CHEMICAL COMPOSITION OF ATMOSPHERIC PARTICLES IN THE AEGEAN REGION

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I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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ABSTRACT

CHEMICAL COMPOSITION OF ATMOSPHERIC PARTICLES IN THE AEGEAN REGION

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Daily aerosol samples were collected at the Çandarlı which is located on Aegean coast of Turkey. A rural site was selected to monitor atmospheric pollution by long range transport. Sampling was performed in both summer and winter seasons, and in total 151 samples were obtained. Concentrations of elements in the samples were measured in order to identify sources and possible source locations of pollutants.

Measured concentrations of trace elements at the Çandarlı station were compared with those measured at various sites around the world and, also in Turkey. As a result of comparison, level of pollution at the Aegean Region was found to be lower than the Mediterranean Region and Black Sea Region.

Air flow climatology at Çandarlı was investigated in order to determine potential source regions for pollutants. Frequency of air flows from Russia and Western Europe are higher suggesting that emissions from these industrial regions affect the chemical composition of particulate matter. Besides these, it was concluded that contributions from Central and Eastern European countries are significantly high because of frequent air mass transport.

Concentrations of elements measured at Çandarlı station were found to show short and seasonal variations. Such variations in concentrations are explained by variations in the source strengths and transport patterns.

Positive matrix factorization (PMF) was applied to determine sources of elements and contribution of sources to each element. This analysis revealed 5 sources, two local anthropogenic emissions factor, one soil factor, one sea salt factor and one long range transport factor.

Distribution of Potential Source Contribution Function (PSCF) values showed that main sources of SO_4^{2-} are observed in Bulgaria, Romania, Poland, Ukraine and central part of Aegean region.

Keywords: Long Range Transport, Positive Matrix Factorization, Aegean Region, Enrichment Factors, Trace Elements

ÖZ

EGE BÖLGESİNDE TOPLANAN ATMOSFERİK PARTİKÜLER MADDENİN KİMYASAL KOMPOZİSYONUNUN BELİRLENMESİ

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Türkiye’nin Ege kıyısında bulunan Çandarlı’da günlük aerosol örnekleri toplanmıştır. Uzun mesafeli taşınımdan kaynaklanan hava kirliliğini izlemek için kırsal bir istasyon seçilmiştir. Örnekleme hem yaz, hem kış mevsiminde yapılmıştır ve toplam 151 örnek elde edilmiştir. Kirleticilerin kaynaklarının ve potansiyel kaynak bölgelerinin belirlenmesi için, örneklerdeki elementlerin konsantrasyonları ölçülmüştür.

Çandarlı’da ölçülen eser element konsantrasyonları, dünyanın ve ayrıca Türkiye’nin çeşitli yerlerinde ölçülen konsantrasyonlar ile karşılaştırılmıştır. Bu karşılaştırmanın sonucunda, Ege bölgesindeki kirlilik düzeyi Akdeniz ve Karadeniz bölgerinden daha düşük olduğu bulunmuştur.

Kirleticilerin potensiyel kaynak bölgelerini belirlemek için Çandarlı’daki hava akım klimatolojisi araştırılmıştır. Rusya ve Batı Avrupa’dan gelen hava akımı frekanslarının yüksek olması, bu endüstriyel alanların emisyonlarının partiküler maddenin kimyasal kompozisyonuna etki ettiği öngörülmektedir. Bunların yanında, hava kütlelerinin taşınım sıklığından dolayı, Orta ve Doğu Avrupa ülkelerininde katkılarının önemli olduğu sonucuna varılmıştır.

Çandarlı istasyonunda ölçülen elementlerin konsantrasyonlarının mevsimsel ve kısa süreli degişiklikler gösterdiği görülmüştür. Bu gibi değişiklikler kaynakların emisyonlarındaki ve hava akımındaki değişikliklerle açıklanmıştır.

Pozitif Matriks Faktörizasyonu (PMF), elementlerin kaynaklarını ve bu kaynakların her elemente katkısını belirlemek için uygulanmıştır. Bu analiz 5 çeşit kaynak belirlemiştir. Bunlardan ikisi lokal antropojen emisyonları faktörü, toprak faktörü, deniz tuzu faktörü ve uzun mesafeli taşınım faktörüdür.

Potansiyel Kaynak Katkı Fonksiyonu (PKKF) değerlerinin dağılımı, SO_4^{2-} ‘ ın ana kaynaklarının Bulgaristan, Romanya, Polonya, Ukrayna ve Ege Bölgesinin iç kısımlarında olduğu göstermiştir.

Anahtar Kelimeler: Uzun Mesafeli Taşınım, Pozitif Matriks Faktörizasyonu, Ege Bölgesi, Zenginleşme Faktörleri, Eser Elementler

To my family...

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CHAPTER 1

INTRODUCTION

It is well known that aerosols have significant impacts on climate, visibility, ecosystems and human health (IPCC, 2001; WHO, 1996). Although a large fraction of aerosols emitted into the atmosphere remains in the boundary layer, some of them may be lifted into the free troposphere and transported over long distances, even between continents. Recently, long range transport of pollutants has received increasing attention due to potential adverse effects hundreds and thousands of km downwind. Sulfate and nitrate particles, for example, lead to acid deposition and acidification of sensitive ecosystems far from source regions.

In order to correctly predict pollution inputs to a particular region from distant sources, rural sampling sites are selected for determining physical and chemical properties of aerosols. In the limited contribution of local anthropogenic sources, long range transport is the most important factor controlling the aerosol concentration when the emission sources at upwind regions are intensive and the meteorological conditions enhance such transport. Knowledge of the possible long range transport contribution will help understanding on the nature of pollutants at a location, in order to develop effective control strategies.

Chemical compositions of aerosols in the eastern Mediterranean atmosphere are fairly well established in previous studies. Anomalously high pollutant concentrations was reported in vastly separated parts of the eastern Mediterranean basin, demonstrating that observed high pollutant concentrations are not specific to a certain location, but a general feature of the whole region (Luria et al., 1996; Güllü et al., 2000; Kubilay and Saydam, 1995; Herut et al, 2001; Sciare et al.; 2003). It is shown that the aerosol composition is significantly affected by both natural and anthropogenic sources. Considerable contribution of anthropogenic emissions from Europe and Asia and Saharan dust transport from North Africa influence Mediterranean atmosphere. Therefore, any data is valuable for identification of similarities and differences in both levels of elements and their transport to the Mediterranean region.

1.1. Aim of the Study

The main aim of this study is 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 Aegean region. In order to assess atmospheric trace metal burden and its relationship with the size of particulate matter, daily fine and coarse aerosol samples were collected at Çandarlı. Contrary to the urban sites that remain under stress of anthropogenic emissions, the sampling site was independent from local pollution effects confirming that this was a representative rural background site. Therefore, it should be expected that the data generated from this site allow to evaluate 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 were rural for reliable comparison. While comparing, the data obtained at different regions in Turkey were also included to demonstrate whether the level and composition of elements observed at Çandarlı is a general feature of the country or specific to the location.

Flow climatology of Aegean region was examined in two ways. Firstly, annual and seasonal wind roses were prepared by using surface wind data obtained at Aliağa during the sampling period. As it is known that Aliağa is the nearest industrial area to Çandarlı, if there was a local pollution effect of this area to sampling site was interpreted clearly to verify the validity of this study. Secondly, upper air data with combining different altitudes were used to investigate the transport of pollutants from different wind sectors. The frequency of flow in each sector was obtained by means of backtrajectories which describe the path of air masses before it is reached at a receptor site. Furthermore, the chemistry data were assigned to sectors to figure out the distributions of species, for both fine and coarse fraction, in each wind sector by visual inspection of trajectories.

In this study, temporal variations were investigated in two ways as short-term and long-term variations. In short-term variations, after determining the background concentrations of measured species, episodic changes and their reasons were discussed whereas in long-term variations seasonal changes and their possible 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, enrichment factors were calculated to evaluate anthropogenic versus natural sources. In addition, positive matrix factorization was applied to estimate the existing sources and apportion the particulate matter mass to each source. After the source profiles and source apportionments were resolved, potential source contribution function was used to identify possible source locations by combining factor scores of samples and backtrajectories.

CHAPTER 2

REVIEW OF LITERATURE

2.1. Characterization of Particulate Matter

Particulate matter (PM) refers to the solid and liquid particles that are suspended in the atmosphere. Combustion-generated particles, such as diesel soot or fly ash; photochemically produced particles, such as those found in urban haze; salt particles formed from sea spray; and soil-like particles from resuspended dust are some examples of atmospheric particles. Atmospheric particles include inorganic ions, metallic compounds, elemental carbon, organic compounds, and crustal compounds (EPA, 2004). Although the term ‘aerosol’ is defined as a suspension of solid or liquid particles in air, it is also used as a synonym of particulate matter. PM can be characterized by size, formation mechanism, origin, chemical composition, and atmospheric behavior, and these properties of PM have temporal and, spatial variations.

Particles are classified as primary or secondary based on their formation mechanism. Primary particles are directly emitted into the atmosphere by anthropogenic activity or wind or can form during condensation of vapours whereas, secondary particles are those formed in the air by chemical transformations of gaseous precursors such as sulphur dioxide, nitrogen oxides and volatile organic compounds (VOCs) (Seinfeld and Pandis, 1998).

2.1.1. Particle Size Classification

Size is the most important parameter for understanding the behaviour of aerosols. The size of particles gives information on their sources, determines the transport scale of particles, residence times, removal mechanism and, their environmental, and human effects.

Atmospheric particles often are not spherical. Therefore, size of particles is expressed by equivalent diameter rather than geometric diameter. The most common equivalent diameter is the aerodynamic diameter. The aerodynamic diameter (D_a) of any irregular shaped particle is defined as the diameter of a spherical particle with a material density of 1 g/cm^3 and the same settling velocity as the particle under consideration (Vallius, 2005), and is given by

$$D_a = D_g K \left(\frac{\rho_p}{\rho_0} \right)^{1/2} \tag{2.1}$$

where D_g is the geometric diameter, ρ_p is the density of particle, ρ_0 is the reference density (1 g/cm^3), and K is a shape factor (1.0 for perfect sphere). From the equation, it can be concluded that a spherical particle with high density will have a larger aerodynamic diameter than its geometric diameter.

The diameters of atmospheric particles range from 0.001 micrometers to 100 micrometers (µm) (EPA, 2005). Typical size distribution of atmospheric particles, including some formation pathways is depicted in Figure 2.1. Particles with diameter greater than 2.5 µm are referred as coarse particles (PM_{10}), and particles with diameter less than 2.5 µm are referred as fine particles ($PM_{2.5}$). Chemical compositions, as well as sources of particles in coarse and fine fractions are quite different. Fine fraction can be further divided into two sub regions; nucleation (aitken) and accumulation range. Particles in the aitken range have diameters less than 0.08 µm. Particles in the accumulation range, on the other hand, have diameters between 0.08 and 2.5 µm. In practice, only two major modes of particles, namely fine and coarse mode, can be seen. The size ranges of particles are handled different in literature (EMEP, 1999; EU Second Position Paper on Particles, 2004; Lazaridis et al., 2002). However, the size ranges described in this paragraph will be used throughout the thesis.

Coarse mode particles are usually produced by mechanical disruption of large particles by crushing or grinding, the bursting bubbles in the ocean (sea spray) or dust resuspension. The aerosol mass is mainly found in coarse mode. Although most of the coarse particles are primary, some secondary formed particles may be found in this fraction. Nitrate formed from the reaction of nitric acid with sodium chloride, and sulfate formed from the reaction of sulfur dioxide with basic particles are examples of the secondary particles (EPA, 2004).

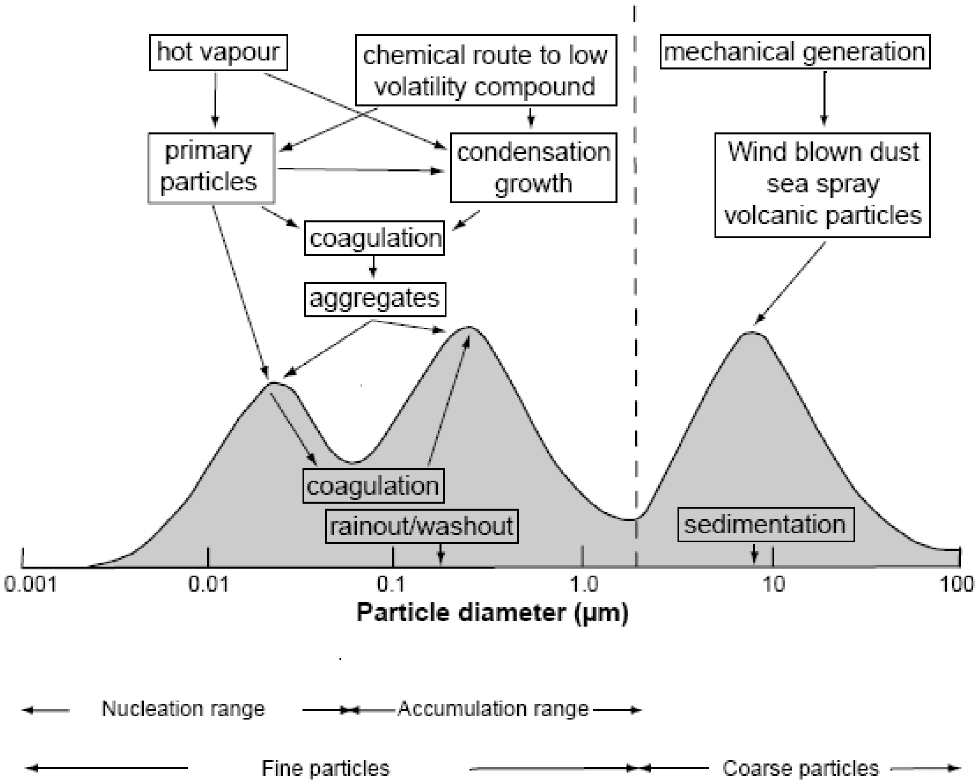


Figure 2.1. Typical size distribution of atmospheric particles, indicating some formation mechanisms (Mathys et al., 2001)

Besides these, fly ash from uncontrolled combustion of coal, oil and wood, oxides of crustal elements (Si, Al, Ti, Fe), pollen, fungal spores, animal and plant fragments are found in coarse mode (Wilson and Suh, 1997). Coarse particles can settle out rapidly from the atmosphere with lifetimes changing between minutes and hours. Larger coarse particles do not travel longer distances due to removal by gravitational settling close to the emission source and impaction on surfaces

(Watson and Chow, 1994). In contrast, smaller coarse particles have longer lifetimes and are transported across larger regions.

Accumulation mode particles are produced by condensation of low vapor pressure vapors from combustion process and coagulation of particles in the aitken range either with themselves or with particles already in the accumulation range. This range is mainly composed of sulphate, nitrate, ammonium and hydrogen ions, large variety of organic compounds, metals (Pb, Cd, V, Ni, Cu, Zn, Mn, Fe) and particle-bound water (Wilson and Suh, 1997). Condensation usually occurs on smaller particles, and the rate for coagulation of two particles decreases as the particle size increases. Therefore, aitken particles grow into the accumulation mode; but accumulation mode particles do not grow into the coarse mode (EPA, 2005). Particles in accumulation mode have long residence times in the atmosphere, ranging from days to week. As a result, they can be transported over long distances until they are removed by wet or dry deposition mechanisms (EPA, 2005). Wet deposition is the main sink for not only the condensation nuclei but also other aerosol particles which are scavenged by precipitation on the way to the surface. On the other hand, dry deposition is particle deposition without precipitation but by convective transport, diffusion, and adhesion to the Earth's surface and is less important on a global scale, but is highly relevant with respect to local air quality, health effects, and the soiling of buildings (Pöschl, 2005).

Aitken (nucleation) mode particles are formed by gas-to-particle conversion in ambient atmosphere and as a result of combustion. Their lifetime is short as they rapidly coagulate and form accumulation mode particles. Although their number concentration is high in atmosphere as most particles are initially produced in aitken size, their contribution to the total mass is small. However, their number concentration decreases rapidly due to the coagulation of them into the larger particles. These particles are very important since they act as cloud condensation nuclei, therefore effect cloud formation (Watson and Chow, 1994).

2.1.2. Sources of Particulate Matter

Atmospheric particles are emitted by natural and anthropogenic sources. Natural sources are dominant on a global scale because of their emission from large area sources. Anthropogenic sources, on the other hand, dominate relatively small areas, such as industrialized regions (Mathys et al., 2001). Natural sources are wind blown dust, sea spray, volcanic emissions, natural fires, and biogenic sources; while anthropogenic sources are fossil fuel combustion, industrial activities, transportation, and construction works (Seinfeld and Pandis, 1998).

Natural and anthropogenic sources give rise to both primary and secondary fraction of particulate matter. Sea spray, volcanic emissions, wild fires, erosion, plant and insect fragments, and biogenic sources such as pollen, spores, and minor amounts of micro-organisms are natural sources of primary particles (Seinfeld and Pandis, 1998).

Sulphate, nitrate and organic aerosol are the main components of natural atmospheric particles with secondary in nature. Natural sulphate is formed from the oxidation of reduced sulphur gases emitted by the oceans and, SO_2 and H_2S emitted by volcanoes. Natural nitrate is formed from the oxidation of NO_x produced by soils, forest fires and lighting (EU Second Position Paper on Particles, 2004). Production of natural secondary organic aerosol is enhanced by the oxidation of organic species such as terpene emitted from vegetation (Librando and Tringali, 2005).

Fossil fuel combustion, motor vehicle exhaust, dust from paved and unpaved roads, agriculture, abrasion of brakes and tires, industrial activities such as building, mining, manufacturing of cement, ceramic and bricks, and smelters are the anthropogenic sources of primary particles. In addition, antropogenic activities result in the formation of secondary particles. Oxidation of SO_2 emitted from fossil fuel combustion , NO_x emitted from fossil fuel combustion and, motor vehicle exhaust and, hydrocarbons emitted from motor vehicles and wood burning give rise to the presence of secondary sulphate, nitrate and organic carbon, respectively (EMEP, 1999).

2.2. Trace Elements

Trace elements are good tracers to estimate the sources that contribute to the pollution at a receptor site. They are found in almost all aerosol size fractions depending on the nature of emissions as reported in fairly high number of studies (Allen et al., 2001; Rizzio et al., 1999). Therefore, for a better understanding of various pollution sources, the aerosol composition, and, in particular, the size differentiated composition is essential.

Trace metals are released to the atmosphere by natural and, mainly, anthropogenic sources. Natural sources include volcanism, wind erosion, forest fires and oceans whereas the latter one includes combustion of fossil fuels and wood, high temperature industrial activities and waste incinerations. Specifically, combustion of fossil fuels is the main anthropogenic source for Be, Co, Hg, Mo, Ni, Sb, Se, Sn and V, and also, it contributes to release of As, Cr, Cu, Mn and Zn. Industrial metallurgical processes emit the largest percentage of As, Cd, Cu, Ni and Zn. Exhaust emissions from gasoline contain variable quantities of Pb, Cu, Zn, also associated with tire rubber abrasion, Ni and Cd (Wang et al., 2005).

Although the above mentioned elements release as a result of anthropogenic activities, natural sources, substantially, are responsible for their concentrations in the atmosphere. On a global scale resuspended surface dusts account for >50% of Cr, Mn and V, and >20% of Cu, Mo, Ni, Pb, Sb and Zn, while volcanic activity probably generates 20% of atmospheric Cd, Hg, As, Cr, Cu, Ni, Pb and Sb. Sea salt aerosols generated by spray and wave action may contribute around 10% of these trace metal emissions (Allen et al., 2001).

Besides, elements like Na, Mg, Al, Si, K, Ca, Ti, Mn and Fe are known to be of crustal origin (Zhang et al., 1998; Han et al., 2005). Among these elements, a certain fraction of Na, Mg, K, Ca and also Cl are the markers of sea salt (Maenhaut and Cafmeyer, 1998; Perrone et al., 2006).

Trace elements are distributed between different size ranges when constituting PM_{10}. In the fine particle size range, there have been found various trace metals including mainly Pb, Zn, Cd, As, Sb, Ag, In, La, Mo, I, and Sm, whereas in the coarse mode there have been found mainly Ca, Al, Ti, Mg, Sc, La, Lu, Hf and Th. Furthermore, depending on the different origin of sources and mechanisms, there have been found Na, K, Fe, V, Cr, Co, Ni, Mn, Cu, Se, Ba, Cl, Ga, Cs, Eu, W, and Au in both fine and coarse modes (EMEP,1999). An example of K in coarse particles comes from soil. However, high concentration of K in fine mode due to the biomass burning (Huang et al., 1994).

2.3. Receptor Modeling

The identification and apportionment of pollutants to their sources is an important step in air quality management. Receptor modeling uses measurements of pollutant concentrations, thus providing a means of achieving this identification task. Chemical mass balance (CMB) and multivariate receptor models are widely used to apportion sources of PM. In addition to chemical measurements at a receptor, CMB requires the additional inputs of the source emission profiles. However, measurement of source profiles have a diffucult methodology and time-consuming. In contrast to CMB, multivariate receptor models do not require source profiles as an input, as this is part of the solution. In other words, these models estimate the number and compositions of the sources, also their contributions to the measured PM. Multivariate receptor models commonly used are principal component analysis (PCA), factor analysis (FA) and positive matrix factorization (PMF).

Multivariate models base on the idea that the time dependence of chemical species at receptor will be the same for species from the same source. Measured species in a large number of samples that have similar variability are grouped together in a minimum number of factors that explain the variability of the data set. It is assumed that each factor is associated with a source type (Liu et al., 2003).

2.3.1. Positive Matrix Factorization (PMF)

PMF is an extensively used tool to apportion sources of PM. Among the receptor models, PMF is a relatively new technique and has some advantages. PMF uses realistic error estimates to weight the data values. As a result, it can handle chemical species more effectively. In addition, non-negativity constraints are integrated in the factor computational process to decrease the rotational freedom. These are very important features for evaluating environmental data because of error estimates that are found in the air pollution monitoring data and mass contributions or source profile composition fractions can not be less than zero. In order to get the complete information in the data set, missing or below detection limit data can be included in the analysis by assigning appropriate values with large error estimates (Huang et al., 1999; Xie et al., 1999a).

PMF has been succesfully applied in atmospheric studies in many regions (Juntto and Paatero, 1994; Song et al., 2001; Anttila et al., 1995; Xie et al., 1999a; Liu et al., 2003; Chueinta et al., 2000; Wang and Shooter, 2005).

The PMF model was developed by Paatero and Tapper (1994) and Paatero (1997). PMF uses a weighted least-squares fit with the known error estimates of the elements of the data matrix used to derive the weights. A conventional factor analysis model can be written as,

$$X = GF + E \text{ ,} \tag{2.2}$$

where X is the known n x m matrix of the m measured chemical species in n samples. G is an n x p matrix of source contributions (time variations). F is a p x m matrix of source compositions (source profiles). Both G and F are factor matrices to be determined. E is the matrix of residuals and is defined as

$$e_{ij} = x_{ij} - \sum_{k=1}^{p} f_{ik} g_{kj} \text{ ,} \tag{2.3}$$

where i = 1,..., n; j = 1,..., m; k = 1,..., p.

PMF applies non-negativity constraints to the G and F which means that sources can not have negative species concentration ($f_{kj} \geq 0$) and sample cannot have a negative source contribution ($g_{ik} \geq 0$). The objective of PMF is to minimize $Q(E)$, which is defined as

$$Q(E) = \sum_{i=1}^{n} \sum_{j=1}^{m} (e_{ij} / s_{ij})^2 \text{ ,} \tag{2.4}$$

where s_{ij} is the error estimate in the jth element measured in the ith sample, and e_{ij} $/s_{ij}$ is the scaled residual.

In addition to the ad hoc computation of error estimates, the program can take outliers into account. It is any data that significantly deviates from the distribution of the other data. The robust mode was selected to handle outlier values in the data matrix. The robust factorization based on the Huber influence function is a technique of iterative reweighing of the individual data values. The least-squares formulation becomes to

$$Q(E) = \sum_{i=1}^{n} \sum_{j=1}^{m} (e_{ij} / h_{ij} s_{ij})^2 \ , \tag{2.5}$$

where $h_{ij}^2 = 1$, if $\left| e_{ij} / s_{ij} \right| \leq \alpha$; otherwise, $h_{ij}^2 = \left| e_{ij} / s_{ij} \right| / \alpha$,

where α is the outlier threshold distance and, in general the value of $\alpha = 4.0$ is chosen.

For the determination of optimal number of factors in PMF, analysis of a good fit of model to the original data set is required. It is assumed that correct values of error estimates have been used, the theoretical value of Q should be approximately equal to the number of data points in the data set. However, in the absence of reasonable error estimates, and in the presence of outliers, it is hard to examine whether Q value is normal or too large. For this reason, the scaled residuals (e_{ij}/s_{ij}) should be examined. They should fluctuate between -2 and 2 with a random distribution of positive and negative values (Chueinta et al., 2000; Liu et al., 2003).

2.4. Trajectories

In order to develop effective control strategies, knowledge of long range transport is an important step in understanding air pollution at a location. Although receptor modeling identifies the nature of sources that contribute pollution, they are unable to determine the locations of sources by which the aerosol materials are transported to the receptor site. When the place of release is not exactly known but there is information about concentration from measurement then trajectories providing geographical information allow to find possible location of the release. A trajectory is the time integration of the position of an air parcel as it is transported by the wind. A back trajectory model is applied to track the origin of air masses in problems connected with source-receptor relationship. Back trajectories, back in time, as the name implies, can be defined as the succesive locations of an air parcel arriving at a given height, location and time.

Horizontal advection component of trajectory is computed with usage of observed or model analyzed winds in most methods. However, one of three assumptions is used to compute the vertical component of the trajectory. These assumptions are isobaric (follow lines of constant pressure), isentropic (follow lines of constant potential temperature) and kinematic (moves with the vertical velocity wind fields generated by a diagnostic or prognostic meteorological model) (NOAA - ARL, 2007).

In order to illustrate the vertical structure of the atmosphere, trajectories are generally run at different altitudes above ground level (AGL). The period of back trajectories must be long enough to include distances covering the major source regions expected to affect the area under consideration. In addition, they must not be so long as to cause uncertainties in their locations.

2.4.1. Flow Climatology

Flow climatology is a statistical evaluation of trajectories to identify the potential for pollution inputs to a receptor from distant sources. It is expected that locations with high pollution inputs are responsible for the observed concentrations in a receptor site. By means of flow climatology, providing a better understanding of air-flow patterns in a region, the frequency of flow from that location can be identified. In the case of frequent flow, the location can be an important source region for the receptor site and if opposite occurs, than the location can be less effective source region. As a result, flow climatology is a useful tool that can at least give preliminary information on possible locations of source regions of pollutants affecting the receptor (Güllü and Tuncel, 2004).

In this approach, calculated trajectories are divided into segments and then, each segment is assigned to a wind sector. The number of segments in each wind sector is calculated. Hence, a measure of the residence time of air masses in a sector is determined by the number of segments in that sector. If high residence time in a sector is coupled with strong emission sources, the countries in that sector are intercepted as potential source regions of pollutants.

2.4.2. Potential Source Contribution Function

Although the receptor modeling can identify the possible sources and apportion aerosol mass to each source, they are unable to determine the geographic locations of sources. After the source profiles and contributions are resolved by PMF, potential source contribution function (PSCF) is applied to identify the source locations. The meteorological data and chemical data is combined by PSCF with using chemical compositon information and wind trajectories. Zeng and Hopke (1989) defined PSCF as the conditional probability, in other words, how often that an air parcel passing through a location before arriving at a receptor and cause pollution at this receptor site.

In the literature, PSCF has been used in a number of prior studies to identify possible locations of sources (Zeng and Hopke, 1989; Gao et al., 1996; Plaisance et al., 1997; Güllü et al., 2005; Hwang and Hopke, 2007).

In this model, the possible source region covered by trajectories is divided into a grided i by j array. Size of the grid cells depends on the geographical scale of the problem. If a trajectory endpoint lies in the ijth cell, it is assumed that trajectory collects material emitted in the cell and the material is assumed to be transported along the trajectory to the receptor site. In addition to these, other assumption in PSCF is that atmospheric removal and chemistry are not considered as an air parcel transports to the receptor site (Plaisance et al., 1997).

If the total number of trajectory endpoints over the whole study period T is N and if the total number of endpoints that fall in the ijth cell is n_{ij}, then the probability of an event, A_{ij}, representing the relative residence time of randomly selected air parcel on the ijth grid is given by

$$P[A_{ij}] = \frac{n_{ij}}{N} \qquad (2.6)$$

If there are m_{ij} endpoints among n_{ij} in the same ijth cell that correspond to the trajectories that arrived at the receptor with pollutant concentration higher than a pre-specified value, then the probability of these event, B_{ij}, representing the relative residence time of contaminated air parcel on the ijth grid is given by

$$P\left[B_{ij}\right] = \frac{m_{ij}}{N} \tag{2.7}$$

PSCF is then defined as a conditional probability that an air parcel with specified pollutant concentration resided in the ijth cell before arriving at the receptor site (Plaisance et al., 1997; Xie et al., 1999b) and formulated as

$$PSCF_{ij} = \frac{P\left[B_{ij}\right]}{P\left[A_{ij}\right]} = \frac{m_{ij}}{n_{ij}} \tag{2.8}$$

Cells with high PSCF value that aproaches 1 are the potential source regions and cells having a PSCF value of 0 are unlikely to be source regions. A sufficient number of endpoints, n_{ij}, should provide accurate estimates of the probability that material emitted from a location affects the sample at the receptor site if the location errors are random and not systematic (Liu et.al, 2003). However, if the total number of endpoints, n_{ij}, in a cell is small, it results in a high $PSCF_{ij}$ value with a high uncertainty. To minimize the effect of small values of n_{ij}, an arbitrary weight function (Yli-Tuomi et al., 2003; Lin et al., 2001; Owega et al., 2006) or a non-parametric bootstrap method (Hopke et al., 1995; Lupu and Maenhaut, 2002; Güllü et al., 2005) is necessary.

The bootstrap (Wehrens et al., 2000) is a statistical tool to provide better estimates of the probability values and their uncertainties. The method assumes that the concentration values are independent and identically distributed. From the original concentration data set, $C = \{c_1, c_2, ..., c_N\}$, B random subsamples of size equal to the length of the data set, $C^* = \{c_1^*, c_2^*, ..., c_N^*\}$, are drawn with replacement. For each bootstrapped sample k, the corresponding PSCF spatial distribution, $P^*_{k;ij}$, is calculated. These values are ordered as $P^*_{(1);ij} < ... < P^*_{(B);ij}$, where $k = 1, ..., B$, and α is the chosen significance level. If

$$P_{ij} \geq P^{*}{}_{((B+1)(1-\frac{\alpha}{2}));ij} \tag{2.9}$$

the null hypothesis that there is no association between concentrations and trajectories is rejected at (1 – α) 100% confidence level. For further analysis, only the PSCF values satisfying the above relation are retained (Lupu and Maenhaut, 2002).

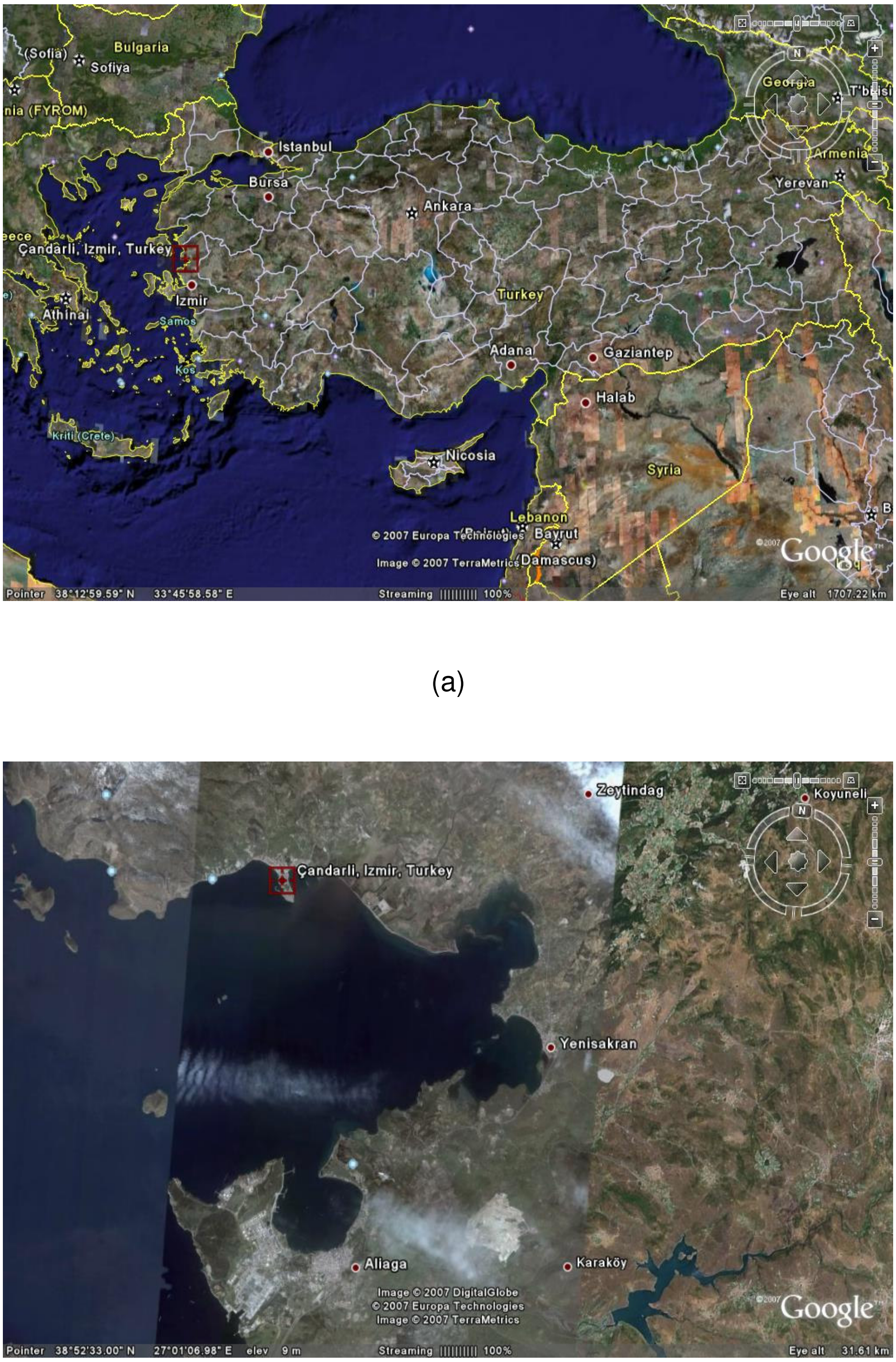
CHAPTER 3

MATERIALS AND METHODS

3.1. Study Area

Sampling was performed at Çandarlı, which is located on the west coast of Turkey (26.99 longitude east of Greenwich and 38.93 latitude north of the Equator), and approximately 80 km north from the city of İzmir. The station is on the coast and located approximately 30 m away from the shoreline. The climate in the region is typical Mediterranean with warm and rainy winters, and hot and dry summers. Local landscape comprises mainly agricultural field.

The sampling site, which is depicted in Figure 3.1, was surrounded by summer housings, and hence can be considered to be near a residental area in summer. However, during winter, there was no residence within a few kilometers. Furthermore, there were no dense traffic ways close to the station, as only local and secondary roads cross this area. Nearest industrial town, Aliağa, including a petroleum refinery, a petrochemical complex, a fertilizer plant, iron and steel industries, is located at 20 km south of Çandarlı. There is no close industrial area around the sampling site and tourism is a sub-sector mainly in summer. This place was chosen for sampling, for the reason that there were no local or proximal industrial activities. In addition, the sampling site was not influenced much by the nearest industrial area, Aliağa, mainly owing to its being upwind from the sources. Dominant winds in the area are from North and Northeast, whereas industries are located to the South of the sampling point. Level of influence was of concern in this study and will be discussed more extensively in the next chapter. From an air quality point of view the measurement site can be considered as a rural or regional background station. A rural sampling site has been chosen to monitor atmospheric pollution by long range transport.



(a)

(b)

Figure 3.1. Location of sampling station (a) and (b)

3.2. Sampling

3.2.1. Sampling Equipment

Daily fine and coarse aerosol samples were collected between December 15, 2005 and March 16, 2006 in winter and samples were also collected between July 24 and October 31, 2006 in summer. The sample collection period was 24 h for all collected samples and sampling were interrupted only to change filters. In total, 74 daily samples for both fine and coarse particles were obtained in winter and 77 in summer.

Samples were collected using a “GENT” stacked filter unit (SFU). The device has a PM_{10} pre-impactor and contains two filters, a coarse and a fine filter, placed in series. The air enters the unit through the preimpactor 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 (d_{50}-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 $PM_{2.5}$ 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). The complete unit design of SFU is shown in Figure 3.2.

In literature, there are various studies conducted with SFU for sample collection. Yatin et al. (2000), Al-Momani et al. (2005), Graham et al. (2004), and Artaxo et al. (1999) are some of these studies.

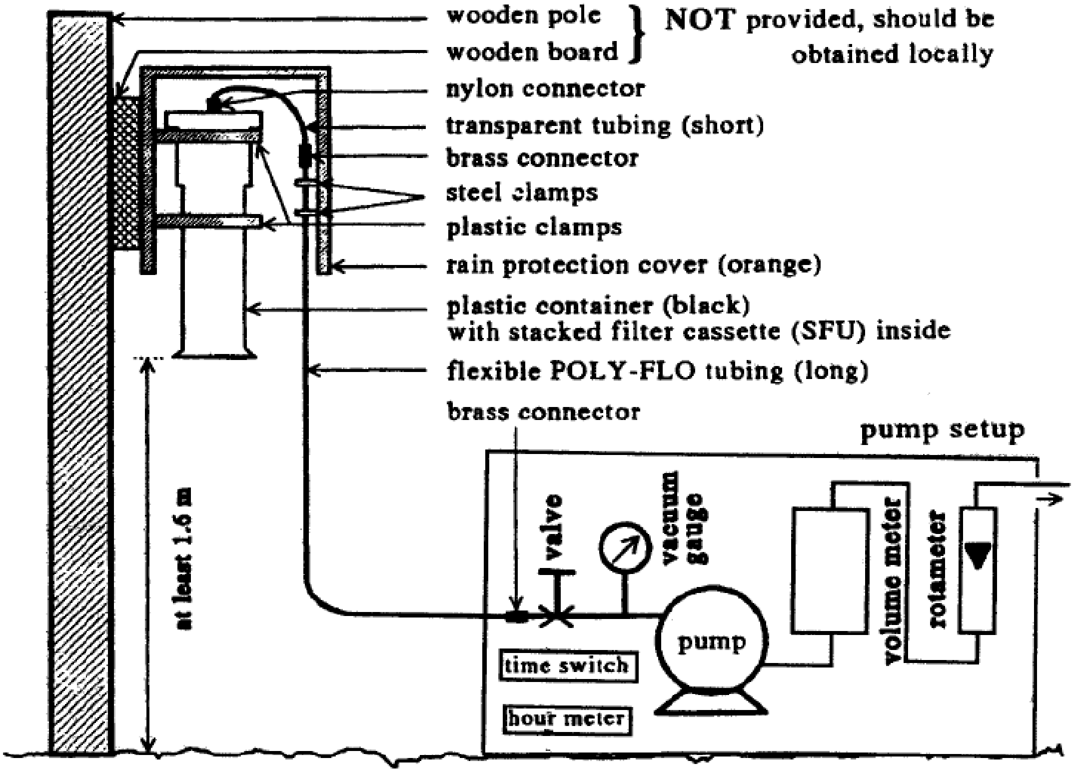


Figure 3.2. Schematic of the SFU as typically deployed in the field including the pump, flow control system, and rain shield (Hopke et al., 1997)

3.2.2. Gravimetric Analysis

Before sampling, the coarse and fine filters were placed into a constant humidity chamber at room temperature, 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. Static electricity had been eliminated using an ionizer prior to weighing. 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.

3.3. Elemental Analysis of Samples

Analysis of filters was performed using an energy-dispersive X-ray fluorescence (EDXRF) in the Sarayköy Nuclear Research and Training Center of the Turkish Atomic Energy Authority in Ankara. Samples were analyzed for a total of 13 elements which are Mg, Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Zn, Pb.

3.3.1. General Information about XRF

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). Among these, XRF is a rapid, nondestructive and comparatively inexpensive method for determining elements in airborne particulate matter collected onto filters. XRF displays high analytical specificity combined with high sensitivity and high dynamic range covering several concentration decades. Furthermore, it is useful for the short- and long-range sampling studies and provide accurate elemental concentration data (Bandhu et al., 2000).

XRF is available in two separate configurations; energy-dispersive (EDXRF) and wavelength-dispersive (WDXRF). Although WDXRF displays a higher sensitivity for low-atomic number elements than EDXRF, the latter technique was used for the analysis of air filters for two main reasons:

- The WDXRF method is characterized by high spectral resolution minimizing peak overlap. It requires high excitation power, which may produce potential degradation of the filter material. EDXRF applies a 100 to 1000 times lower excitation energy and hence avoids sample damages.

- High sensibility WDXRF is a sequential method where the investigated analyte has to be known a-priori. EDXRF is basically a simultaneous method, where the entire information is stored as an energy spectrum, and is analysed after exposure (Mathys et al., 2001).

In the literature EDXRF has been used in fairly high number of studies for characterization of aerosol samples collected in different regions (Vallius et al., 2003; Marcazzan et al., 2004; Ariola et al., 2006; Hoornaert et al., 2004; Bandhu et al., 2000).

As mentioned previously, polycarbonate filters were used for sampling. One important point that should be kept in mind is filter material must fit the method of analysis. Polycarbonate filters have less contaminations and give rise to lower background of scatterred radiation than other types of filters (Öblad et al., 1982). Hence, filters used for sampling was found to be reliable for analysing by EDXRF.

One other important thing for polycarbonate filters is deposited material is distributed homogeneously over the entire surface of filter (Horvath et al., 1996). This avoids the erroneous results during quantification of elements. Because heteregeneously loaded filters are expected to reflect more or less values than true concentrations of trace elements depending on the assesment location.

3.3.2. EDXRF Analysis

EDXRF with the ED2000 spectrometer manufactured by Oxford Instruments used for analysis in this study consists of a source for sample excitation, a Si(Li) solid phase detector, a sample chamber and an emission or fluorescence energy analyser, such as a multichannel analyser (MCA). An Ag anode X-ray tube with maximum current of 1000 µA and with maximum voltage of 50 kV was used as a source of excitation. Five measuring conditions, presented in Table 3.1, were fixed to optimise the sensitivy for groups of elements.

When sample is exposed to X-rays having energy greater than the binding energy of the inner shell electrons of the element, an inner shell electron is discharged. Then, outer shell electrons fill the electron vacancies. As electrons in outer shells have higher energy states than inner shell electrons, the outer shell electrons give X-rays while filling the vacancies (Mathys et al., 2001). Emergent X-rays were detected using a liquid nitrogen cooled Si(Li) semiconductor detector with a resolution of 180 eV. MCA coupled with detector was used to collect the fluorescent X-ray spectra from the samples. It should be noted that each element emits X-rays of different energy levels. The specific type or energy of the emitted X-ray is unique to a given element and is called a “characteristic” X-ray (Mathys et al., 2001). After storage of spectra over a set of period, each spectra was analyzed for aerial concentration of each detected element using Oxford XpertEase software.

Exposure times of samples is an important criteria for precision in EDXRF. While selecting analysis time, it kept in mind that counting times must be long enough to get reliable results. When exposure time of sample is increased, more emission counts are obtained. Consequently, the data gathered for a sample increase which, in turn, averages variations in emissions and more precised measurements.

Table 3.1. Measuring conditions of EDXRF

	Condition-1	Condition-2	Condition-3	Condition-4	Condition-5
	Very light elements	Solids	Steel	Medium elements	Heavy elements
Tube curren(µA)	1000	800	900	127	213
Time (s)	200	100	100	100	100
Elements	Mg, Al, Si,S	K, Ca	Ti, Cr	Mn, Fe, Ni	Zn, Pb

3.3.2.1. Calibration and Limit of Detection

Calibration of EDXRF was carried out to establish an intensity-concentration relationship for analyte quantification by using SRM 2783 of the National Institute of Standards and Technology (NIST) as standard reference material. The NIST has a variety of SRMs, but the SRM used in the study has to have similar matrix with the sample. There is one SRM for trace elements on air particulate filter, that is SRM 2783. SRM 2783 is an air particulate sample reduced in particle size to simulate $PM_{2.5}$ air particulate matter and deposited on a polycarbonate filter membrane. It is primarily intended for use in the evaluation and calibration of methods of analysis for common and toxic elements contained in various fractions of airborne particulate matter collected on filter media (SRM 2783 Material Safety Data Sheet, 2005).

The correctness of the selected working equation that describes the relationship between intensity and concentration for a given calibration model is important. This equation depends on both experimental conditions and sample matrix composition. The experimental conditions include the characteristic radiation selected for the analysis, the energy distribution of the radiation selected for excitation, the detector efficiency and the geometric design. The absorption of primary radiation and absorption and enhancement of fluoresced characteristic lines are termed as matrix effects which generally result in a nonlinear working equation. To overcome this problem, necessary corrections are made by the use of theoretical methods (Álvarez et al., 2007). However, the matrix effects in thin samples are less important than in thick ones. In thin samples, background is low and absorption effects are negligible (Sitko, 2006). Therefore, by choosing special conditions for sample excitation a linear equation is possible. In this study, linear intensity/concentration functions for all elements were obtained by selecting five different conditions. These conditions are listed in Table 3.2.

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 RíoBocio et al., 2003; Szilàgyi and Hartyàni, 2005; 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 also given in Table 3.2.

The detection limit is a theoretical concept, and was not a limiting factor in measurements performed in this study, as typical concentrations of elements in this study are two-to-three orders of magnitude higher than their corresponding detection limits.

3.3.2.2. Quality Assurance

As mentioned earlier, EDXRF is a non-destructive method allowing repeated measurements of same filters. In order to eliminate uncertainty, some of the filters which had unreasonable high results or filters associated with wrong ID numbers reanalyzed and corrected.

Table 3.2. Analytical curve equations and detection limits of measured elements

Element	Calibration curve equations	R^2	LOD (ng m^{-3})
Mg	y = 0.0015x	0.991	0.0001
Al	y = 0.0066x	0.995	0.0007
Si	y = 0.0167x	0.998	0.0055
S	y = 0.0909x	0.998	0.1436
K	y = 0.0092x	0.995	0.0013
Ca	y = 0.0122x	0.998	0.0038
Ti	y = 0.0087x	0.987	0.0004
Cr	y = 0.0239x	0.985	0.0012
Mn	y = 0.0147x	0.991	0.0003
Fe	y = 0.0156x	0.999	0.0031
Ni	y = 0.0025x	0.983	0.0001
Zn	y = 0.0034x	0.997	0.0003
Pb	y = 0.0083x	0.988	0.0006

* y = concentration of element (ng), x = intensity of element (cps)

** The average flowrate is 28.8 m^3 for 24 h sampling period.

For quality control, laboratory and field blanks were used in order to determine level of contamination for each type of filter. Contamination due to sampling system or during transportation can be determined by field blanks. Air was pulled through field blanks for 1 min. Then, filters were removed from the SFU and analyzed in the same way as the samples. Laboratory blanks were also analyzed to minimize sample contamination during processing in the laboratory. Six field blank filters and six laboratory blank filters were analyzed with EDXRF, and their average concentrations for each element was used for correction of measured values. Blank concentrations and percentages of blank contributions on samples are presented in Table 3.3.

Higher blank contribution, greater than 75%, is observed for Cr and Pb. Besides these, blank contribution for Ti to fine fraction is high but not as high as Cr and Pb. As a result, contribution of blank subtraction to the uncertainties in measured concentrations is considerable for these 3 elements. On the contrary, for the rest of the elements blank contribution is less than 30% which indicates that blank subtraction does not have a significant contribution on uncertainties in measured concentrations.

Table 3.3. Blank concentrations and percentages of blank contributions on samples

Element	Blank (ng filter^{-1})	Fine %	Coarse %
Mg	0.00	0.00	0.00
Al	295.61	22.80	6.87
Si	140.13	5.27	1.44
S	294.71	3.65	13.55
K	161.44	3.84	5.70
Ca	155.53	6.48	1.14
Ti	41.94	43.40	11.51
Cr	99.67	100.48	89.21
Mn	44.11	25.67	13.55
Fe	601.75	26.60	9.74
Ni	0.00	0.00	0.00
Zn	0.00	0.00	0.00
Pb	198.21	75.49	112.77

CHAPTER 4

RESULTS AND DISCUSSION

4.1. General Characteristics of Data

Concentrations of elements observed in Çandarlı aerosol from December, 2005 to March, 2006 and from July to October, 2006 are presented in this study. Concentrations of 13 elements (Mg, Al, Si, S, K, Ca, Ti,Cr, Mn, Fe, Ni, Zn and Pb) were measured in both fine and coarse fraction by EDXRF.

Statistical summaries for all measured species in fine and coarse fraction are given in Table 4.1 and 4.2, respectively. The values given in the tables include the number of samples, arithmetic means, together with standard deviations and median values. Median concentrations of elements are reported because frequency diagrams indicated that data for most elements are log-normally distributed which is discussed hereafter. Arithmetic means are reported to be consistent with the literature.

Elements measured with the highest frequency are Ca and K which are measured in 149 and 150 samples, respectively. As can be seen from Tables 4.1 and 4.2, 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 log-normal distribution of data (Koçak et al., 2004a).

Concentrations of elements in the fine fraction vary between 970 ng m^{-3} for SO_4^{2-} and 0.25 ng m^{-3} for Pb. Concentration range in the coarse fraction is between 289 ng m^{-3} for Ca and 0.42 ng m^{-3} for Pb. The results indicated that, concentrations of SO_4^{2-} in fine fraction, Ca and Si in coarse fraction are high compared to concentrations of other elements.

Table 4.1. Summary statistics of elemental concentrations in fine fraction aerosols (ng m^{-3})

Parameter	N	Arithmetic mean	Median
Mg	67	33 ± 45	25.5
Al	94	76 ± 134	39
Si	145	152 ± 257	80
SO_4^{2-}	148	1097 ± 844	970
K	149	83 ± 74	66
Ca	146	85 ± 120	57
Ti	97	5.1 ± 8.1	3
Cr	65	0.45 ± 0.37	0.37
Mn	54	5.7 ± 8.2	3.6
Fe	144	73 ± 83	47
Ni	13	0.43 ± 0.24	0.37
Zn	28	126 ± 124	71
Pb	11	0.39 ± 0.31	0.25
$PM_{2.5}$	149	16205 ± 10359	15540

Although Zn was quantified in 28 samples for fine fraction and 19 samples for coarse fraction out of 151 samples, measured concentrations were found to be unreasonably high. It could be arised from erroneous calibration or from an error while appliying measurement conditions. As a result, average or median values of Zn in Tables 4.1 and 4.2 are affected by samples reported with extremely high concentrations. Therefore, concentrations determined for Zn is excluded in most of this study. However, Zn is only included during the application of positive matrix factorization to apportion the sources.

The European Air Quality Directive 1999/30/EC set an annual mean limit value of 40 µg m^{-3} for PM_{10} and more recently, the limit on $PM_{2.5}$ concentrations introduced by the European Commission would be 25 µg m^{-3}, averaged over a year. The values given in the tables for PM_{10} and $PM_{2.5}$ are quite lower than these limits. In fact, comparison the data from rural regions with regulatory standards is not very meaningful, as rural stations are not under direct influence of emission sources.

Table 4.2. Summary statistics of elemental concentrations in coarse fraction aerosols (ng m^{-3})

Parameter	N	Arithmetic mean	Median
Mg	105	61±91	45.85
Al	141	189±340	106.81
Si	147	436±810	238.54
SO_4^{2-}	141	185±216	138.22
K	149	77±136	53.22
Ca	150	411±778	288.67
Ti	124	15±37	8.12
Cr	91	0.84±0.84	0.61
Mn	80	8.09±18.01	3.37
Fe	146	185±454	120.62
Ni	18	0.68±0.58	0.42
Zn	19	124±121	115.56
Pb	23	0.48±0.46	0.42
PM_{10}	138	29811±23307	25020

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, depicted in Figure 4.1, vary between approximately 5 for Ca and 0.2 for SO_4^{2-}. Crustal elements, such as Ca, Al, Ti, Si, Mg and Fe are mostly found in the coarse fraction, with coarse-to-fine ratios varying 2 and 5. This observation is not surprising as soil particles bearing these elements are known to be coarse (Yatin et al., 2000; Salma et al., 2002; Almeida et al., 2005). On the other hand, anthropogenic specie, SO_4^{2-}, dominates in the fine fraction as reported in previous studies (Marcazzan et al., 2001; Han et al., 2005; Kuloglu and Tuncel, 2005).

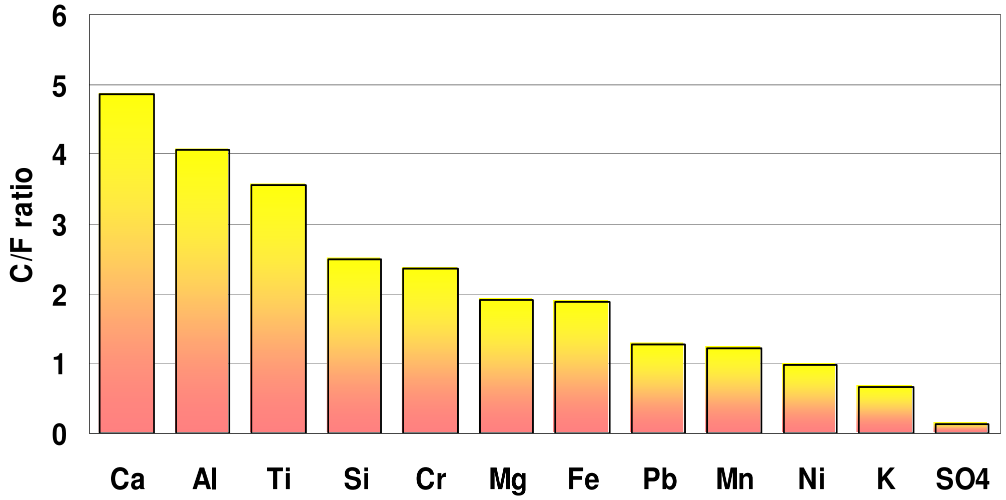


Figure 4.1. Coarse-to-fine concentration ratios (C/F) of elements

Elements Mn, Ni have ratios close to unity. These elements have anthropogenic sources but significant fractions of these elements also originate from resuspended soil particles. That is the reason for having these elements equal amounts in coarse and fine fractions. Although atmospheric Cr concentrations are also contributed by anthropogenic sources, it is mostly observed in coarse fraction. It is indicated that high contribution of atmospheric soil particles enriched with Cr may be related with the observed concentration. K 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 (Gatari et al., 2005; Huang et al., 1994). This issue will be further discussed in the source apportionment section.

4.1.1. Distribution Characteristics of Data

The concentrations of air pollutants usually vary randomly and fluctuates with the emission levels and meteorological conditions. The frequency distribution of air pollutants can be used to understand the statistical characteristics of data and to estimate how frequently a critical concentration level is exceed while developing air pollution control strategies (Lu and Fang, 2002). Distribution characteristics also dictate the type statistics that represent the data best.

Although 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 distribution of the ambient concentrations (there are too many references for this issue, some examples from our group are Güllü et al., 1998; Al-momani et al., 1998; Yatın et al., 2000). As presented in Table 4.1 and 4.2, arithmetic means are different from median values, suggesting that a deviation from symmetric Gaussian distribution.

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 4.3, skewness values are positive which means all measured parameters are positevely skewed. Due to positive skewness of all variables, it was assumed that distributions are log-normal. This distribution of elements is not unique to Çandarlı, but observed in almost all aerosol studies.

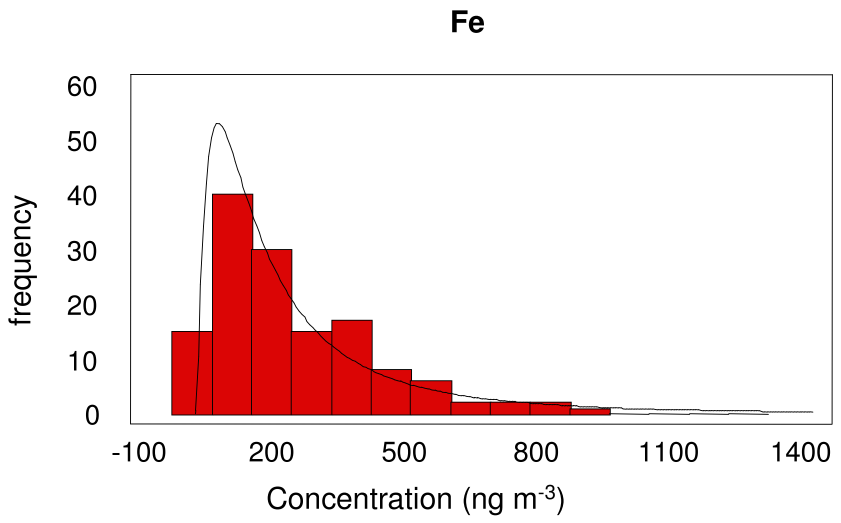
In this study, Statgraphics Software was used to determine whether the log-normal distribution fits the data adequately by performing Kolmogorov-Smirnov (K-S DN) and Chi-square tests. The chi-square test divides the range of the variable into nonoverlapping intervals and compares the number of observations in each class to the number expected based on the fitted distribution. The Kolmogrov-Smirnov test computes the maximum distance between the cumulative distribution of the variable and the cumulative distribution function of the fitted log-normal distribution.

Table 4.3. Results of skewness, K-S DN and Chi-square

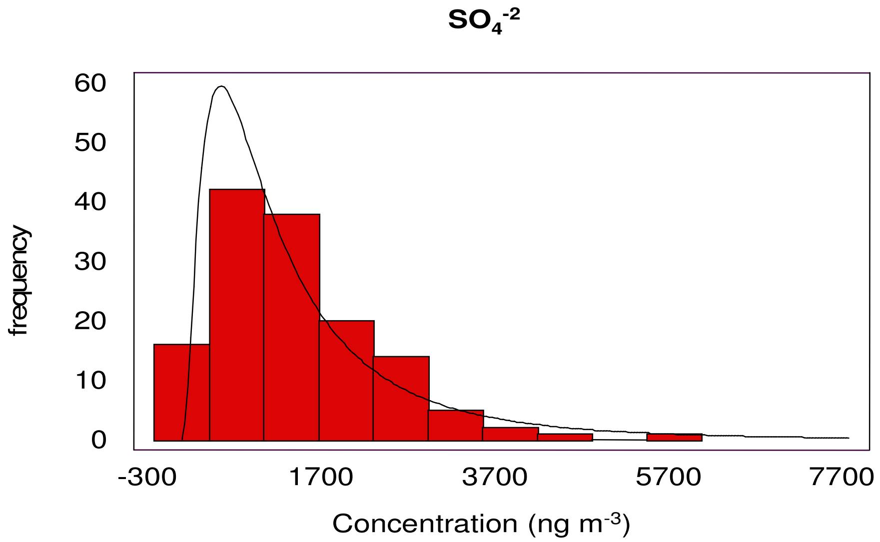
Element	Skewness	p-value	Distribution Type
Mg	7.56	0.35	Log-normal
Al	7.98	0.71	Log-normal
Si	7.36	0.19	Log-normal
SO_4^{2-}	1.29	0.02	Weibull
K	6.12	0.34	Log-normal
Ca	8.92	0.31	Log-normal
Ti	9.63	0.58	Log-normal
Cr	1.98	0.04	Weibull
Mn	3.42	0.48	Log-normal
Fe	9.72	0.57	Log-normal
Pb	0.13	0.80	Log-normal

For each of the goodness of fit tests applied, namely K-S DN and Chi-square, a p-value was calculated which is the probability that the population of data measured is log-normally distributed. They are used to determine whether there is a statistically significant difference in the mean values of the measured data and log-normal distribution (Costabile et al., 2006). Among the two tests, lowest p-value was selected by Statgraphics. If the p-value selected is greater than an acceptable level of significance, the data can be considered log-normal. As can be seen from Table 4.3, p-values computed by the test for all variables is greater than 0.05, except for SO_4^{2-} and Cr, meaning concentrations of these elements show log-normal distribution within 95% confidence interval. When the goodness of fit tests was applied to SO_4^{2-} and Cr, Weibull distribution was the best fitted one with 95% confidence interval. Figure 4.2 illustrates the frequency histograms of Fe which shows log-normal distribution and SO_4^{2-} which shows weibull distribution.

Median and geometric mean values represent log-normally distribured data sets better than arithmetic mean values. Due to this reason, median values, robust against the outliers, will be used in throughout the manuscript.



(a)



(b)

Figure 4.2. Frequency histograms of (a) Fe and (b) SO_4^{2-}

4.1.2. Comparison with Literature

Comparison of the measured concentrations of elements in this study with those obtained in previous studies allows to evaluate the level of pollution at Çandarlı. For this purpose, various sampling sites were selected around the world and also in Turkey. However, selection of sites was not done randomly. Instead, rural regions where parameters measured agrees with those measured in this study were preferred to be compared. When comparing these data, it should be noted that the concentrations of elements depend on several factors such as physical and chemical transformations, the strength of sources and meteorological factors. Although the sites used in this section are rural areas, the measured concentrations follow either similar pattern or significantly different pattern among the sites. Brief information about site characteristics can be useful to determine underlying factors for observed similarities or differences between stations.

The studies selected for comparison include Nam Co Region (China) (Cong et al., 2007), Chaumont (Switzerland) (Hueglin et al., 2005), Bemantes (Spain) (Salvador et al., 2007), Alert (Canada) (Xie et al., 1999a), Tien Shan (Kazakhstan) (Hoornaert et al., 2004), Amasra (Turkey) (Doğan, 2005) and Antalya (Turkey) (Güllü, 1996).

Brief description of sampling sites are given below.

a) Nam Co Region, China (Cong et al., 2007)

This station was set up at the southeast shore of Nam Co which is the largest lake in Tibet at an elevation of 4718 m. The collected samples were analyzed using particle induced x-ray emission (PIXE) method. The arithmetic means of elemental concentrations were listed. Reported concentration of S was converted to SO_4^{2-} for valid comparison.

b) Chaumont, Switzerland (Hueglin et al., 2005)

Sampling was performed at various sites of Switzerland. Measured concentrations of elements collected at rural one was selected for comparison. The site was located in the north-western part of the country with an elevation of 1140 m a.s.l. Trace elements were determined by inductively coupled plasma mass spectrometry (ICP-MS). Arithmetic means of elemental concentrations were listed.

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

The monitoring station was located in the north-western part of Spain and 2 km inland along the main axis of the estuary named Ria de Betanzos at the Atlantic Ocean. The techniques used for chemical analysis of selected elements for comparison included inductively coupled plasma atomic emission spectroscopy (ICP-AES), ICP-MS and ion chromatography (IC). Arithmetic means of elemental concentrations were listed. For valid comparison reported concentration of Al_2O_3 and SiO_2 were converted to Al and Si, respectively.

d) Alert, Canada (Xie et al., 1999a)

Sampling was performed at Alert, North-west Territories of Canada in order to understand the extend of Arctic air pollution. The samples were analyzed by ICP, IC and instrumental neutron activation analysis (INAA). Geometric means of elemental concentrations were reported.

e) Tien Shan, Kazakhstan (Hoornaert et al., 2004)

Sampling was done at a remote astronomical observatory in the region of Tien Shan mountains at an elevation of 2760 m above sea level. Samples were analyzed by EDXRF and arithmetic means of elemental concentrations were listed. Reported concentration of S was converted to SO_4^{2-}.

e) Amasra,Turkey (Doğan, 2005)

The station was located in the north coast of Turkey with a distance of approximately 3 km to the Black Sea. The altitude of the station was 150 m. Samples were analyzed by INAA, IC and atomic absorption spectrometry (AAS). Geometric means of elemental concentrations were reported.

f) Antalya, Turkey (Güllü, 1996)

Sampling was performed at a coastal site at the Mediterranean coast of Turkey, at approximately 20 km to the east of Antalya. The altitude of station was 20 m above sea level. Analytical techniques used for measurement of species were INAA, AAS and IC. Arithmetic means of elemental concentrations were chosen from the data set.

The concentrations of trace elements measured in the aforementioned sites and in this study are given in Table 4.4 and Figure 4.3 for visual comparison. Since arithmetic means are tabulated in most of the selected studies, average concentrations obtained in this study also used for comparison.

In comparison with Alert, the elemental concentrations measured in our station, except for Pb which is comparable, are higher at least a factor of three, indicating the atmosphere in Alert is more pristine than that in Çandarlı.

The average concentrations of the crustal elements, like Mg, Al, K, Ca, Ti, Si, Fe, are significantly lower in this study than the values reported in the Antalya station and much higher than those reported in the Nam Co Region, Chaumont and Tien Shan. In addition, except Mg and K, concentrations of almost all elements of crustal origin are fairly higher than corresponding concentrations measured in Bemantes. Among crustal species concentrations of K, Ca and Fe are slightly higher than the concentrations measured in the Amasra station. From the picture emerging, it can be concluded that concentrations of crustal elements collected in different stations located at several parts of Turkey are considerably higher than the values reported in other rural parts of the world. This not surprising considering the aridity of the Mediterranean and Middle East regions. When three stations located on the Mediterranean, Black Sea and Aegean coasts of Turkey are compared, the highest concentrations for crustal elements are reported on the Mediterranean coast, followed by Black Sea coast. The highest concentrations measured in the Mediterranean coast can be partly due to low annual rainfall in the region and partly due to frequent transport of dust from north Africa.

Table 4.4. Comparison of elements measured in this study with those measured in other locations (ng m-3)

[a]Cong et al., 2007 [b]Hueglin et al., 2005 [c]Salvador et al., 2007 [d]Xie et al., 1999a [e]Hoornaert et al., 2004 [f]Doğan, 2005 [g]Güllü, 1996

	Nam Co Region, China[a]	Chaumont, Switzerland[b]	Bemantes, Spain[c]	Alert, Canada[d]	Tien Shan, Kazakhstan[e]	Amasra, Turkey[f]	Antalya, Turkey[g]	This study
Mg	12	40	153			110	365	77.0
Al	131	91	85	65	140	900	540	239.9
Si	550		450	190	540			600.5
SO_4^{2-}	303	2000	2995	490	1050	4150	5540	1325.0
K	82	91	175		110	135	365	160.0
Ca	251	138	134	70	250	270	2100	504.0
Ti	10		7	5	16	20.3	40	18.0
Cr	1		1		1.3	0.87	3.75	1.5
Mn	3.7	2.4	5	0.75	3.4	8.68	8.93	11.0
Fe	94	93	137		150	200	390	265.0
Ni	0.95	1.3	3		0.61	1.13	2.5	1.1
Pb		5.4	8	0.6	4.4	12.06	21	0.5

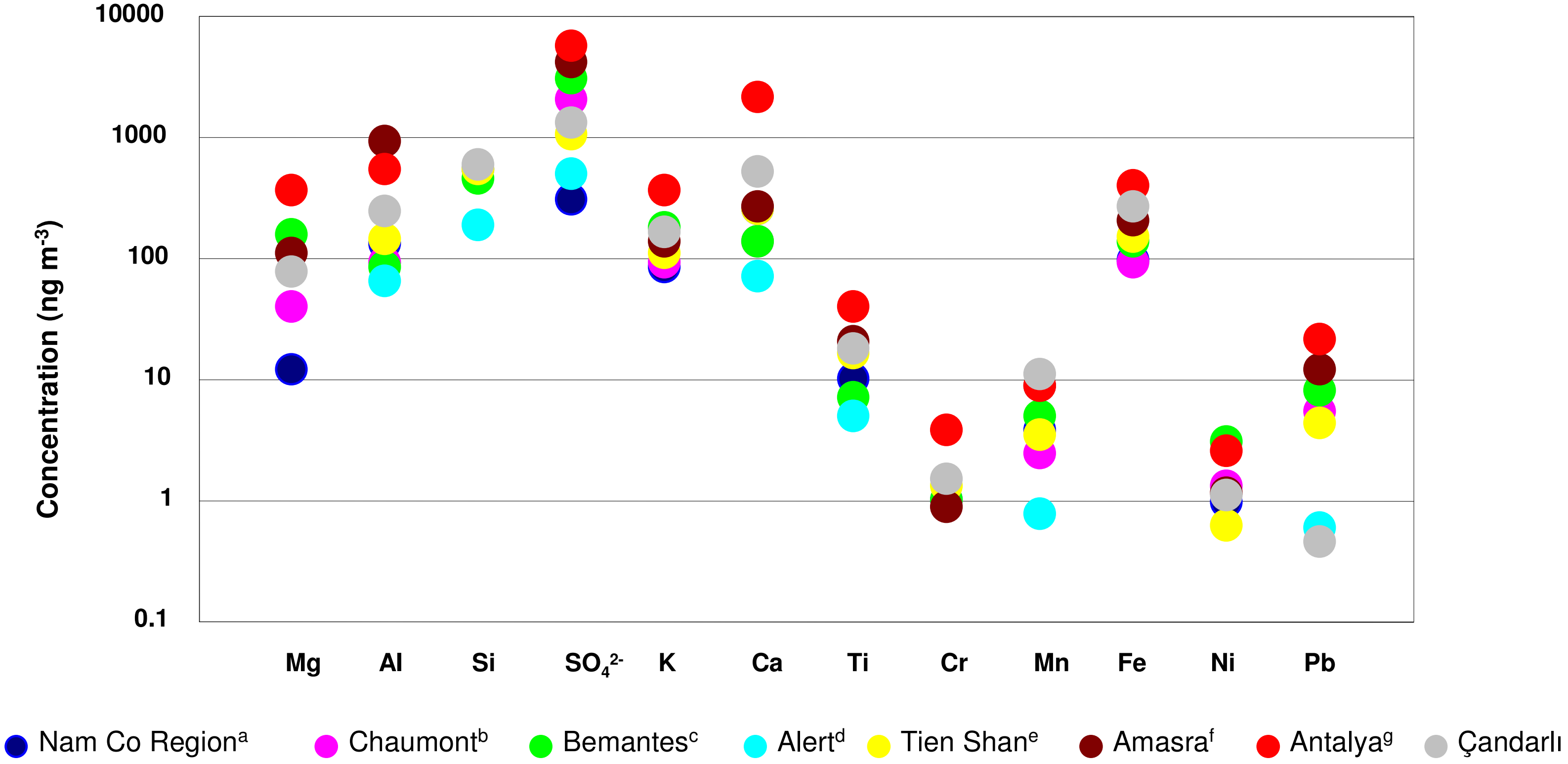


Figure 4.3. Comparison of elements measured in this study with those measured in other locations (ng m^{-3})

[a] Cong et al., 2007 [b] Hueglin et al., 2005 [c] Salvador et al., 2007 [d] Xie et al., 1999a [e] Hoornaert et al., 2004 [f] Doğan, 2005 [g] Güllü, 1996

Hence, composition of soil determines the contribution of each element to the total particulate matter collected in sampling station. The difference in the concentrations of crustal elements measured at different parts of the world can be related to (1) the different abundance of each element in the soil at these sites, particularly for elements like Ca that show a significant variation from one place to another and (2) different emissions depending on the different precipitation frequency and intensity. Based on this discussion, high calcium content at Çandarlı may correspond to calcareous soils around the station. Even though concentrations of crustal elements mainly depend on resuspended local soil, a portion of them can be from soil transported to the region.

Mg and K in the aerosol can be considered to exist as a mixture originated from marine salt and soil at the coastal sites. Concentrations of these elements are remarkably higher than concentrations measured at the Nam Co Region, Chaumont and Tien Shan stations, which are located far away from sea indicating that source of Mg, K is only crustal material at these stations. Concentrations of these two elements are not dramatically high compared to concentrations observed at the Antalya station. Among the coastal stations, concentration of Mg is lowest at the Çandarlı station, whereas concentration of K is comparable at Çandarlı, Amasra and Bemantes stations and higher at the Antalya station.

In fact, concentrations of sea salt particles depend on the relative distances of stations to the coast. The sea salt particles generated via bubble bursting tend to settle out quickly due to their relatively large size. Then, their concentrations are expected to be higher at the Çandarlı and Antalya stations. Because these two stations are located at the coast and conversely, Amasra and Bemantes stations are located approximately 3 km away from the coast. There is a very good agreement between the concentration of Ca and proximity of stations to the sea. However, this statement contradicts with lower or similar concentrations of Mg and K at the Çandarlı station in comparison with the Amasra and Bemantes stations. This pattern can be attributed to the different contribution of soil to these elements or different wind speeds.

As it is previously stated, Cr, Mn and Ni have mixed sources. Although some portion of them are associated with anthropogenic emissions, significant fractions of them also originate from resuspended soil. As the sites selected for comparison are rural, the contributions from local anthropogenic sources to these elements tend to be lower and it is not surprising that the contributions to concentrations of them are dominated by soil enriched with Cr, Mn and Ni. It is also worthy to point that they may also reach to the sampling stations from distant anthropogenic sources by transport. The concentration of Mn is highest at the Çandarlı station among the concentrations reported in other studies. Actually, Mn concentrations are significantly higher in all three stations located at the coastal sites of Turkey. This was also observed previously on the samples collected from Black Sea atmosphere and attributed to the dense ferromanganese industries in Central Russia (Hacısalihoğlu et al., 1992). Significantly higher concentrations of Ni and Cr are reported in the Antalya station than Çandarlı station and it is attributed to soil enrichment with these elements in the eastern Mediterranean (Kubilay and Saydam, 1995). In comparison with other sites except Antalya, the concentration of Cr is slightly higher, whereas Ni concentration is significantly less than those measured in the Bemantes station and comparable with the rest of the selected sites.

In addition to Cr, Mn and Ni, some fraction of which are emitted from anthropogenic sources, two other truly anthropogenic species (Pb and SO_4^{2-}) were measured in this study. Pb concentration measured at the Çandarlı station is significantly smaller than Pb concentrations measured in all other stations, and the highest concentration of Pb is reported at the Antalya station, followed by the Amasra station. It is known that Pb is emitted from burning of leaded gasoline and smelters (Simonetti et al., 2004; Sun et al., 2006). Therefore, relatively low concentrations of anthropogenic elements, in a region fairly close to an industrial area, indicates that the sampling point is not strongly influences by local anthropogenic emissions. It should also be noted that Pb concentrations in atmospheric data sets strongly depends on the sampling year. Samples collected before 2002 (Antalya and Amasra) are expected to be enriched in Pb, because leaded gasoline was commonly used in the vehicle fleet in Turkey. However, the use of leaded gasoline was banned in 2002, after installation of catalytic converters. Due to this transition, atmospheric Pb concentrations are expected to be higher in Antalya and Amasra data sets, where samples are collected before 2002, compared to the concentrations measured at Çandarlı where samples were collected last year.

Concentration of SO_4^{2-} measured in this study is significantly lower than the concentrations measured in the Antalya, Amasra, Bemantes and Chaumont stations and higher than the values reported at more remote sites, namely Nam Co Region, Alert and Tien Shan. Sulfate is an anthropogenic specie associated with long range transport. From such knowledge, it is expected that concentration of SO_4^{2-} reported in Çandarlı station is higher than that reported in the Antalya station due to the proximity of Çandarlı to the most likely source regions, like Eastern and Western Europe. Because of extensive industrialization in Western Europe and lack of emission controls in Eastern Europe, emissions at these regions are high and if high emissions coupled with frequent flows, then Çandarlı station receives more pollution derived elements than the Antalya station. However, when compared with Antalya and Amasra, significantly lower concentration of SO_4^{2-} may be attributed to different flow pattern at these sites. High variability in SO_4^{2-} concentration measured in different parts of Turkey was reported previously (Yörük, 2004; Doğan, 2005) and attributed to different flow patterns affecting coastal and high-altitude sites.

Discussions presented up to this point provided information on the general characteristics of the generated data and level of pollution in the Çandarlı region. Sources of the observed concentrations of elements at the Çandarlı station will be discussed in subsequent sections.

4.2. Flow Climatology of Aegean Region

4.2.1. Local Meteorology and the Influence of Industries in Aliağa Region

Aliağa is a highly industrialized area located at approximately 20 km south of Çandarlı. The industrial activities include a petroleum refinery, a petrochemical complex, LPG storage plants and some chemical industries. In addition, several iron-steel plants, a fertilizer plant and a natural gas burning power plant operate at 5 km south of Aliağa. Due to the lack of effective emission control technologies, pollutants are emitted in large amounts from these sources. As a result, high emission rates create serious threat endangering the air quality in the Aegean Region. It is fairly well established in the literature that elevated levels of anthropogenic pollutants are observed in Aliağa region, its surroundings and also in

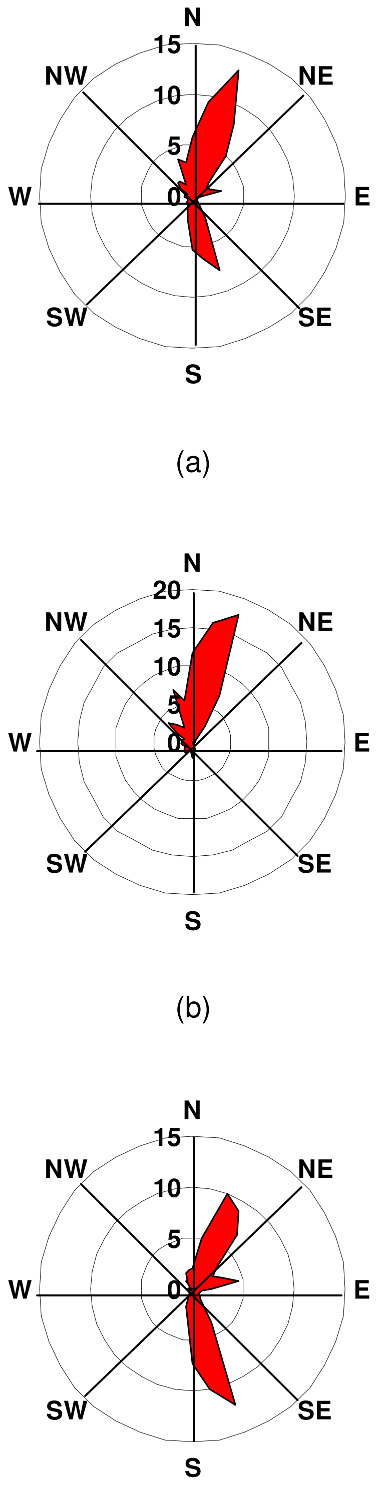
İzmir which is located 50 km south of this industrial area (Muezzinoglu et al., 2003; Cetin et al., 2005; Ulu et al., 1994; Dincer et al., 2003).

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 from Aliağa region. 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, the impact of industries on the Çandarlı station is investigated. The observed concentrations of elements at a specific location depend not only strength of sources but also meteorological parameters. Despite high emissions of pollutants in Aliağa region, the sampling site can be accepted as a representative rural background site if no or limited transport of pollutants from industrial area can be demonstrated.

To clarify this discussion, firstly, annual and seasonal wind roses were prepeared for the sampling period. These roses are depicted in Figure 4.4. The surface meteorological data used in this study is obtained from General Directorate of Meteorology. In addition to meteorology, hourly SO_2 concentrations were measured for 13 days in November 2006. The objective of these two-week-long measurements was to detect episodes that show transport of pollutants from local sources at the Aliağa industrial zone. The time series plots of SO_2 data are given in Figure 4.5.

The main source of SO_2 in the atmosphere is combustion of fossil fuels with high sulfur content (Badr and Probert, 1994). Among the fossil fuels, fuel oil usage is high in Aliağa region because of presence of a petroleum refinery (TUPRAS) and a petrochemical complex (PETKIM). They were found to be significant sources of air pollution via SO_2 emissions with values amounting to 27,900 ton yr^{-1} for TUPRAS and 25,730 ton yr^{-1} for PETKIM by Elbir and Muezzinoglu (2004).

Sulfur dioxide has short residence time in the atmosphere and is oxidized to sulfate within few days. Therefore, SO_2 cannot be associated with regional-scale transport, which requires longer times to observe the concentrations of any specie at a receptor site. Consequently, SO_2 concentrations obtained at the Çandarlı station are



(a)

(b)

(c)

Figure 4.4. Wind roses prepeared with meteorological data measured at Aliağa during the measurement campagins (a) annual, (b) summer and (c) winter

most probably due to the transport of local SO_2 emissions from Aliağa region. Another important point is that the oxidation rate of SO_2 to SO_4^{2-} is enhanced in summer months due to increased solar radiation, and this, in turn, results lower concentration of SO_2 at a receptor site in summer. Hourly concentrations of SO_2 were measured in November as to figure out the impact of local sources more clearly. Çandarlı is a touristic city with high population during summer months. In November and in other winter months population is at its lowest and observed episodes represent transport from industrial area located to the south of Aliağa.

As discussed in the chapter on experimental procedures, the distribution of emission sources around Çandarlı is not uniform. Aliağa industrial zone is approximately 20 to the south of the sampling point and there is no other significant industrial activity within 100 km in other sectors. This means that the only contribution of local sources can be from the south sector.

As can be seen from Figure 4.4, the most frequent annual flows are from NNE and SSE sectors, and also there is a relatively less frequent flow from S sector. Flow from NNE sector is characteristic for this region and observed in previous studies (Ulu et al., 1994). Flows from southerly (S and SSE) directions, on the other hand, are infrequent in the region. In summer season, prevailing flows are from NNE sector and there is no flow from southerly directions. Similar to annual flow pattern, flows from NNE and SSE sectors are more dominant accompanied with a small S component in winter season. One important point to remember, these wind roses were plotted by using meteorological data obtained during the sampling period which is relatively short. Therefore, it is unlikely to make a generalization about flow pattern in Aliağa which can be different from this pattern by using meteorological data for longer periods. Hence, this factor should be taken into consideration while discussing the relation between flow patterns at Aliağa region and measured SO_2 concentrations at the Çandarlı station.

Another important point to consider is that flow from SSE is not likely to bring pollutants from industrial region. As Aliağa region is located at south of Çandarlı, flow coming from S direction is expected to affect the sampling station. Hence, frequency of flow from S sector is of concern in this study. In order to have clearer vision about the influence of wind direction, annual wind roses, shown in Figure 4.6, were prepared with two-hour periods of each day. The most frequent flow from S

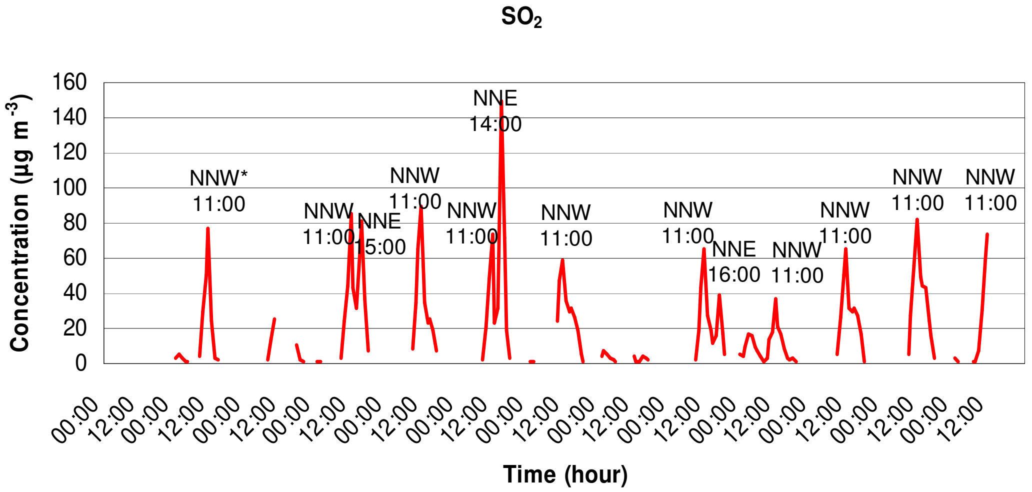
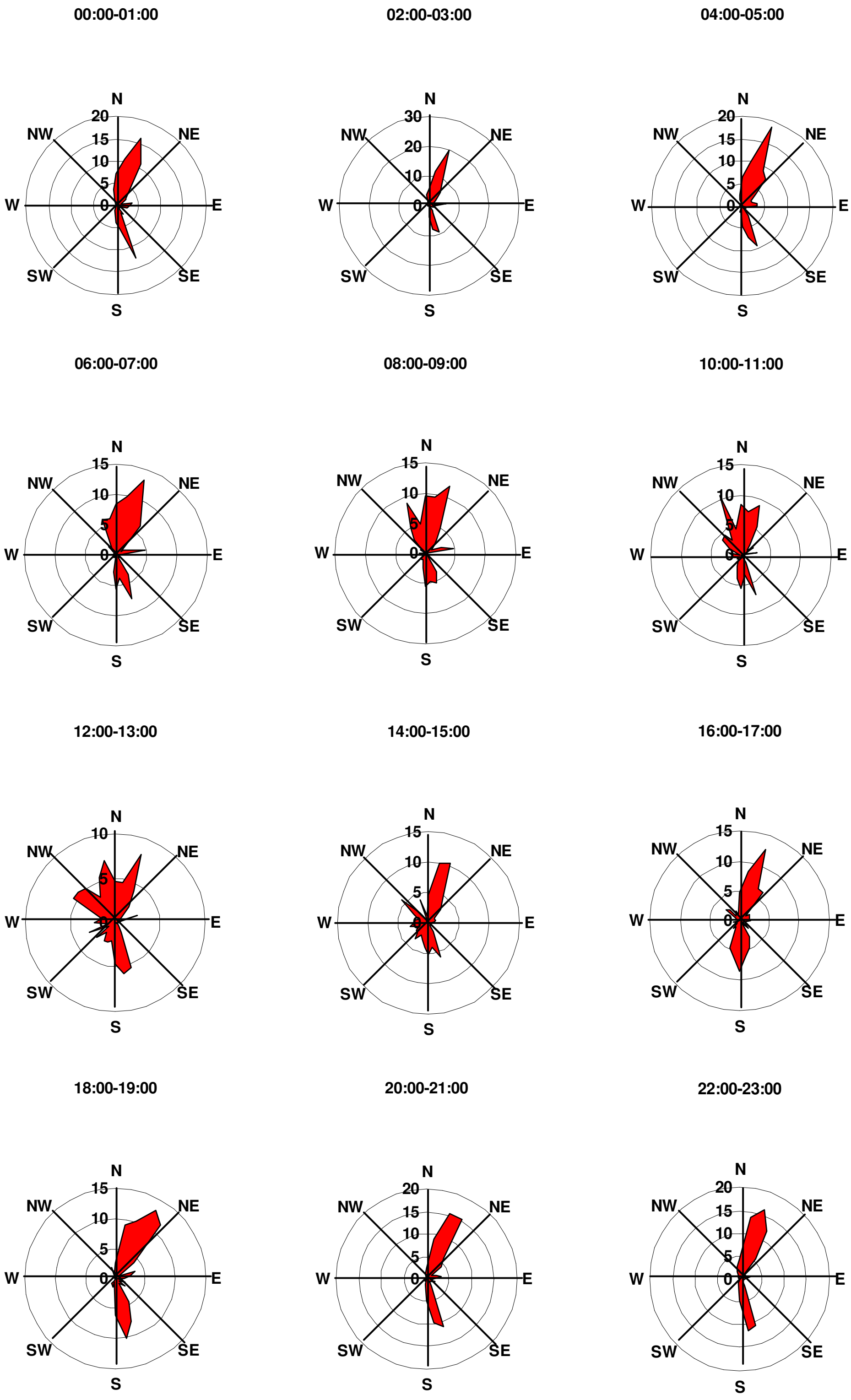


Figure 4.5. Time series plot of SO_2 measured at Çandarlı in a 13 day period between November 4 and 16, 2006

* annual dominant wind direction at Aliağa associated with high concentrations of SO_2 measured at Çandarlı

sector is at 16:00-17:00 pm and also fairly less frequent or no southerly flows are seen at different time periods. Detected flow from S sector is a periodic flow occuring at specific time of a day, and these types of flows are generally observed depending on land-sea breezes and the location of sampling station with respect to sea.

Based on the above discussion, it is expected to measure higher SO_2 concentrations at the Çandarlı station at 16:00-17:00 pm. However, the situation is different. As shown in Figure 4.5, highest concentrations of SO_2 are reported at 10:00-11:00 am despite the less frequent flow from S sector. Concentrations of SO_2 reported are significantly low, and most of the time they are near zero. The average concentration of SO_2 is 56 µg m^{-3} between 10:00 and 11:00 am, whereas the average concentration is 16 µg m^{-3} except this two-hour. During this time, SO_2 concentration reaches up to 90 µg m^{-3}. The only exception to this trend is a maximum value of 149 µg m^{-3} reported at 14:00 pm. The period at which southerly flow becomes most frequent is not associated with high concentrations of SO_2



00:00-01:00

02:00-03:00

04:00-05:00

06:00-07:00

08:00-09:00

10:00-11:00

12:00-13:00

14:00-15:00

16:00-17:00

18:00-19:00

20:00-21:00

22:00-23:00

Figure 4.6. Annual wind roses with 2-hour periods at Aliağa

measured in the Çandarlı station. The reason is not clear. Highly periodic SO_2 episodes may not be due to transport from industrial area and may be a totally different source. However, sampling point where SO_2 measurements were also recorded is a fairly deserted area in November and such a source that can generate SO_2 at the immediate vicinity of the station is not known. Another possibility is malfunctioning of the clock either in the meteorological station or in SO_2 monitor. Such a malfunctioning is not detected in the instrument and also it is very unlikely in the automated meteorological station.

Whatever the reason is, it is clear that the industrial area affects the sampling point for at most two hours in a day (if the source of the SO_2 episode is not the transport from industrial area than the impact of the industrial zone is even smaller). Therefore, it is considered that pollutants transported from distant regions are not masked by those from Aliağa region and concentrations of elements measured in this study represent regional levels.

4.2.2. Annual and Seasonal Flow to Çandarlı Area

In previous section, surface wind observations obtained at Aliağa during the sampling period were discussed to figure out the impact of local emission sources. Surface winds are a determining factor in local-scale transport. However, upper air wind observations must be investigated in order to assess regional-scale transport. While determining contribution of distant sources to measured concentrations at a receptor site, both strength of emission and frequency of flow from source region are significant parameters. When frequent flow is associated with high emissions, then the region is assigned to be a potential source region for receptor site. Therefore, priority should be given to understand flow climatology of the region to gain insight into the possible origin of sources. So, this analysis, in turn, gives a better way of interpretation of temporal variations on measured concentrations of trace elements.

Air mass backtrajectory analysis was applied in present study. Backtrajectories can be defined as the succesive locations of an air parcel before it is arrived to a receptor at a given height, location and time.

In this study, the HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resources Laboratory was used with “Final Run” meteorological data archieves (FNL) to calculate 5-day isentropic back trajectories (Draxler and Rolph, 2003). Five-day back trajectories were long enough to include distances covering the major source regions expected to affecting Çandarlı, and they were also not so long as to cause unreliable uncertainties in their locations. Trajectories ending at 22:00 UTC, which was the midpoint of sampling, were calculated for a one-year period between November 2005 and November 2006. The resulting backtrajectory data consisted of time, latitude, longitude and altitude information for every hour of the 5 days of calculations. Each of the hourly location of the puff is called a “segment” or “endpoint”.

Each backtrajectories were modeled at three different starting point altitudes to average the possibility of transport at different levels. The starting levels of calculations were 100, 500, 1500 m above ground level (AGL). This is a procedure commonly used in literature. 100 m, 500 m or 1500 m refer to the starting altitude of the trajectory calculations, in other words, when starting altitude is 100 m, it is assumed that the first 100 m of the atmosphere is well mixed during sampling. The same argument is also true for 500 m and 1500 m starting points as well.

With the described procedure, 120 segments were determined at each altitude for each day. As about 2% of the segments in calculated trajectories was missing values in meteorological data archieves, a total of approximately 128600 segments were obtained instead of 131400.

In order to understand flow pattern, each 1-hour segment obtained from backtrajectories was assigned to a wind sector and the number of segments in each of the eight wind sectors were counted by using GIS software. The total number of the segments in each wind sector is the residence time of air masses in that particular sector. By means of this technique, annual and seasonal frequencies of air masses arriving at Çandarlı were calculated. Annual and seasonal flow patterns were calculated by using the trajectories of 1-year period and the trajectories associated with sampling period, respectively. Therefore, the trajectories were combined including the months from December to March for determining winter season flow pattern, and from July to October for summer season flow pattern.

The frequencies of annual airflow from each sector are presented in Figure 4.7. The most frequent airflows are from NE and W sectors. Approximately 48% of total air mass arriving at Çandarlı is from these two sectors. In other words, the region is expected to be mostly affected by the pollutants coming from the sources located in NE and W sectors. Even though the frequency of air mass transport from NW and N sectors are not as high as NE and W sectors, their contribution to the total flow is significant when compared to the rest of the sectors. The frequency of air flow from NW and N sectors accounts for 27% of total flow. From such knowledge and understanding about the annual flow pattern and, as anthropogenic sources are mostly found in the regions that are N, NE, NW and W of receptor site, it can be concluded that high emissions from these sources can reach to Çandarlı and have potential to influence measured concentrations. On the contrary, less contribution of E and SW sectors to the total flow is observed with frequencies of 7% and 10%, respectively. Air flows from S and SE sectors are relatively infrequent and accounts for approximately 8% of total flow. Therefore, the pollutants from S and SE sectors have less influence on the composition of the aerosol.

Countries associated with annual flow frequencies are depicted in Figure 4.8. Since air mass transport is more frequent from NE sector, the countries lying in this sector are more likely to affect the aerosol composition at the sampling station. As can be seen from the figure, NE sector includes Central Russia, a significant part of Ukraine and industrial areas like İzmit and İstanbul located in Turkey. Due to the heavy industries and lack of emission control in these industries, trajectories originating in Russia and Ukraine, which pass through İstanbul and İzmit, are expected to bring pollution derived elements to Çandarlı. In addition, industrialized countries like Italy, Spain, a part of France and Western Mediterranean Sea are located in the W sector from which considerable air mass movement occur. Then, these regions can be attributed to the source for marine elements and a large fraction of anthropogenic elements. Since flow frequencies are approximately similar from N and NW sectors and high when compared to the rest of the sectors, emissions in Central and Eastern European countries have also significant impact on the aerosol composition at the sampling site.

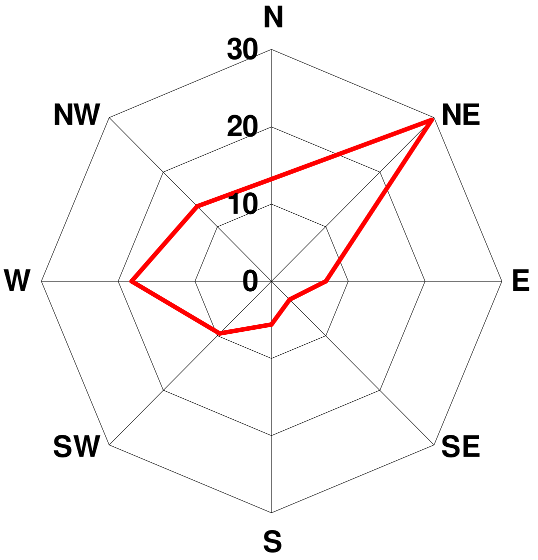


Figure 4.7. Annual flow pattern at Çandarlı

Although frequency of flow from SW sector is higher than that from E sector, emissions in E sector have more pronounced effect than emissions in SW sector. Because absence of industrial activities in northwest of Africa lying in the SW sector indicates that the region is less likely to be source for pollutants. Contribution of flow from E sector to the observed concentrations of pollutants is supposed to be high but not as high as N, NE, NW and W sectors. Almost all parts of Turkey, except northwest, are included in E sector and many industrial activities like Soma (Manisa), Tunçbilek (Kütahya) and Afsin-Elbistan (Kahramanmaraş) Thermal Power Plants are present in Turkey. Therefore, air masses coming from Anatolia region bring pollutants without effective scavenging as the distance traveled is short.

Seasonal differences in flow frequencies can have a significant impact on seasonal variations in concentrations of measured elements. In order to reach such a conclusion, the presence of significant differences in the flow patterns between summer and winter seasons must be demonstrated. The frequency of airflow from each sector is given in Figure 4.9 for both seasons.

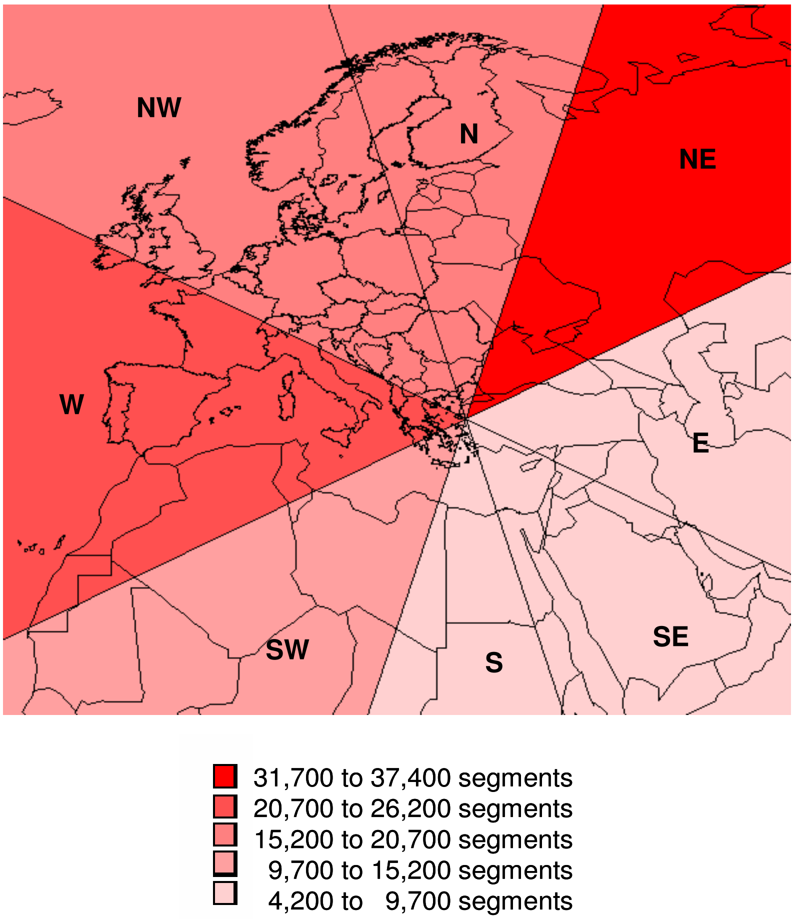


Figure 4.8. Countries associated with annual flow frequencies

There are some differences in air mass transport from each sector between summer and winter season. Summer flow pattern is closely similar to annual flow pattern, and frequency of flow changes from one sector to another, with highest frequencies in NE, N and W sectors. During winter season, on the other hand, air flow frequencies between sectors are not as variable as those observed in summer season. In summer season, flows from NE and N sectors are more frequent than the flows observed from these two sectors in winter season. There are smaller seasonal differences in air mass transport from W and NW sectors. Contribution of E, SE, S and SW sectors to total flow in winter season are higher than corresponding contributions in summer months. The difference between summer and winter frequencies of flow from SE, S, SW sectors are 4%, but slightly higher from E sector which is 6%.

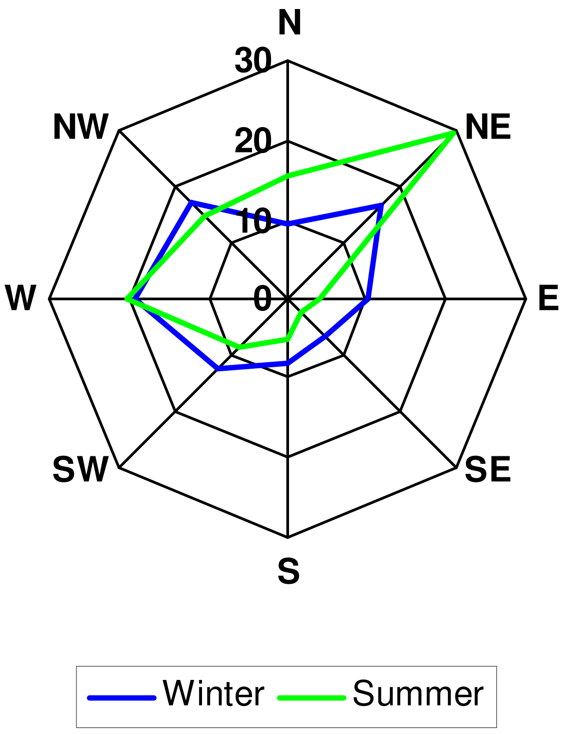


Figure 4.9. Seasonal flow patterns at Çandarlı

Countries associated with seasonal flow frequencies are depicted in Figure 4.10. As can be seen from the figure, emissions from Central Russia, a large portion of Ukraine reach to the sampling site more frequently in summer. However, contributions to the aerosol composition from Western European countries are nearly same in both seasons. During winter, air mass movements from Central European countries are slighty higher, whereas during summer air flow from Eastern European countries are higher. In addition, emissions from central part of Turkey arrive more frequently in winter than in summer. In summary, almost all parts of Europe and Central Russia are more likely to be source regions for pollutants measured at Çandarlı due to frequent air mass transport from these regions combined with heavy industrial activities.

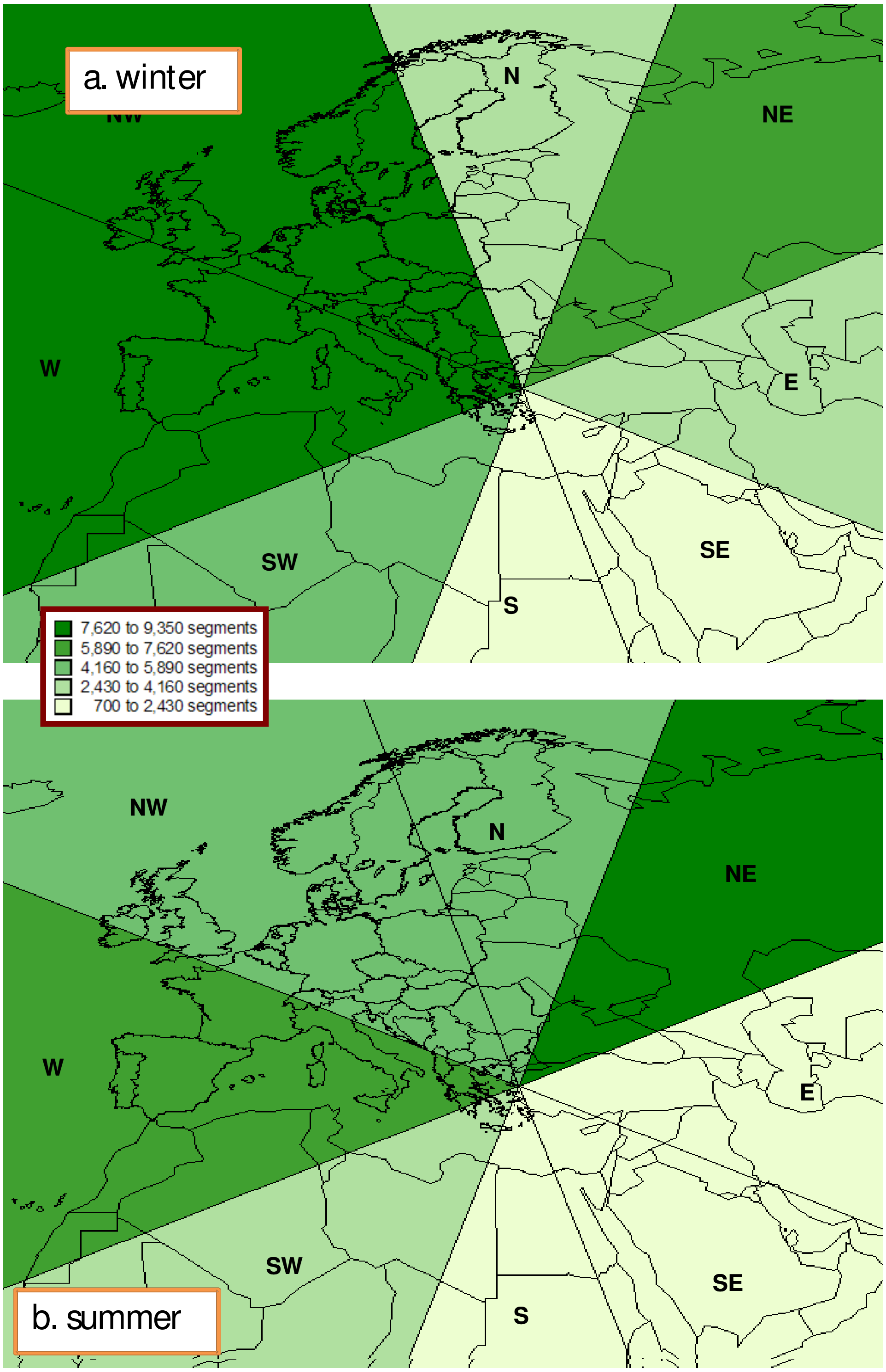
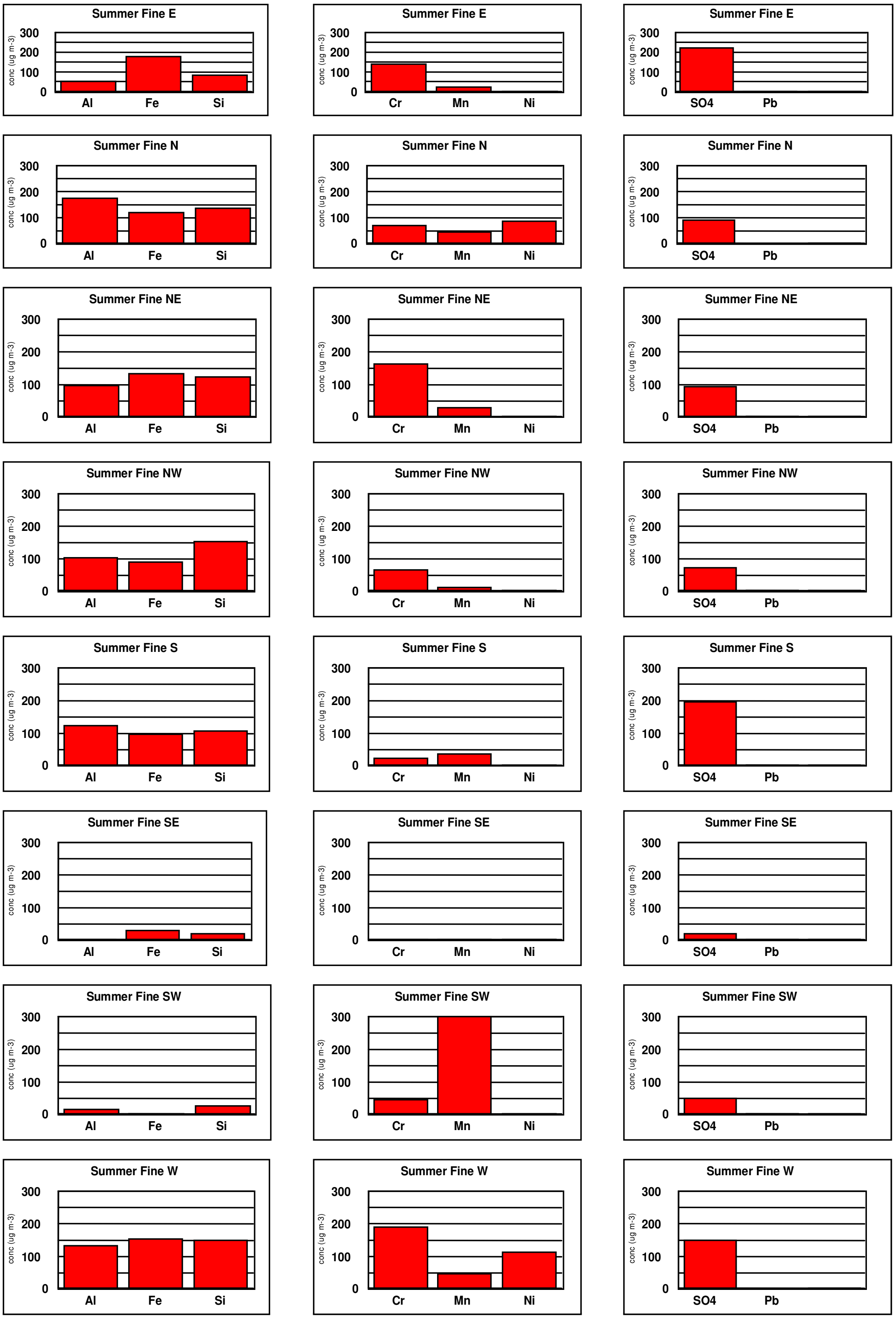


Figure 4.10. Countries associated with seasonal flow frequencies

Up to this point, frequency of air flow from different wind sectors has been considered. However, source strength is another determining factor in relation with flow frequency in the measured concentrations of pollutants. In order to gain a better understanding of potential source regions, sectorial fine and coarse concentrations of selected elements during summer season are presented in Figure 4.11. Average concentrations in each of the eight sectors were multiplied by some factors indicated below the figure for easier visual comparison. While discussing concentrations of elements on sectors, only summer season is considered due to favourable meteorological conditions giving chance to transport of pollutants more frequently for longer distances. In winter season, influence of local sources becomes clear, and upper air data contradicts with the winter concentrations of elements. Because low mixing height meaning that the air is generally stagnant with very little vertical motion trap pollutants near the ground surface in winter season. Furthermore, scavenging by precipitation is an effective mechanism which decreases the loads of air masses during winter season.

Sectorial elemental concentrations were determined by the method described by Katsoulis (1999). Trajectories were assigned to a particular sector visually as if they resided over it for all the time of travel to the sampling site. However, uncertainties can arise from this approach. Trajectories usually do not spend all the time in one of the sectors. They, instead, cross the borders of other sectors. Therefore, concentration of an element on any of the sectors does not necessarily imply that the sources located at that sectors are totally responsible for them. But, an appreciably large fraction of this element can be attributed to sources in that sector. Another limitation of this method is that frequency of flow is not considered. If high emissions from sources are present at a region, but few trajectories carrying higher amounts of these emissions reach to the sampling site, then the region cannot be regarded as potential source region for pollutants.

Elements were divided into three groups. First group consists of Al, Fe and Si which are crustal elements. Second group includes Cr, Mn and Ni. The source of them in coarse fraction is crustal material, whereas anthropogenic sources increase concentrations of them in fine fraction. Anthropogenic elements, including Pb and SO_4^{2-}, are in the third group.



* Al, Fe, Si, Cr, Mn, Ni, SO_4^{2-}, Pb are multiplied by 1.48, 1.56, 0.71, 275.32, 9.49, 176.88, 0.10, 200, respectively.

Figure 4.11. Average concentrations of selected elements in different wind sectors

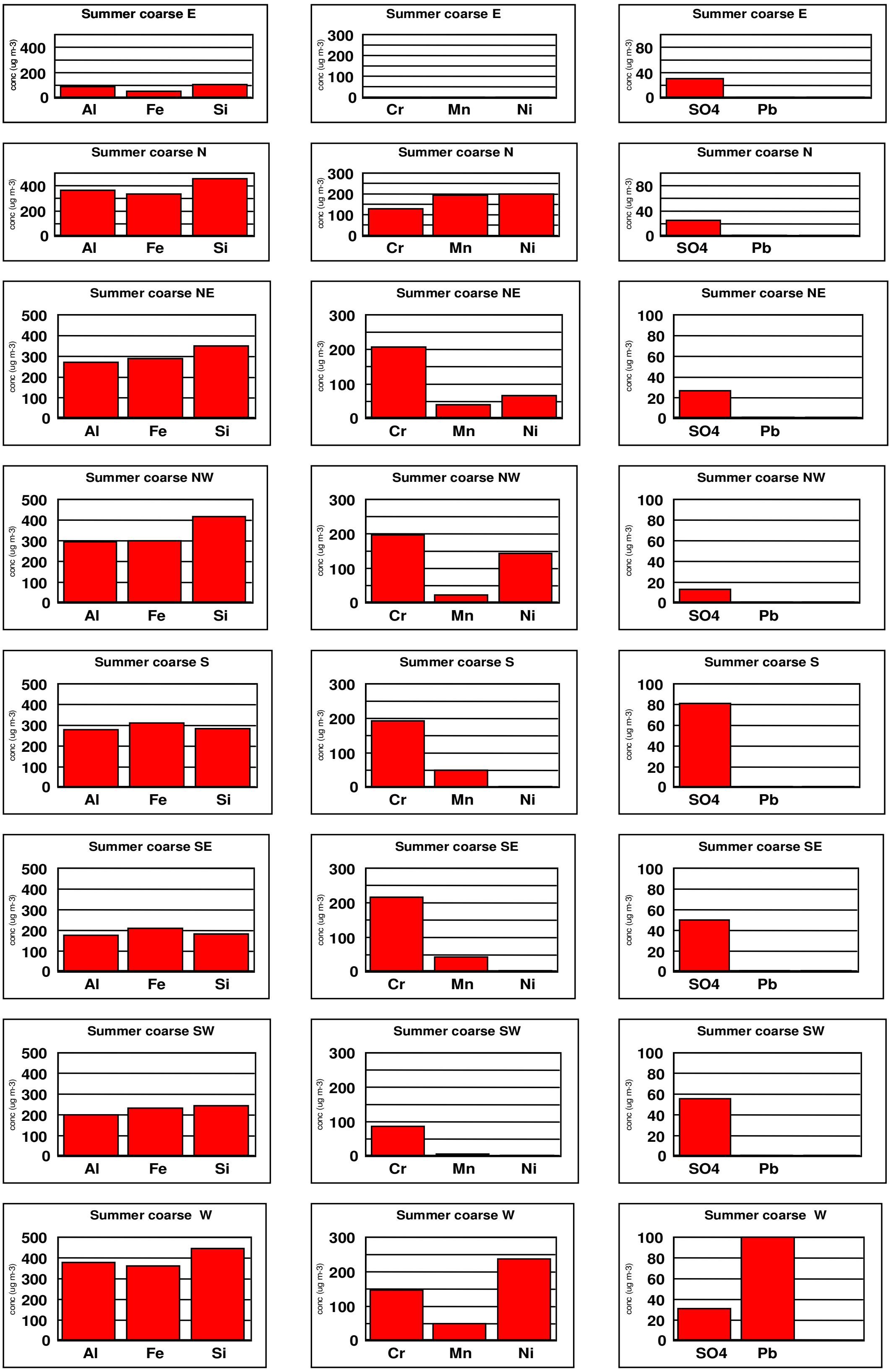


Figure 4.11. Cont’d.

Concentrations of crustal elements in fine fraction are noticeably low as it is expected. They distribute uniformly in almost all sectors except SE and SW sectors. Least loaded air masses originating from SE and SW sectors suggest that the sources in the regions lying on these sectors are not strong enough to increase concentrations of crustal elements or generation of them is limited by the meteorological conditions such as low wind speed. Concentrations of soil-related elements in fine fraction are not very informative, because only a small fraction crustal mass occurs at dimeters smaller than 2.5 µm.

Similarly, concentrations of soil-derived elements in coarse fraction do not show a significant variation from one sector to another.

Only for E sector, reported concentrations in coarse fraction are significantly low. Previous studies have shown that Eastern Mediterranean aerosol is strongly affected from Saharan dust transport events (Herut et al., 2001; Kubilay et al., 2000; Güllü et al., 2000; Kubilay et al., 1997; Koçak et al., 2004b). During these events, highest concentrations of crustal elements were observed. However, relatively low and uniform concentrations of crustal elements on the sectors indicate that the effect of local soil resuspension is the most important factor on observed concentrations of crustal elements. Apparently, the sampling site is not as much influenced as the other sites in the Eastern Mediterranean by such episodic transport from North Africa or any other regions. However, it should be noted that the period used to determine sectorial concentrations includes August, September and October in this study. These months are not the months at which Saharan dust transport occur (April, May and October). Probably a different conclusion can be reached if the sampling were done in Saharan dust transport months.

Contrary to the precedent, fine concentrations of Cr, Mn and Ni, having both natural and anthropogenic sources, show some differences within the sectors. Concentration of Cr in fine fraction is high in air masses coming from NE and W sectors, whereas it is significantly low in air masses coming from S, SE and SW sectors. Taking into consideration high concentration of Cr in NE and W sectors as well as frequent flow from these sectors during summer season, it can be concluded that Western Europe and Central Russia are potential regions for sources of Cr. This behaviour characterizes the influence of industries such as ferrochrome processing extensively operating in Central Russia and France on Cr concentration. Manganese in fine fraction has its maximum concentration in SW sector, while Mn concentration is low and comparable in the rest of the sectors. However, it still cannot be claimed that main location of Mn sources are in SW sector. Because number of trajectories assigned to SW sector is 2 out of 77. As already mentioned, high emissions must associate with frequent flow in order to determine source regions. Although Ni is included in this part of the study, sectorial concentrations of Ni, measured in few samples, can be statistically insignificant. Nickel concentration in fine fraction is higher in N and W sectors which does not indicate an important source area for Ni as it is detected only two of the samples associated with these sectors.

Concentrations of Cr, Mn and Ni in coarse fraction are higher than in fine fraction and, like crustal elements, do not show any significant sectorial variations. There are no reported concentrations of these elements in E sector. Average concentrations of Mn and Ni are slightly higher in N and W sectors, respectively.

Third group includes Pb and SO_4^{2-}, which are originated from anthropogenic sources. Similar to Ni, lead is detected in low number of samples. Therefore, discussion of sectorial preferences of anthropogenic elements is limited with sulfate. Concentrations of SO_4^{2-} in fine fraction are slightly higher in air masses coming from E, S and W sectors. However, it should be noted that in none of these sectors concentration is dominant over the others. The observed concentrations in E and S sectors do not correspond to dominant flow direction. The numbers of trajectory cases are 1 for E sector and 4 for S sector. An interesting point is that all high concentrations of SO_4^{2-} in E and S sectors are reported in October. This observation is most probably due to effects of local sources. Heavily industrialized region, Aliağa, and Yatağan Power Plant lie in S sector, while Soma and Tunçbilek Power Plants are located in E sector. Hence, air masses coming from these sectors are affected by the emissions from these industrial areas. However, Aliağa region and regions in which several power plants operate cannot be accepted as potential source regions of SO_4^{2-} because of the low number of trajectories. On the contrary, it can be claimed that sources of pollution are in W sector. This is not only due to the high concentration of SO_4^{2-} in this sector but also due to relatively high frequency of air mass arrival from that sector. Five days-long backtrajectories corresponding to the highest 40% of measured concentrations of fine SO_4^{2-} for 100, 500 and 1500 m above the ground level is shown in the Figure 4.12. As seen from the figure, trajectories are mainly in westerly and northerly directions supporting high concentration of SO_4^{2-} in W sector. Coarse concentrations of SO_4^{2-} do not show any remarkable variations among the sectors. Only in S sector, a slightly higher concentration of SO_4^{2-} is observed. It should be noted that, since only a small fraction of SO_4^{2-} is in the coarse fraction, even if there are regions with dominating influence on coarse SO_4^{2-} concentrations, that contribution would not be important on the total SO_4^{2-} concentrations.

In this section, wind direction is attempted to be related to the observed concentrations of elements. This treatment would provide an idea on the potential source regions, but cannot provide information on the contribution of these source regions, because contribution of sources or source regions depends not only on the emission strength (measured by concentrations observed in sectors) but also on the frequency of transport. For example, SO_4^{2-} concentration may be very high in one of the sectors due to a strong emitter, such as a power plant, but contribution of that power plant will not be important if air masses do not come to Çandarlı from that sector. More detailed treatment of sources contributions, taking into account not only concentrations of elements in different regions, but also frequency of transport will be presented in subsequent sections in the manuscript.

4.3. Temporal Variations

4.3.1. Seasonal Variations

In order to quantify the differences in concentrations of elements between summer and winter seasons and to identify the reasons behind those observed differences, the average and median concentrations of elements are presented in Table 4.5 for both fine and coarse fraction. Winter season includes the period between mid-December and mid-March, and summer season includes the period between August and October. As can be seen from the table, summer and winter concentrations of elements show some differences changing from one element to another. In order to have clearer vision about the differences, summer-to-winter ratios calculated by using median values of total elemental concentrations are depicted in Figure 4.13.

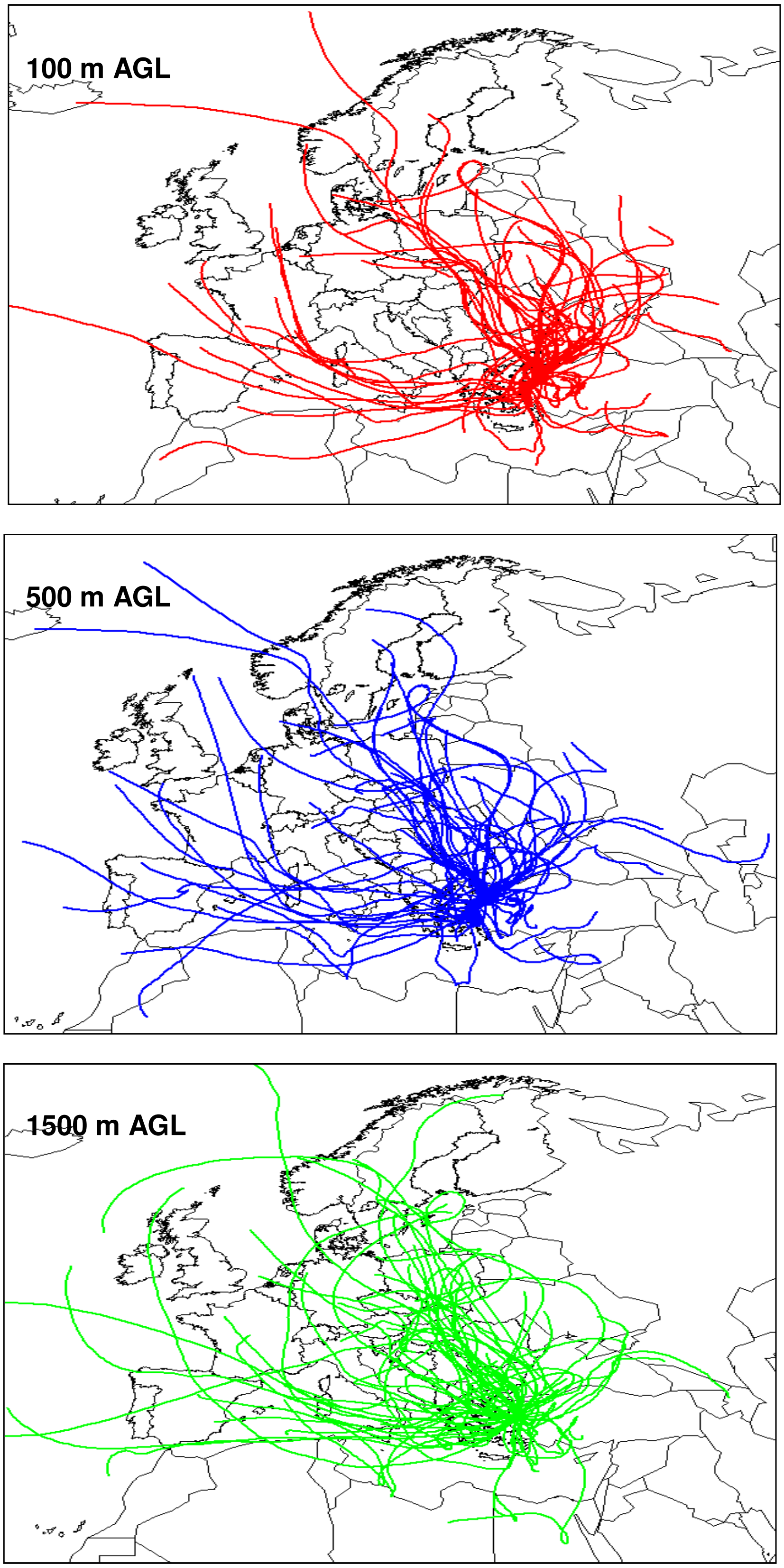


Figure 4.12. Trajectories representing the highest 40% of measured concentrations of fine SO_4^{2-}

Table 4.5. Winter and summer season average mass (μg m^{-3}) and elemental (ng m^{-3}) concentrations

	Winter				Summer			
	Fine		Coarse		Fine		Coarse	
	Average	Median	Average	Median	Average	Median	Average	Median
Mg	33.36	22.93	69.70	41.99	31.39	28.76	50.84	48.19
Al	75.99	35.70	170.58	66.81	76.42	41.26	206.06	150.29
Si	122.17	72.30	325.21	125.19	180.07	112.52	542.81	368.60
SO_4^{2-}	1153.88	988.82	220.23	161.60	1041.21	925.95	148.60	119.17
K	86.54	79.74	65.80	39.71	78.71	58.95	88.04	68.09
Ca	92.10	54.64	453.88	207.82	78.49	58.52	368.26	302.75
Ti	4.81	2.33	15.95	5.74	5.31	3.49	13.78	11.50
Cr	0.46	0.41	1.08	0.73	0.43	0.36	0.62	0.51
Mn	6.38	4.61	9.18	3.47	5.13	2.94	7.53	2.83
Fe	69.61	41.20	173.42	70.08	77.14	59.08	195.95	166.44
Ni	0.37	0.29	0.62	0.36	0.57	0.63	0.92	0.99
Pb	0.39	0.25	0.43	0.39			1.02	1.02
PM	19.73	17.97	13.84	9.40	12.82	12.24	13.95	11.60

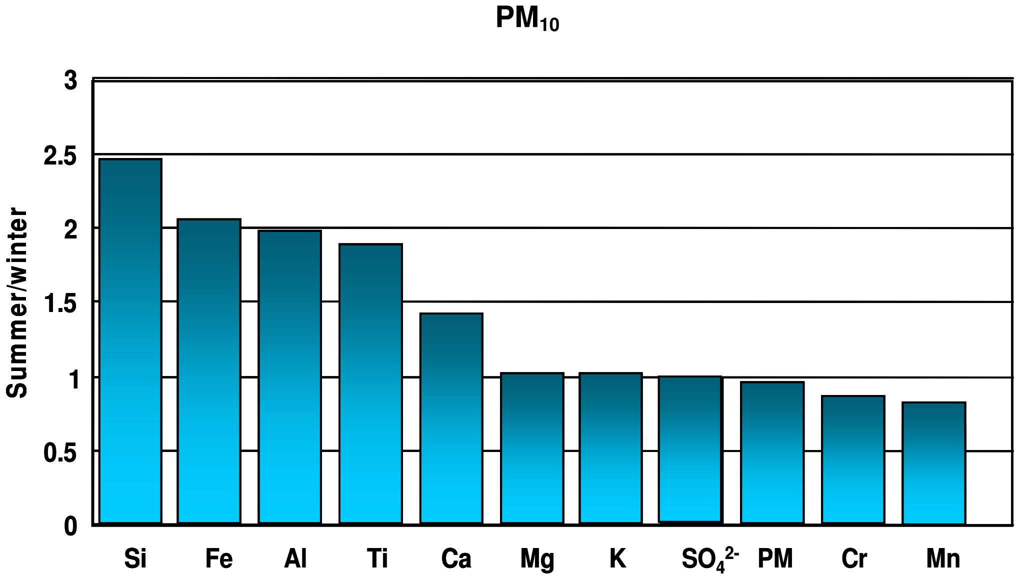


Figure 4.13. Summer to winter ratio of elements

As shown in Figure 4.13, summer-to-winter ratios of elements vary from 2.5 for Si to 0.7 for Mn. Lead and nickel are excluded from the figure as their infrequent existence in samples cause uncertainties in summer and winter concentrations of these two elements.

A students 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 Si, Fe, Al, Ti, Ca are included in the first group. Concentrations of these elements in summer season are higher than their concentrations in winter season. Concentrations of Mg, K, SO_4^{2-} and PM_{10}, on the other hand, do not show statistically significant differences between summer and winter seasons. The two elements, namely Cr and Mn made up the third group. Concentrations of these elements in winter season are higher than their concentrations in summer season. 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.

First group associated with crustal elements, Si, Fe, Al, Ti, Ca, 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. As can be seen from Table 4.5, both winter and summer concentrations of crustal elements are dominated in coarse fraction. Approximately 70% of Al and Si are associated with coarse particles, which is not surprising as association of soil related elements with coarse particles are well documented in the literature. Differences observed between seasonal concentrations of them in coarse fraction are substantially higher than those observed in fine fraction.

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.

Before discussing the seasonal variations in the concentrations of anthropogenic species, the mechanisms leading to these variations should be discussed. Concentrations of anthropogenic species differ from one season to another due to several factors. First of all, certain fraction 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. Secondly, photochemical reactions are another reason for observed seasonal variations of species like SO_4^{2-}. SO_2 is oxidized to SO_4^{2-} quite rapidly in summer months due to the intense solar radiation. So, higher summer concentration of SO_4^{2-} is expected during summer season.

One other reason is that variations in transport patterns can explain the observed seasonal differences. Emissions originating from industrialized regions are more frequently transported to the sampling site in one of the seasons, then it is not surprising to have higher concentrations of pollution-derived elements in that 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.

As stated in previous studies, concentrations of anthropogenic elements do not show as clear seasonal differences as crustal and marine elements. However, summer concentration of SO_4^{2-} is found higher in the studies performed in the Eastern Mediterranean (Güllü et al., 2000; Koçak et al., 2004b; Luria et al., 1996, Mihalopoulos et al., 1997; Kouvarakis and Mihalopoulos, 2002), and attributed to frequent precipitation scavenging in winter season and intense photochemical reactions in summer. Moreover, change in airflow patterns are reported as an another reason for the observed situation in some of these studies. In this study, SO_4^{2-} has comparable summer and winter concentrations, which is not consistent with the results observed over the Mediterranean by the other studies indicating a higher local source contribution on the measured SO_4^{2-} concentration in the Çandarlı station.

PM_{10} concentrations are similar in both seasons meaning that total aerosol intercepted at the sampling site do not differ between the seasons. Concentration measured in fine fraction is dominating in winter season, whereas fine concentration is comparable to coarse concentration in summer season. This behaviour can be explained by variations in generation and scavenging mechanisms.

Third group consists of Cr and Mn. Their concentrations are higher in winter season and lower in summer season. Therefore, it can be concluded that their sources are local, and scavenging mechanism is not as effective as long range transported elements.

4.3.2. Short-term Variations

Average concentration of an element measured at a sampling site is the combination of regional background concentration and inputs from local and distant sources. Regional background is defined as the mean concentration of a species not impacted by local emissions, and theoretically expected to be uniform over the region. The difference between average and background concentrations of elements indicates strong or weak influence of emissions from local sources and meteorological factors.

In this study, regional background concentrations of elements were calculated by deleting all peak concentrations of an element in the data, which correspond to episodic transport to the sampling site. Calculated background concentrations of elements are given in Table 4.6 together with their average concentrations. Contributions of episodes on total concentrations of elements are also included in the table. Average concentrations measured in this study vary between 0.45 ng m^{-3} for Pb and 1326 ng m^{-3} for SO_4^{2-}, while corresponding background concentrations of these species are 0.25 ng m^{-3} and 813 ng m^{-3}, respectively. As can be seen from the table, contribution of episodes to observed concentrations varies from one element to another. The most episodic behavior is observed for Si (where, 76% of total concentration is accounted for by episodes) and the least is observed for SO_4^{2-} (where 38 percent of measured concentration is due to the episodic transport).

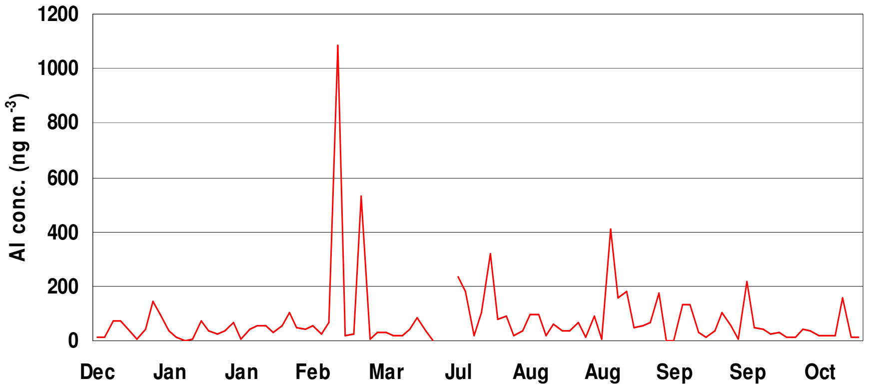
Short-term variations refer to the unusual (episodic) changes in the concentrations of elements. In order to gain better understanding in episodic behaviours, the temporal variations in the concentrations of Al and SO_4^{2-} are illustrated in Figure 4.14 for both fine and coarse fractions. Aluminum is a typical crustal element. Sulfate, on the other hand, is an example of anthropogenic elements. As seen in the figure, their concentrations show fluctuations over the study period. Strong short term variations are also observed for all other elements. This is expected and observed in most of the aerosol data (Karakaş et al., 2004; Bergametti et al., 1989; 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.

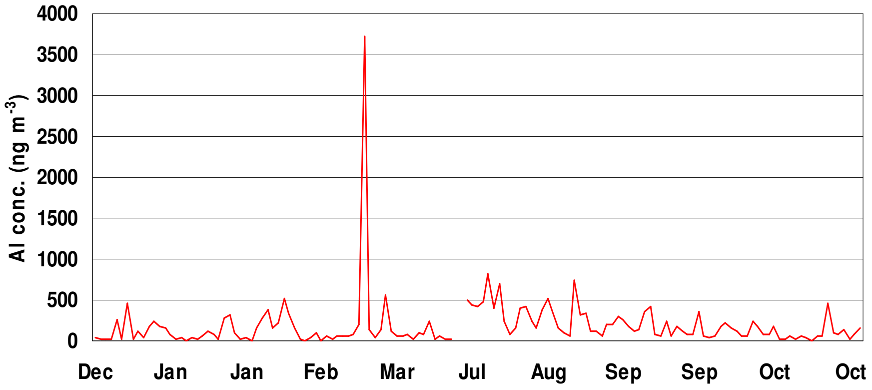
Table 4.6. Contribution of episodes on concentrations of elements

Element	Background concentration (ng m^{-3})	Average concentration (ng m^{-3})	% of episodes
Mg	46	76.97	40.24
Al	79	239.90	67.07
Si	142	600.45	76.35
SO_4^{2-}	813	1325.71	38.67
K	80	160.43	50.13
Ca	150	504.69	70.28
Ti	6.56	18.61	64.75
Cr	0.65	1.54	57.91
Mn	5.16	11.31	54.36
Fe	81	265.28	69.47
Pb	0.25	0.45	44.70

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 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 4.14, the most episodic behaviour is detected on February 24, 2006. Backtrajectories corresponding to this day indicates high concentrations of elements are due to transport from North Africa. Hence, this variation can be explained by change in transport pattern. Air mass movements from



Fine



Coarse

Figure 4.14. Temporal variations of Al and SO_4^{-2}

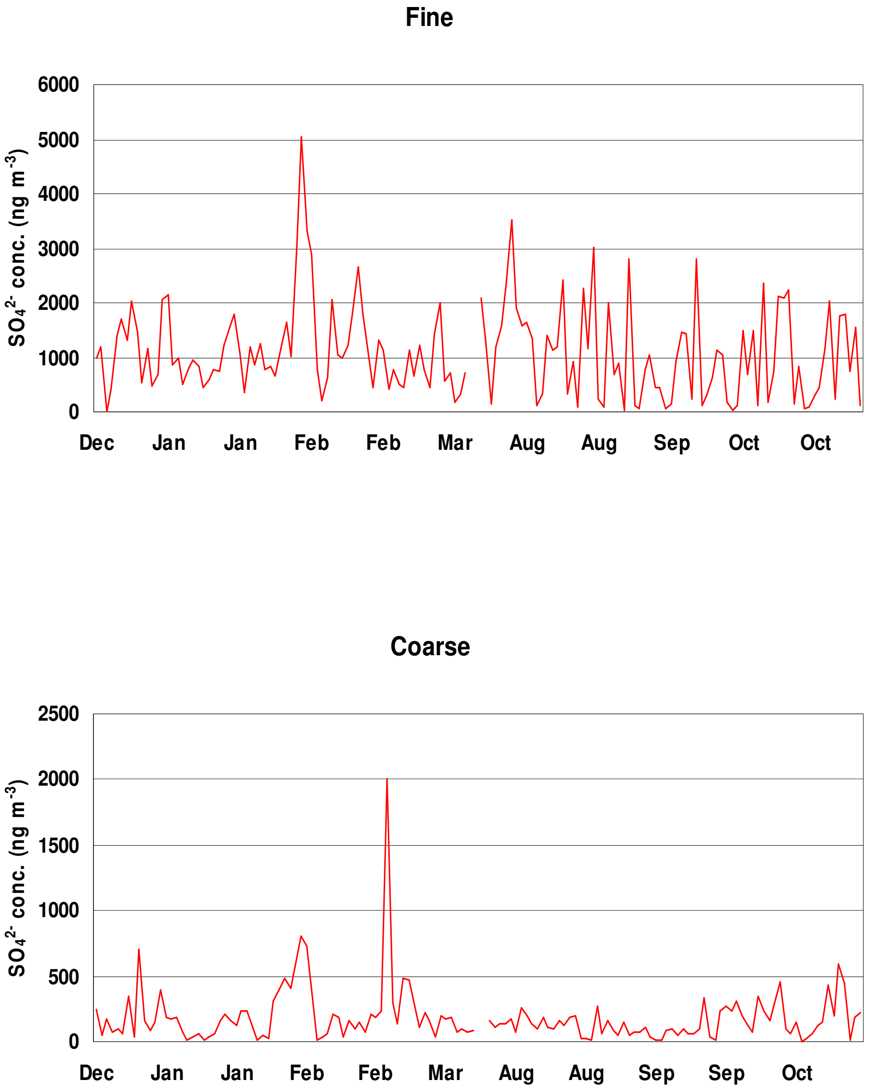


Figure 4.14. Cont'd.

southerly sector, which is a rare occasion for our sampling site, on that day bring desert dust aerosol without effective scavenging.

As seen from Table 4.6, contribution of episodes on measured concentrations of crustal elements like Al, Si, Ca, Ti and Fe is higher than that of anthropogenic elements. As crustal particles and elements are associated with them are locally generated, strong episodes in their concentrations is not surprising. During dry period concentrations of soil related elements depends strongly on the wind speed. Since wind speed shows episodic changes in a daily time-scale, it generates similar episodes in atmospheric concentrations of soil related elements.

Contribution of episodes on concentrations of pollution derived elements, such as Pb and SO_4^{2-} are the smallest among all elements measured in this study. This is an indication of distant sources of Pb and SO_4^{2-}, because strongly episodic nature in temporal variations of elements suggests influence of local sources on concentrations of that particular element. Since concentrations of elements smears out during transport, concentrations of elements reaching to sampling site are not expected to as episodic as the locally generated species.

4.4. Source Apportionment and Quantification

4.4.1. Correlations between Parameters

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 positive matrix factorization 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 coefficients (r) between the concentrations of elements are calculated for both coarse and fine fractions by using S-plus 6.0 software and given in Table 4.7 and 4.8, respectively. As can be seen from Table 4.7, all parameters measured in this study are strongly correlated [P(r,n)<0.01] in the coarse fraction. Strong correlations among crustal or anthropogenic elements are expected. But such strong correlations between anthropogenic and crustal elements is interesting. This observation indicates a dominating influence of crustal material in the coarse fraction. Concentrations of elements with mixed crustal-anthropogenic sources, such as Mn and Cr originate largely from soil in the coarse fraction. Strong correlation between SO_4^{2-} with crustal elements indicates that main source of this anthropogenic specie is also soil in the coarse fraction.

Similar to coarse fraction, crustal elements (Mg, Al, Si, Ca, Ti and Fe) are correlated well in fine fraction suggesting that the sources of these elements are soil in the fine fraction as well. Although soil is the dominating source of Mn, Cr, SO_4^{2-} in the coarse fraction, lack of correlation between these elements and crustal elements in fine fraction indicate that anthropogenic sources determine their fine fraction concentrations. In the fine fraction Mn and Cr are correlated (P[r, n]<0.05), probably indicating the role of steel industry on composition of aerosols in this region.

As SO_4^{2-} is generally associated with long range transport, moderate correlation of SO_4^{2-} and Cr in fine fraction can be related to either similar sources such as fossil fuel burning or similar transport patterns and scavenging mechanisms.

The correlations between K and crustal elements are relatively weak when compared with the correlations among crustal elements in fine fraction. Although K is a soil-originated element, it is known that biomass burning is one of the major sources of K (Liu et al., 2000; Park and Kim, 2004). Taking into account that particles emitted from biomass burning is small in size, then the weak correlation of

Table 4.7. Correlation coefficients between coarse fraction of the parameters

Mg	**Mg**									
Al	0.932	**Al**								
Si	0.919	0.996	**Si**							
SO_4^{2-}	0.812	0.804	0.755	**SO_4^{2-}**						
K	0.946	0.988	0.988	0.794	**K**					
Ca	0.906	0.955	0.931	0.887	0.952	**Ca**				
Ti	0.948	0.984	0.977	0.817	0.993	0.969	**Ti**			
Cr	0.808	0.848	0.828	0.753	0.865	0.886	0.885	**Cr**		
Mn	0.923	0.928	0.913	0.843	0.945	0.931	0.947	0.859	**Mn**	
Fe	0.952	0.980	0.972	0.822	0.991	0.968	0.997	0.890	0.964	**Fe**

Table 4.8. Correlation coefficients between fine fraction of the parameters

Mg	**Mg**									
Al	0.966	**Al**								
Si	0.953	0.992	**Si**							
SO_4^{2-}	-0.215	-0.218	-0.212	**SO_4^{2-}**						
K	0.569	0.663	0.604	-0.049	**K**					
Ca	0.976	0.942	0.920	-0.324	0.594	**Ca**				
Ti	0.953	0.981	0.979	-0.219	0.573	0.940	**Ti**			
Cr	-0.091	-0.087	-0.161	0.465	0.109	-0.184	-0.117	**Cr**		
Mn	0.029	0.046	-0.054	0.138	0.318	0.063	0.015	0.681	**Mn**	
Fe	0.952	0.974	0.954	-0.135	0.655	0.938	0.977	-0.004	0.182	**Fe**

K and crustal elements in fine fraction can be explained by contribution of this source.

Correlations between fine and coarse fractions of elements are given in Table 4.9. As seen from the table, fine and coarse fractions of crustal elements show strong correlations indicating that the main source of crustal elements both in fine and coarse fractions is soil. Besides, the correlations between coarse fraction of SO_4^{2-}, Cr, Mn and crustal elements both in fine and coarse fractions are strong. This observation suggests that these elements have similar source with crustal elements. On the other hand, lack of correlations between fine fraction of Cr, SO_4^{2-} and crustal elements indicates anthropogenic sources affect the concentrations of Cr and SO_4^{2} in fine fractions.

4.4.2. Crustal Enrichment Factors

Crustal source by low-temperature crustal weathering, marine source by sea salt generation and anthropogenic source by a variety of mainly high-temperature anthropogenic processes are globally important sources of trace metals to aerosols. The use of enrichment factors (EF), incorporating reference elements which are indicators of a specific source, is one of the ways of identifying the principal sources of trace metals (Chester et al., 2000).

Soil is found everywhere, and due to rich elemental content, it is the main natural source of aerosols in rural studies. Soil absolutely contributes the measured concentrations of all elements more or less. Crustal enrichment factors (EF_c) show the degree of enrichment of a measured element in the air compared to the relative abundance of that in earth' s crust. EF_c is calculated by using the following equation:

$$EF_c = \frac{(C_x / C_R) sample}{(C_x / C_R) crust} \tag{4.1}$$

where C_x is the concentration of the element of interest; C_R is the concentration of reference element. The sample and crust subscripts refer to particles in the aerosol samples and crustal material, respectively. In this study, the ratio of elements in the

Table 4.9. Correlation coefficients between fine and coarse fractions of the parameters

Mg$_f$	**Mg$_f$**											
Mg$_c$	1.00	**Mg$_c$**										
Al$_f$	0.97	0.98	**Al$_f$**									
Al$_c$	0.99	1.00	0.99	**Al$_c$**								
Si$_f$	0.96	0.97	1.00	0.98	**Si$_f$**							
Si$_c$	0.99	0.99	0.99	1.00	0.99	**Si$_c$**						
SO_{4f}^{2-}	-0.47	-0.47	-0.50	-0.53	-0.51	-0.54	**SO_{4f}^{2-}**					
SO_{4c}^{2-}	1.00	1.00	0.98	1.00	0.98	1.00	-0.51	**SO_{4c}^{2-}**				
K$_f$	0.87	0.89	0.94	0.89	0.95	0.90	-0.27	0.88	**K$_f$**			
K$_c$	1.00	1.00	0.98	1.00	0.98	1.00	-0.52	1.00	0.88	**K$_c$**		
Ca$_f$	0.99	1.00	0.99	1.00	0.98	1.00	-0.54	1.00	0.88	1.00	**Ca$_f$**	
Ca$_c$	1.00	1.00	0.97	1.00	0.96	0.99	-0.53	1.00	0.85	1.00	1.00	**Ca$_c$**
Ti$_f$	0.94	0.96	1.00	0.97	1.00	0.98	-0.48	0.96	0.97	0.96	0.97	0.94
Ti$_c$	1.00	1.00	0.98	1.00	0.97	1.00	-0.53	1.00	0.87	1.00	1.00	1.00
Cr$_f$	-0.44	-0.47	-0.60	-0.54	-0.63	-0.56	0.78	-0.50	-0.57	-0.51	-0.53	-0.48
Cr$_c$	0.99	0.98	0.93	0.97	0.91	0.96	-0.46	0.98	0.79	0.98	0.97	0.99
Mn$_f$	0.76	0.75	0.68	0.69	0.65	0.69	0.21	0.72	0.70	0.71	0.69	0.71
Mn$_c$	1.00	1.00	0.97	0.99	0.96	0.99	-0.52	1.00	0.85	1.00	1.00	1.00
Fe$_f$	0.96	0.97	1.00	0.98	1.00	0.98	-0.44	0.97	0.97	0.97	0.97	0.96
Fe$_c$	1.00	0.99	0.97	1.00	0.96	0.99	-0.54	1.00	0.85	1.00	1.00	1.00

Table 4.9. Cont'd.

Ti$_f$	**Ti$_f$**							
Ti$_c$	0.96	**Ti$_c$**						
Cr$_f$	-0.64	-0.50	**Cr$_f$**					
Cr$_c$	0.89	0.98	-0.34	**Cr$_c$**				
Mn$_f$	0.65	0.71	0.16	0.77	**Mn$_f$**			
Mn$_c$	0.94	1.00	-0.47	0.99	0.72	**Mn$_c$**		
Fe$_f$	1.00	0.97	-0.58	0.91	0.70	0.95	**Fe$_f$**	
Fe$_c$	0.94	1.00	-0.49	0.99	0.70	1.00	0.96	**Fe$_c$**

crustal material is obtained from Mason's (1966) compilation for trace elements in earth crust. Although this is one of the globally accepted compilations, calculated enrichment factors must be used with caution to assess sources of trace metals. The ratio of elements in the crustal material is only an approximation due to differing types of crustal material and soils in various source areas and uncertainties concerning fractionation during weathering processes (Toscano et al., 2005).

An element that is selected as the reference element should meet some criteria. It should be a non-volatile lithophile element, abundant in crustal material, accurately measured with available analytical techniques. Also, only crustal material should be the source of reference element (Güllü, 1996). For these reasons, Al was selected as the reference element for EF_c calculation in this study. When Al is not measured in a study, other elements such as Fe, Si, Sc, Ti can be used as reference element.

The EF_c value close to unity suggests that the element is dominantly from crustal materials or non-crustal sources contribute only a minor fraction, whereas the EF_c value higher than 1 may indicate sources other than crustal material. However, there are some differences between the local soil composition and the average earth's crust composition given by Mason (1966) as already mentioned. Therefore, another classification was made. An EF_c value less than 10 indicates that an element has a significant crustal source and these are termed the non-enriched elements (NEEs). In contrast, an EF_c value greater than 10 indicates that a significant proportion of an element has a non-crustal source and these are termed the anomalously enriched elements (AEEs).

Figure 4.15 shows the crustal enrichment factors of elements for both fine and coarse fractions. As shown in the figure, SO_4^{2-} and Pb with EF_c values ranging between 100 and 10000 are highly enriched in both fine and coarse fractions. These high EF_c values indicate that these elements mainly originate from anthropogenic sources, and contribution of crustal sources on their measured concentrations is negligible. This result contradict with the findings of previous section. Because when correlation coefficients was investigated, strong correlations were found between SO_4^{2-} and crustal elements in coarse fraction suggesting almost all of observed coarse concentrations of them are due to crustal sources.

This apperent dilemma reveals an important feature in the region. High EF_c values of SO_4^{2-} and Pb 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. However, correlation analysis implied that SO_4^{2-} is strongly correlated with crustal elements like Al, Fe, etc and hence its source in the coarse fraction should be soil. These two conditions can only be satisfied if S and Pb have high concentrations in local soil due to prolonged deposition from atmosphere. Such contribution of polluted soil on atmospheric concentrations of elements is frequently reported in literature (Yatın et al., 2000). Polluted nature of soil in the Aegean region is also reported in the literature (Odabasi et al., 2002).

Elements Ni, Cr, Mn, K, Ca and Mg have EF_c values greater than 10 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 EF_c values are less than 10 which confirms that their coarse concentrations can be attributable predominantly to crustal sources. It is known that Ni, Cr and Mn have mixed sources. 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. Fossil fuel combustion, steel industry and waste incineration are the main anthropogenic sources of Cr, while fuel burning and vehicular emissions are regarded as Ni sources. Similarly, Mn can be considered as a marker element of emissions from ferro-manganese industries (Pacyna, 1984).

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; Gatari et al., 2001).

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. As marine aerosols are coarse particles, enrichment of Mg and Ca in fine fraction cannot be explained by the contribution of sea salt. In fact, the reason behind this behaviour is not known. One likely source for enrichment of Mg and Ca in the coarse fraction is variation of the chemical composition of soil as a function of size. Number of studies in the literature showed that chemical composition of fine soil particles may be different from the composition of coarse soil particles (Schütz and Rahn, 1982; Eltayeb et al., 1992).

Elements Fe, Si and Ti are not enriched to higher than 10 in both fine and coarse fractions. However, it still indicates a non-crustal source for these elements. Because elements are size-differentiated and fine particles are known to be the indicators of anthropogenic sources. Fine particles have larger EF_c values than coarse ones implying that fine fraction of these elements are more influenced by non-crustal sources. Non-crustal sources of Fe and Ti in the atmosphere are steel industry. Hence, the observed enrichments of these elements can be due to the iron-steel plants operating at 5 km south of Aliağa region. Although dominant source of Si is the crustal material, a minor fraction can be emiited from diesel vehicles (Han et al., 2005).

Crustal enrichment factors of elements for summer and winter seasons are illustrated in Figure 4.16. Most of the elements are more enriched in winter season. Higher enrichment of Cr and Mn in winter season can be due to two reasons. Firstly, as discussed in Section 4.3.1, concentration of them in winter is higher than that in summer indicating a local source contribution. Secondly, Al concentration in winter is lower as soil is damp leading to limited generation of crustal particles. Hence, high EF_c values of Mn and Cr in winter months can be explained by higher concentrations of these elements and lower concentration of Al in winter season. Concentration of SO_4^{2-} is comparable in summer and winter and concentrations of Pb and Ni are higher in summer. Therefore, higher enrichments of these three species in winter cannot be attributed to seasonal variations in their concentrations. The only reason for this behaviour is lower concentration of Al in winter months.

The EF_c values of crustal elements like Fe, Ti, Si, Ca are similar in both summer and winter seasons, as it is expected. Because their seasonal variations follow same pattern with seasonal variation of Al. However, winter enrichments of Mg and K are significantly higher. Even if contribution of marine source has an influence, it cannot be regarded as the sole responsible for the high EF_c values of Mg and K in winter months. Based on the above discussion, another reason for the observed situation is contribution of non-crustal sources on their measured concentrations.

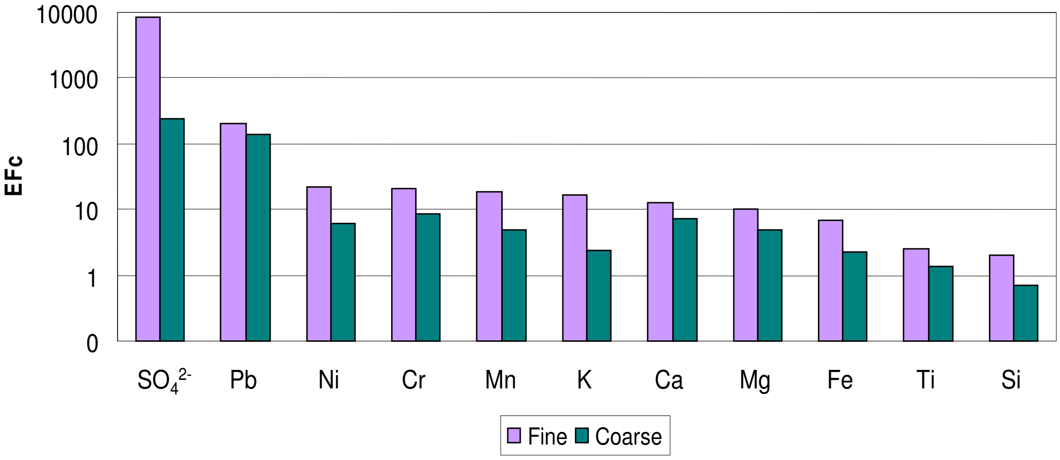


Figure 4.15. Annual crustal enrichment factors

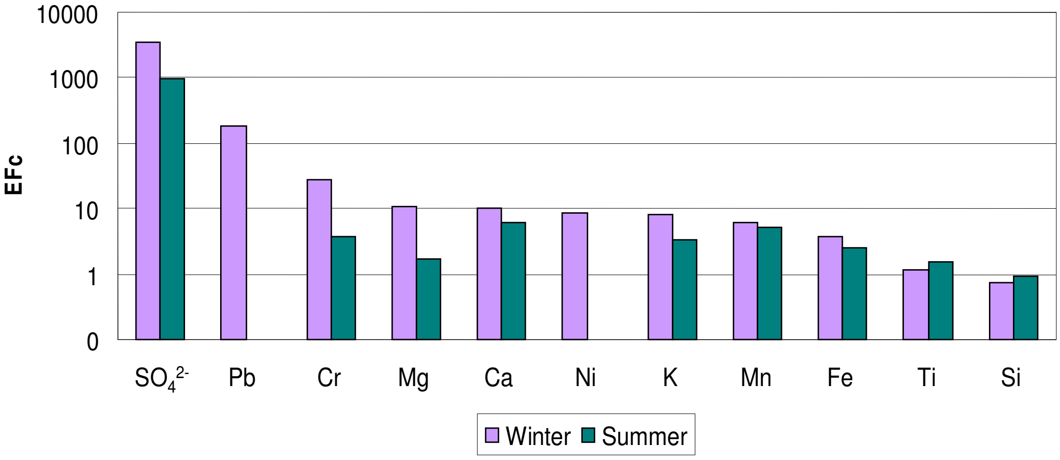


Figure 4.16. Seasonal crustal enrichment factors

Enrichment factor diagrams can be used to identify crustal and non-crustal contributions on measured concentrations of elements. Crustal enrichment factor vs. Al plots of Si, SO_4^{-2}, Cr, Ca, K and Fe are depicted in Figure 4.17. Since concentrations of purely crustal elements vary together with Al concentration, EF_c values are independent of Al concentration. Hence, the plot is a horizantal line for purely crustal elements. However, concentrations of non-crustal elements are independent of Al concentration. So, EF_c values of them decrease with increasing Al concentration.

As can be seen in Figure 4.17, crustal enrichment factors of Si, Ca, K and Fe in coarse fraction are independent of Al concentration exhibiting a horizantal line. Therefore, coarse fractions of these elements are attributed to crustal sources.

The EF diagrams for SO_4^{-2} and Cr in fine fraction suggest that enrichments of these elements are due to the non-crustal sources as expected. Although K is a crustal element, fine fraction of K is originated from non-crustal sources such as biomass burning. Because EF_c values of K generate a decreasing line in the EF diagram for fine fraction, which indicates that concentrations of K and Al does not change similarly.

As shown in Figure 4.17, crustal enrichment factors of Ca, Si and Fe in fine fraction decrease with increasing Al concentrations at low Al concentrations, but become independent of Al concentrations at high Al concentrations. This behaviour can be explained by contribution of non-crustal sources at low Al concentrations and contribution of crustal sources at high Al concentrations. Consequently, these non-crustal sources are observed when loading of crustal particles is low, whereas masked by dominating crustal source.

Another important point to consider is that for Si, the data points with few exceptions are around the horizantal line at the EF_c value close to 1 in coarse, fine and total fractions. However, for Fe and Ca horizantal lines are generated at the EF_c values higher than 1 indicating the Fe-to-Al and Ca-to-Al ratio in the sample is different from that ratio in the reference. Therefore, enrichment of Si in fine fraction can be attributed to the contribution of non-crustal sources, while enrichments of Fe and Ca in the fine fraction are due to both non-crustal sources contribution and differences

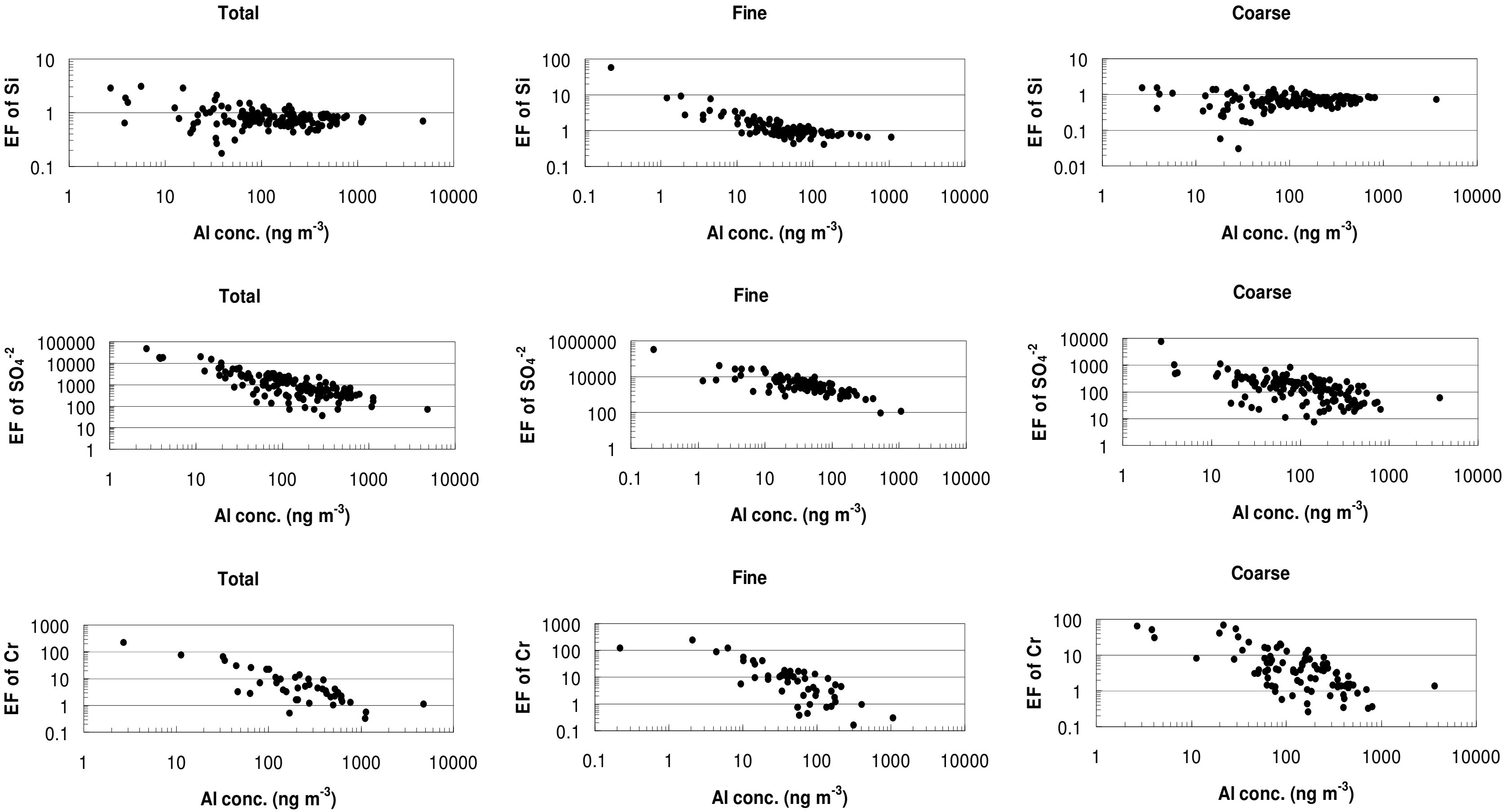


Figure 4.17. EF plots of Si, SO_4^{-2}, Cr, Ca, K and Fe

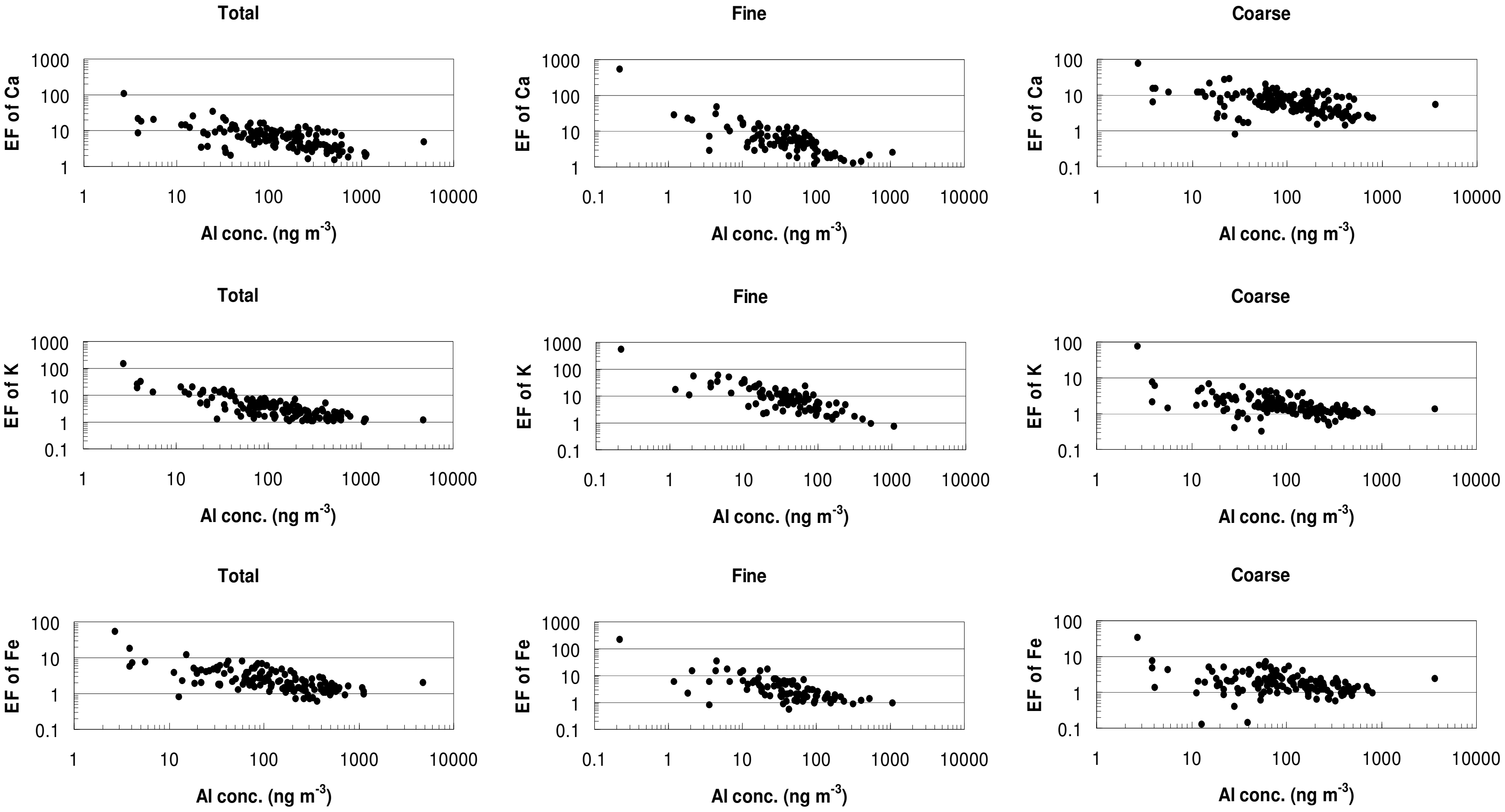


Figure 4.17. Cont'd

between the local soil composition and the average earth's crust composition given by Mason (1966).

4.4.3. Positive Matrix Factorization

Multivariate statistical receptor models have been extensively used for source apportionment of airborne particles. The approach to obtaining a data matrix for receptor modeling is to determine pollutant concentrations in a number of samples collected at a receptor site (Hopke, 2003). Multivariate models are based on the idea that the time dependence of a chemical species at the receptor site will be the same for species from the same source (Chueinta et al., 2000). Principle component analysis (PCA) (Thurston and Spengler, 1985), factor analysis (FA) (Hopke, 1985) and positive matrix factorization (PMF) (Paatero and Tapper, 1993) are multivariate models commonly used in atmospheric studies for aerosol source identification. Among these models, PMF is a relatively new technique developed by Paatero and Tapper (1993, 1994) and Paatero (1997) and, as mentioned in Chapter 2, has some advantages over the other techniques. PMF uses a least squares approach by integrating non-negativity constraints to factor loadings and factor scores during the optimization process and utilizing the error estimates for each data value as point-by-point weights.

A special advantage of PMF is the ability of the model to handle incomplete data such as missing data and below detection limit data. Increasing the error estimates permits the reduction of their influence. As the input to the PMF program, the concentration data and the associated error estimates should be constructed. In this study, they were determined by the following methods.

For the measured data, the method described by Paatero (2002) was used. According to this approach, the concentration values are used directly and the error estimates are built using the summation of detection limit value of the element and a certain ratio of concentration of that element. The ratio takes values between 0.01 and 0.1. In this study, the ratio was chosen as 0.05.

Data less than the detection limit were replaced with a half value of the detection limit for each element and 5/6 of the detection limit value was used as its error estimate. Missing values were used for the geometric mean of the measured elemental concentration and the value of the error estimate was used four times the geometric mean to obtain a larger value of the standard deviation (Polissar et al.,1998, 2001). This approach minimize the wieght of the missing values on the fit.

PMF analysis was applied using PMF version 4.2 software compiled by Paatero (2002). In this study, the robust mode was selected for handling outlier data. That is, a data point is processed as an outlier if the residual exceeds α times the standard deviation. The ‘‘processing as an outlier’’ means that the standard deviation value is increased so that the influence of this value is decreased. The α value of 4.0 was used in this work.

A critical step in PMF analysis is the determination of the number of factors. In order to find the optimal one with most physically reasonable results, it is necessary to test different numbers of factors. However, some criteria should be taken into account in assigning the number of factors as an input. Using too few factors will combine sources of different nature together and, also the unexplained parts for some species can be too large. On the contrary, using too many factors will dissociate a real factor into non-existing sources (Hien et al., 2004). Besides, careful choice of chemical species included in PMF is important. In this study, PMF was run for different numbers (4,5,6,7) of factors to obtain explainable results. After several trials, some of the chemical species were excluded due to too many missing values in the data set.

Analysis of the goodness of model fit, Q, as defined in Eq. (2.5), can be used to help determine the optimal number of factors. The theoretical Q value should be approximately equal to the number of data points in the data set, provided that correct values of error estimates have been used. In this case, theoretical value of Q is the total number of daily measurements times the total number of species used minus the number of factors times the number of species. In this study, in order to find global minimum solution of Q, PMF was run by using different seeds for pseudo-random starting points.

In the PMF, there is a parameter (FPEAK) that is used to control the rotation. Examination of Q value by varying FPEAK between 0.1 and 1.0 was performed.

When the Q value did not change very much, the FPEAK value was selected as an optimum solution.

Finally, an appropriate solution was determined by a method of trial and error based on the evaluation of the scaled residual matrix, Q value and source profiles. The optimum number of factors extracted for the fine data set was 5 and each factor was well defined. Besides, plots of factor score values for each factor versus those for other factors were investigated. As a result, there were no autocorrelations between factors, meaning that factor score values are randomly distributed. The calculated Q value (FPEAK=0.3) was higher than the theoretical Q value. Fine mass was included as a variable in the input data, while Cr and Pb was excluded from the analysis. Lead was excluded due too many missing data points, and Cr was excluded as it detoriated the quality of the fit in all of our attempts.

PMF was only applied to fine data set. As explained in Section 4.4.1, strong correlations between all elements are obtained in coarse fraction indicating soil is a dominating source for all of the measured parameters

Factor loadings, explained variances and calculated enrichment factors for the 5 factor PMF solution for fine fraction are given in Figure 4.18. In order to identify sources associated with factors, evaluations were based on all three of these graphs. Factor loading values are the concentrations of measured elements in each factor. Factor profiles in PMF analysis are equivalent to source profiles in chemical mass balance (CMB). CMB requires inputs of source profiles and speciated data to determine source contributions (Watson et al., 1984). PMF, on the other hand, is advantageous in that source profiles are the part of the solution. As can be seen from Figure 4.18, Factor 3 has high loadings of K, Ca, Ti and Fe. However, high concentrations of these elements in Factor 3 do not necessarily indicate that this factor represent the most significant source for them. Factor 4 has relatively lower loading of K than Factor 3. But, K is mostly explained by Factor 4 which will be discussed hereafter. Another example is that concentration of sulfate in soil is higher than concentrations of purely crustal elements such as Ti, Sc, Co. Therefore, it is misleading to identify sources only by investigation of factor loading values. In addition, explained variance (EV) of each element in each factor, an output of PMF, is plotted. It is a way of presenting factor characteristics in a qualitative way. In other

Figure 4.18. Explained variations, factor loadings and enrichment factors for fine fraction

words, explained variance shows how much of the variance of an element is explained by each factor. Besides, crustal enrichment factors of parameters are calculated by using factor loading values of each factor. Al is used as the reference element for the crustal enrichment factor calculations.

Factor 1 represents a mixed source of local industrial emissions. This factor provide high fine particulate mass concentration. Most of the variances of Mn, Fe and Zn is explained by this factor. Besides, Factor 1 explains small fraction of the variances of SO_4^{2-}, K and Ca. All of these 6 species are highly enriched. Although Mn, Fe, K and Ca are soil-related elements, their higher enrichments with anthropogenic species indicating contribution of the non-crustal sources. Steel industry operating at Aliağa region can be related to the measured concentrations of Mn and Fe. Influence of anthropogenic sources on Ca and K concentration in fine fraction was also explained in previous sections.

Factor 2 is a crustal factor. This factor is associated with high loadings of crustal elements such as Al, Si, Ca, and also explains most of variances of these elements. EF_c values are around one confirming that the source is purely crustal material.

Factor 3, similar to Factor 1, describes a source of local industrial emissions. Concentration of Fe is high. This factor explains most of the variances of Fe, Ti and Ni. Crustal enrichment factors of these 3 elements are greater than 10000 suggesting that their concentration is mostly influenced by anthropogenic sources. Iron and Ti are markers of soil where there is no industrial activities. However, in the presence of industrial emissions, like steel industry which is the case for this sampling site, their measured concentration, particularly in the fine fraction, can be attributed to these sources. Nickel is the indicator of oil burning and vehicular emissions. It is also produced by the steel industry. Therefore, Factor 3 clearly represents anthropogenic emissions.

The fourth factor with the highest fine particulate matter mass concentration is identified as long range transport factor. Because it explains most of the variance of SO_4^{2-}. Due to the slow oxidation of SO_2 to SO_4^{2-}, sulfate is accepted as an indicator of long range transport in such studies. As seen from Figure 4.18, Factor 4 also explains a large fraction of variance of K. When total or coarse aerosol mass is considered, the most significant source of K is undoubtly soil. However, in fine fraction, K originates from biomass burning as well as soil (Andreae, 1983). Hence, presence of K in the same factor with SO_4^{2-} indicates that air masses carrying potassium to the receptor site may come from a high K emission region, causes that air parcel to be loaded with elevated levels of K. The regions where large number of forest fires occur can be associated with high emission areas of K. Besides, SO_4^{-2} and K are significantly enriched, and the rest of the elements have lower EF_c values. In the factors representing local sources, EF_c values of elements are much higher. Owing to all reasons mentioned above, Factor 4 is identified as long range transport factor.

Factor 5 is a clearly sea salt factor. This factor explains a significant portion of the variances of Mg and Ca. Moreover, a small fraction of variances of K, and anthropogenic elements, Zn and Ni, are explained by this factor. When crustal enrichment factors are considered, Mg, SO_4^{-2}, K, Ca are significantly enriched. It is known that concentrations of these enriched elements are high in sea salt. The marine component of Na is a good tracer of sea salt aerosol. Unfortunately, Na was not measured in this study. However, except Na, enrichment of the elements known to have high concentrations in sea salt makes it reasonable that fifth factor represents sea salt.

Besides factor loading and explained variance, another output of PMF is G (source contribution) matrix. It includes factor score values (one score for every measurement day) for each factor. Factor scores are the weight of each factor in sampling days. Daily concentrations of elements due to each factor are computed by multiplying factor score for that particular day with the factor profile. Summation of the concentrations of an element in each factor determine the predicted concentration of that element in that particular day.

A good evidence to effectiveness of PMF model is the observed to predicted ratios of elements. These ratios have to be close to unity for PMF to be considered successful. Figure 4.19 represents the observed to predicted ratios of elements. This ratio for each element was calculated one by one for each sample and then, averaged. As seen from the Figure 4.19, observed concentrations of Zn and Ni is higher than the predicted concentrations of these elements and the ratios are around 1.5. This can be due to the detection of Zn and Ni in a fairly low number of samples. Measured Mn concentration, on the other hand, is smaller than the predicted Mn concentration. The observed to predicted ratios of rest of the parameters are approximately equal to 1. Consequently, the PMF model is used successfully for source apportionment of particulate matter.

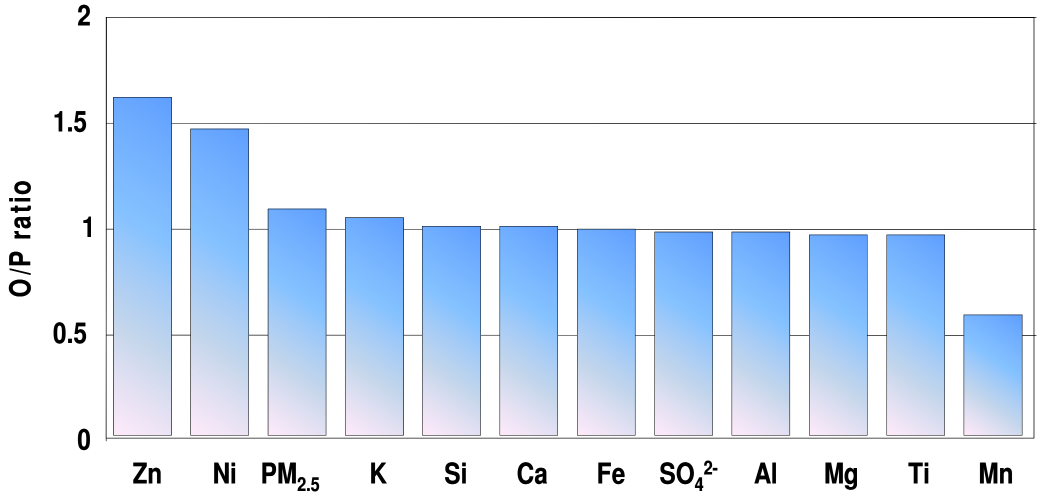


Figure 4.19. Observed-to-predicted concentration ratios of parameters

In PMF model, a good fit of the mass concentrations of fine particles is more important than the quality of fit of the other elements as air quality directives are based on mass concentrations. For this reason, the total $PM_{2.5}$ mass concentration measured for each sample regress against the predicted $PM_{2.5}$ mass for each sample. Figure 4.20 presents observed versus predicted $PM_{2.5}$ mass concentrations and the relation between the observed and predicted $PM_{2.5}$ concentrations. As seen from the figure, these concentrations show a similar trend within a small deviation and closely related to the observed mass concentration indicating that the modelling approach is appropriate.

The solution provided by PMF analysis allows to calculate contribution of each factor to each element. This can be achieved by dividing the daily concentration of element

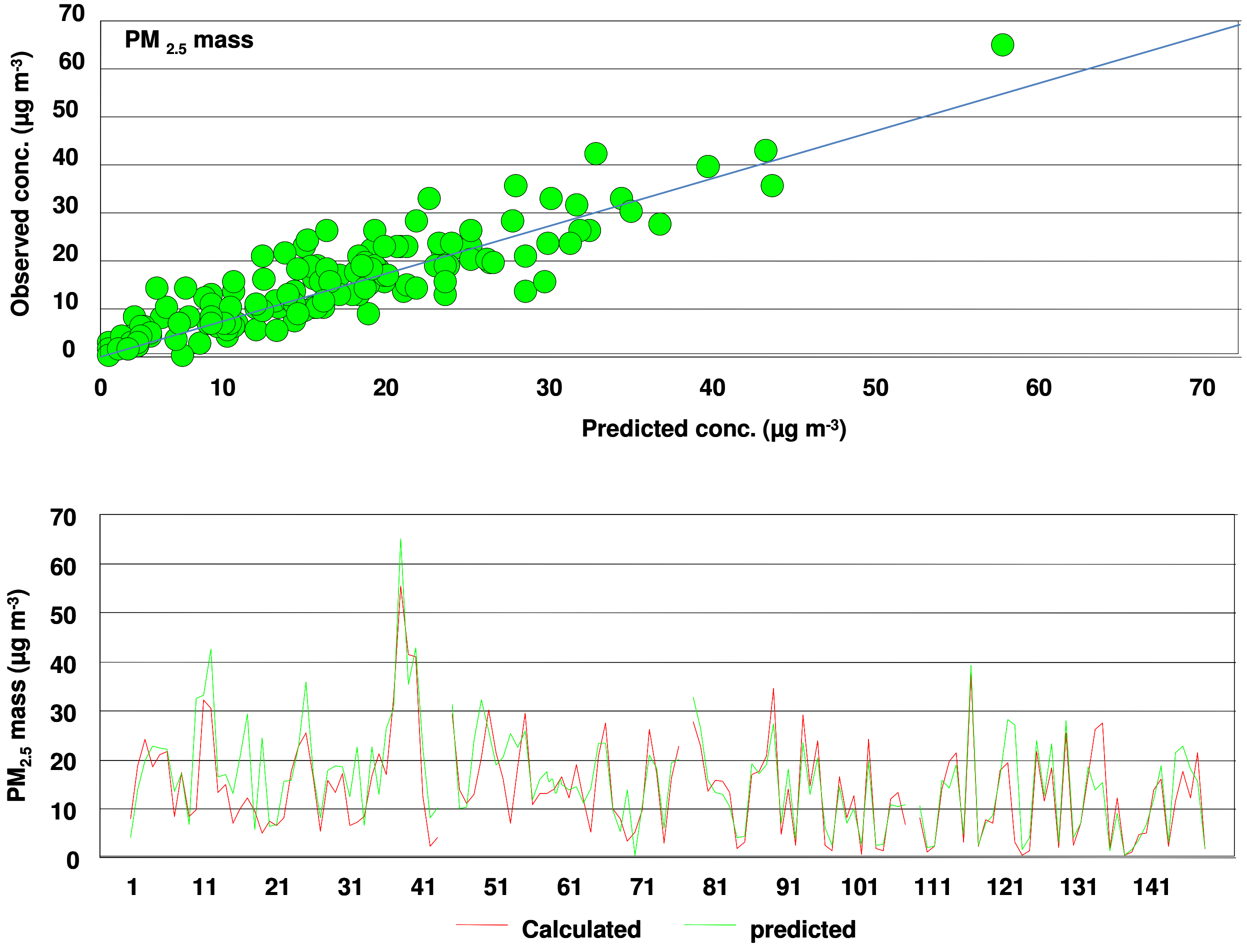


Figure 4.20. The relation between the observed and the predicted fine particulate mass concentrations

in each factor to total predicted concentration of that element in that particular day. This procedure is repeated seperately for all days. Then, the results for each element are averaged for each factor. The calculated values are converted to percent contributions and given in Figure 4.21.

As seen from the figure, almost all concentrations of soil-originated elements, Al and Si, is due to Factor 2 which is identified as a crustal factor. Although K, Ca, Ti are known as soil related elements, there is less or no contribution of crustal sources. A significant portion of K is attributed to long range transport, while the main source for Ti is local anthropogenic emissions. Sea salt accounts for 95% of measured Mg concentration and 47% of observed Ca concentration. Considering the fact that our station is by the sea, high contribution of marine factor on Mg and Ca concentrations is not surprising. Similar to Ti, local anthropogenic emissions are important sources for Fe and Zn. As it is expected, sulfate is mostly associated with long range transport. Besides, fine particulate mass concentration is dominated by long-range transported concentrations of species.

The most important outcome of the PMF analysis contribution of local sources to the concentrations of elements, such as Fe, K, Ti, Mn. In most data sets reported in the literature these elements are found to originate from crustal particles in the atmsophere, but their concentrations are accounted for mostly by local anthropogenic sources and not by resuspension of crustal material. It should be noted that PMF in this study is applied to fine particles that has diameters smaller than 2.5 µm. In fine fraction, sources of these elements at a location close to an industrial area are anthropogenic and not crustal. It is also worthwile to point that only one of the factors among five are identified as long-range transport. However, approximately 80% of the fine particulate mass is accounted by this factor, owing to higher concentrations of SO_4^{2-}, which is the main specie associated with this factor, compared to the concentrations of other elements.

4.4.4. Potential Source Contribution Function

Potential source contribution function (PSCF) is used to identify the possible locations of sources of pollution that is being detected at a given location (Zeng and Hopke, 1994). PSCF is defined as the conditional probability that an air parcel with a

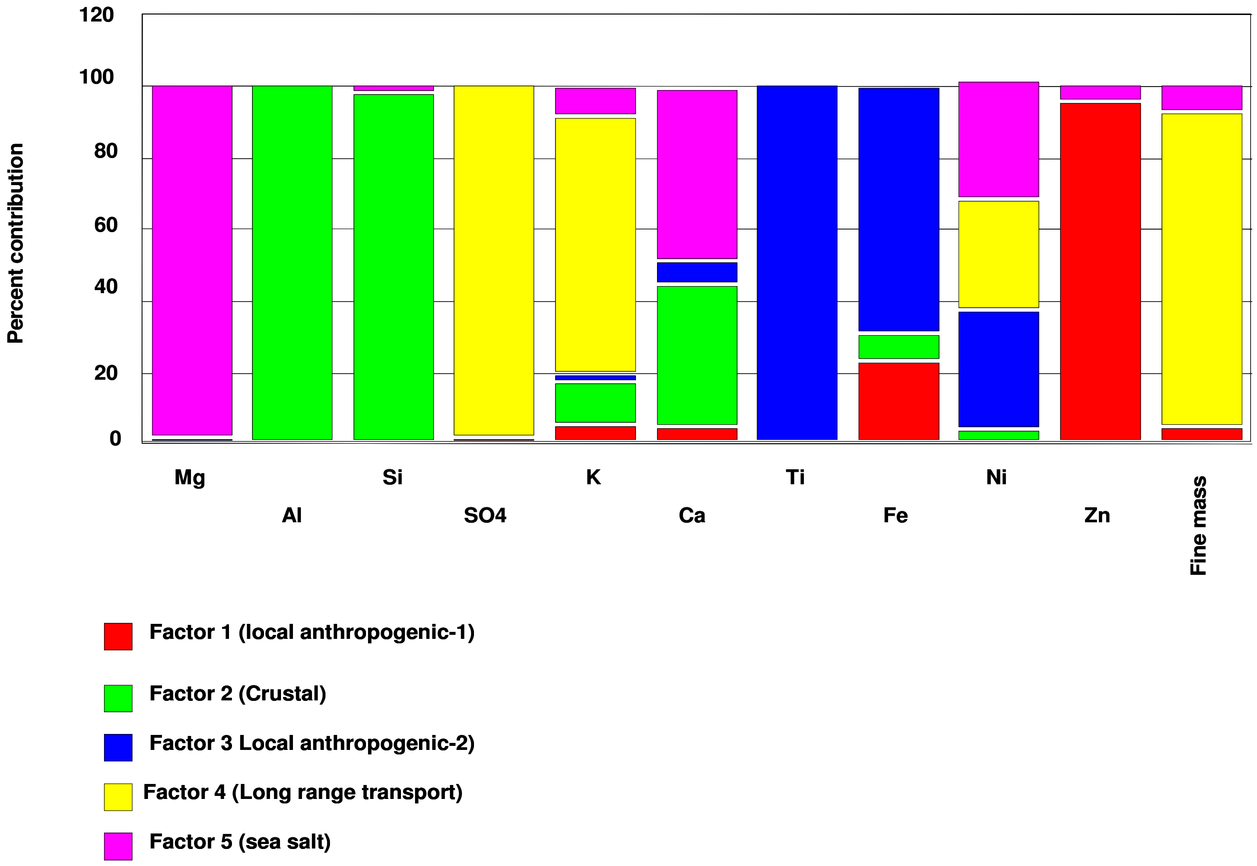


Figure 4.21. Percent contribution of each factor to each parameter

level of pollutant concentration above a criterion value arrives at a receptor site after having passed through a specific geographical area (Gao et al., 1993). PSCF model combines chemical data and meteorological data by using the chemical concentrations and wind trajectories.

The PSCF of an element x in subregion ij is given by

$$PSCF_{x,j} = \sum m_{ij} / \sum n_{ij}$$

where $\sum n_{ij}$ is the total number of trajectory segments in the *ij*th subregion and $\sum m_{ij}$ is the total number of polluted trajectory segments in the same *ij*th subregion during the study period. Cells with high PSCF value that aproaches 1 are the potential source regions and cells having a PSCF value of 0 are unlikely to be source regions. However, if the total number of endpoints, n_{ij}, in a cell is small, it results in a high $PSCF_{ij}$ value with a high uncertainty. To minimize the effect of small values of n_{ij}, a non-parametric bootstrap method was used in this study. As this method is discussed in Chapter 2, it is not further explained in this section.

In this study, a 1° x 1° grid size was used to divide the geographical region covered by trajectories. This region lies between 75°N latitude at north, 15°N latitude at south, 20°W longitude at west and 60°E longitude at east. 151, 5 day-long, 900 hPa backtrajectories with 1-hour segments were used and these segments were counted in each subregion.

In this study, bootstrapped PSCF maps was prepared by using the trajectories corresponding to the highest 40% of fine SO_4^{-2} were selected as polluted trajectories. Besides, PSCF values was calculated at the 95% confidence level. The grid cells that have less than 5 trajectory segments were excluded. The reason for selecting SO_4^{-2} in fine fraction is that this specie is associated with long range transport. Application of PSCF is meaningful when pollutants are imported from distant regions. PSCF bootstrapped distribution of fine SO_4^{-2} calculated with the highest 40% of measured concentrations is depicted in Figure 4.22.

The regions identified by PSCF analyses showed that Bulgaria, Romania, Poland, Ukraine and central part of Aegean region are the important potential source regions that may contribute to SO_4^{-2} concentrations in the Aegean region. The secondary potential source regions are Greece and south of Italy. Emissions from Mount Etna in the eastern Sicily most probably affect the concentration of SO_4^{-2} as reported in previous studies in the eastern Mediterranean (Doğan, 2005; Yörük, 2004). Since distribution of PSCF values for highest 40% scores of Factor 4 show no difference with this one, it is excluded.

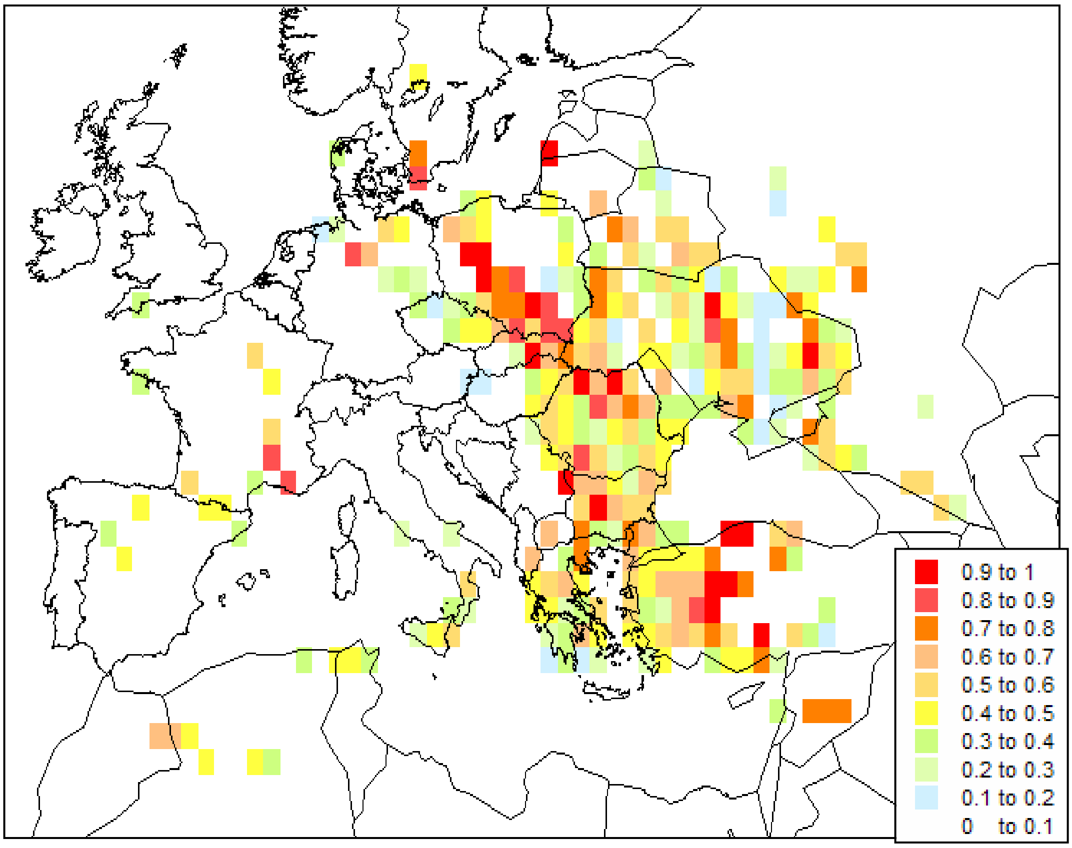


Figure 4.22. PSCF bootstrapped distribution of fine SO_4^{-2} calculated with the highest 40% of measured concentrations

Potential source contribution calculations were performed for a number of different stations in Turkey, including data sets generated on the Mediterranean coast (Güllü et al., 2005), Black Sea coast (Doğan, 2005), Central Anatolia (Yörük, 2004). It is interesting to note that an important source region for SO_4^{2-} in Ukrain was found to be important source regions in other studies as well. Obviously this region at central Ukrain affects most parts of Turkey. Poland, on the other hand, are expected to be important source for most parts of Turkey, owing to poor quality of coal used in power plants and poor technology used in energy generation. But regions in Poland appeared as important source region affecting composition of fine particles at Çandarlı and also Black Sea coast of Turkey, but not an important source for particles collected at the central Anatolia and Mediterranean coast of Turkey. These similarities and differences between sites, in terms of source regions affecting them, indicates complex and different flow patterns affecting different parts of Turkey. To obtain a country-wide assesment of potential source regions either measurements has to be performed at a large number of sites representing whole country (simultaneous measurement at 6 – 7 carefully selected stations for > 3 years can be okay) or a regional model has to calibrated using mesurements, and applied for the whole country. Short term measurement campaigns performed at a specific part of the country is very useful to gain insight for that particular location and for that particular time, but can not be generalized both in space and time.

CHAPTER 5

CONCLUSION

Daily fine and coarse aerosol samples were collected for three months both in winter and in summer seasons between 2005 and 2006. Sampling was performed at the Çandarlı station which is a rural sampling site located on the west coast of Turkey. Collected samples were analyzed by EDXRF for a total of 13 elements.

Concentrations of SO_4^{2-} in fine fraction and Ca in coarse fraction are highest among the species, whereas concentration of Pb is lowest in both fractions. As the sampling site is not under direct influence of local sources, total and fine particulate mass concentrations are quite lower than urban areas. As a result of calculation of coarse-to-fine concentration ratios, crustal elements are mostly found in the coarse fraction as expected. Sulfate dominates in the fine fraction. On the other hand, elements, which are known to have mixed sources, have comparable concentrations in both fractions.

In order to evaluate the level of pollution at Çandarlı, measured concentrations of elements in this study were compared with those obtained in previous studies performed at various sites of world and also in Turkey. Concentrations of crustal elements reported in the Çandarlı station are higher than those reported in the stations located outside Turkey and lower than those measured in Turkey. Relatively higher concentrations of crustal elements are attributed to the arid nature of Mediterranean and Middle East regions. In addition to that, different abundance of each element in the soil can be identified as another reason for differences in crustal element concentrations measured at different parts of the world. Manganese concentration observed in Çandarlı station is higher than all the other sites. Contrary to Antalya and Amasra stations, lower concentration of SO_4^{2-} can be due to different flow patterns affecting these sites. This comparison clearly demonstrates that concentrations of elements significantly differ from one site to another despite all sites are located in Turkey due to several reasons. Consequently, based on the results obtained from a few sampling stations, general feature of the country can not be clarified, levels and also compositions of elements are then specific to the sampling location.

In order to discuss features of long range transport, no or limited transport of pollutants from Aliağa, industrial zone, should be demonstrated. For this reason, by means of surface wind data flow pattern at Aliağa and hourly SO_2 concentrations were investigated. In addition, to have clearer vision about the influence of wind direction, annual wind roses, were examined with two-hour periods of each day. Concentrations of measured SO_2 are low, but at a periodic time of each day relatively higher concentrations of SO_2 and southerly flows are detected although the time of flow and reported high concentrations are not associated with each other. The reason behind this is not so clear. However, since the industrial area affects the sampling point for at most two hours in a day, the sampling site is accepted as a representative background site.

In Çandarlı station, most frequent flows are from NE and W sectors. Even though the frequency of air mass transport from NW and N sectors are not as high as NE and W sectors, their contribution to the total flow is significant when compared to the rest of the sectors. Therefore, emissions from the sources located in Central Russia and European countries are most likely to affect the aerosol composition in the sampling site.

Calculation of seasonal flow patterns revealed that there are some differences in air mass transport from each sector between summer and winter seasons. During summer season, flow is more frequent from NE, N and W sectors. Air masses reaching to sampling station come from W, NW and NE sectors more frequent than those from other sectors in winter season. Besides, air flows from E, SE, SW and S sectors are more frequent in winter. Consequently, with heavy industrial activities, emissions from Central Russia, and Eastern European countries are more influential in determining aerosol composition in summer, whereas contributions to the aerosol composition from Western European countries are nearly same in both seasons.

Crustal elements have higher concentrations in summer season due to their generation mechanisms. Only Mg and K do not show this trend. Concentrations of anthropogenic elements do not show as clear seasonal differences as crustal elements. Their concentrations are at least comparable or slightly higher in winter season suggesting higher local source contribution on their measured concentrations.

Concentrations of all elements were found to show short term variations. Contribution of episodes on measured concentrations of crustal elements is higher than that of anthropogenic elements due to variations in source strengths. Relatively lower contribution of episodes to the observed concentrations of truly anthropogenic species is an indication of variations in transport patterns.

Correlations between parameters indicate that all parameters measured in this study are strongly correlated in coarse fraction suggesting that major source of elements are soil in coarse fraction. Similarly, crustal elements are correlated well in fine fraction. Lack of correlations between Mn, Cr, SO_4^{2-} and crustal elements show that anthropogenic sources determine their fine fraction concentration.

Calculation of enrichment factors revealed that in both fine and coarse fractions, Pb and SO_4^{2-} are highly enriched, and the rest of the elements are not significantly enriched. Higher enrichments of crustal elements in fine fraction than those in coarse fraction is observed. Enrichment factor diagrams of these elements in fine fraction indicate that when loading of crustal particles is low, contribution of non-crustal sources become appear. Consequently, concentrations of these elements are influenced by sources, which are not commonly seen in rural locations.

Positive Matrix Factorization (PMF) was applied to data in order to identify sources and contribution of each source to measured concentrations of elements. PMF identifies two local emission component, one crustal component, one long range transport component and one sea salt components. Calculation of observed-to-predicted ratios of parameters included in PMF show that the modeling approach is effective.

To identify source regions of pollutants, Potential Source Contribution Function was used. Distribution of PSCF values showed that main sources of SO_4^{2-} are observed in Bulgaria, Romania, Poland, Ukraine and central part of Aegean region.

5.1. Recommendations for Future Research

In this study, analysis were performed by EDXRF for 13 elements. The number of species should be increased and the fingerprint species must be detected in order to get more accurate source apportionment. Hence, long range transport contribution can be clearly identified.

In addition to aerosols, dry and wet deposition samples were not collected for the time being. However, collection of them leads examining all the aspects of long range transport.

Sampling should be performed for longer periods and at different parts of the country. Then, levels and also compositions of elements are not specific to the sampling location and can determine factors affecting the aerosol compositions in the whole country.

Persistent organic pollutants (POPs) are organic compounds that are stable for long period. Hence, they can be transported over long distances. So, their sampling are recommended.

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