soil particles enriched with Co may be related to the observed concentration. Potassium is expected to have high C/F ratio, but it is largely in fine fraction. High fine K concentrations were observed in the literature and attributed to biomass burning (Chan et al., 1999). This issue will be further discussed in the source apportionment section.

3.1.1. Distribution Characteristics of Data

The distribution characteristics of atmospheric data depend on the meteorological conditions and source emission variables. While the emissions from sources may be approximately constant, the successive mixing and dilution of pollutants as they are transported from source to receptor site results in a log-normal distribution for the ambient concentrations (Güllü, 1996).

In general, a data matrix is generally treated as normally distributed values and described with arithmetic mean and standart deviation in which it is assumed that there is a symmetric Gaussian distribution. However, in a data set affected by different pollution sources, elements generally follow a log-normal distribution. The distribution type of aerosol composition over a long period of time is dependent on the fluctuations in the meteorological conditions and source strength variations. Frequency distributions of pollutants are useful to search for similarities and differences among the components which may help to understand processes that influence the ambient levels.

As can be seen from Tables 3.1 and 3.2, there are large differences between arithmetic and geometric mean values whereas median and geometric mean values

are comparable. This is an indication that the data set is generally log-normal distributed.

Table 3.3 Results of skewness and K-S DN for $PM_{2.5}$ mode elements

Element	Skewness	K-S DN	*p*- value	Distribution Type
Li	8.1	0.10	0.01	Lognormal
Be	1.6	0.07	0.49	Weibull
Na	2.7	0.07	0.10	Lognormal
K	1.0	0.04	0.66	Weibull
Mg	3.1	0.07	0.14	Lognormal
Al	5.6	0.12	$5x10^{-4}$	Lognormal
P	5.0	0.07	0.12	Lognormal
Ca	5.1	0.05	0.49	Lognormal
Ti	4.0	0.05	0.38	Lognormal
V	1.8	0.06	0.25	Weibull
Cr	7.0	0.08	0.08	Lognormal
Mn	3.6	0.07	0.14	Lognormal
Fe	15.7	0.08	0.04	Lognormal
Co	5.9	0.16	$2x10^{-6}$	Lognormal
Ni	10.1	0.08	0.04	Lognormal
Cu	5.4	0.07	0.10	Lognormal
Zn	2.8	0.10	0.01	Lognormal
Ge	5.8	0.08	0.08	Lognormal
As	2.2	0.05	0.54	Lognormal
Se	0.7	0.04	0.90	Weibull
Rb	1.0	0.03	0.98	Weibull
Sr	12.0	0.11	$2x10^{-3}$	Lognormal
Y	3.4	0.05	0.59	Lognormal
Mo	6.5	0.07	0.18	Lognormal
Cd	12.1	0.12	$1x10^{-3}$	Lognormal
Sn	9.5	0.07	0.16	Lognormal
Sb	7.3	0.07	0.16	Lognormal
Cs	9.1	0.05	0.45	Lognormal
La	5.5	0.05	0.55	Lognormal
Ce	9.6	0.07	0.12	Lognormal
Pr	5.0	0.05	0.49	Lognormal
Nd	5.4	0.05	0.47	Lognormal
Eu	5.5	0.10	0.10	Lognormal
Sm	4.4	0.06	0.36	Lognormal
Gd	4.8	0.08	0.07	Lognormal
Tb	2.9	0.20	0.03	Lognormal
Dy	3.3	0.08	0.11	Lognormal

Table 3.3 Results of skewness and K-S DN for $PM_{2.5}$ mode elements (continued)

Element	Skewness	K-S DN	*p*- value	Distribution Type
Ho	2.6	0.15	0.16	Lognormal
Er	13.6	0.11	$5x10^{-3}$	Lognormal
Yb	3.5	0.07	0.28	Weibull
Hf	3.4	0.11	0.01	Lognormal
W	7.5	0.05	0.51	Lognormal
Au	3.6	0.16	0.39	Lognormal
Pb	6.1	0.11	$3x10^{-3}$	Lognormal
Bi	6.4	0.08	0.10	Lognormal
Tl	1.9	0.05	0.62	Weibull
Th	6.1	0.06	0.22	Lognormal
U	2.9	0.15	$1x10^{-4}$	Lognormal

Skewness characterizes the degree of asymmetry of a distribution around its mean. In symmetric Gaussian distribution, the value of skewness is zero. Positive skewness indicates a distribution with an asymmetric tail extending toward more positive values. In contrast, negative skewness indicates a distribution with an asymmetric tail extending toward more negative values. In the case of positively (right) skewed data, arithmetic means are larger than median and geometric mean values. If opposite is true, then data is negatively skewed. As given in Table 3.4, skewness values are positive which means all measured variables are positively skewed. In describing the positively skewed data, log-normal or Weibull distributions can be used.

In this study, Statgraphics Centurion XV.II Software was used to determine whether the log-normal distribution fits the data adequately by performing Kolmogorov-Smirnov (K-S DN) As can be seen in Tables 3.3 and 3.4, most of the elements are log-normally distributed according to a Kolmogorov-Smirnov test. This statistic is used to test the goodness of fit of the data to lognormal distribution. Kolmogorov-Smirnov test involves the entire distribution of the examined variable, not just its

central value and compares the empirical cumulative distribution function to that of the hypothesized distribution. In case of the log-normal distribution, the maximum absolute distance between the data and the hypothesized distribution is calculated to test the conformance to the two cumulative distribution functions. Therefore, smallest DN value indicates the good fit of the data to distribution type. The observed significance levels for the Kolmogorov-Simirnov DN statistic are also given in Tables 3.3 and 3.4. If the smallest *p*-value amongst the tests performed is less than 0.05, we can reject the hypoyhesis that these elements come from a lognormal distribution with 95% confidence. Then we run the test for Weibull distribution type whether it is appropriate or not. If both of these distributions have *p*-values smaller than 0.05 such as Fe, Co, Ni, Zn, Sr, Cd, Er, Hf and Pb, smallest DN value specify the distribution type. Figure 3.2 illustrates the frequency histograms of fine fraction elements shows log-normal distribution while K, Rb, Yb, Tl and Se fit Weibull distribution. This result indicates that the coal combustion originated K and Se affect the receptor site from local sources. Also, less than 20 times observed elements such as Tm, Pt and Lu concentrations show a distribution similar to log-normal. In this situation, alterations in data set may vary depending on the meteorological factors (Karaca et al., 2006).

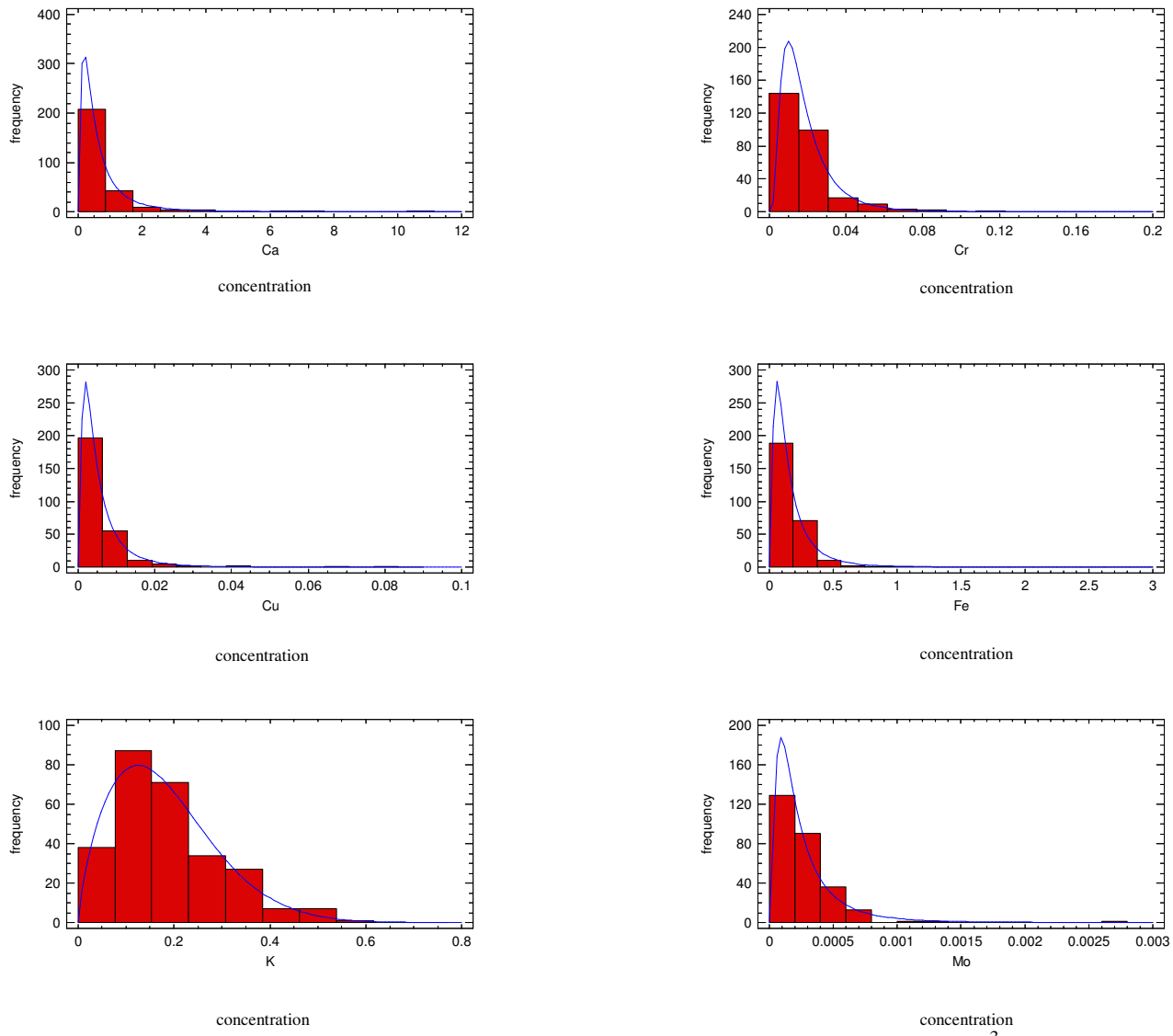


Figure 3.2 Frequency histograms of $PM_{2.5}$ mode elements (ng m^{-3})

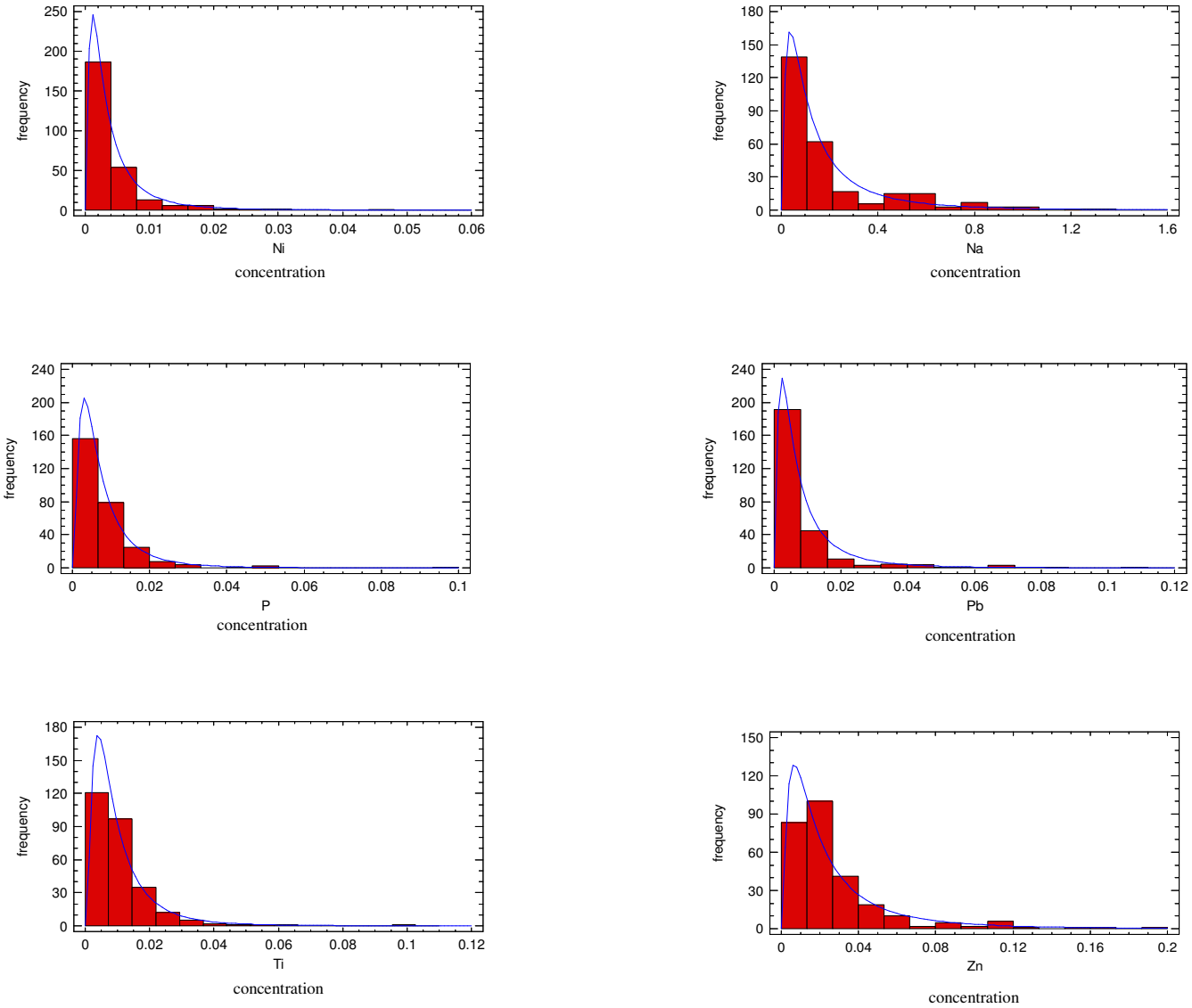


Figure 3.2 Frequency histograms of $PM_{2.5}$ mode elements (ng m^{-3}) (continued)

As can be seen from Table 3.4, p-values computed by the test for all variables are greater than 0.05, except for Co, As, Sn, Ce, Er, W and Pb, meaning concentrations of these elements show log-normal distribution out of 95% confidence interval. When the goodness of fit tests was applied to $PM_{2.5-10}$ Co, As, Sn, Ce, Er, W and Pb, these elements fit neither log-normal nor Weibull distribution with 95 % confidence. High DN values indicate the deviation from log-normal and Weibull distribution. If both of these distributions have *p*-values smaller than 0.05, smallest DN value specifies the distribution type. Figure 3.3 illustrates the frequency histograms of coarse fraction elemental concentrations.

Table 3.4 Results of skewness and K-S DN for $PM_{2.5-10}$ mode elements

Element	Skewness	K-S DN	p- value	Distribution Type
Li	5.0	0.05	0.62	Lognormal
Be	1.3	0.03	0.98	Weibull
Na	2.0	0.07	0.12	Lognormal
K	1.9	0.06	0.29	Lognormal
Mg	2.3	0.04	0.70	Lognormal
Al	10.4	0.08	0.05	Lognormal
P	2.2	0.05	0.46	Lognormal
Ca	1.7	0.05	0.57	Weibull
Ti	2.1	0.06	0.25	Weibull
V	4.0	0.06	0.40	Weibull
Cr	5.9	0.06	0.31	Lognormal
Mn	1.6	0.05	0.45	Weibull
Fe	2.3	0.06	0.26	Weibull
Co	13.1	0.15	$1x10^{-5}$	Lognormal
Ni	5.7	0.04	0.73	Lognormal
Cu	14.6	0.05	0.56	Lognormal
Zn	6.9	0.05	0.62	Lognormal
Ge	2.1	0.09	0.11	Lognormal
As	3.8	0.09	0.03	Lognormal
Se	3.6	0.04	0.91	Lognormal
Rb	2.2	0.06	0.34	Lognormal
Sr	3.2	0.05	0.51	Lognormal
Y	2.1	0.06	0.40	Weibull
Mo	3.1	0.07	0.12	Lognormal
Cd	4.1	0.07	0.17	Lognormal
Sn	13.6	0.09	0.03	Lognormal
Sb	2.3	0.06	0.32	Lognormal
Cs	1.8	0.04	0.74	Lognormal
La	5.1	0.05	0.56	Lognormal
Ce	8.6	0.09	0.04	Lognormal
Pr	2.7	0.07	0.19	Lognormal
Nd	2.7	0.07	0.20	Weibull
Eu	3.5	0.05	0.55	Lognormal
Sm	2.5	0.07	0.22	Lognormal
Gd	2.8	0.07	0.20	Weibull
Tb	1.9	0.06	0.86	Lognormal
Dy	2.1	0.06	0.29	Weibull
Ho	1.5	0.06	0.94	Lognormal

Table 3.4 Results of skewness and K-S DN for $PM_{2.5-10}$ mode elements (continued)

Element	Skewness	K-S DN	p- value	Distribution Type
Er	8.6	0.15	$4x10^{-5}$	Lognormal
Yb	1.6	0.06	0.27	Weibull
Lu	1.7	0.12	0.29	Lognormal
Hf	3.5	0.04	0.87	Lognormal
W	5.5	0.10	0.01	Lognormal
Au	2.2	0.15	0.58	Lognormal
Pb	12.7	0.10	0.01	Lognormal
Bi	3.1	0.06	0.42	Lognormal
Tl	3.0	0.04	0.92	Lognormal
Th	2.3	0.06	0.22	Lognormal
U	5.1	0.08	0.09	Lognormal

When the frequency histograms of elements are compared, it can be seen that Weibull distributed elements Ca, Ti, Mn, Fe, Y, K, V, Rb, Nd, Gd, Dy and Yb arise from soil particles. These results could be supported by factor analysis in next sections. In terms of the antropogenic elements, a large group of distribution function show log-normal distribution. Many studies in the past indicate that the log-normal function fits air quality data reasonably well (Ott, 1990; Deacon, 1997; Karakaş, 1999). These studies showed that a concentration resulting from a series of independent random dilution's tends to be log-normally distributed. Therefore, while the emissions from sources may be approximately constant, the successive mixing and dilution of pollutants as they are transported from source to receptor results in a log-normal frequency distribution for the ambient concentrations measured at the receptor.

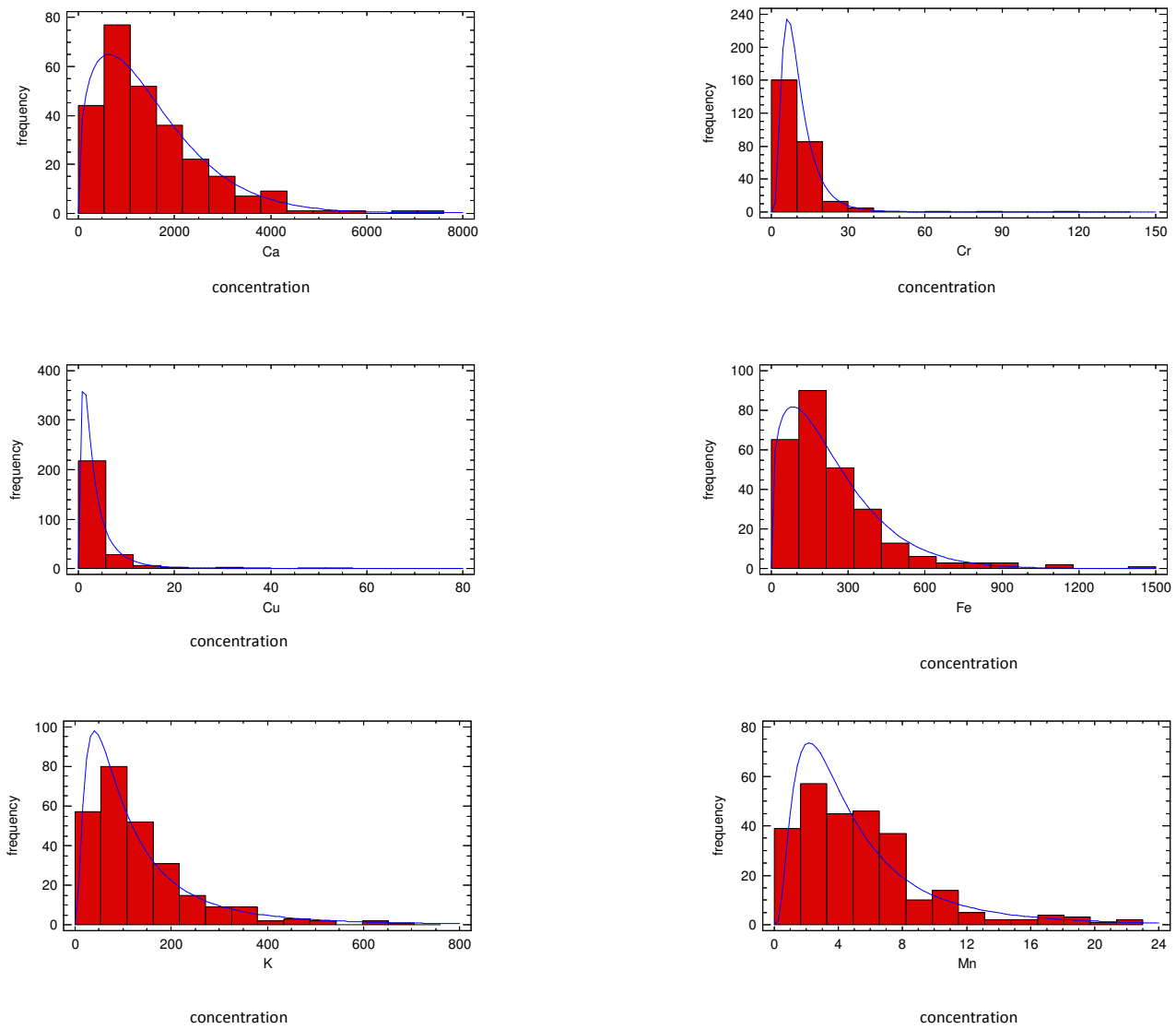


Figure 3.3 Frequency histograms of $PM_{2.5\text{-}10}$ mode elements (ng m^{-3})

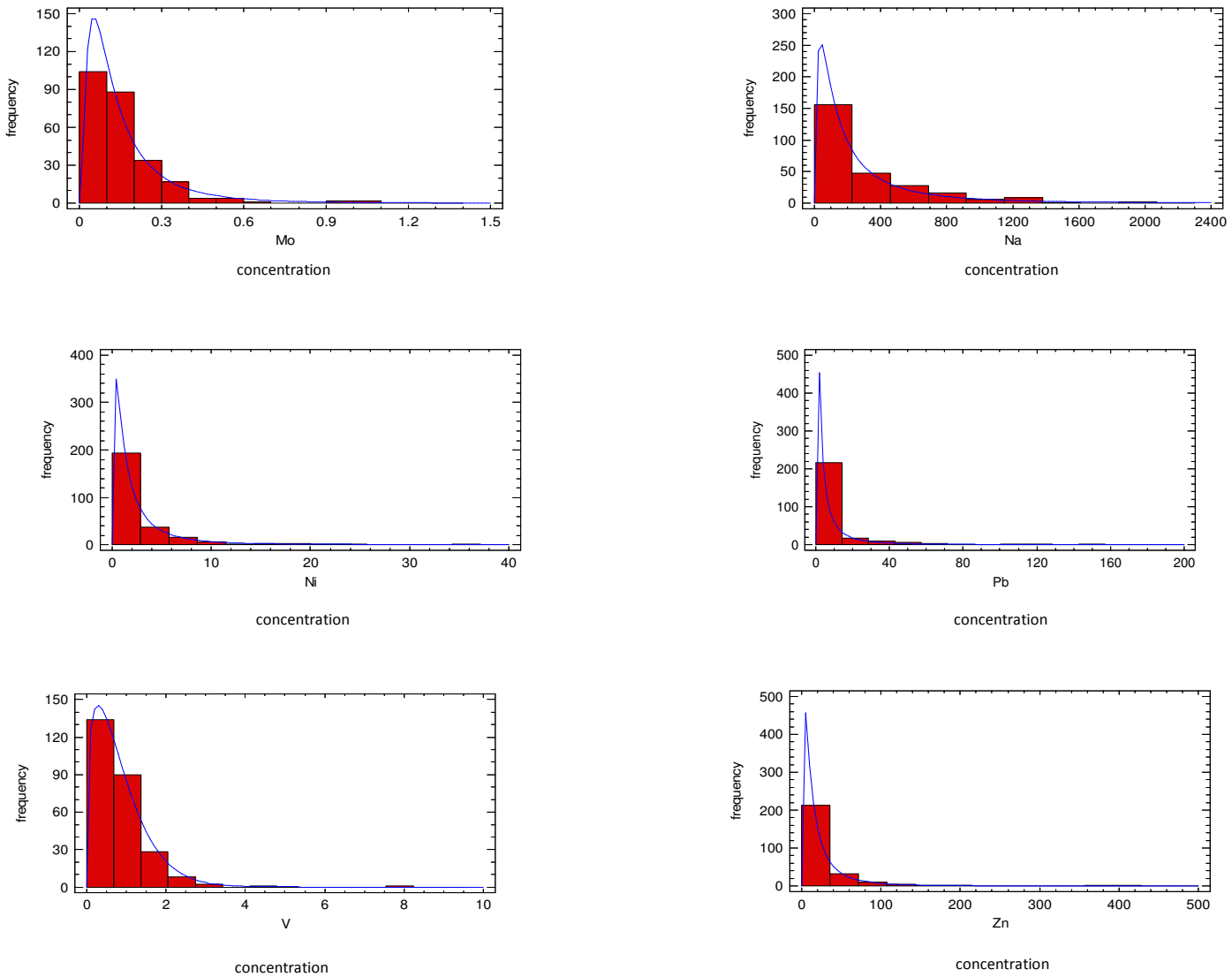


Figure 3.3 Frequency histograms of $PM_{2.5\text{-}10}$ mode elements (ng m^{-3}) (continued)

3.1.2. Comparison with Literature

In order to assess the extent of pollution in the study area, the observed concentrations of elements are compared with earlier observations of trace elements reported for comparable sites from other parts of the world.

For comparision of the data obtained in this study with those reported for other comparable sites, arithmetic mean values of elements have been preferred because most of the previous results were reported with arithmetic means. The results of urban and industrial sites were included to see the levels of pollutants in our site.

The reference sites selected for $PM_{2.5}$ particle composition comparison include Rajshahi, Bangladesh (Bilkis et al. 2004), Bemantes, Spain (Salvador et al., 2007), Mira Loma, California (Na and Cocker, 2009), Basel, Switzerland (Hueglin et al., 2005), Ho Chi Minh City, Vietnam (Hien et al., 2001). These sites are described below.

a) Rajshahi, Bangladesh (Bilkis et al., 2004)

Airborne particulate matter was collected in an urban area of Rajshahi from August 2001 to May 2002. Rajshahi, a metropolitan city, is situated in the northern region of Bangladesh and near the border with India. The samples were analyzed for elemental concentrations by proton induced X-ray emission (PIXE). Particulate matter mean concentrations are given in the table.

b) Bemantes, Spain (Salvador et al., 2007)

The Bemantes monitoring station (altitude 170m ASL) is located 2 km inland along the main axis of the estuary named Ria de Betanzos, in a rural area. Topography of Galicia, the north-westernmost region of Spain, is characterised by a framework of

low mountains and small rivers that run into the Atlantic Ocean forming estuaries named Rias that conform a complex coastal relief. The techniques used for chemical analysis of selected elements for comparison included inductively coupled plasma atomic emission spectroscopy (ICP-AES) and ICP-MS.

c) Mira Loma, California (Na and Cocker, 2009)

Concentrations of trace elements in ambient fine particulate matter were measured from September 2001 to January 2002 in Mira Loma, a semi-urban area in southern California. The community of Mira Loma is located inwestern Riverside County, California, approximately 90 km east of downtown Los Angels. According to the 2000 United States census, Mira Loma has a population of 17,617 and a total area of 16.9 km^2. Analysis of trace elements was performed by Energy Dispersive X-Ray Fluorescence (EDXRF) technique.

d) Basel, Switzerland (Hueglin et al., 2005)

Sampling was performed at various sites of Switzerland. Measured concentrations of elements collected at sub-urban one was selected for comparison. Sampling was done between April 1998 to March 1999 in Basel and trace elements determined by inductively coupled plasma mass spectrometry. Mean concentrations are given in the table.

e) Ho Chi Minh City, Vietnam (Hien et al., 2001)

Aerosol samples were collected for two years in Ho Chi Minh City that is the biggest industrial and commercial centre in Vietnam with 4.5 million inhabitants (7% of the Vietnam population), producing one-third of the country's industrial output. The area

is characterized by compact housing, narrow streets and busy traffic and there are no major industrial plants within 10 km of distance.

The studies selected for $PM_{2.5-10}$ particle composition comparison include Budapest, Hungary (Muranszky et al., 2011), Lancastar, Los Angles (Cheung et al., 2011), Florence, Italy (Lucarelli et al., 2000), Basel, Switzerland (Hueglin et al., 2005), Edinburgh, United Kingdom (Heal et al., 2005). Brief description of sampling sites is given below.

a) Budapest, Hungary (Muranszky et al., 2011)

Budapest is thecapital of Hungary and its biggest city as well, with a population of 1.7 million. During the past two decades, the industrial activity has decreased in the general area of Budapest. The sampling site was located at the Szena Square where the main pollution source is the traffic and a few other companies. Aerosol samples were collected monthly between September 2004 and August 2007. Inductively coupled plasma sector field mass spectrometer was used for trace element determination. The arithmetic means of elemental concentrations were listed.

b) Lancastar, Los Angeles (Cheung et al., 2011)

The sampling station is situated in a desert-dominated rural region in the City of Lancaster in the north of the Los Angeles County. It is a typical desert site over 2 km west of freeway CA-14. Ambient coarse PM was collected over a year long in 24-hour periods once per week during weekdays. Filters were analyzed by the Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) to determine the concentrations of the metals. The arithmetic means of elemental concentrations were reported.

c) Florence, Italy (Lucarelli et al., 2000)

The sampling station is in the eastern part of the urban area close to a heavy traffic road (about 2000 vehicles/h on four lanes). The sampling campaign lasted from February 1997 to January 1998. The elemental analysis was carried out using the external PIXE-PIGE beam facility of the INFN Van de Graaff accelerator. Given average values are calculated considering only the days when the element concentrations are above the MDL.

d) Basel, Switzerland (Hueglin et al., 2005)

Sampling was performed at various sites of Switzerland. Measured concentrations of elements collected at sub-urban one was selected for comparison. Sampling was done between April 1998 to March 1999 in Basel and trace elements determined by inductively coupled plasma mass spectrometry. Mean concentrations are given in the table.

e) Edinburgh, United Kingdom (Heal et al., 2005)

Particulate matter samples were collected from 16 September 1999 to 15 September 2000 at an urban background site in Edinburgh. Edinburgh has a population of about 450,000, does not contain major heavy industry, and is bounded by coastal estuary to the north and comparatively rural environs elsewhere. At 18 m elevation above neighbouring streets, the site is representative of urban background air in the city. Quantification of elements was performed using a VG Elemental Plasma Quad 3 ICP-MS.

The concentrations of $PM_{2.5}$ and $PM_{2.5-10}$ trace elements measured in the reference sites and in this study are given in Table for comparison. Previous study done at Bolu

station with the support of TÜBİTAK (108Y089) is also referred in comparision to observe long-time variations.

Table 3.5 Comparison of fine mode elements measured in this study with those measured in other locations (ng m^{-3})

	Rajshahi, Bangladesh[a]	Bernantes, Spain[b]	Mira Loma, California[c]	Basel, Switzerland[d]	Ho Chi Minh City, Vietnam[e]	Bolu, Turkey[f]	This study
	urban	rural	sub-urban	sub-urban	industrial	previous study	semi-rural
$PM_{2.5}$	22465	13467	41800	18900	16110	15400	17782
Al	386		292	37	528	1670	1342
Ca	116		553	64	207	2830	756
Na	92			117	196	5801	217
Fe	114		581	66	261	295	199
K	551	175	122	224	832	354	184
Mg	314	153	50	16	266	972	73
Zn	17	16	26		245	38	27
Cr	5	1	15		4	20	20
Pb	15	8	39	19	79	20	12
Ti	14	7	101		101	128	11
P	223	14	113			127	8
Cu	2	8	75	6	2	10	6
Ni	2	3	12	2		35	6
Cd			43	0.5		1	5
Mn	5	5	17	3	14	11	4
Sr		1	12				4
Co			16		1	2	2
As			6	0.4	3	2	1
V		5	33	2	8	4	1
Sn		1	68			3506	1
Sb			76	0.4	2	1.4	1
Rb		1	6	1			1
Se			7	0.4	1	0.2	0.4
Mo		3	75	0.4		3	0.3
La				0.1	0.2	0.2	0.1
Bi						0.3	0.1
Tl			5	0.03		0.1	0.1
Y			6			0.1	0.05
Th					0.1	0.04	0.03

[a]Bilkis et al., 2004 [b]Salvador et al., 2007 [c]Na and Cocker, 2009 [d]Hueglin et al., 2005 [e]Hien et al., 2001 [f]Yenisoy-Karakaş and Aga, 2011

The average concentration of P is significantly lower in this study than the values reported in the Rajshahi station as expected since Rajshahi station is located in urban area. In addition, concentration of territorial Al, Cr, Cu, Ni, Ca and Na elements are fairly higher than corresponding concentrations measured in Rajshahi while Zn, Fe, Ti and Mn concentrations are found to be comparable.

Manganese and K concentrations at a rural side of the Bernantes are comparable with this study. Among crustal species concentrations of Mg and V are slightly higher than the concentrations measured in the Bolu station while Zn, Cr, Pb, Ni concentrations are higher at Bolu station. Besides that Mo concentration is determined 10 times higher in Spain.

In comparison with riverside Mira Loma, the elemental concentrations measured in this study, except for Zn and Cr which is comparable, are higher at least a factor of three. In consequence of studying in winter period in Mira Loma, heating source elements are found higher than our annual means. Also, soil originated elements (Al, Ca and Na) except for Ti, Fe and Y are higher at Bolu station.

The study performed in a sub-urban area of Switzerland is very convenient for comparision of the long range transport because of the similarities with Bolu station. From Table 3.5, it can be pointed that concentrations of lithophilic elements collected in Bolu station are 2 to 30 times higher than the values reported in Basel. At the same time, industrial elements such as Ni, Cd, Sb, Tl and As are higher than Basel. This is not surprising considering the air flow from northwestern industrial areas of the Marmara region. The concentrations of V, Pb in the Basel are higher

than these of Bolu. Lastly concentration of Rb, Cu, Mn, Se, Mo, K, La and Pb are at considerable levels.

Concentrations of Ti, Fe, Mg, K, Zn, Mn, As, V, Se, Th, La and Sb in this study are lower than the values reported for Ho Chi Minh City. This industrial site also attracted attention to the high Pb concentration as a result of motor vehicle emissions. Also, Al, Ca, Cr, Cu and Co concentrations are higher in Bolu station.

The previous study performed at Bolu station in 2009-2010, includes 3 month winter and 3 month summer samples. Both of these studies are referred in comparision to observe short-time variations at the sime time elucidating the distinction of local and long range transport. Aluminum, Mo, Bi, Fe, K, Zn, Ni, Mn, V and As concentrations are higher than this study because the usage of pronounced natural gas for heating had not yet begun in those years. Higher Pb concentration indicates the effect of E-80 and D-100 highways in the previous study.

Table 3.6 illustrates the comparison of elements measured in this study with those measured in other locations of Turkey. PM_{10} aerosol data in these stations were generated by Güllü (1996) at the Mediterranean station, by Karakaş (1999) at the Black Sea station and Yenisoy-Karakaş (1995) at the Uludağ station.

The Mediterranean station is located at the coast approximately 20 km to the east of Antalya (31.0°E, 36.8°N). The station is located on a rock structure at a height of 20 meters above the sea level. One difficulty to establish a reference station on the Mediterranean coast was the extensive domestic and foreign tourism in the region. A rest area owned by the Ministry of Forestry was selected as the site where the station is established. The nearest population center was the city of Antalya, which was approximately 20 km away. In this study, results of 1992 and 1993 aerosol samples

will be discussed. During this period, a total of 600 daily aerosol samples were collected.

The station on the Black Sea coast is implemented at at a storage area, which belongs to the Ministry of Forestry. The storage area is located 20 km to the east of the town of Amasra. The distance between the station to the Black Sea coast is approximately 3 km (32.3°E, 41.5°N). The altitude of the station is approximately 150 m. Daily aerosols samples were collected in between April 1995 and July 1997. During this time period 354 daily aerosol samples were collected.

Uludağ Station is located in Sarıalan region of the Uludağ Mountain, which has a 1685 m altitude and located at approximately 20 km south of the city of Bursa. This station is approximately 7 km away from the ski resort area and approximately 30 km from the Marmara Sea. One hundred and eighty-four daily aerosol samples collected between September 1993 and March 1994 were used in this study.

In comparision with other locations of Turkey, the elemental concentrations of Al, Cr, Co, Ni, Cd, Ce, Cs and Zn are found quite high in this study where As, Fe, Sb and K concentration are moderately high. Also concentrations of other listed elements have higher values in general in this study.

Table 3.6 Comparison of PM_{10} mode elements measured in this study with those measured in other locations of Turkey (ng m^{-3})

	Antalya[a]	Amasra[b]	Uludağ[c]	This study
	coastal	coastal	rural	semi-rural
Mg	280	110	50	201
K	250	135	45	319
Ca	1550	270	830	2250
Na	750	300	350	527
V	1.8	2.1		1.9
Pb	14	12		23
Al	300	900		2735
Ti	27	20		33
Cr	2.6	0.9		31
Mn	6	9		9
Fe	230	200		436
Co	0.14	0.13		4.2
Ni	1.6	1.1		8.5
Zn	8	11		55
As	1.2	1.2		2
Se	0.2	0.3		0.7
Rb	0.6	0.6		0.9
Mo	0.3	0.4		0.5
Cd		0.2		18
Sb	0.3	0.3		1.0
Cs	0.07	0.09		0.2
La	0.2	0.2		0.3
Ce	0.4	0.2		1.3
Sm	0.03	0.02		0.03
Nd	0.3	0.8		0.2
Eu	0.006	0.012		0.019
Tb	0.003	0.016		0.009
Dy	0.03	0.04		0.03
Yb	0.011	0.008		0.016
Lu	0.002	0.001		0.007
Hf	0.02	0.01		0.07

[a]Güllü, 1996 [b]Karakaş, 1999 [c]Yenisoy-Karakaş, 1995

Comparation in coarse fraction concentrations pointed comparable levels with literature values. In comparison with urban site Budapest, concentrations of some antropogenic elements such as Mo, Pb and Mn are higher than the elemental concentrations measured in this study. In addition, concentrations of Fe, Zn, Cu, Sb and Rb have higher values while Cr, Ni, V, have comparable values. Lastly, Cd, Co and Tl concentrations are found higher in this study when comparing Budapest.

The average concentration of Cu at desert site Lancastar station is significantly higher than this study. Titanium and Fe have comparable results while Al, Ca and Zn are dramatically high at Bolu station.

Magnesium and Cr concentrations at a rural side of the Florance are comparable with this study. Among crustal and antropogenic species concentrations of Ca, Fe, K, Zn and Ni are slightly higher than the concentrations measured in the Bolu station while Mn and Al concentrations are higher in this study. Also antropogenic species As and V concentrations are determined 10 times higher in Italy.

As a result of comparision with the study done in Basel, concentrations of some crustal elements such as Al, Ca, Na, K and Mg are found quite high in this study. Some antropogenic components such as Pb, Ni, Cd, V and As have dramatically high concentrations in this study with comparable levels of Cu, Fe, Mn, Sb, Rb, Se, Mo La and Tl.

From the table, it can be pointed that concentrations of Zn is observed extremely high in Edinburg. However concentration of Fe, Cr, Ti and Mn are found higher in this study. The average concentrations of Pb, Cu, Ni Co and Sb are comparable while As concentration is determined 4 times higher in Edinburg.

Table 3.7 Comparison of coarse mode elements measured in this study with those measured in other locations (ng m^{-3})

	Budapes, Hungary[a]	Lancastar, Los Angeles[b]	Florence, Italy[c]	Basel, Switzerland[d]	Edinburg, United Kingdom[e]	Bolu, Turkey[f]	This study
	urban	desert site	rural	sub-urban	urban	previous study	semi-rural
$PM_{2.5-10}$	27800	9373	47000	24800	14100	28400	15476
Al		335	400	51		1600	1393
Ca		213	1880	196			1494
Na				147			310
Fe	2115	307	1730	221	183	310	237
K			370	41			135
Mg			140	34			128
Zn	54	5	80		13300	140	28
Cr	7		12		2	13	11
Pb	30		280	4	14	10	11
Ti		30			4		22
P							17
Cu	37	22	90	3	5	6	5
Ni	3		9	0.5	3	50	3
Cd	1			0.04	0.3	5	13
Mn	27		0.2	5	3	10	5
Co	0.3					1	2
As			10	0.1	4	4	1
V	3		11	0.3	1	3	1
Sb	8			0.3			0.4
Rb	2			0.1			0.4
Se				0.1			0.3
Mo	3			0.4			0.2
La				0.1			0.2
Tl	0.1			0.01			0.04

[a]Muranszky et al., 2011 [b]Cheung et al., 2011 [c]Lucarelli et al., 2000 [d]Hueglin et al., 2005 [e]Heal et al., 2005 [f]Yenisoy-Karakaş and Aga, 2011

Comparision with the previous study at Bolu in 2009-2010 shows that concentrations of Al, Fe, Zn, Ni Mn, As and V are higher in this period. For all that, Cr, Pb, Cu and Co concentrations are at comparable levels and Cd have higher concentration in this study.

3.1.3. Short-term Variations

Short-term variations refer to the episodic changes in the concentrations of elements. In order to gain better understanding in episodic behaviours, the temporal variations in the concentrations are illustrated in Figure 3.4 for both fine and coarse fractions. Coarse fraction is generally originated from natural sources while fine fraction, on the other hand, is emitted from anthropogenic sources. As seen in the figure, their concentrations show fluctuations over the study period. This is expected and observed in most of the aerosol data (Karakaş et al., 2004; Güllü et al., 2000).

The reasons for short-term variability are variations in source strengths, transport patterns and meteorological factors. The urban sampling sites which are under influence of local emissions are mostly affected by variations in source strengths as they are located in the immediate vicinity of sources. However, since pollutants are transported from distant regions and composition becomes more homogeneous during transport, in rural studies episodes are expected to account for a smaller fraction of the system variance.

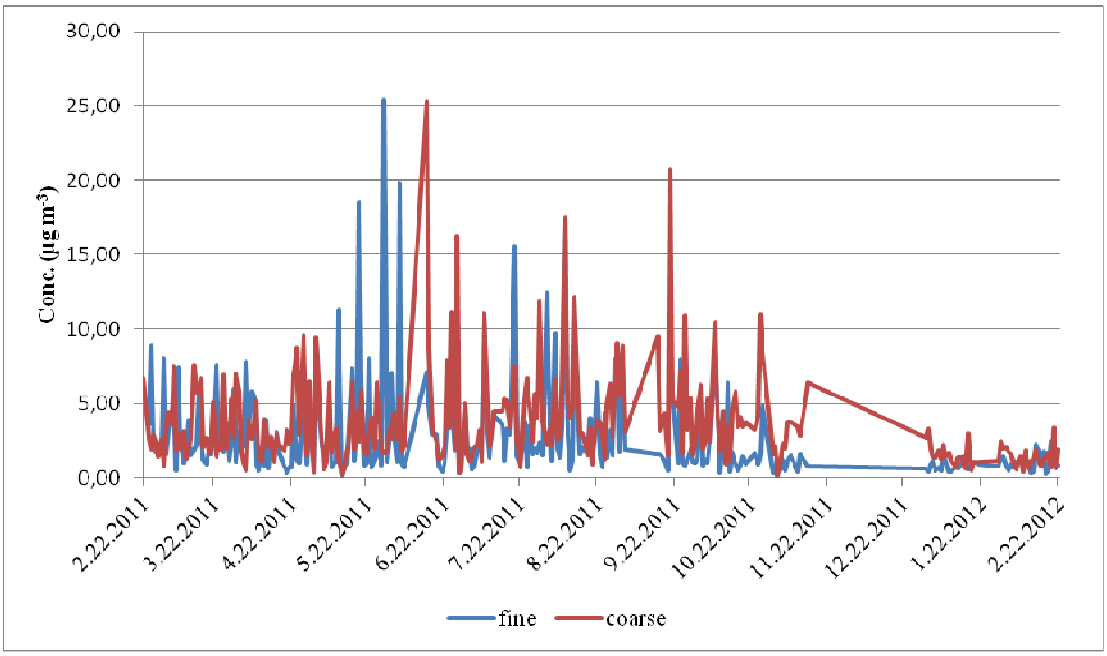


Figure 3.4 Temporal variations of fine and coarse fractions

In rural studies, episodes are generally explained by variations in flow pattern. Air masses passing through areas where emissions are stronger becomes enriched with individual parameters, and result in higher measured concentrations of elements at the receptor. After a few days, direction of upper air flow changes and, clean air masses may reach to the sampling site, resulting in low concentrations of elements. This sequence of events results in rapid increase followed by a quick drop in concentrations resulting in a peak or an episode. Therefore, trajectories corresponding to days with high concentrations of species indicate potential source areas for pollutants. As seen from Figure 3.4, the most episodic behaviours of fine particles are detected on May, 2011. Backtrajectories corresponding to these days indicate high concentrations of elements are due to transport from Russia, Middle East and Europe. Hence, this variation can be explained by change in transport pattern. On the other hand, the most episodic behaviours of coarse particles are detected on various dates which pointed to Russia, Europe and Black Sea.

3.1.4. Seasonal Variations

The observed differences in summer and winter concentrations of elements can be due to the seasonal variations in transport of elements to the receptor site and their removal and generation mechanisms.

To illustrate the seasonality in the elemental concentrations the sampling period has been divided into two seasons, heating season winter (October-April) and the non-heating season summer (June-September). The average and median concentrations of elements are presented in Table 3.8 for both fine and coarse fraction. As can be seen from Table 3.8, summer and winter concentrations of elements show some differences changing from one element to element. In order to have more clear vision about the differences, summer-to-winter ratios calculated by using median values of total elemental concentrations are depicted in Figure 3.5.

Table 3.8 Winter and summer season elemental (ng m^{-3}) concentrations

	Winter				Summer			
	Fine		Coarse		Fine		Coarse	
	Average	**Median**	**Average**	**Median**	**Average**	**Median**	**Average**	**Median**
Li	0.2	0.1	0.3	0.2	0.3	0.1	0.4	0.3
Be	$5x10^{-3}$	$4x10^{-3}$	0.01	0.01	0.01	0.01	0.02	0.01
Na	202	94	297	148	234	114	325	164
K	163	143	122	90	208	193	152	119
Mg	70	35	118	86	76	53	141	121
Al	760	178	809	364	1997	268	2084	527
P	7	5	13	11	11	8	22	17
Ca	641	347	1280	901	888	594	1748	1471
Ti	8	6	17	14	14	11	28	24
V	0.9	0.8	0.7	0.5	1.3	1.1	1	0.8
Cr	17	12	10	7	23	18	12	10
Mn	3	3	4	3	6	5	7	6
Fe	132	111	193	157	275	169	288	238
Co	0.7	0.1	1.4	0.1	3	0.2	4	0.2
Ni	5	2	3	2	6	3	3	1
Cu	5	4	4	2	7	5	7	3
Zn	24	17	24	11	31	20	32	13
Ge	0.12	0.08	0.08	0.05	0.1	0.08	0.07	0.05
As	1.7	1.2	0.7	0.4	1.3	1	0.4	0.3
Se	0.3	0.2	0.2	0.1	0.5	0.4	0.3	0.2
Rb	0.4	0.4	0.3	0.3	0.7	0.6	0.6	0.5
Sr	3	1	6	4	4	2	5	4
Y	0.04	0.03	0.07	0.06	0.06	0.05	0.1	0.1
Mo	0.23	0.17	0.17	0.12	0.32	0.28	0.15	0.11
Cd	5	0.5	11	2	6	0.4	15	1
Sn	0.5	0.4	0.4	0.2	0.8	0.6	0.6	0.2
Sb	0.6	0.5	0.3	0.3	0.7	0.6	0.4	0.3
Cs	0.06	0.04	0.05	0.03	0.12	0.09	0.07	0.05
La	0.1	0.1	0.1	0.1	0.2	0.1	0.2	0.2
Ce	0.2	0.1	0.5	0.2	0.4	0.2	0.6	0.3
Pr	0.01	0.01	0.03	0.02	0.03	0.02	0.04	0.03
Nd	0.05	0.04	0.10	0.08	0.08	0.06	0.15	0.13
Eu	0.01	$4x10^{-3}$	0.01	$6x10^{-3}$	0.01	$5x10^{-3}$	0.02	0.01
Sm	0.01	0.01	0.02	0.01	0.02	0.01	0.03	0.02
Gd	0.01	0.01	0.02	0.01	0.02	0.01	0.03	0.02

Table 3.8 Winter and summer season elemental (ng m^{-3}) concentrations (continued)

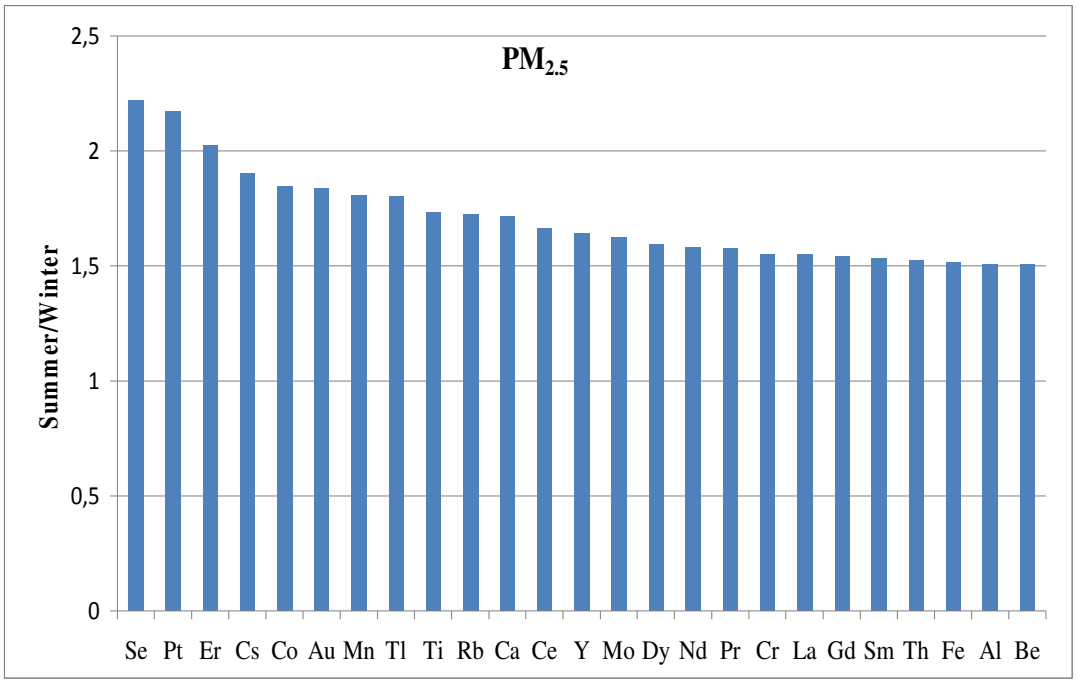
	Winter				Summer			
	Fine		Coarse		Fine		Coarse	
	Average	Median	Average	Median	Average	Median	Average	Median
Tb	$3x10^{-3}$	$3x10^{-3}$	$4x10^{-3}$	$4x10^{-3}$	$4x10^{-3}$	$3x10^{-3}$	0.01	$5x10^{-3}$
Dy	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.02
Ho	$3x10^{-3}$	$3x10^{-3}$	$5x10^{-3}$	$4x10^{-3}$	$4x10^{-3}$	$3x10^{-3}$	0.01	0.01
Er	0.04	$5\ 10^{-3}$	0.3	0.01	0.1	0.01	0.3	0.01
Tm	$4x10^{-3}$	$4x10^{-3}$	$4x10^{-3}$	$3x10^{-3}$	$4x10^{-3}$	$3x10^{-3}$	$4x10^{-3}$	$3x10^{-3}$
Yb	$4x10^{-3}$	$4x10^{-3}$	0.01	0.01	0.01	$5x10^{-3}$	0.01	0.01
Lu	$3x10^{-3}$	$3x10^{-3}$	$3x10^{-3}$	$3x10^{-3}$	$3x10^{-3}$	$3x10^{-3}$	$4x10^{-3}$	$3x10^{-3}$
Hf	0.03	0.02	0.04	0.03	0.04	0.02	0.04	0.03
W	0.2	0.1	0.5	0.1	0.2	0.1	0.3	0.1
Pt	0.01	$3x10^{-3}$	$2x10^{-3}$	$2x10^{-3}$	0.01	0.01	$5x10^{-3}$	$4x10^{-3}$
Au	0.1	0.04	0.2	0.1	0.2	0.1	0.2	0.1
Pb	7	5	6	2	18	7	16	2
Bi	0.1	0.04	0.04	0.02	0.1	0.1	0.03	0.02
Tl	0.1	0.03	0.04	0.02	0.1	0.1	0.03	0.02
Th	0.02	0.01	0.04	0.03	0.03	0.02	0.1	0.05
U	0.1	0.02	0.1	0.02	0.04	0.01	0.05	0.02

There are factors that affect the seasonal variations of parameters measured. The first one is the scavenging of pollutants from atmosphere during their long-range transport. Removal of the pollutants from atmosphere via rain is an important factor that affects their seasonal variations (Güllü et al., 1996). Pollutants which have distant sources are washed out from the atmosphere as the air mass which carries them passes through rain events. As the frequency of rain is higher in winter months, the pollutants which have source regions far away from the receptor site can hardly reach to the receptor site in winter. So, for the pollutants which are long-range transported to Northwestern Turkey, winter concentrations are expected to be lower than summer concentrations. The species, which have local sources, on the other hand, have less chance to be removed from the atmosphere via rain, because the

distance, which they travel before they are intercepted at the station, is shorter. If we have a ratio of unity, this means that these elements have local sources.

In fine fraction, some of the elements have same concentrations in both summer and winter such as Tb, Ho and Lu. Besides that, some of the elements have higher concentrations in winter such as Ge, Li, As, Cd, Tm and U. Other elements show high concentrations in summer. Arsenic, Cd, and U have higher concentrations in winter probably due to the coal burning in this period. The crustal elements like Er, Cs, Mn, Ti, Rb, Ce, Co, Y, Dy, Nd, Pr, Cr, La, Gd, Sm, Th, Fe, Al, Be, P, Mg, V, Eu, Yb, Na, Hf and Sr are normally higher concentrations in summer than in winter. There are re-suspended particulate matters in air in dry season. However, the concentrations of antropogenic elements may come from the long-range transport such as Se, Pt, Co, Au, Tl, Mo, Ni, Cu, Sn, K, and Bi.

As shown in Figure 3.5, summer-to-winter ratios of fine mode elements vary from 2 for Se to 0.6 for U. A student's t-test revealed that elements can be categorized into three groups based on their summer-to-winter concentration ratios. Statements "lower" or "higher" in this discussion refer to statistical significance of 95%. Elements Se to Sr are included in the first group. Concentrations of these elements in summer season are higher than their concentrations in winter season. Concentrations of Tb, Ho and Lu, on the other hand, do not show statistically significant differences between summer and winter seasons. The elements, namely Li, As, Cd, Tm and U made up the third group. Concentrations of these elements in winter season are statistically higher than their concentrations in summer season.



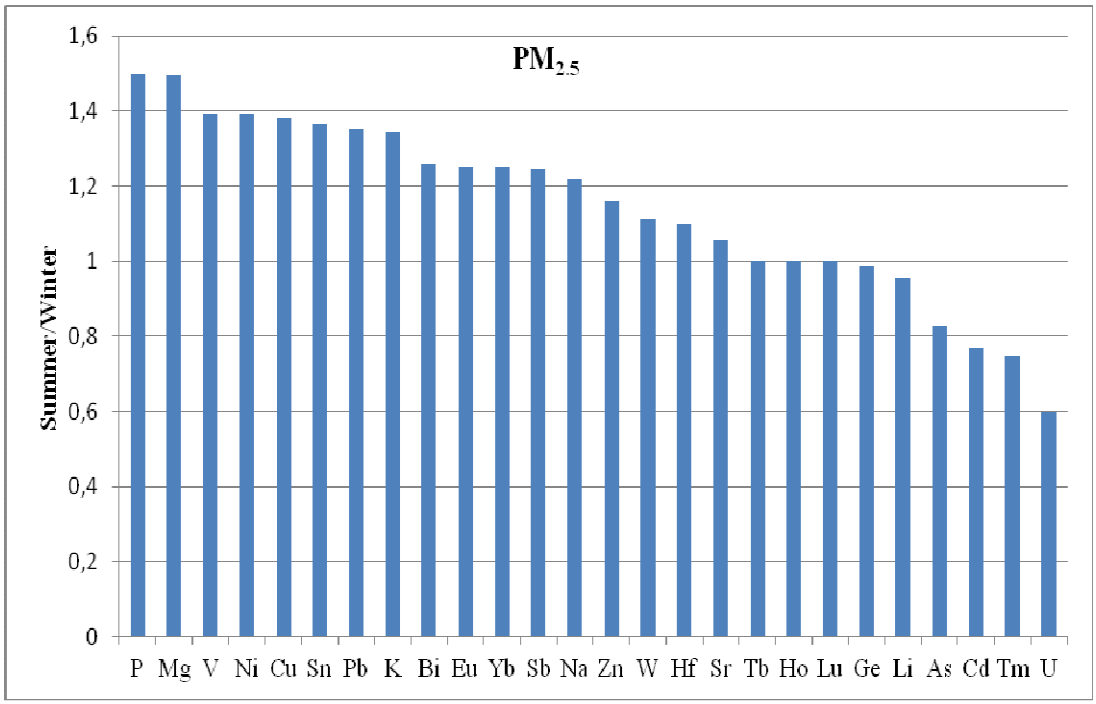


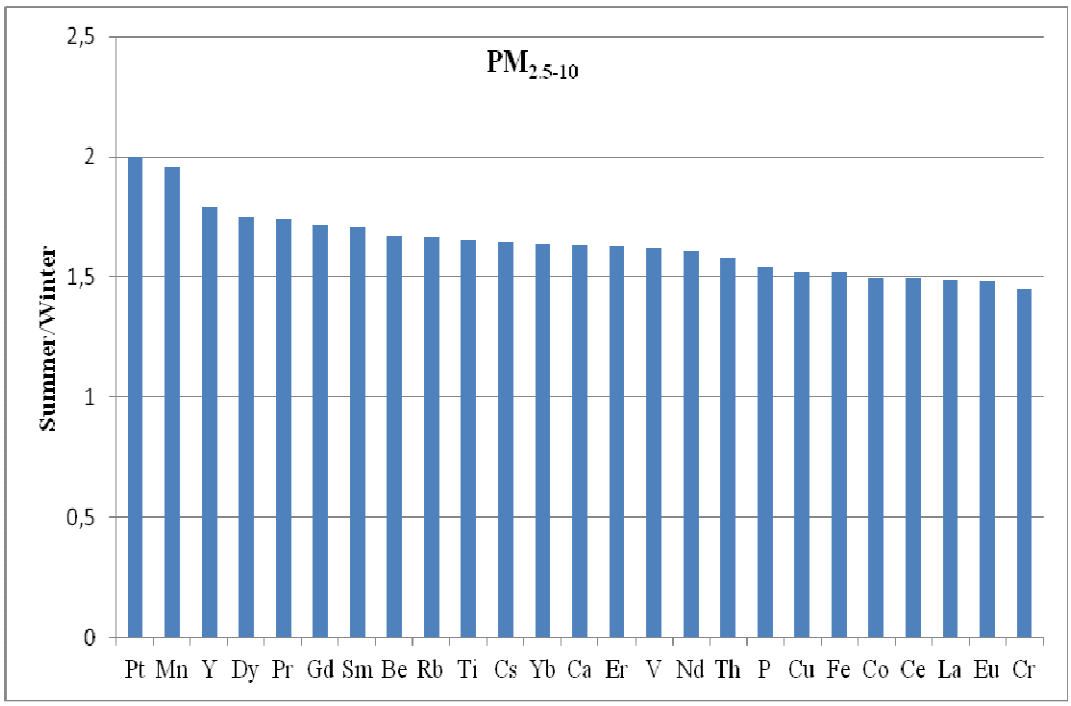
Figure 3.5 Summer to winter ratio of $PM_{2.5}$ elements

However, concentrations of anthropogenic elements do not show as clear seasonal differences as crustal and marine elements, change in airflow patterns are reported as a reason for the observed situation in this study. First group associated with antropogenic elements have higher concentrations during summer season due to the low scavencing events. Certain fractions of them are removed from the atmosphere by rain scavenging before reaching to the receptor site. Since rain events occur more frequently in winter months, and the distance is long enough to meet with rain before intercepted at the sampling station, extensive scavenging of species results in lower winter concentrations than summer concentrations.

As shown in Figure 3.6, summer-to-winter ratios of coarse mode elements vary from 2 for Pt to 0.5 for Cd. According to the student's t-test, elements Pt, Mn, Y, Dy, Pr, Gd, Sm, Be, Rb, Ti, Cs, Yb, Ca, Er, V, Nd, Th, P, Cu, Fe, Co, Ce, La, Eu, Cr, Al, Ho, Mg, K, Li, W, Tb, Sb, Zn, Tl, Hf, Na and Se are higher in winter season while Sr, Tm, Lu, Bi and Pb do not follow a seasonal trend. Concentrations of elements Mo, Ge, U, Ni and Sn in summer season are moderately higher than their concentrations in winter season and the most clear difference observed in the concentrations of As, Au and Cd. First group generally associated with crustal elements have higher concentrations during summer season due to the easier resuspension of soil. In winter season, soil is damp and hence resuspension of soil is limited leading low concentrations of these elements despite stronger winds. However, in summer season, soil is dry and formation of crustal aerosols is enhanced even if there is less wind. The higher concentration of soil-related elements in coarse mode indicates that contributions to measured concentrations from surrounding regions are much more pronounced than contribution from distant regions. It is well documented in the literature that coarse particles settle out quickly from the atmosphere preventing their

transport over long distances. Consequently, observed seasonal variations in concentrations of crustal elements are mainly influenced by the difference in their generation mechanisms between summer and winter season.

The variations in transport patterns can explain the observed seasonal differences. Emissions originating from industrialized regions are more frequently transported to the sampling site and it is not surprising to have higher concentrations of pollution-derived elements in summer season. Lastly, emissions from local sources can not be removed by wet deposition as the time is short between emitting from source and arriving to receptor. Then, it is expected to have higher winter concentrations or at least comparable at winter and summer.



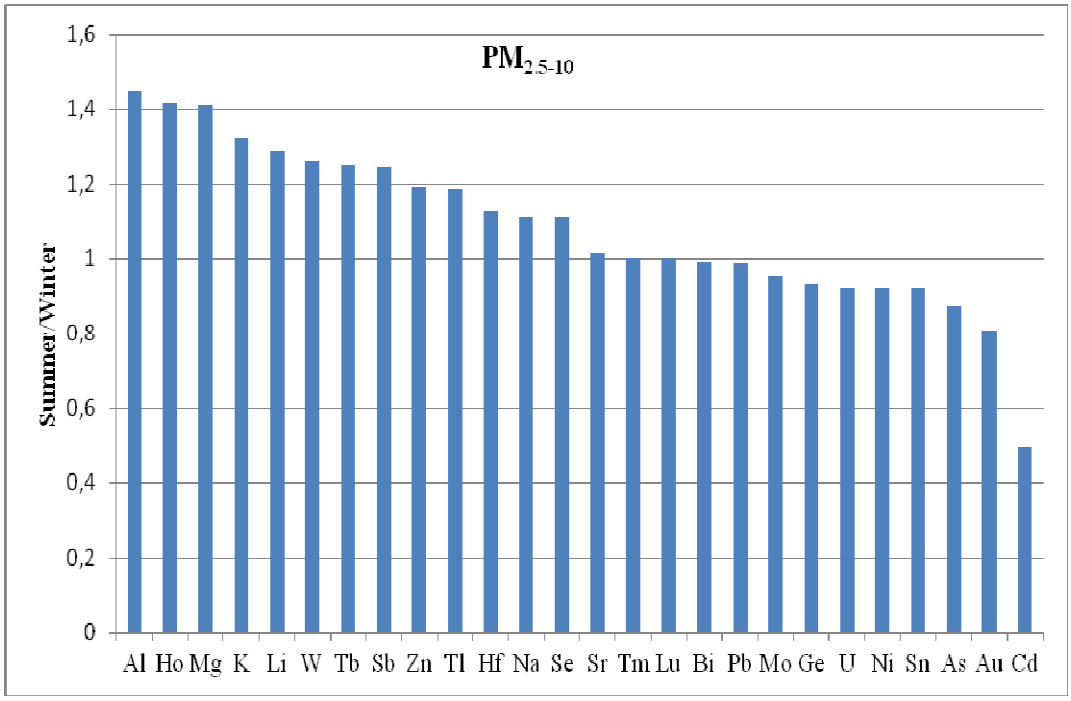


Figure 3.6 Summer to winter ratio of $PM_{2.5-10}$ elements

3.2. Source Apportionment

3.2.1. Enrichment Factors

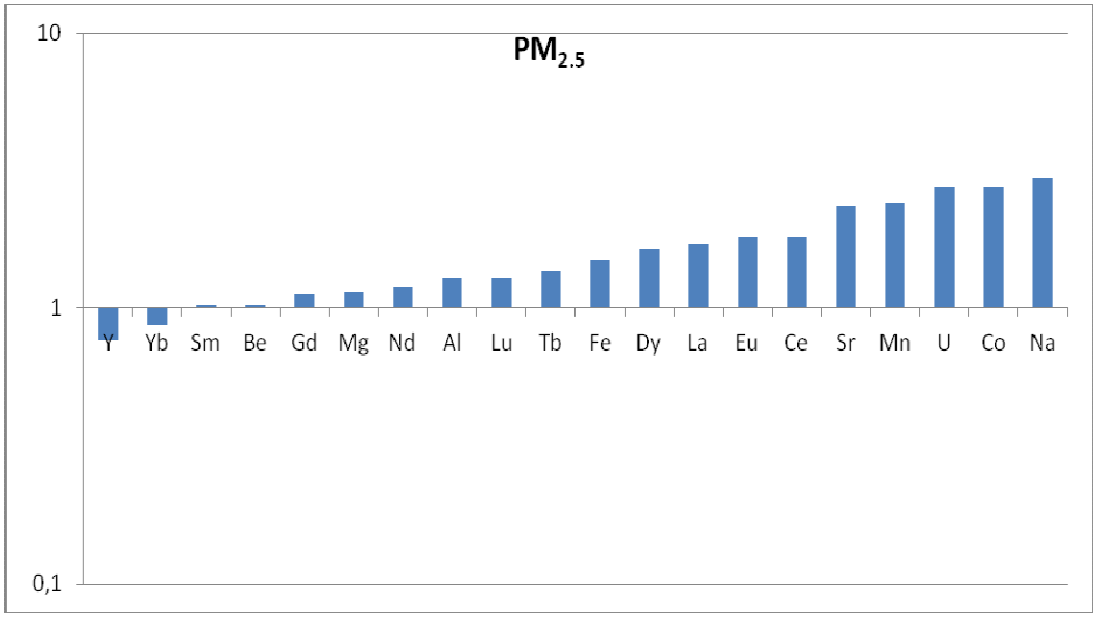
As discussed previously (Section 1.7.1), the elemental concentrations of atmospheric particles vary over several orders of magnitude depending on the geographic location of the sampling site, meteorological conditions and the seasonal changes in the intensities of the sources venting particles into atmosphere. There are many factors affecting the atmospheric concentrations of the elements over short time and space scales, it is difficult to characterize the composition of the aerosol by observing their regional atmospheric concentrations. The identification of source areas was found to be difficult because the origin of individual emissions was masked by the mixing which occurs in the reservoir (Yatin et al., 2000).

The primary constituent of the aerosols arriving at the sampling site was the crustal component transported both from the surrounding desert areas and from within the region as a result of deforestation, agricultural activities and over exploitation of vegetation for domestic use.

One way of evaluating the chemical character of the aerosol is by the use of Enrichment Factors (EFc) providing information on the extent to which trace metal concentrations in aerosols are enriched or depleted relative to crustal sources. EFc which are straightforward and informative parameters were utilized for the characterization of aerosols.

Crustal enrichment factors (EFc) for the various elements in the coarse and fine size fractions were calculated relative to the average crustal rock composition of Taylor (1972), with Ti as a reference element. Enrichment factor value more than 10 can be considered as the influence of man-made sources. If EF value is 1 that means earth

crust is only contributor to the given element. Calculated crustal enrichment factors of elements with their ranges and median values in aerosol samples for all data set are illustrated in Figures 3.7 and 3.8. Elements in Figures are arranged according to increasing median enrichment factors, which indicate the increasing antropogenic content.



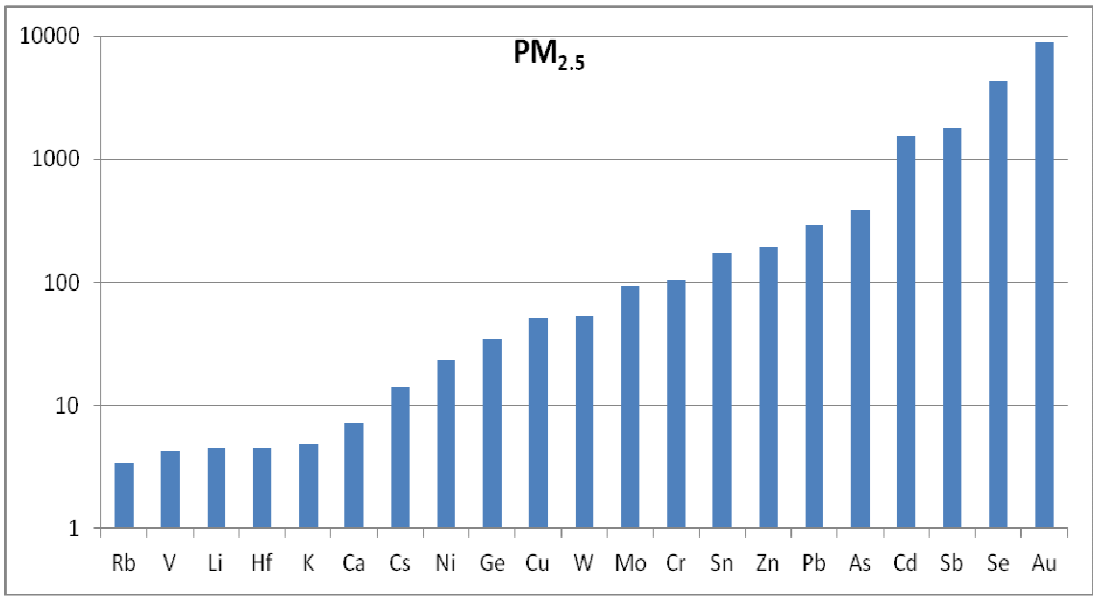


Figure 3.7 Crustal enrichment factor (EF's) of fine mode elements

Figure 3.7 shows the crustal enrichment factors of elements for fine fraction. As shown in Figure, Cd, Sb, Se and Au with EFc values ranging between 1000 and 10000 are highly enriched in fine fractions. These high EFc values indicate that these elements mainly originate from anthropogenic sources, and contribution of crustal sources on their measured concentrations is negligible. High EFc values of Cd, Sb, Se and Au in the coarse fraction suggests that these elements are enriched in aerosols relative to soil and should have non-soil sources even in coarse fraction. Correlation analysis implied that these elements strongly correlated with each other and hence their sources in the coarse fraction could be common.

Elements Sn, Zn, Pb and As have EFc values greater than 100 in fine fraction suggesting high contribution of non-crustal sources on fine concentrations of these elements. Conversely, these group of elements are not significantly enriched in coarse fraction. Their EFc values are less than 100 which confirm that their coarse concentrations can be attributable slightly to crustal sources. It is known that Zn and Pb could be source from contaminated road dust. Therefore, it is not surprising that fine fraction of these elements are more affected by emissions from a wide variety of anthropogenic sources, whereas coarse fraction of them are more affected by crustal sources. Iron-steel industry and motor vehicles are the main anthropogenic sources of Sn, Zn and As elements Similarly, Pb can be considered as a marker element of emissions from road traffic (Sterbeck et al., 2002).

Although K is a soil-related element, fine fraction of K are likely to have originated from biomass burning. Such enrichments of K is also reported in previous studies for fine aerosol samples collected from rural and urban regions (Yatin et al., 2000).

One of the attractive point is Fe which is non-enriched in coarse fraction and moderately enriched in fine fraction. Iron generally indicates the iron-steel industry but soil component seems higher than antropogenic factor. Also, soil originated elements without any known antropogenic component such as Yb, Sm, Y and Be have ratios close to 1.

Calcium and Mg have soil origin in sampling sites far from coastal areas. Besides crustal material, sea salt contributes on their observed concentrations at the stations located close to sea. Enrichment of Na, Mg and Ca in coarse fraction can be explained by the contribution of sea salt. One likely source for enrichment of Na, Mg and Ca in the coarse fraction is variation of the chemical composition of aerosols as a function of size.

Elements Cu, W, Mo and Cr are enriched to higher than 10 in both fine and coarse fractions. It indicates a non-crustal source for these elements with soil component. Because elements are size-differentiated and fine particles are known to be the indicators of anthropogenic sources. Fine particles have larger EFc values than coarse ones implying that fine fraction of these elements are more influenced by non-crustal sources. Non-crustal sources of these elements in the atmosphere can be long range transport.

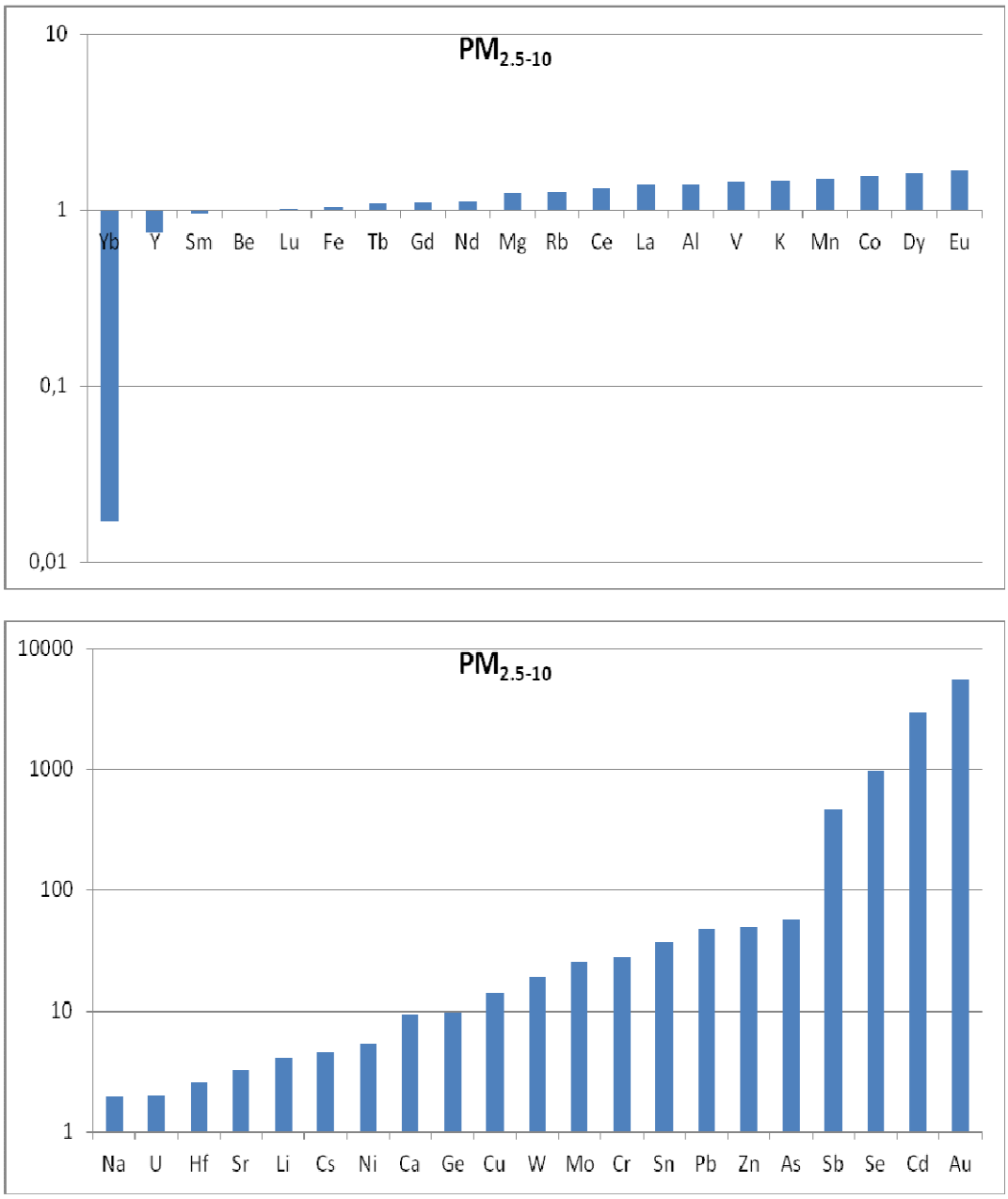


Figure 3.8 Crustal enrichment factor (EF's) of coarse mode elements

3.2.2. Wind Sector Analysis

Particulate matter concentrations in the atmosphere are governed by climate and weather. Climate and weather factors play an important role in transport, wet/dry removal processes, and chemical transformations of aerosols (Seinfeld and Pandis, 1998). The dispersion of particulate matter is dependent on the complex combination of emissions as well as weather conditions (Giorgi and Meleux, 2007). The main meteorological factors are wind (speed and direction), temperature, monsoon, rain effects and dust storms (Barmpadimos et al., 2010; Chang et al., 2000).

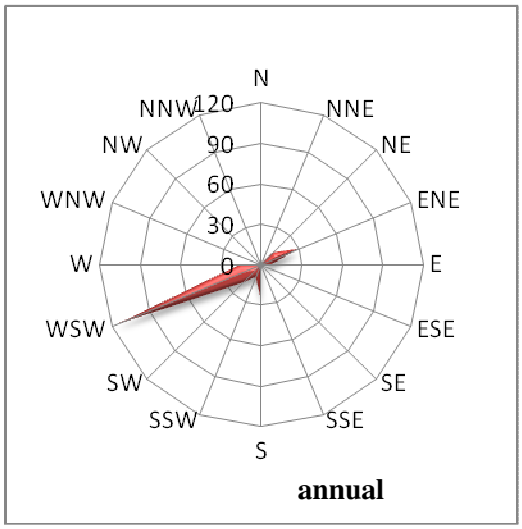
The observed concentrations of elements at a specific location depend not only strength of sources but also meteorological variables. As the main aim of this study is to monitor long range transport, the sampling station must not be under direct influence of local emissions. Since the impact of the local emissions on measured concentrations of elements would be dominating compared to long-range transported concentrations, it would not be possible to discuss the features of long range transport if the site is under direct influence of local sources. Hence, before interpreting the findings from present study, possible pollution sources around the Bolu station are investigated. Wind sector analysis carried out to determine wind directions that have experienced the highest number of extreme pollution episodes at Bolu.

In this study, prevaling wind directions for each day were counted and average elemental concentrations on these directions were calculated to associate with pollution sources around the sampling station. Possible emission sources around the station were given in Table 3.9 with wind directions.

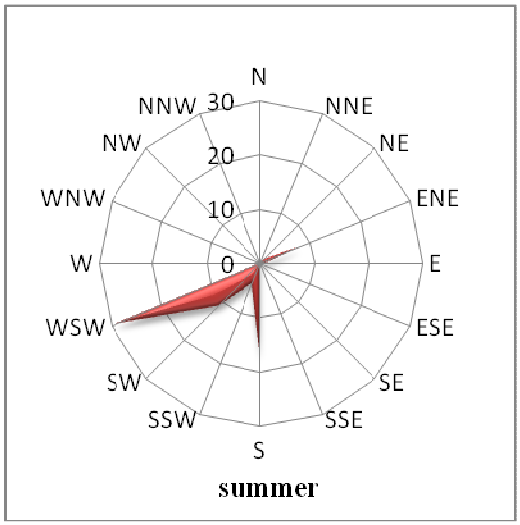
Table 3.9 Local pollution sources near the sampling site

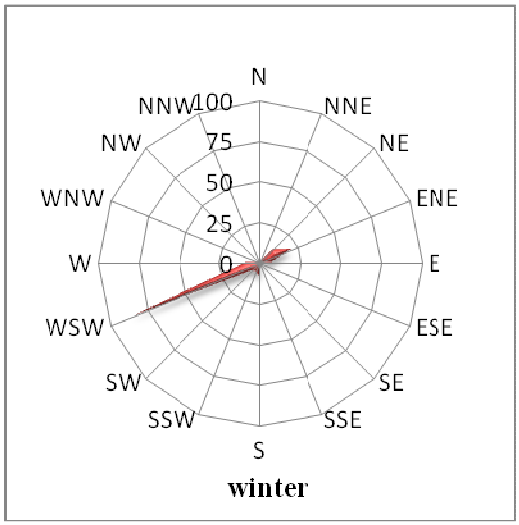
Wind direction	Pollution sources	Tracer Elements
North (N) North-North-East (NNE)	Traffic (E-80 and D-100 highways), forest area	Pb, Br, Cu, Zn, Cd, Sb, Ba and crustal elements
North-East (NE)	City center (Bolu), farmlands (Karaköy), industrial area (polymer production, aluminum joinery, petrochemistry), petrol station	As, Se, V, S, La, K, Al and crustal elements
East-North-East (ENE)	Residental area, farmlands, asphalt production plant	Crustal elements, Ni, V, Pb, Cr, As, Se
East (E)	Residental area, farmlands (Dörtdivan), industrial area, leather factory (Gerede), cement factory, city center	Crustal elements, Ca, Al and antropogenic elements
East-South-East (ESE) South-East (SE) South-South-East (SSE)	Industrial area (potato processing factories), residental area (Karaköy, Doğancı) Farmlands (Karacasu, Seben, Kıbrıscık), industrial area (pulp mill) Industrial area (pulp mill), farmlands	Al, As, Cr, Ni, Cu, Fe, Co, Cd, V, Zn, Se, Mo Sb and crustal elements
South (S) South-South-West (SSW)	Farmlands (Seben), Gölköy Lake Forest and farmlands (Mudurnu, Göynük)	Crustal elements
South-West (SW)	Farmlands (Mudurnu), forest area, residental area (Gölköy), heating center (A.İ.B.Ü)	V, S, La and crustal elements
West-South-West (WSW) West (W)	Forest area Residental area (Bolu)	Crustal elements
West-North-West (WNW) North-West (NW) North-West-North (NWN)	Traffic (E-80 and D-100 highways), forest area Traffic (E-80 and D-100 highways), forest area Traffic (E-80 and D-100 highways), forest area	Pb, Br, Cu, Zn, Cd, Sb, Ba and crustal elements

In this way, if high concentrations related directions are not predominant and there is no local source in these directions during the sampling period, it is deemed that these pollutants will be reach the receptor site by long-range transport and detected by back trajectories. To clarify this discussion, firstly, annual and seasonal wind roses were prepeared for the sampling period. These roses are depicted in Figure 3.9.



(a)





(b) **(c)**

Figure 3.9 Wind roses prepeared with meteorological data measured at Bolu during the measurement periods (a) annual, (b) summer and (c) winter

As can be seen from Figure 3.9, the most frequent annual flows are from WSW sector, and also there is a relatively less frequent flow from SW, S and ENE sectors. Flows from S and ENE directions, on the other hand, are infrequent in the region. In summer season, prevailing flows are from SW and S sectors besides WSW sector. Similar to annual flow pattern, flows from WSW sector is more dominant without any S component in winter season.

Based on the above discussion, it is expected to measure higher particulate matter concentrations at the Bolu station on WSW direction. If the local sources dominate, the suggestion is not enough to explain the sources of the pollutant since there are no local sources on WSW direction. As shown in Figure 3.10, the highest concentrations of some particulate matters in fine mode are also reported on NNE and NE sectors despite the frequent flow from WSW, S and ENE sectors. That means, high concentration on these sectors are originated from long-range transport.

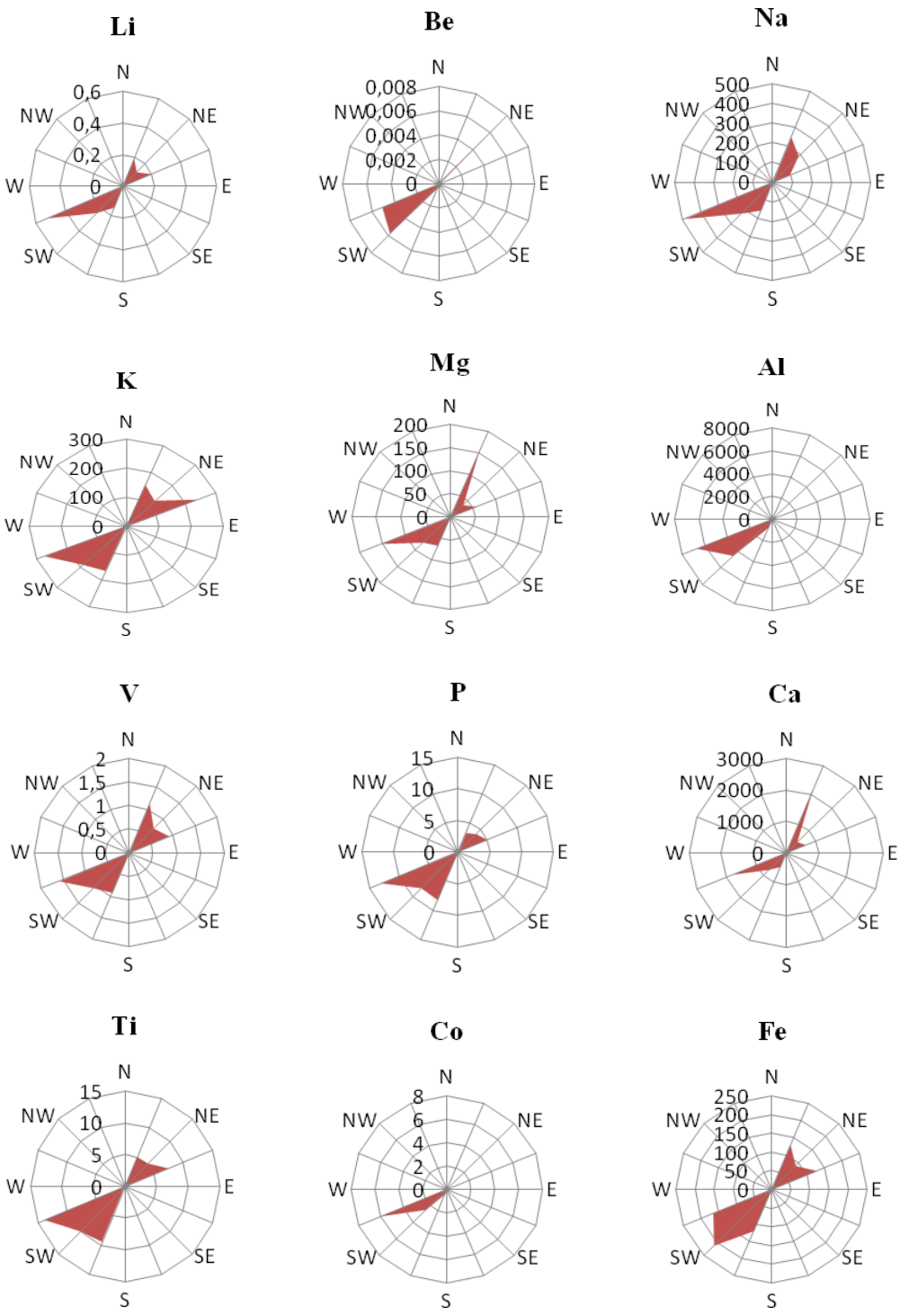


Figure 3.10 Annual pollution roses of $PM_{2.5}$ mode elements at the sampling station (ng m^{-3})

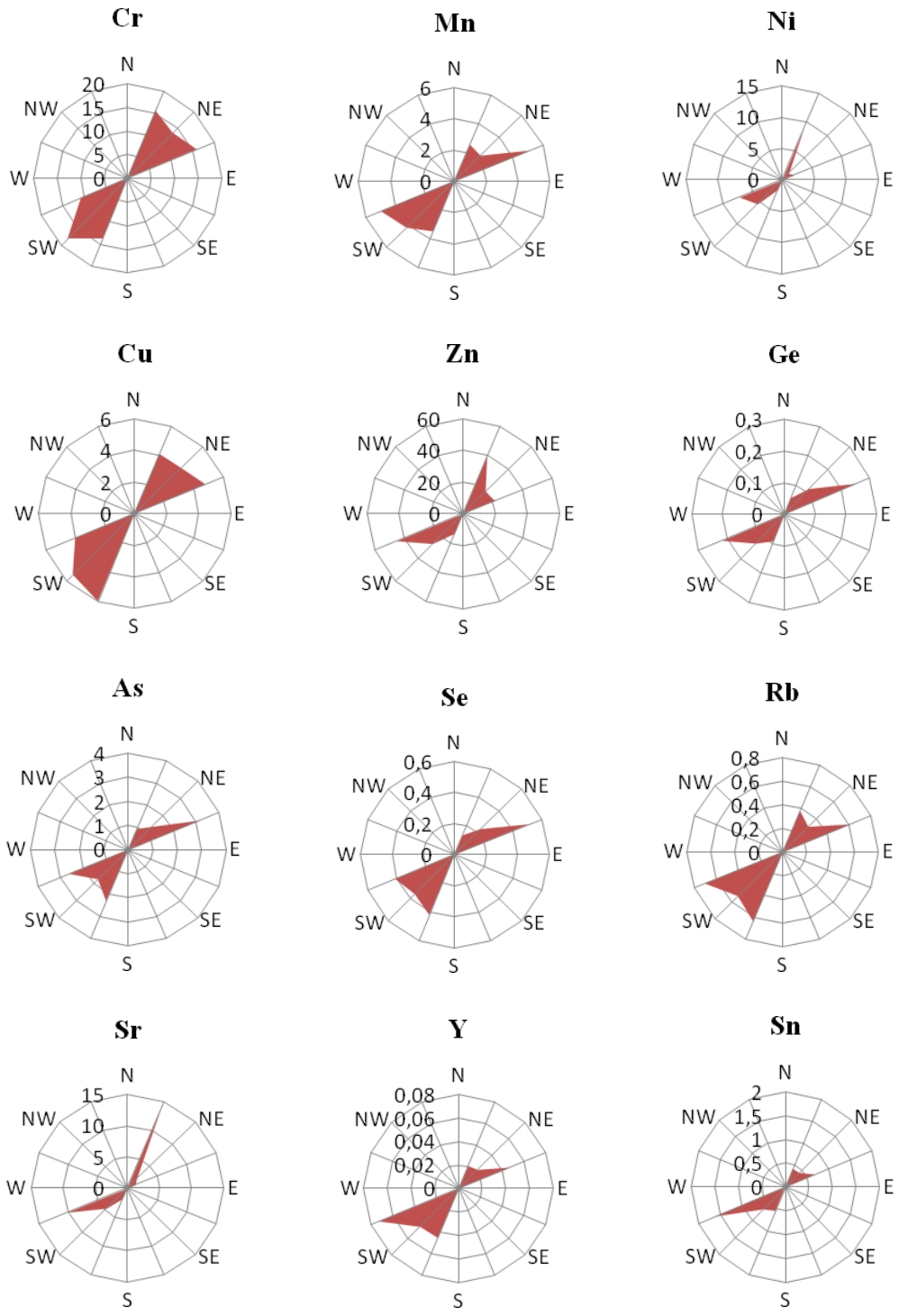


Figure 3.10 Annual pollution roses of $PM_{2.5}$ mode elements at the sampling station (ng m^{-3}) (continued)

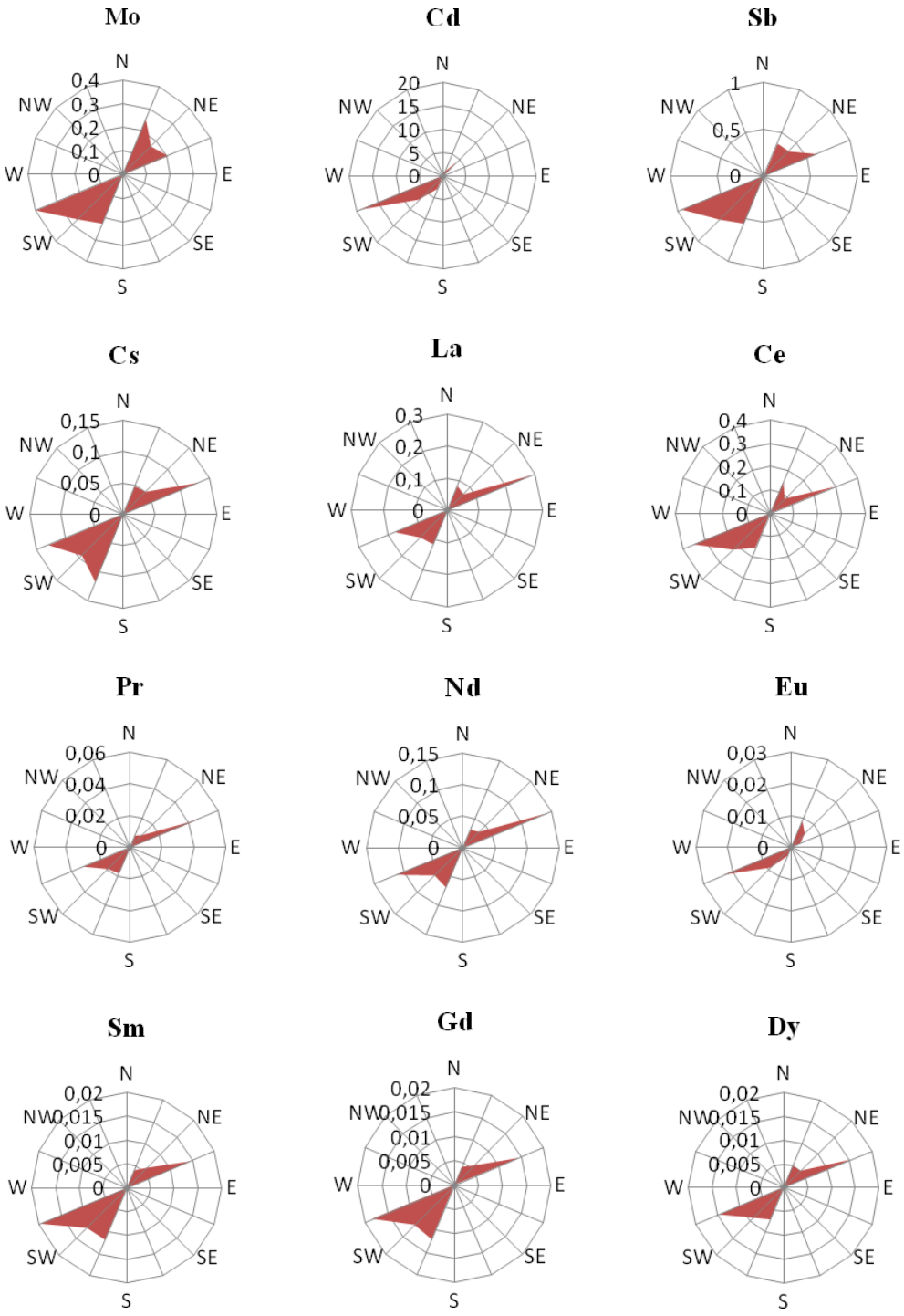


Figure 3.10 Annual pollution roses of $PM_{2.5}$ mode elements at the sampling station (ng m^{-3}) (continued)

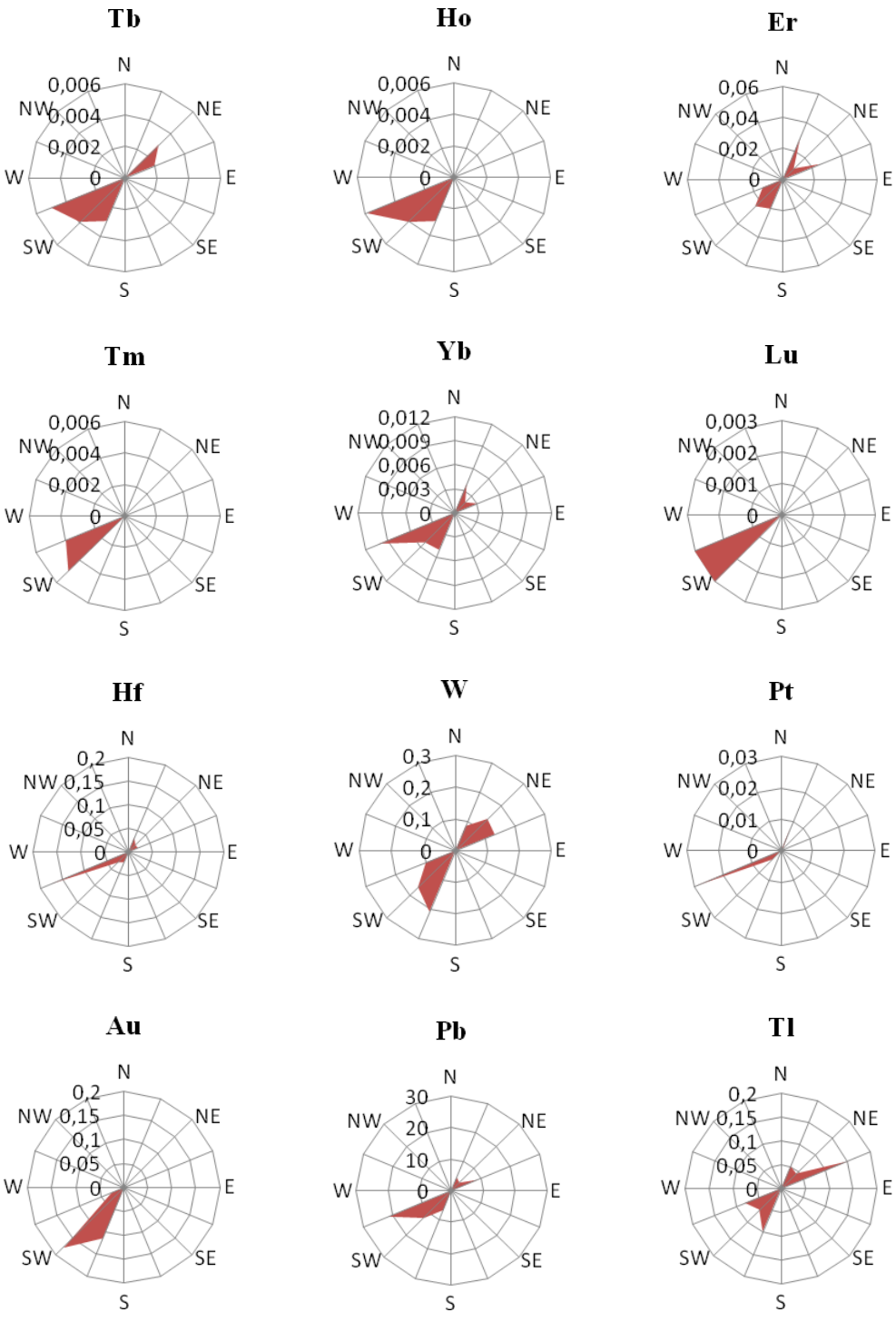


Figure 3.10 Annual pollution roses of $PM_{2.5}$ mode elements at the sampling station (ng m^{-3}) (continued)

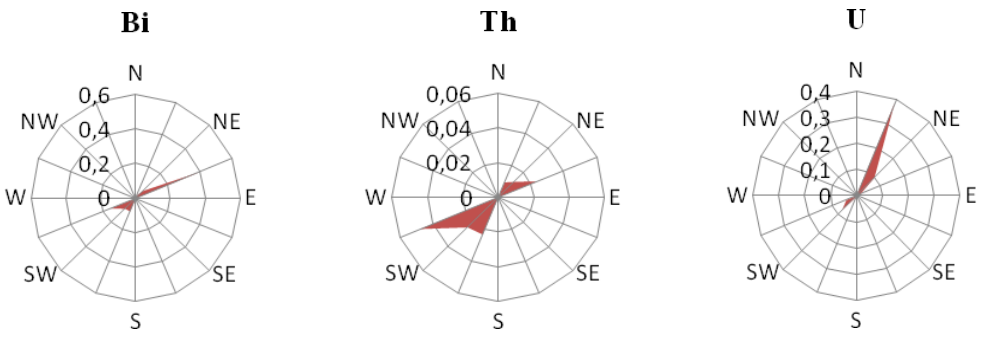


Figure 3.10 Annual pollution roses of $PM_{2.5}$ mode elements at the sampling station (ng m^{-3}) (continued)

High concentrations of both antropogenic and crustal elements such as K, Mn and Fe on ENE, WSW and NE directions indicate the effects of forest area with contribution of industrial area and city center. These elements are known as coal and burning emission particles besides soil originated character.

Pollution roses also indicate WSW and NNE sector contributions of sodium, Na, Mg, K and Sr. So, sea-salt affect may be seen on NNE sector in addition to the crustal affects of farmlands. Some elements such as Be, Al, Co, Cd, Tm, Ho, Lu, Hf and Au only dispersed on WSW and SW sectors. These elements show a characteristic soil affect as a group.

Vanadium, Mn, Fe, Ni and Mo concentrations are observed mostly in NE, NNE and WSW sectors. Similar concentration contribution trends of these elements may be originated from iron-stell works from NE site since there is no known antropogenic emission source on WSW direction. Besides that NNE tendency of these elements can point to the long range transportation.

Annual pollution roses of coarse fraction elements are illustrated in Figure 3.11. High Ca, Mg, Al, V and Mn concentrations at the direction of the forest areas and farmlands located ENE and WSW sectors indicate the wind erosion.

Iron-steel work tracer elements such as K, V, Cr, Fe, Ni, Cu, Zn and Mo have high concentrations in ENE and WSW sectors. Besides the known soil effect on WSW direction, industrial area near the sampling site can dominate ENE sector.

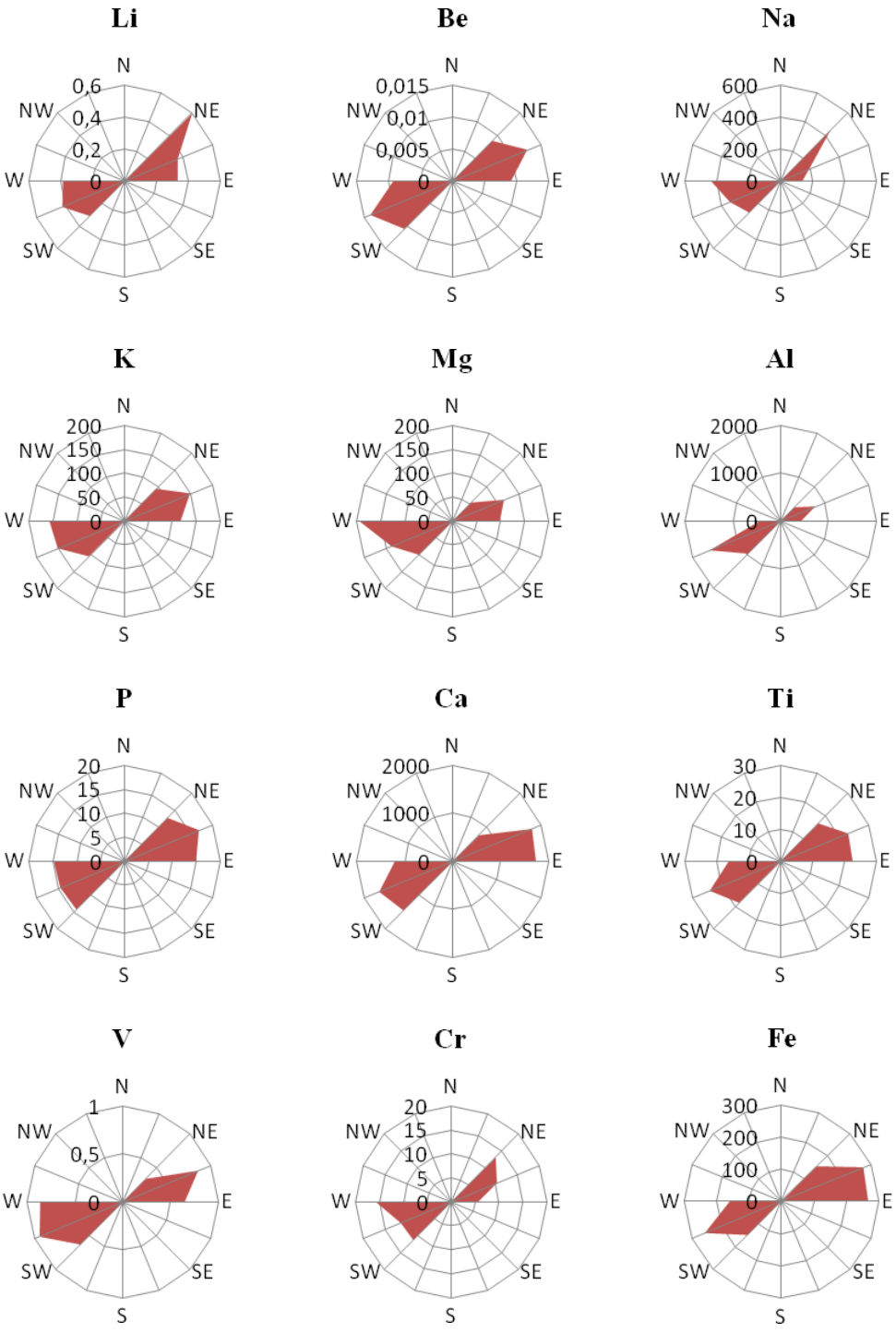


Figure 3.11 Annual pollution roses of $PM_{2.5-10}$ mode elements at the sampling site (ng m^{-3})

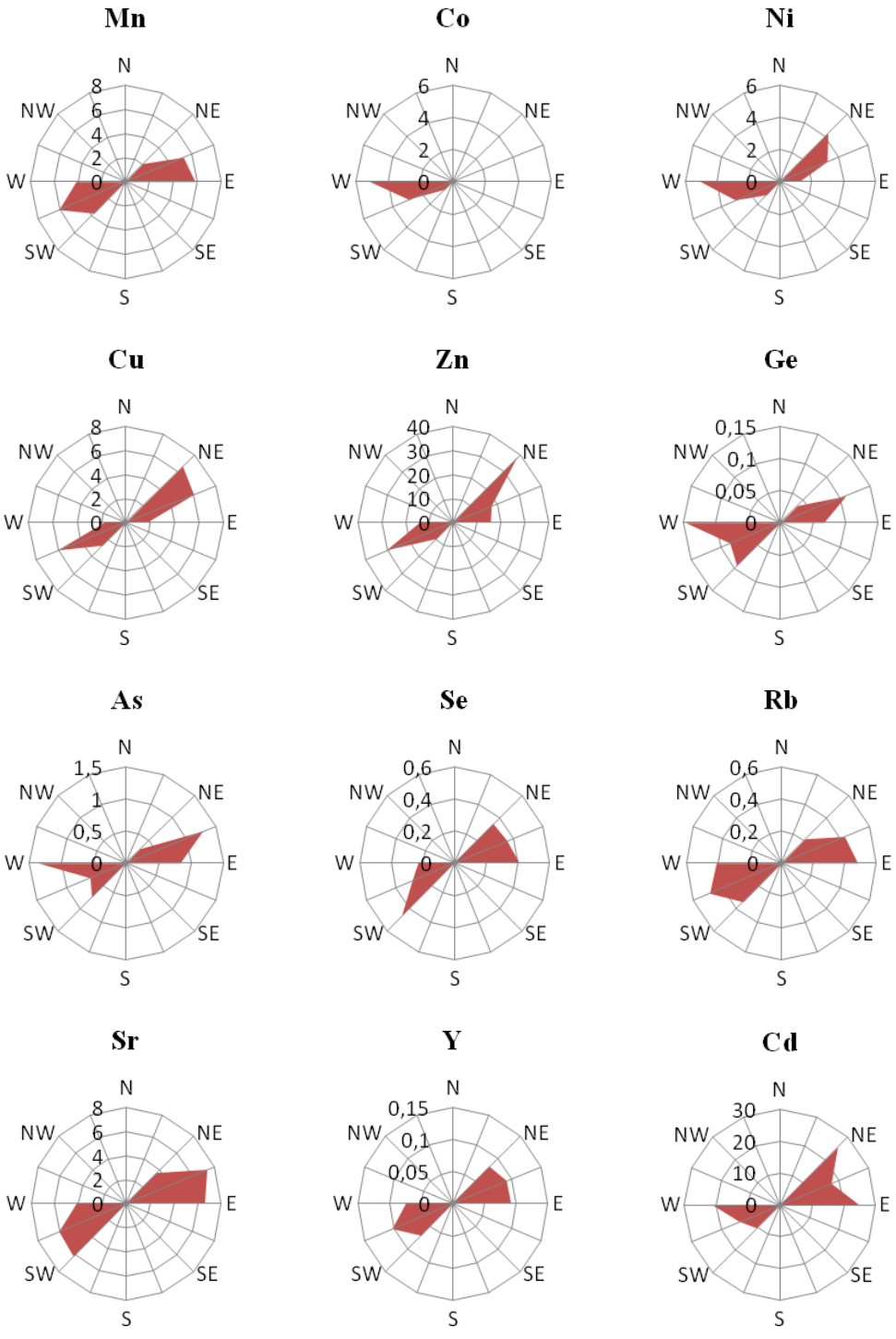


Figure 3.11 Annual pollution roses of $PM_{2.5-10}$ mode elements at the sampling site (ng m^{-3}) (continued)

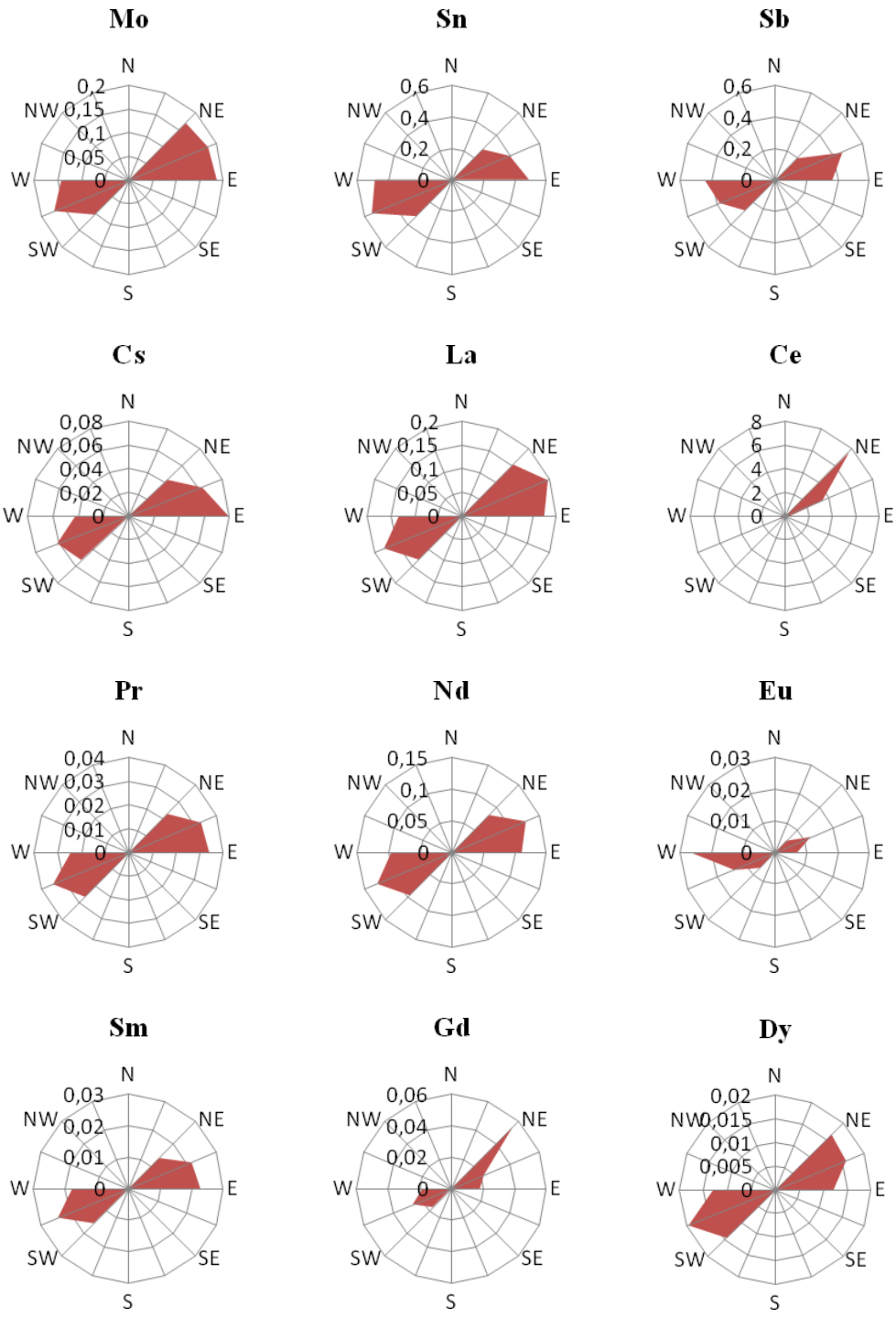


Figure 3.11 Annual pollution roses of $PM_{2.5-10}$ mode elements at the sampling site (ng m^{-3}) (continued)

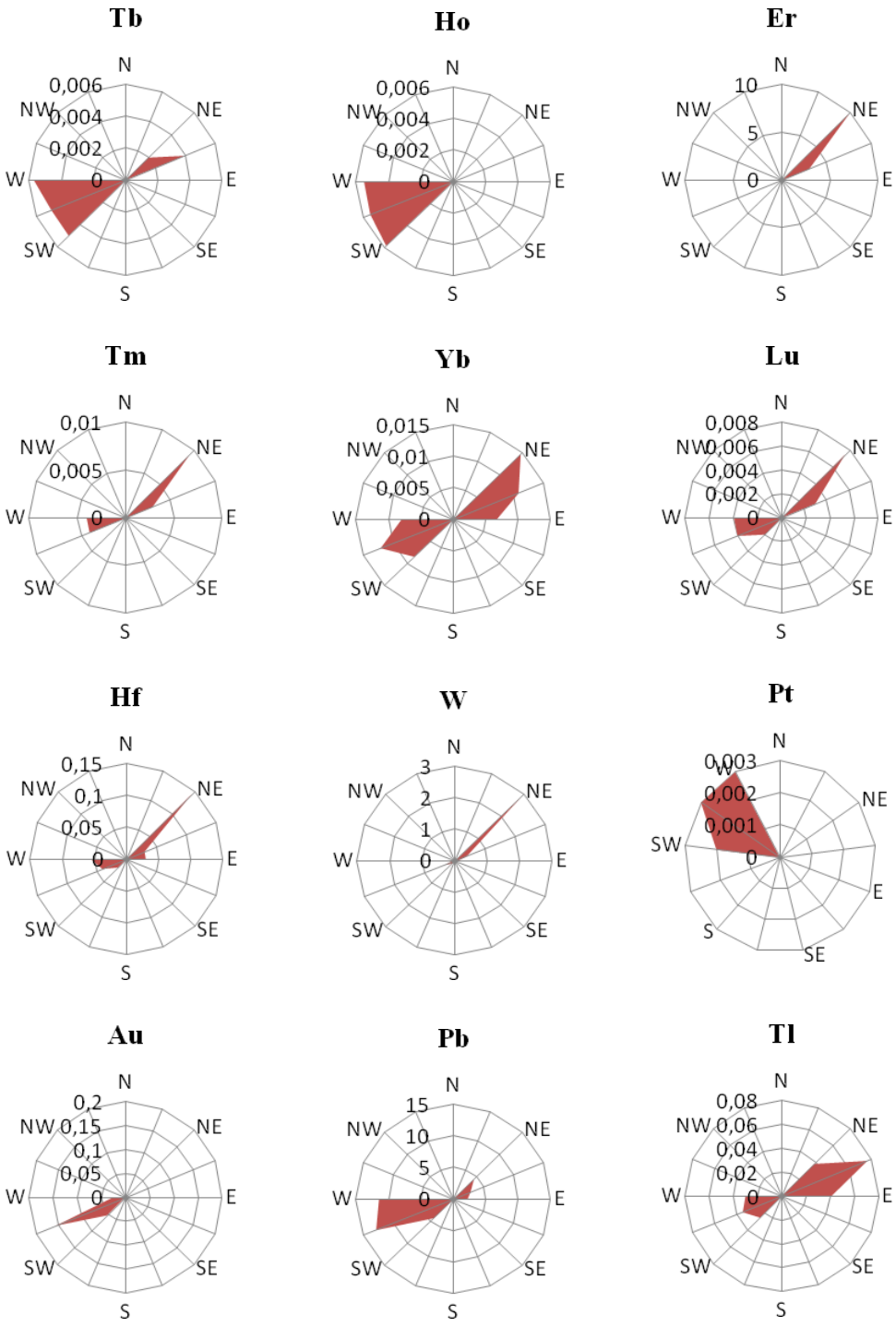


Figure 3.11 Annual pollution roses of $PM_{2.5\text{-}10}$ mode elements at the sampling site (ng m^{-3}) (continued)

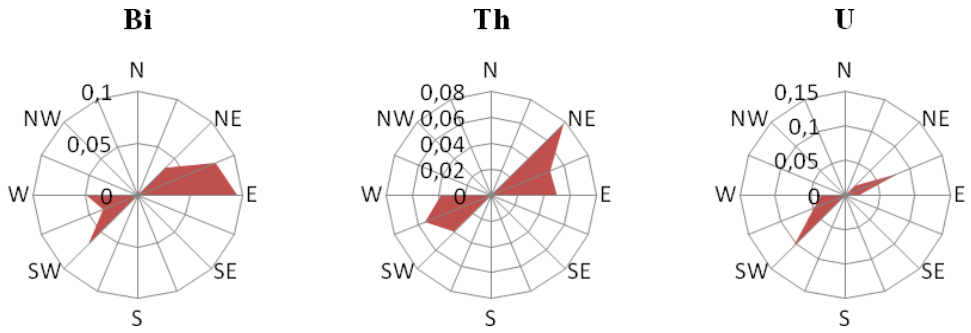


Figure 3.11 Annual pollution roses of $PM_{2.5-10}$ mode elements at the sampling site (ng m^{-3}) (continued)

3.2.3. Correlations between Variables

Binary correlations between parameters are one of the useful statistical tools used to estimate possible sources of pollutants, or the chemical processes that affect the chemical composition of aerosol at the receptor site. Although simple, this method gives fair amount of information on how the species co-vary in the data set. However, correlation analysis is a qualitative approach and cannot provide quantitative information on source contributions. Therefore, further analyses such as factor analysis are required to reveal source contributions.

Strong correlations between parameters in aerosol samples collected from urban regions indicate that these parameters have similar sources. Because particles are collected in a short time after they are emitted from sources. However, in rural areas aerosols are transported from long distances. During transport, pollutants mix well in the air mass and a good correlation between two parameters may indicate similar transport path as well as similar sources. Hence, correlations between parameters in aerosol samples collected from rural regions imply either similarities and differences in sources or physical and chemical processes during transport of these pollutants.

The correlation coefficient (*r*) between the concentrations of elements is calculated for both coarse and fine fractions by using Statgraphics XV.II software and given in Tables 3.10 and 3.11, respectively. Conventional correlation coefficients can not be a good indicator of relationship between parameters by itself, because relation also depends on number of data points included in the statistical test. In this section the term "correlation" is used only if the probability of chance correlation between parameters is less than 5% ($p<0.05$). For a better view, correlations between the values of ±0.25 were excluded from Table.

In fine fraction, soil elements except for Al and Fe, have strong correlations among them. Aluminum shows correlation with Lu, V and Zn, while iron have correlation with Be, Ge, Ho, Lu, Mn, Tb, and Yb. Strong correlation is also seen among As, Bi, Ge, and Lu ($r>0.50$). Bismuth is also correlated with Cs, Ge, Ho, K, Lu, Rb, Se, Tb, Tl. These elements (As, K, Se, Tl) generally originate in coal combustion and indicates the long range trasportation (As, Se). Most of the elements (Cd, Cs, Gd, Ho, Li, Lu, Nd, P, Pr, Sm, Sr, Tb, Th, Ti, Y and Yb) have strong correlations with soil originated elements and this indicates a local pollution source. Cobalt and lead show a strong correlation ($r=0.97$) as a result of motor vehicle emissions. Chromium is correlated with iron/steel work originated elements Cu ($r=0.30$), Lu ($r=0.37$), Mn ($r=0.35$), Mo ($r=0.61$), Ni ($r=0.32$) and Tb ($r=0.33$). Correlation among manganese, antropogenic elements and crustal elements is an expected since Mn is originated from both antropogenic and crustal sources. Correlation values are generally less than 0.50 except for Fe ($r=0.62$). Significant correlation of Sb with Se and As, is a sign of long range transportation. Tin just gives a poor correlations with Hf, K, Lu and Rb ($r<0.31$). Vanadium shows correlation with both antropogenic and crustal

elements. Zinc gives a correlation with crustal elements unexpectedly and this fact will be discussed in factor analysis section.

Correlation values in coarse fraction are greater than fine mode values (Table 3.10). All soil originated elements are related with each other except for aluminum. Aluminum is related with Co, Eu, Ge Pt and V. Arsenic have strong correlation with antropogenic elements Bi, Ge, Sb, Tl and V (0.54-0.76), while having poor correlation with Mo(r=0.36) and Ni (r=0.27). Gold is correlated with antropogenic elements like Bi, Cd, Se, Hf, Mo, P and W as a result of industrial applications. Coal burning indicator element Cd is related with Cs, Li, Pr, Se, Sr and Th. Elevated chromium correlation with lead (r=0.98) signs motor vehicle emissions. Chromium also shows correlations with crustal elements as the same with antropogenic elements Bi, Lu, Mo, Ni and W. Copper have significant correlation with Pt (r=0.64). Iron shows correlation with both crustal and some antropogenic elements such as Sb, Mn, As, Mo, Ni, Sn and V. Iron/steel work could be the possible source for this relation. Manganase correlation with both crustal and antropogenic elements could be associated with caol burning. Correlation of molybdenum with some antropogenic elements (As, Au, Bi, Cr, Fe, Hf, Ni, Tl, V and W) indicate metal-work and coal burning. Strong correlation of Ni with Cr (r=0.76), Ge (r=0.39) and W (r=0.69) could be originated from long range transportation. Lead is primarly correlated with Co, secondly with Al (r=0.34) and lastly some crustal elements (Na, Eu). Tin, Fe, Ge, Mn and Zn correlations could be arised from solder production.

Table 3.10 Correlation matrix among fine fractions of the variables (p<0.05)

	Al	As	Au	Be	Bi	Ca	Cd	Ce	Co	Cr	Cs	Cu	Dy	Er	Eu	Fe	Gd	Ge	Hf	Ho	K	La	Li	Lu	Mg	Mn	Mo	Na	Nd	Ni	P	Pb	Pr	Rb	Sb	Se	Sm	Sn	Sr	Tb	Th	Ti	Tl	U	V	W	Y	Yb	Zn
Al	1.00																																																
As		1.00																																															
Au			1.00																																													
Be				1.00																																												
Bi		0.54			1.00																																										
Ca				0.28		1.00																																										
Cd				0.36		0.66	1.00																																									
Ce				0.29		0.27	0.29	1.00																																								
Co									1.00																																						
Cr			0.40	0.26						1.00																																					
Cs		0.31		0.40	0.30	0.64	0.84	0.30			1.00																																				
Cu			0.39	0.32						0.30		1.00																																			
Dy				0.51		0.60	0.57	0.43			0.62		1.00																																		
Er			0.26					0.85						1.00																																	
Eu						0.29			0.58				0.30		1.00																																
Fe				0.44												1.00																														
Gd				0.55		0.63	0.67	0.57			0.66		0.92				1.00																													
Ge		0.53			0.41											0.70		1.00																												
Hf						0.51	0.42	0.34	0.44		0.40		0.41		0.52		0.42		1.00																											
Ho		0.42	0.45	0.70	0.35	0.75	0.71	0.75			0.72	0.39	0.95	0.32	0.30	0.51	0.89		0.46	1.00																								
K		0.46	0.30		0.37	0.25					0.41		0.46				0.38	0.30	0.30	0.34	1.00																							
La				0.37		0.50	0.46	0.50			0.48		0.63				0.70		0.27	0.68	0.37	1.00																						
Li				0.32		0.68	0.80	0.34	0.42		0.75		0.62		0.58		0.64		0.58	0.69	0.32	0.42	1.00																					
Lu	0.54	0.84	0.44	0.67	0.73	0.81	0.79	0.53	-0.33	0.37	0.83	0.38	0.83	0.25	0.37	0.44	0.92	0.65	0.45	0.97		0.86	0.85	1.00																			
Mg						0.58					0.45		0.30				0.41		0.47	0.45	0.34	0.34	0.31	0.33	1.00																			
Mn				0.40						0.35	0.27		0.40			0.62	0.36	0.48		0.51	0.39	0.41				1.00																		
Mo				0.25				0.60		0.61				0.65						0.53				0.37		0.42	1.00																	
Na						0.34		0.26	0.44				0.29		0.66				0.55	0.27	0.47		0.41		0.52			1.00																
Nd				0.51		0.67	0.71	0.45			0.72		0.93				0.95		0.44	0.92	0.42	0.68	0.70	0.85	0.42	0.35			1.00														
Ni										0.32														0.33		0.43	0.29			1.00														
P				0.45		0.63	0.63	0.35			0.70		0.80		0.32		0.79		0.43	0.90	0.36	0.58	0.69	0.76	0.35	0.35		0.35	0.84		1.00													
Pb									0.97						0.48				0.47					0.40	-0.31				0.40			1.00											
Pr				0.56		0.66	0.68	0.47			0.69		0.87				0.92		0.39	0.91	0.37	0.81	0.65	0.85	0.40	0.42			0.93		0.78		1.00										
Rb		0.33		0.32	0.37	0.28					0.55		0.56				0.47	0.27	0.32	0.48	0.84	0.43	0.29	0.34	0.31	0.54		0.35	0.51		0.50		0.46	1.00									
Sb		0.31																		0.35	0.32			0.43										0.33	1.00								
Se		0.29			0.35						0.49		0.27							0.33	0.47			0.53		0.37			0.27		0.28		0.26	0.62	0.25	1.00							
Sm				0.49		0.63	0.65	0.39			0.65		0.95		0.28		0.93		0.41	0.92	0.41	0.61	0.67	0.81	0.42	0.37			0.97		0.82		0.89	0.50		0.26	1.00					
Sn																			0.30		0.31			0.31										0.29				1.00				
Sr				0.37		0.74	0.97	0.31			0.84		0.61		0.26		0.70		0.45	0.75		0.48	0.82	0.83	0.29			0.75		0.66		0.71			0.69		1.00				
Tb		0.39	0.53	0.71	0.29	0.75	0.76	0.75		0.33	0.77	0.33	0.97			0.51	0.94		0.41	0.99	0.31	0.67	0.71	0.96	0.37	0.45	0.44		0.96		0.90		0.95	0.46	0.37	0.34	0.97		0.80	1.00			
Th				0.42		0.67	0.80	0.54			0.76		0.83		0.26		0.89		0.53	0.83	0.32	0.60	0.76	0.84	0.34			0.28	0.90		0.77		0.84	0.39			0.87		0.82	0.88	1.00		
Ti				0.52		0.56	0.54	0.43			0.65		0.82				0.82		0.37	0.88	0.37	0.59	0.61	0.79	0.29	0.43		0.26	0.85		0.95		0.80	0.54		0.30	0.82		0.58	0.89	0.77	1.00	
Tl		0.52			0.67						0.35							0.48			0.51					0.38								0.59	0.29	0.52						1.00	
U						0.31														0.37				0.29						0.34								0.31	0.44	0.28	0.25		1.00
V	0.44	0.25		0.25		0.25					0.34		0.47				0.43			0.48	0.49	0.48	0.32	0.48		0.37	0.28	0.29	0.44		0.51		0.42	0.53		0.38	0.43			0.42	0.34	0.49		
W								0.70						0.84														0.55														
Y				0.49		0.62	0.54	0.47			0.62		0.95		0.27		0.92		0.42	0.97	0.48	0.63	0.61	0.86	0.48	0.45		0.30	0.93		0.82		0.86	0.60		0.32	0.95		0.58	0.97	0.84	0.86		
Yb				0.50		0.61	0.63	0.49			0.63		0.92		0.37	0.38	0.88		0.48	0.92	0.40	0.60	0.68	0.91	0.40	0.40	0.27	0.34	0.88		0.79		0.82	0.47			0.89		0.67	0.94	0.86	0.80		
Zn	0.33					0.54					0.30		0.25							0.25	0.28		0.33	0.50	0.26			0.31		0.39									0.27		0.33		0.38	0.29		0.29		1.00

Table 3.11 Correlation matrix among coarse fraction of the variables (p<0.05)

	Al	As	Au	Be	Bi	Ca	Cd	Ce	Co	Cr	Cs	Cu	Dy	Er	Eu	Fe	Gd	Ge	Hf	Ho	K	La	Li	Lu	Mg	Mn	Mo	Na	Nd	Ni	P	Pb	Pr	Pt	Rb	Sb	Se	Sm	Sn	Sr	Tb	Th	Ti	Tl	Tm	U	V	W	Y	Yb	Zn
Al	1.00																																																		
As		1.00																																																	
Au			1.00																																															
Be				1.00																																														
Bi		0.58	0.26	0.28	1.00																																												
Ca		0.30		0.47	0.28	1.00																																												
Cd			0.60			0.42	1.00																																												
Ce			-0.32					1.00																																										
Co	0.31		-0.26						1.00																																									
Cr					0.33			0.47		1.00																																									
Cs		0.33		0.52	0.44	0.77	0.48				1.00																																							
Cu			-0.26									1.00																																						
Dy		0.27		0.57		0.71					0.68		1.00																																					
Er								0.99		0.46				1.00																																					
Eu	0.33		-0.25			0.36			0.57				0.30		1.00																																				
Fe		0.28		0.46	0.27	0.51		0.26		0.25	0.55		0.70			1.00																																		
Gd		0.26	-0.26	0.48		0.58		0.64		0.34	0.58		0.86	0.54	0.26	0.66	1.00																																
Ge	0.44	0.76	-0.33	0.32	0.53	0.42				0.29	0.44		0.45		0.27	0.50	0.43	1.00																																
Hf			0.40		0.31			0.66		0.33				0.64	0.35		0.50		1.00																																
Ho		0.39		0.70	0.37	0.56				0.32	0.53	0.28	0.87		0.30	0.54	0.73	0.53	0.26	1.00																														
K		0.40	-0.32	0.44	0.25	0.54					0.49		0.67		0.36	0.53	0.60	0.56	0.24	0.60	1.00																														
La		0.31	-0.26	0.49		0.61					0.62		0.82			0.62	0.79	0.41		0.70	0.55	1.00																													
Li				0.26		0.50	0.35	0.28	0.66		0.50		0.47		0.61	0.33	0.52	0.29	0.41	0.40	0.37	0.45	1.00																											
Lu				0.49		0.35		0.64		0.34	0.40		0.62	0.58		0.54	0.90	0.26	0.64	0.65	0.51	0.66	0.68	1.00																										
Mg		0.34	-0.27	0.40		0.64					0.44		0.68		0.41	0.50	0.57	0.47		0.67	0.71	0.55	0.39	0.38	1.00																									
Mn		0.33		0.58	0.34	0.67					0.65		0.85		0.30	0.80	0.71	0.58		0.80	0.71	0.65	0.37	0.42	0.63	1.00																							
Mo		0.36	0.28		0.46			0.44		0.59				0.42		0.35	0.34	0.36	0.50	0.29	0.29		0.29	0.45		0.29	1.00																						
Na			-0.37			0.34		0.33	0.38	0.24			0.29	0.31	0.62		0.38	0.43	0.47	0.27	0.63		0.41	0.39	0.51	0.36	0.35	1.00																				
Nd		0.27		0.58		0.71					0.71		0.96		0.28	0.70	0.85	0.42		0.81	0.64	0.91	0.49	0.63	0.66	0.80			1.00																		
Ni		0.27	-0.31		0.33			0.47		0.76				0.46		0.29	0.26	0.35	0.36								0.62	0.33		1.00																		
P			-0.31	0.46		0.70		0.34		0.28	0.60		0.81	0.24	0.39	0.61	0.78	0.49	0.38	0.77	0.61	0.69	0.51	0.73	0.62	0.78	0.26	0.52	0.78		1.00																	
Pb	0.34								0.98						0.56			0.39										0.39				1.00																
Pr		0.27	-0.27	0.57		0.71	0.28				0.71		0.93		0.28	0.68	0.84	0.39		0.79	0.61	0.93	0.50	0.66	0.63	0.76			0.98		0.76		1.00													
Pt	0.62		0.34	0.51	0.39			0.47			0.53	0.64	0.44	0.48		0.50	0.44	-0.53		0.35	0.59	0.46		0.32		0.62			0.50	-0.33	0.49		0.47	1.00													
Rb		0.33	-0.27	0.58	0.26	0.63					0.65		0.87		0.28	0.67	0.71	0.52		0.79	0.83	0.68	0.34	0.46	0.71	0.90		0.41	0.83		0.73		0.79	0.58	1.00											
Sb		0.54	-0.26	0.48	0.42	0.58					0.50		0.53			0.46	0.41	0.64		0.55	0.56	0.42			0.50	0.64		0.25	0.50		0.46		0.47	0.30	0.64	1.00										
Se			0.75		0.27	0.58	0.68	0.28			0.59		0.29				0.36					0.37	0.46	0.44					0.40		0.31		0.44	0.29		1.00										
Sm		0.26	-0.26	0.57		0.69					0.67		0.96		0.30	0.69	0.83	0.43		0.84	0.67	0.85	0.48	0.60	0.67	0.81		0.26	0.98		0.78		0.95	0.44	0.86	0.50	0.33	1.00							
Sn																0.25		0.36								0.25												1.00							
Sr				0.26		0.73	0.69				0.73		0.45			0.29	0.40				0.25	0.53	0.52	0.30	0.36	0.25			0.54		0.43		0.58	-0.28	0.27		0.78	0.48		1.00						
Tb		0.41		0.74	0.30	0.45				0.29	0.45		0.85			0.45	0.60	0.49		0.95	0.57	0.70		0.51	0.62	0.71	0.25		0.80		0.69		0.77	0.43	0.76	0.55		0.84			1.00				
Th		0.28		0.47	0.33	0.64	0.41	0.54		0.43	0.72		0.77	0.45		0.64	0.88	0.39	0.46	0.64	0.50	0.75	0.59	0.89	0.47	0.64	0.40	0.30	0.81	0.33	0.73		0.81	0.42	0.62	0.35	0.60	0.76		0.61	0.53	1.00			
Ti		0.26		0.57	0.25	0.76		0.32		0.28	0.69		0.87		0.31	0.69	0.83	0.47	0.31	0.75	0.57	0.78	0.53	0.79	0.60	0.80	0.24	0.37	0.88		0.94		0.86	0.47	0.75	0.47	0.45	0.86		0.53	0.67	0.82	1.00		
Tl		0.57		0.28	0.61	0.36					0.50		0.27			0.29		0.46		0.34	0.32			0.26		0.39	0.30		0.24						0.35	0.50		0.24			0.25	0.27	0.24	1.00		
Tm				0.40		0.27		0.70		0.26	0.34	0.25	0.58	0.64		0.48	0.94		0.66	0.57	0.45	0.61	0.64	0.92	0.29	0.34	0.35	0.32	0.57	0.25	0.65		0.60	0.71	0.38		0.33	0.54		0.26	0.35	0.81	0.72		1.00	
U																														0.28															1.00	
V	0.66	0.42		0.33	0.30	0.46		0.29			0.44		0.79		0.34	0.58	0.74	0.72	0.33	0.72	0.58	0.67	0.35	0.59	0.47	0.68	0.35	0.38	0.75	0.25	0.67		0.71	0.37	0.61	0.51		0.76		0.70	0.50	0.65	0.31	0.56	1.00	
W			0.53		0.31			0.74		0.66				0.74		0.39		0.57						0.41			0.56	0.25		0.69			-0.39								0.41		0.41		1.00	
Y		0.29	-0.24	0.59		0.75		0.28			0.72		0.98		0.32	0.73	0.90	0.48	0.29	0.84	0.68	0.86	0.52	0.74	0.68	0.85		0.32	0.97		0.84		0.95	0.48	0.87	0.54	0.37	0.97		0.51	0.80	0.84	0.91	0.29	0.69		0.80		1.00	
Yb		0.28	-0.25	0.56	0.27	0.65		0.46		0.32	0.65		0.90	0.37	0.32	0.70	0.93	0.47	0.43	0.81	0.63	0.77	0.54	0.91	0.60	0.79	0.30	0.37	0.88		0.79		0.86	0.33	0.78	0.48	0.38	0.87		0.44	0.72	0.87	0.86	0.27	0.90		0.76	0.30	0.93	1.00	
Zn																		0.33														0.33						0.67											1.00

3.2.4. Factor Analysis

Principal component of factor analysis provides preliminary information about the possible sources that may influence a given receptor site. In principle, it actually distinguishes groups of elements which concentrations fluctuate together from one sample to another and separates these elements into so called 'factors' (Karakaş, 1999). Ideally, each extracted factor represents a source affecting the samples. Although there are no well-defined rules on the number of factors to be retained, usually either factors that are meaningful or factors with eigenvalues larger than one are retained. In theory, irrelevant factors have zero eigenvalues and eigenvalues less than one indicate the factor contribute less than a single variable. In this study, factors which have eigenvalues larger than unity have been retained.

Although values below or above a DL are "missing," data are not missing at random in the usual sense, because their absence reflects levels of exposure. This type of missing data is called "nonignorable missing," and the simple exclusion of such "interval-measured" data can bias results (Little and Rubin 1987; Schafer 1997). Concentration values below measurement detection limits are a common problem which complicates statistical analysis of measured species in environmental samples. Common methods for handling values below detection limit, one half of detection limit, detection limit or multiplication of detection limit with a random number between zero and one are known to produce biased estimates for means and variance and also lack statistical justification (Helsel 1990; Hornung and Reed 1990).

In this study, for the missing values in the data set, detection limit values were used. It was observed that treating missing values with detection limit values did not alter the results obtained from the factor analysis when the number of missing values was

less than 20% of the whole sample size. In the factor analysis, we included the elements having percent observations greater than 80% in samples. Consequently, the substitution of missing values with detection limits can be used without altering the factor analysis results statistically.

Factor analysis has been performed using the Statgraphics Centurion XV.II Software. In factor analysis, the first step in the derivation of source impacts is to calculate factor scores for each sample. These factor scores are correlated with their respective pollution sources impacting the site with each having a mean of zero. High factor scores indicates the samples impacted by the source more than the average and negative factor scores indicates the samples impacted by the source less than the average. In literature, it is pointed out that if a sample has factor score greater than 6 at least in one of the factor, it is called outlier and should be discarded from the analysis. Totally 42 samples in $PM_{2.5}$ and 47 samples in $PM_{2.5-10}$ had been deleted from the data set. As a result total 236 samples with 31 elements for fine fraction and 220 samples with 31 elements for coarse fraction were used in the analysis.

The results of varimax-rotated analysis is shown for $PM_{2.5}$ and $PM_{2.5-10}$ fractions respectively in Table 3.12 and Table 3.13. Only factor loadings larger than 0.25 were included in the table, because loadings smaller than 0.25 were considered insignificant. Six identifiable factors account with 74% of the total variance in fine fraction data set while five identifiable factors account with 74% total variance in coarse fraction data.

Table 3.12 Varimax rotated factor loadings and probable sources for fine fraction elements

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Communality
Na				0.54	0.43	0.41	0.70
K	0.34	0.70				0.37	0.79
Mg	0.31				0.43	0.63	0.71
P	0.77						0.72
Ca	0.33				0.72		0.70
Ti	0.84						0.79
V	0.42	0.38					0.46
Cr			0.83				0.72
Mn	0.54	0.39	0.55				0.76
Fe	0.53		0.60				0.70
Co				0.96			0.93
Ni			0.62				0.43
As		0.72				0.28	0.65
Se		0.67					0.63
Rb	0.49	0.72					0.82
Sr					0.82		0.73
Y	0.93						0.91
Mo		0.26	0.75				0.68
Sb		0.69					0.63
Cs	0.37	0.65					0.77
La	0.64		0.38				0.58
Ce	0.64						0.51
Pr	0.88						0.85
Nd	0.94						0.92
Sm	0.93						0.89
Gd	0.93						0.90
Dy	0.91						0.89
Pb				0.95			0.91
Bi		0.76					0.62
Tl		0.88					0.82
Th	0.81						0.71
% variance	**37.59**	**12.55**	**8.25**	**6.37**	**5.37**	**3.58**	**73.71**
probable source	soil	coal and wood burning	iron-steel works	road dust	sea-salt	regional background	

The first factor was identified as soil factor, because it included high loadings of crustal elements such as K, Mg, Ca, Ti, V, Mn, Fe, Rb, Y, Cs, La, Ce, Pr, Nd, Sm, Gd, Dy and Th. Also P element present in this factor as a result of agricultural activities around the receptor site. Phosphorus, K, Ca and Mg are typical marker macronutrients of fertilizer. The macronutrients are consumed in larger quantities and are present in plant tissue in quantities from 0.15% to 6.0% on a dry matter (0% moisture) basis (Mills and Jones, 1996). The soil factor accounts for a 37.59 % of the system variance due to inclusion of large number of crustal elements in the factor anaysis and high loadings of these elements in the factor.

Factor two has high loadings of K, As, Se, Rb, Bi, Tl and weak loadings V, Mn, and Cs. This factor is identified as coal and wood burning factor owing to presence of combustion tracers. Arsenic and Se are marker elements for coal combustion and K is amarker element for wood burning. Data from Nriagu and Pacyna (1988) indicate that the coal combustion also may be responsible for Sb and Tl emissions. Besides that fly ash of coal contains trace amounst of Mn and Bi (Huang et al., 2004). However, the factor also includes soil originated elements. Backtrajectories of selected high factor scores (green lines show positive scores and red lines show negative factor scores) are depicted in Figure 3.12. Trajectories corresponding to high scores, with a few exceptions, originate from NE and NNE sectors. These sectors include majority of high heating process emission area in the city center of Bolu.

The third factor is higly loaded with Cr, Mn, Fe, Ni, Mo and moderately loaded in La. Antropogenic elements such as Cr, Ni, Mn, Fe and Mo are released from iron-steel works (Dragovic and Mihailovic, 2009). The backtrajectories corresponding to the highest factor scores of Factor 3 are given in Figure 3.13. The backtrajectories of

the highest factor scores contributing this factor derive usually from W and NNE sectors. Air masses coming from Europe or Russia convey the pollution of Karabük. Negative scored air masses sweep in the receptor site from Anatolia. Oil combustion product such as La is also identified under this factor.

Factor four has high loadings of Pb, Co and weak loading of Na. This factor is idenfied as road dust factor, because automobile exhaust elements Pb, Co (Mouli et al., 2006) with crustal element Na (Nagpal, 2004). Sodium has high factor loading (0.54) in this factor as a result of salted road in long snowy winters. The backtrajectory depiction of Factor 4 for 500 m is given in Figure 3.14 and it originates from NNE sector which includes the heavy traffic of D-100 and E-80 highways.

The fifth factor is loaded in Ca, Na, Mg and Sr with 5.37 % variance. This factor is clearly a marine factor with high factor loading of Sr (0.82), Ca (0.72), Mg (0.43) and Na (0.43). Sodium, Ca and Mg are very well-known tracers of sea salt. Strontium is also given under sea salt factor in recent literature studies (Lowenthal and Kumar, 2006; Hsu et al., 2010). The mean strontium content of ocean water is 8 mg L^{-1} (Angino et al., 1966). At a concentration between 82 and 90 µmol L^{-1} of strontium the concentration is considerable lower than the calcium concentration which is normally between 9.6 and 11.6 mmol L^{-1} (Sun et al., 2005). The backtrajectories of the highest scores of Factor 5 are given in Figure 3.15. From the top view, the trajectories arriving to the station site mainly approaches from Black Sea and Aegean Sea however negative scored air masses reaches from European lands.

Different anthropogenic and natural species are enriched in factor six which implies regional background. The combination of Na, K, Mg and As in this factor confirm this. This factor explains 0.28 of the % variance in As concentrations in the data set and it is clear that it is an anthropogenic factor which is originated from coal combustion. Also sea affect is seen clearly in this sector with factor loadings of Na, K and Mg. Generally, the air masses come from all around Black Sea. The backtrajectory depiction of Factor 6 for 1500 m is given in Figure 3.16.

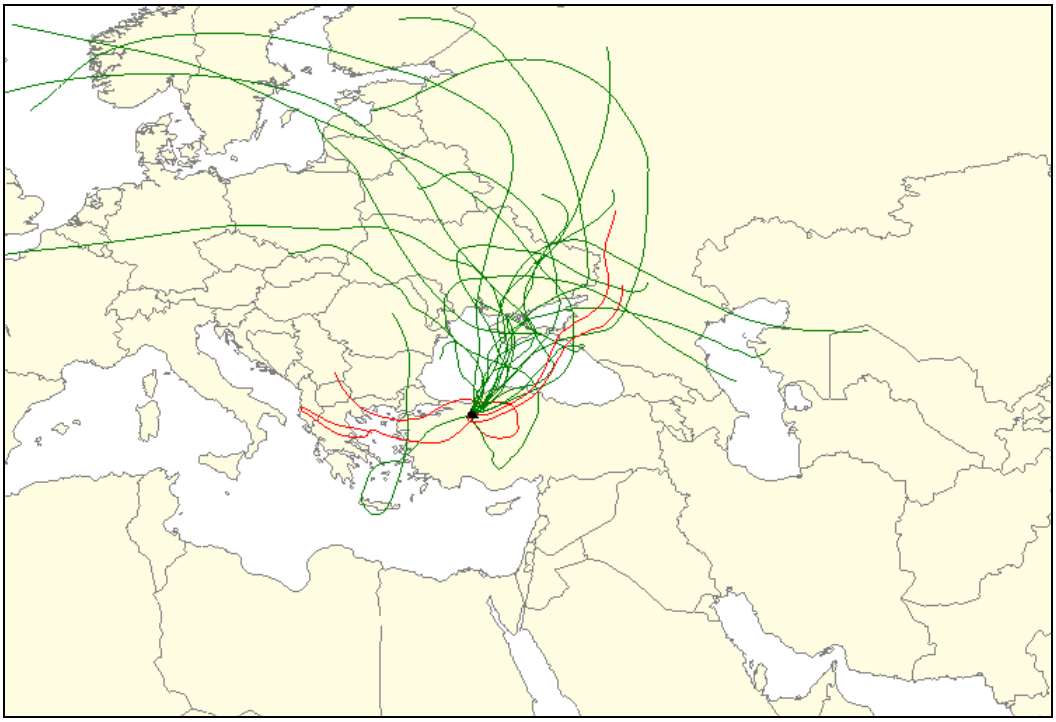


Figure 3.12 Backtrajectories corresponding to the highest factor scores of $PM_{2.5}$ Factor 2 (500 m)

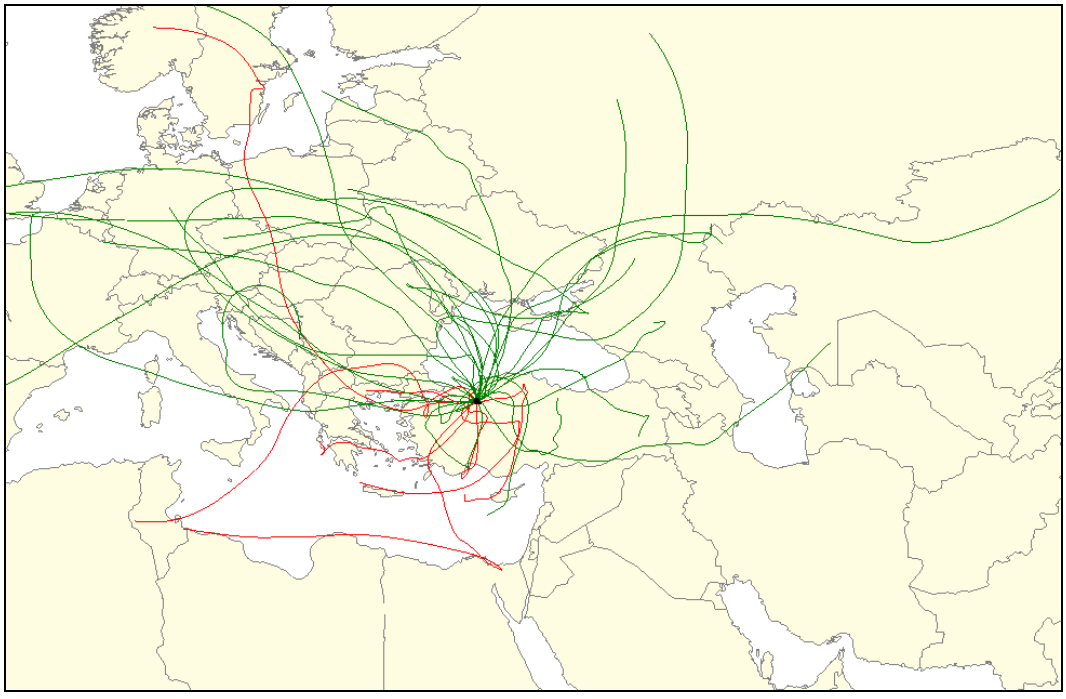


Figure 3.13 Backtrajectories corresponding to the highest factor scores of $PM_{2.5}$ Factor 3

(1500 m)

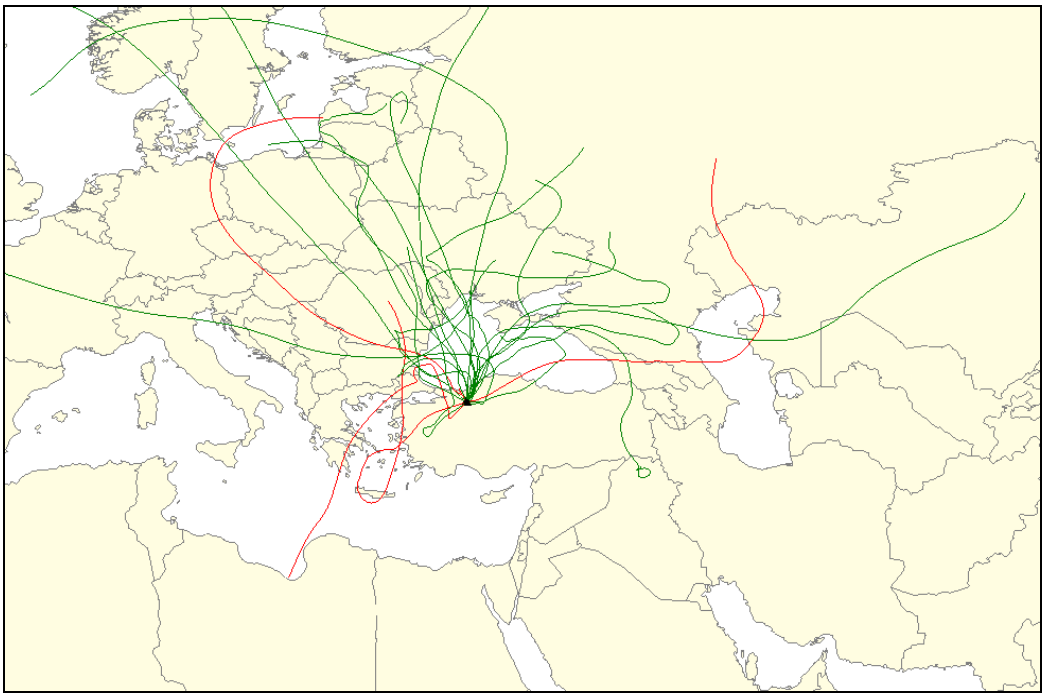


Figure 3.14 Backtrajectories corresponding to the highest factor scores of $PM_{2.5}$ Factor 4 (500 m)

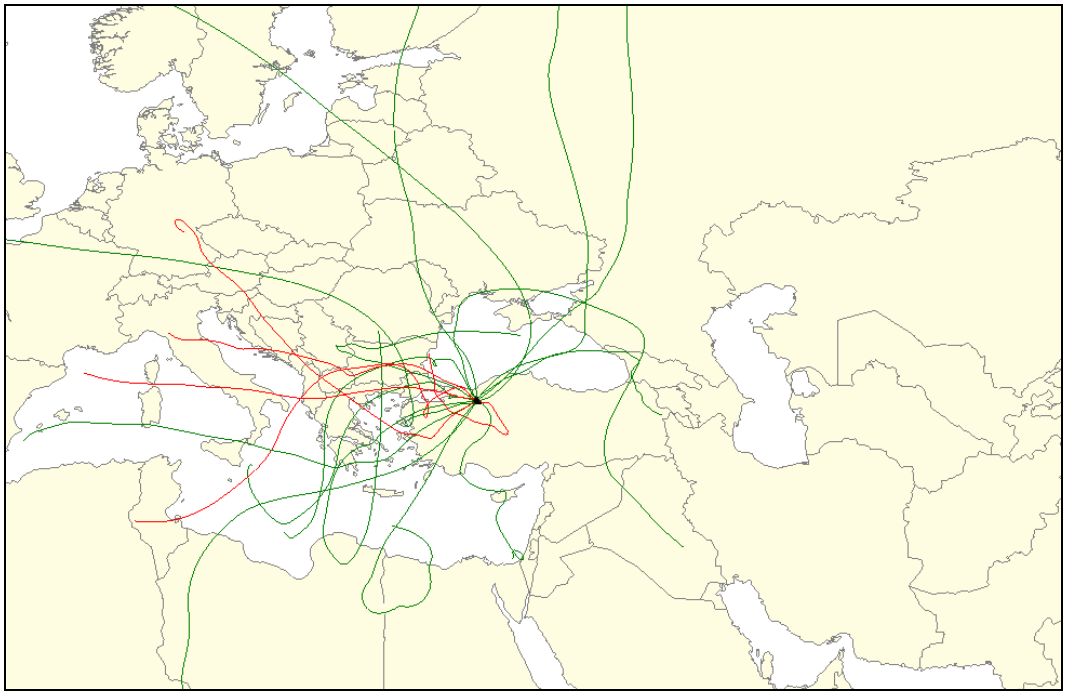


Figure 3.15 Backtrajectories corresponding to the highest factor scores of $PM_{2.5}$ Factor 5

(1500 m)

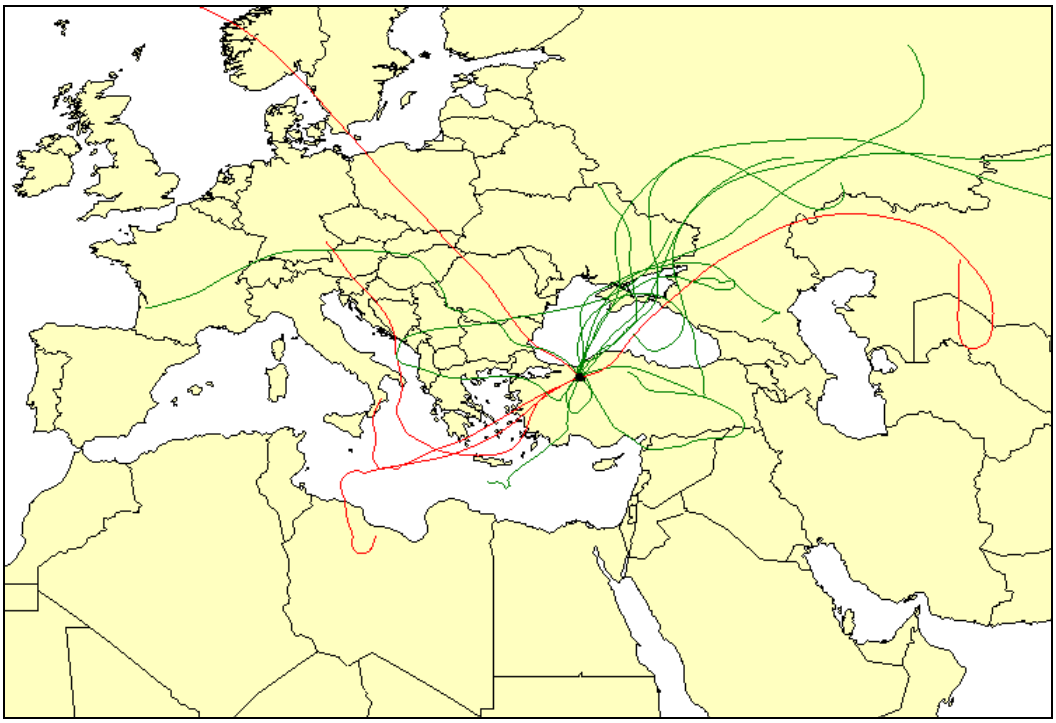


Figure 3.16 Backtrajectories corresponding to the highest factor scores of $PM_{2.5}$ Factor 6

(1500 m)

The first factor in coarse mode was idenfied as soil factor, since all the crustal elements and REE appeared in this factor. As seen in Table 3.13, factor one has high factor loading of P, Ti, Mn, Rb, Y, Yb, Ce, Pr, Nd, Sm, Gd, Dy, Th and modarate factor loadings of Ca, V, Fe, Cs and La. Potassium, Mg, Cr, Sr and Sb also have weak factor loadings in this factor. Fertilizer traces are also seen in this group as fine mode soil factor. The soil factor accounts for a 47.1% of the system variance which is the highest percent variance in this analysis.

Factor two contains coal combustion marker elements such as As, Sb, Tl, Mn and Bi as mentioned before. Besides that, this sector includes fuel oil burning tracers V, Mo and some crustal elements such as Ca, Rb and Cs with weak factor loadings. Unlike fine fraction, coarse fraction do not include biomass burning tracer K in coal burning factor. The top view backtrajectories corresponding to the highest factor scores are given in Figure 3.17. The view of this trajectory reminds the $PM_{2.5}$ Factor 2 (coal and wood burning) except SW sector. Heating center of university in the SW sector may have affected the receptor site.

Road dust factor for coarse fraction includes Na, K, Mg, V, Co and Pb same as fine fraction with close factor loading values. Factor three accounts for 6.99% of the total varince in coarse mode while fine mode accounts for 6.37% of the variance. The backtrajectories of the highest scores of Factor 3 are given in Figure 3.18. Unlike $PM_{2.5}$ road dust factor, some trajectory patterns are seen from SW sector. Coarse fraction road dust may have originated from the campus traffic as well as from the highways.

Factor four explained only 5.03% of the total variance. This factor is identified as sea salt factor with high loadings of Sr and weak loadings of Na, Mg, Ca, Cs, La and Th which can be emitted from the Black Sea. However the factor also includes soil originated elements. The backtrajectory depiction of Factor 4 for 1500 m is given in Figure 3.19 and it is similar to fine fraction sea salt factor trajectories.

The last factor, factor five, contained just Ni element with high loading and Na, K, Mg, V, Cr, As and Mo with weak loadings. The presence of antropogenic elements with sea salt elements indicates that this factor is caused by long range trasport of pollutants to our site. Because, this factor do not includes crustal or REE except for sea originated Na, K, Mg. That's why, there is no local pollution trace in this factor. The backtrajectories of the highest scores of Factor 5 are given in Figure 3.20.

Table 3.13 Varimax rotated factor loadings and probable sources for coarse fraction elements

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Communality
Na			0.73	0.27	0.39	0.77
K	0.38		0.51		0.41	0.66
Mg	0.38		0.30	0.27	0.48	0.57
P	0.84					0.77
Ca	0.65	0.32		0.42		0.74
Ti	0.91					0.86
V	0.55	0.52	0.27		0.26	0.73
Cr	0.29				0.43	0.38
Mn	0.86	0.25				0.87
Fe	0.62					0.50
Co			0.88			0.79
Ni					0.81	0.67
As		0.71			0.30	0.64
Rb	0.81	0.25				0.79
Sr	0.36			0.81		0.81
Y	0.97					0.96
Mo		0.46			0.27	0.44
Sb	0.39	0.58				0.55
Cs	0.57	0.32		0.52		0.72
La	0.78			0.29		0.71
Ce	0.84					0.77
Pr	0.92					0.89
Nd	0.97					0.96
Sm	0.93					0.90
Gd	0.94					0.91
Dy	0.94					0.90
Yb	0.88					0.80
Pb			0.89			0.83
Bi		0.74				0.56
Tl		0.72				0.58
Th	0.86			0.33		0.88
% variance	47.12	10.33	6.99	5.03	4.36	73.83
probable source	soil	coal burning	road dust	sea-salt	long range transportation	

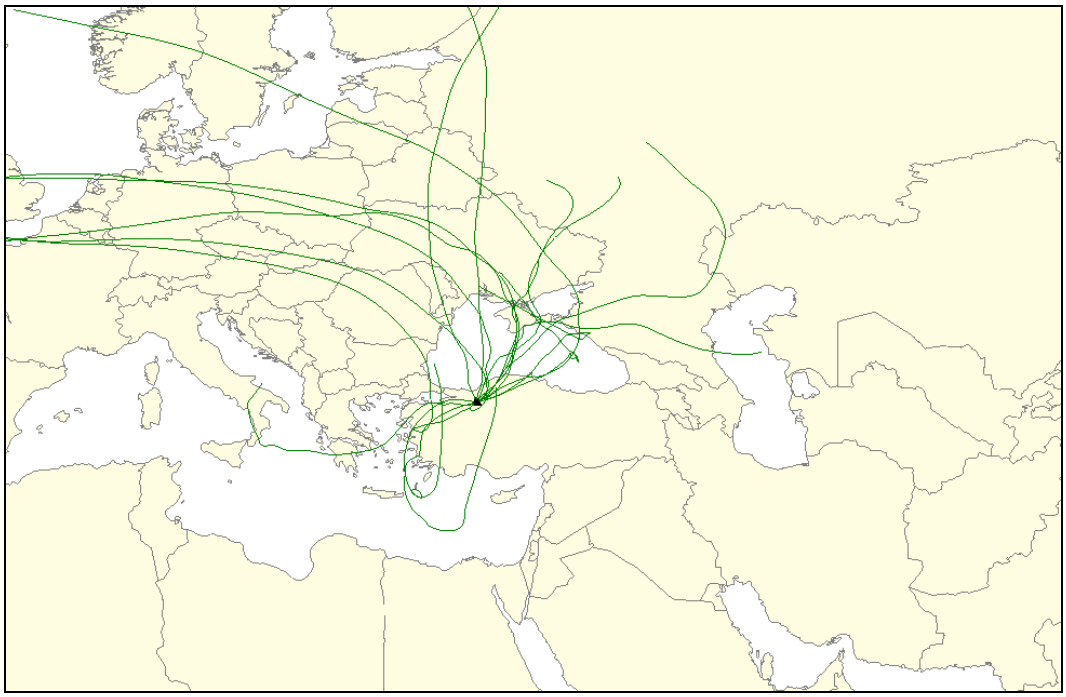


Figure 3.17 Backtrajectories corresponding to the highest factor scores of $PM_{2.5\text{-}10}$ Factor 2

(500 m)

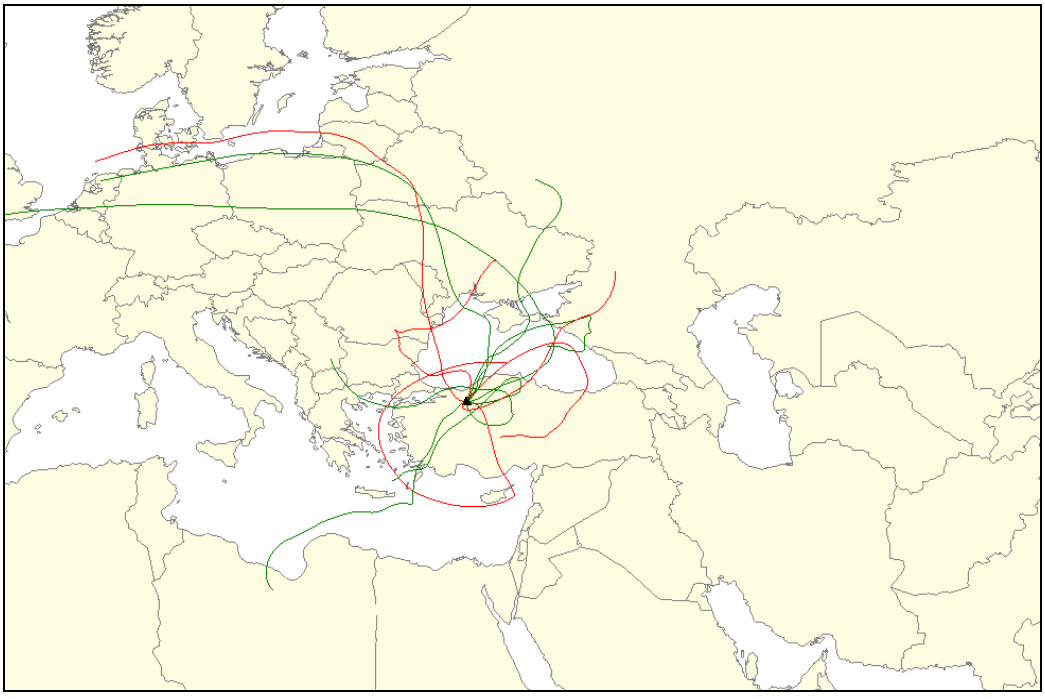


Figure 3.18 Backtrajectories corresponding to the highest factor scores of $PM_{2.5\text{-}10}$ Factor 3

(500 m)

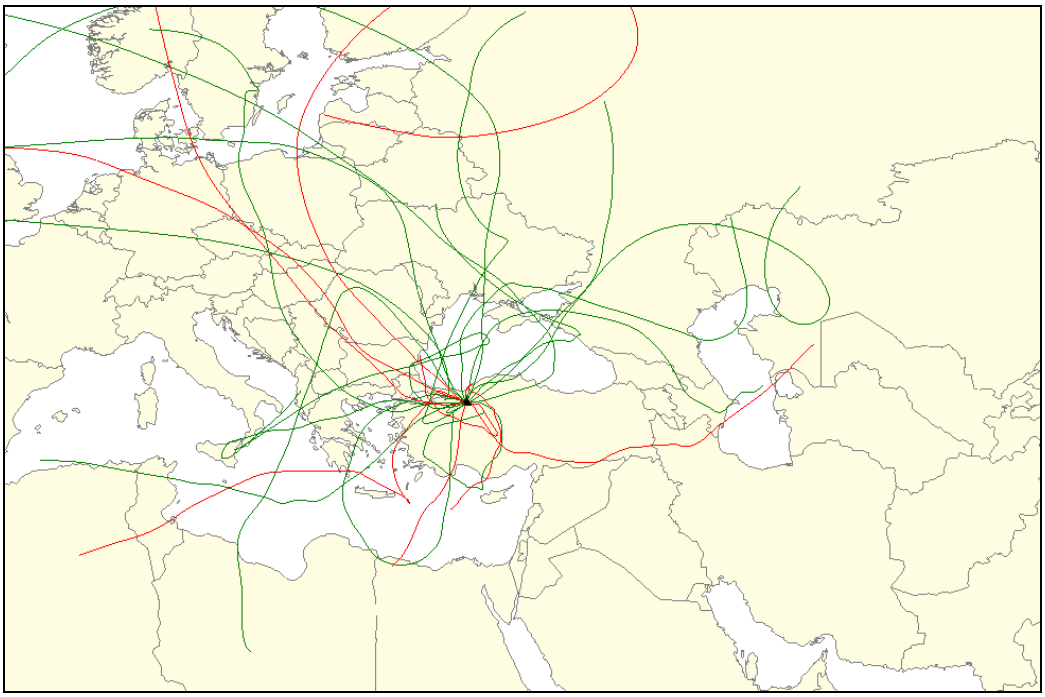


Figure 3.19 Backtrajectories corresponding to the highest factor scores of $PM_{2.5\text{-}10}$ Factor 4

(1500 m)

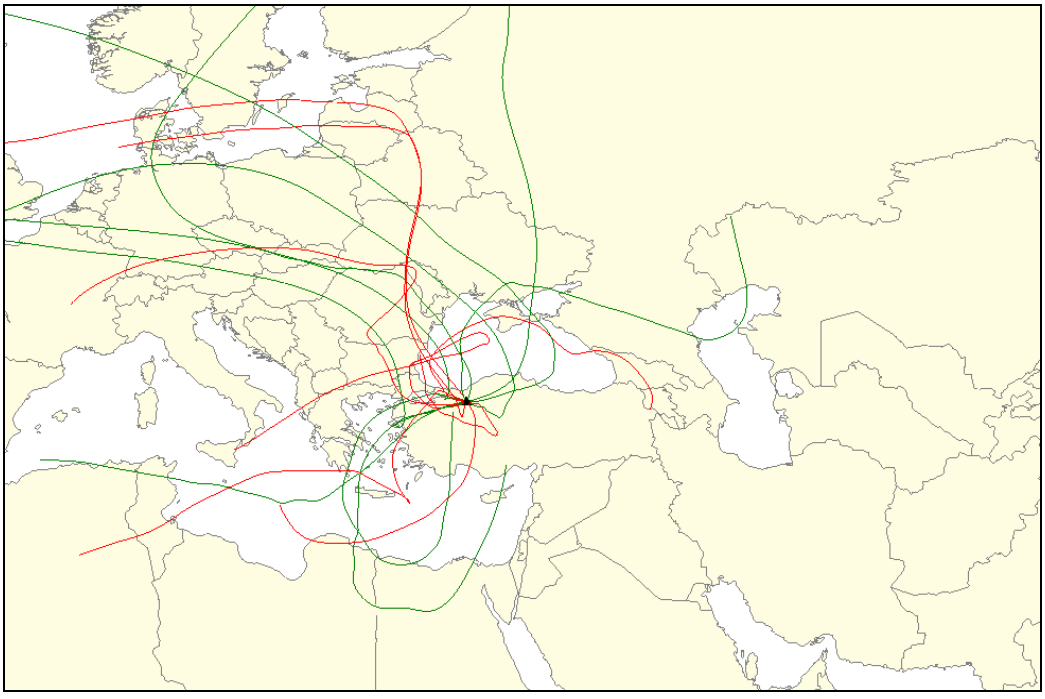


Figure 3.20 Backtrajectories corresponding to the highest factor scores of $PM_{2.5\text{-}10}$ Factor 5

(1500 m)

4. CONCLUSION

Daily fine and coarse aerosol samples were collected at the Bolu station which is a semi-rural sampling site located in the western Black Sea Region of Turkey between February 2011 and February 2012.

The selected samples were analyzed by ICP-MS for a total of 51 elements. Concentrations of Al and Ca in fine and coarse fraction are the highest among the elements, whereas concentration of Tb, Ho and Tm in fine mode and Pt in coarse mode are the lowest ones. Although the sampling site is not under direct influence of local sources, total and fine particulate mass concentrations are at comparable levels with urban areas. As a result of calculation of coarse-to-fine concentration ratios, the crustal elements are mostly found in the coarse fraction as expected. Cadmium and S dominate in the coarse fraction. On the other hand, elements, which are known to have mixed sources, have comparable concentrations in both fractions.

Almost all measured variables follow a log-normal distribution. When the dynamics of atmosphere are considered, these have shown that there would be more than one possible pollution source for each element.

In order to evaluate the level of pollution at Bolu, measured concentrations of the elements in this study were compared with those obtained in previous studies performed at various sites of the world. Concentrations of the crustal elements except for REE reported in the Bolu station are generally higher than those reported in the stations located outside Turkey. Chromium concentration in fine mode and Cd concentrationin coarse mode in the Bolu station are higher than all the other sites.

Consequently, based on the results obtained from a few sampling stations, the general feature of the country can not be clearified; levels and also compositions of the elements are then specific to the sampling location.

In order to discuss features of long range transport, no or limited transport of pollutants from city center and industrial area should be demonstrated. For this reason, by means of surface wind flow pattern data at the Bolu station were investigated and annual pollution roses were examined. As a result, it is observed that concentrations of the crustal species dominate on WSW direction, while concentrations of antropogenic species are higher in the NNE, NE and ENE sectors. Elements, which are known to have mixed sources, are contributed from the WSW, NNE and ENE directions.

In the Bolu station, the most frequent annual flows are from WSW sector and also there is relatively less frequent flow from the SW, S and ENE sectors. Even though the frequency of air mass transport from the NNE and ENE sectors are as high as the WSW sector, its contribution to the total flow is significant when compared to the rest of the sectors. Therefore, emissions from the sources located in Central Russia countries are most likely to affect the aerosol composition in the sampling site.

The crustal elements have higher concentrations in summer season due to their generation mechanisms. Only Ge and Li in fine fraction and Ge and U in coarse mode do not show this trend. Concentrations of the anthropogenic elements do not show as clear seasonal differences as the crustal elements. Their concentrations are at least comparable or slightly higher in the summer season except for As and Cd which indicate coal burning in the winter season.

Correlations among the variables indicate that all the variables measured in this study are strongly correlated in the coarse fraction suggesting that major source of the elements is soil. Similarly, the crustal elements are correlated well in the fine fraction except for Al and Fe. Lack of correlations of Sb with Se and As in the fine fraction is a sign of long range transport.

Calculation of enrichment factors revealed that in both fine and coarse fractions, Cd, Sb, Se and Au are highly enriched, and the rest of the elements are not significantly enriched. High EFc values of these elements in fine fraction indicate that these elements mainly originate from antropogenic sources. High EFc values of these elements also in the coarse fraction suggest that these elements are enriched in aerosols relative to soil.

Factor Analysis (FA) was applied to data in order to identify sources of the elements. FA identified six possible emission sources such as soil, coal and wood burning, iron-steel works, road dust, sea-salt and regional background. Also five possible pollution sources were determined for coarse fraction and include soil, coal burning, road dust, sea-salt and long-range transportation.

To identify source regions of the pollutants, backtrajectories were used. High factor loading values were determined for each factor and flow patterns of these factors were figured coincidently. Distribution patterns showed that main sources of long-range transported elements are observed mainly from the NE sector.

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