DETERMINATION OF THE EUROPEAN CONTRIBUTION ON THE AEROSOL COMPOSITION IN THE BLACK SEA BASIN AND INVESTIGATION OF TRANSPORT MECHANISMS

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ABSTRACT

DETERMINATION OF THE EUROPEAN CONTRIBUTION ON THE AEROSOL COMPOSITION IN THE BLACK SEA BASIN AND INVESTIGATION OF TRANSPORT MECHANISMS

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Concentrations of trace and major elements and ions measured in aerosol samples collected between April 1995 and July 1997 were investigated to understand the general features of elemental concentration, sources and source regions affecting the chemical compositions of the aerosols in the western Black Sea atmosphere of Turkey. This study was the most extensive and longterm one carried out at the region among all the Black Sea countries. We have collected a total of 354 daily aerosol samples and the samples were analyzed by atomic absorption spectrometry, instrumental neutron activation analysis, ion chromatography and UV/VIS spectrometry for about 46 elements and major ions.

Three dimensional (3D), four-day long back trajectories of the air masses arriving daily at the sampling site (20 km east of Amasra town and about 4 km to southern Black Sea coast) at 900, 850 and 700 hPa (mbar) barometric pressure levels, have been calculated. The calculation of the back trajectories was achieved by utilizing the operational model on the computer of the European Centre for Medium Range Weather Forecast (ECMWF, Reading, England). The calculated back trajectories were used to determine the locations of the aerosol sources affecting our sampling site.

Various statistical methods like distribution tests, factor analysis and potential source contribution function were applied on the generated data to determine the sources, source compositions and source regions of the atmospheric particles. Almost all of the measured parameters showed lognormal distribution type which mean that aerosol composition is altered by several contributing sources during transport from distant and local sources. The local and distant rain events are the determining factors for most of the observed variations in the elemental concentrations.

Calculation of enrichment factors have revealed three general source groups, namely a crustal source, a marine source, and an anthropogenic source. The main components of the collected aerosol samples were formed by these three contributing sources. Factor analysis identified four basic sources affecting the elemental concentrations in the aerosol samples. The most effective source was found to be the earth crust and then a local mixed pollution source, a marine source and a distant pollution source. Moreover, factor analysis identified two crustal components when applied to elements contributed mainly by the earth crust. The most promising markers to distinguish between the local soil and the soils from other regions like Africa, Ex-USSR Countries, western Europe and Middle East were the element to aluminum ratios of Mg, Ca, Fe, Mn and K. Concentrations of these elements are significantly different in local and other crustal aerosol regions. Potential Source Contribution Function (PSCF) technique showed that there are two principal components in the western Black Sea cost of Turkey. The main source regions of crustal elements are eastern Turkey, Central Asian countries, North Africa and Middle East countries. On the other hand, the anthropogenic components usually originates from western and eastern European countries and Russian Federation and Turkey.

Keywords: Aerosol, Turkish Western Black Sea Region, Trace Element, Ion, Enrichment Factor, Factor Analysis, Back Trajectory, Potential Source Contribution Function, INAA, AAS, Long Range Transport .

ÖZ

KARADENİZ HAVZASI ÜZERİNDEKİ AEROSOLLERİN KOMPOZİSYONUNA AVRUPA' NIN KATKISI VE AEROSOLLERİN TAŞINIM MEKANİZMALARININ İNCELENMESİ

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Nisan 1995 ve Temmuz 1997 tarihleri arasında toplanan aerosol örneklerinde majör ve eser elementlerle majör iyonların konsantrasyonları kullanılarak Türkiye'nin batı karadeniz atmosferininde bulunan aerosollerin kimyasal kompozisyonlarını etkileyen kaynak ve kaynak bölgeleri incelenmiştir. Bu çalışma, Karadeniz ülkeleri de dahil bölgede yapılan en kapsamlı ve uzun süreli olanıdır. Toplam olarak 354 günlük aerosol örneği toplandı ve bu örneklerin analizinde, atomik absorpsiyon spektrometresi, ensrümantal nötron aktivasyon analizi, iyon kromatografisi ve kolorimetri teknikleri kullanılarak yaklaşık olarak 46 element ve majör iyonların konsantrasyonları tayin edildi.

Örnekleme bölgesine (Amasra'nın 20 km doğusu ve karadeniz'in güneyinde, denize 4 km mesafede) 900, 850 ve 700 hPa (mbar) barometrik basınç seviyelerinde ulaşan hava kütlelerinin 4-gün süreli geriye dönük, üç boyutlu (3D) yörüngeleri hesaplanmıştır. Hava kütlelerinin geriye dönük yörüngelerini hesaplanmasında ECMWF'in (Avrupa Orta Ölçekli Hava Tahmin Merkezi, Reading, İngiltere) bilgisayarında kullanıcılara açık olan model kullanılmıştır. Hesaplanan geriye dönük hava yörüngeleri, bölgenin atmosferindeki aerosolleri etkileyen kaynak yerlerinin bulunması için kullanılmıştır. Kaynakların, kaynaktaki aerosollerin kompozisyonlarının ve kaynak bölgelerinin belirlenmesi için, dağılım testleri, faktör analizi ve potensiyel kaynak katkı fonksiyonu (PKKF) gibi çeşitli istatistiksel metotlar kullanılmıştır. Dağılım testleri hemen hemen ölçülen bütün parametrelerin konsantrasyon dağılımlarının lognormal olduğunu göstermiştir ki bu da aerosol kompozisyonlarının, örnekleme bölgesine lokal ve uzun mesafeli taşınımlar sırasında birden fazla ve farklı kaynaklar tarafından etkilendiğini göstermektedir. Elementel konsantrasyonlarda gözlenen değişimlerin en etkili nedeninin lokal ve bölgesel yağışların olduğu bulunmuştur.

Hesaplanan zenginleşme faktörleri üç farklı genel kaynak grubu göstermiştir. Bunlar, toprak kaynağı, deniz kaynağı ve antropojenik (insan aktiviteleri sonucu) kaynaklardır. Toplanan aerosollerin en önemli bileşenlerinin, katkıda bulunan bu üç kaynak tarafından oluşturulduğu belirlenmiştir. Faktör analizi, aerosollerdeki elementlerin konsantras-yonlarına katkıda bulunan 4 ana kaynak göstermiştir. En fazla katkıda bulunan kaynak toprak, sonra lokal ve karışık kirletici kaynağı, deniz kaynağı ve uzun mesafelerde bulunan kirletici kaynakları olarak bulunmuştur. Bunlara ek olarak, faktör analizi sadece toprak elementlerine uygulandığında, toprak kaynağı ikiye ayrılmıştır. Lokal, Afrika kökenli, eski SSCB Ülkeleri, Batı Avrupa ve Orta Doğu'dan gelen toprak kaynaklı aerosollerdeki elementleri ayırt etmekte kullandığımız en önemli "iz" Mg, Ca, Fe, Mn ve K gibi elementlerin konsantrasyonlarının aluminyum konsantrasyonuna olan oranlarıdır. Bu elementlerin local ve diğer kaynak bölgelerinden gelen tozlardaki kompozisyonları bir birilerinden oldukça farklıdırlar. Potensiyel Kaynak Katkı Fonksiyonu (PKKF) tekniği, iki ana potensiyel bileşen belirlemiştir. Buna göre, toprak elementlerinin ana kaynak bölgeleri Türkiye'nin doğusu, Orta Asya Ülkeleri, Kuzey Afrika ve Ortadoğu ülkeleridir. Diğer yandan, antropojenik kökenli bileşenler ise, Batı ve Doğu Avrupa ile Rusya Federasyonunda bulunan ülkeler ve Türkiye'dir.

Anahtar kelimeler: Aerosol, Türkiye Batı Karadeniz Bölgesi, Eser Element, İyon, Zenginleşme Faktörü, Faktör Analizi, Üç Boyutlu Hava Yörüngesi, Potensiyel Kaynak Katkı Fonksiyonu, INAA, AAS, Uzun Mesafeli Taşınım.

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INTRODUCTION

It is now recognised that the atmosphere is an important pathway for the transport of material to the oceans and seas. This atmospheric material consists of a wide variety of components including gases, nutrients, sulfates, nitrates, biological debris, crustal materials and associated major and trace metals. The material transport through the atmosphere can affect a number of global biogeochemical processes, both during its residence time in the air and following its deposition to the sea surface and lands. In the air, atmospherically transported material can influence climatic conditions; for example, by affecting the radiation budget of the atmosphere or by perturbing atmospheric circulation patterns. This influence can occur either directly (e.g., by affecting solar and terrestrial radiation) or indirectly (e.g., by the ability of the aerosol particles to act as condensation nuclei which facilitate cloud formation processes. Following its deposition to the surface atmospherically transported material mixes with material brought to the oceans or seas by other transport pathways (e.g., rivers) and can play an important role in marine sedimentary, biological and trace metal cycles.

The Black Sea is an inland sea lying between southeastern Europe and Asia Minor. It is connected with the Aegean Sea by the Bosphorus, the sea of Marmara and the Dardanelles. Romania, Bulgaria, and the European portion of Turkey bound it on the West. The northern and eastern shores are bordered by Ukraine, Russia, and Georgia; the entire southern shore is Turkish territory.

The Black Sea has a length of about 1200 km from east to west, a maximum width of 610 km, and an area (excluding sea of Azov) of about 436,400 km^2. The sea receives the drainage of a large part of central and eastern Europe through the Dnepr, Dnestr, and Danube rivers. It also receives waters from a considerable section of eastern European Russia, through the Don River and from the western Caucasus region through the Kuban, and a number of smaller rivers; and the Black Sea drains northern Asia Minor through the Çoruh, Yeşilırmak, Kızılırmak and Sakarya rivers. The greatest depth of the Black Sea exceeds 2135 m and severe storms occur frequently on the sea, particularly during the winter seasons. The prevailing winter winds are from the north (Tuncer et al., 1998 and Haccısalihoğlu et al., 1992).

The Black Sea cost at Amasra has mountains behind the beach. Water from the sea evaporates and forms clouds at higher altitudes. If low clouds become too heavy with rain, then they can not move south. They stay over Amasra and pour down rain. The meteorology of Amasra is discussed in detail in the results and discussion chapter with meteorological data available for 12 to 26 years.

The resources of Black Sea and its problems are shared by six coastal countries; Bulgaria, Georgia, Romania, Russia, Turkey and Ukraine. Management of the Black Sea's shared resources is the responsibility of these countries but part of this responsibility for controlling aquatic and airborne pollution should also be shared amongst the other eleven countries which have a major part of their territory in the Black Sea Basin. Protection of the Black Sea can not be achieved on a unilateral basis. Almost every use of the sea and coastal areas has the potential for affecting the well-being of neighbouring countries. Even pollution restricted to the vicinity of an industrial plant may affect the economic development of another country by killing juvenile fish which would have otherwise migrated to its coastal seas. On the other hand, countries may wish to over-exploit their part of a migrating resource in order to deny access (and advantage) to the neighbours. Joint management and protection of shared marine living resources is one of the few available options to countries bordering the Black Sea. In this manner, a better sense of ownership of the sea's resources can be attained and owners tend to protect their property more than those enjoying a free service. There is a strong need for harmonising legal and policy objectives and for developing common strategies for investment in the control of pollution. Furthermore, only concerted international action can hope to do anything to protect the biological diversity of the Black Sea.

The first move was to establish a new legal framework for co-operation. Inspired by the regional Seas Conventions which emerged after the 1972 Stockholm Conference on Environment and Development, representatives of the Black Sea countries drafted their own "Convention for the Protection of the Black Sea Against Pollution". This convention was signed in Bucharest in April 1992, and ratified by six legislative assemblies by early 1994. The "Bucharest Convention" includes a basic framework of agreement and three specific protocols on: the control of land based sources of pollution; dumping of waste; and joint action in the case of accidents (such as oil spills). The convention establishes rules, but it does not set the goals, priorities and timetable needed to bring about environmental actions. For this reason, a Ministerial Declaration on the Protection of the Black Sea Environment was signed by all six Ministers of the Environment in Odessa in April 1993. Based largely upon the Agenda for the 21st Century adopted at the 1992 Rio Summit of World Heads of State, this innovative document sets the stage for three years of change (State of the Environment Georgia, 1997).

The activity centres and their working parties in the Black Sea Environmental Program are as follows:

1. Emergency Response (Varna, Bulgaria),
2. Routine Pollution Monitoring (i.e. Assessment of land-based sources, bathing water quality, etc.) (Istanbul, Turkey),
3. Special Monitoring Programs, biological and human health effects, and environmental quality standards (Odessa, Ukraine),
4. Protection of Biodiversity (Batumi, Georgia),
5. Development of Common Methodologies for Integrated Coastal Zone Management (Novorossiysk, Russian Federation),
6. Fisheries (Constantza, Romania).

The entire network, which was established to ensure the efficient implementation of the Odessa Declaration, will be gradually transferred to the Secretariat of the

Istanbul Commission and in the case of the Fisheries Activity Centre, to the Fisheries Commission.

The Black Sea Environmental Program discussed above does not contain any activity about atmospheric fluxes of pollutants and forest decline on the Black Sea Coastal Zones. However, in our previous studies about land based pollutant fluxes to the Black Sea and Atmospheric Wet and Dry deposition study in the Eastern Mediterranean Basin showed that the fluxes of land based and atmospheric pollutants are at comparable levels (Al-Momani, 1995 and Tuncer et al., 1998). Therefore, the atmospheric depositions of pollutants can not be underestimated in pollution control and management works. In this study, results obtained from daily aerosol sample collection between April 1995 and July 1997 at Western Black Sea Basin were studied extensively. Collected samples were analyzed for a range of inorganic species including major ions and 13 (samples from April 1995 to May 1996) to 40 (samples from May 1996 to July 1997) trace elements. The results of these analyses are discussed in terms of the atmospheric processes controlling the aerosol concentrations and source regions affecting concentrations of these species in the Western Black Sea Basin. The data set generated in this work is the most extensive one at this region. In general, data is extremely limited in the entire Black Sea Coastal Zones. Although there had been a few works in which inorganic species were measured, they are limited either in temporal coverage or in the numbers of parameters determined. The data generated in this work includes the largest set of parameters in the whole Black Sea Basin which is invaluable to identify types and locations of the sources affecting the region. The importance of our data lies not only in the improved data base of concentrations of a number of components in aerosols but also more it allows for the first time a clear evaluation of the meteorological control of the aerosol compositions regime to be considered in the Western Black Sea part of the basin.

In this investigation, the atmospheric long range transport of natural and anthropogenic species to the Black Sea Basin and the transport mechanisms from Russia, Western and Eastern Europe and the Sahara Desert was studied. The main purpose of the investigation was to determine the short and long term variations of the pollutant concentration levels, fluxes of wet and dry depositions (depositions are being studied as a second PhD thesis in the Environmental Engineering department, METU) types and regions of pollution sources and transport mechanisms of pollutants in the Western Black Sea region of Turkey. A previous study done by our group in 1992 inwhich atmospheric samples were collected in the Black Sea atmosphere (Hacısalihoğlu, 1992). This study showed that; 1) concentrations of some of the pollutants were high enough to be harmful to the forest in the Black Sea Region, 2) approximately %70 of the pollutants were transported from Europe, 3) the fluxes of some of the pollutants were comparable with the riverine fluxes of same pollutants to the Black Sea, 4) the concentrations of measured species in the Western Black Sea Region was observed to be two times higher than the concentrations of same species measured in the Eastern Black Sea Region, and 5) the concentrations of the pollutants showed a strong variation with the short (daily) and long terms (seasonal).

To achieve the above goals, daily aerosol samples were collected in between April 1995 and July 1997. During this time period 354 daily aerosol samples were collected. Trace elements and major ions were determined in these aerosol samples. For the determination of pollution sources the following methodologies will be used in the discussions section;

a) **Determination of concentration levels:** The data obtained in this study will be compared with the literature values and the levels of measured species will be discussed in order to understand their effects on forest decline in the Western Black Sea Basin.

b) **Determination of short term and long term variations of the pollutant concentrations:** The short and long term variations in the concentrations of pollutants is a very strong clue for the transport mechanisms of the pollutants to the region. The atmospheric transport mechanisms of the pollutants can be affected by the local and upper atmospheric meteorological parameters and the transport mechanism of a pollutant changes with seasonal changes in the meteorologic conditions. Therefore, the pollutants transported to the receptor site can be from different regions in different seasons. In order to understand the long range transport of pollutants to the Black Sea Basin, the short and long term concentration variations of the marker elements and factors affecting these variations should be well understood. The upper atmospheric meteorologic parameters are used to understand the transport mechanisms of the pollutants. For this reason *back trajectory* modelling is used in literature. By using this model, the origin or sources of pollutants transported to the receptor site can be determined.

c) **Determination of components of the aerosol mass:** The aerosol particles collected on the filters are the mixtures of particles from different sources. The aerosols contain crustal, marine and anthropogenic (pollution) components. Before the determination of anthropogenic source types and source regions, the contributions of these three components to the total aerosol mass will be calculated and temporal changes in their contributions will be determined.

d) **Determination of pollution source types:** The types of sources responsible for the atmospheric input of the pollutants will be evaluated. The *key* here is the differences in the chemical compositions of the aerosols emitted from different sources. For this purpose, *Enrichment Factors* of the elements and *Factor Analysis* will be used. By means of using these two methodologies, the anthropogenic component of the aerosol mass and the types of pollutant sources will be determined.

e) **Determination of Regional Sources:** After determining the source types affecting the Western Black Sea Basin, the regions where these sources exist will be determined. For this purpose, the measured trace elements and major ions concentrations will be combined with the upper atmospheric meteorological parameters and air mass movements, the pathway in which the measured species in the aerosol samples were transported to the Western Black Sea will be determined. In this study, Turkey was divided into three regions as west, central, and east subregions. In addition to Turkey, some regions of Middle East, Asia, Europe and Africa were also divided in subregions. The contributions of these subregions to the aerosol compositions are calculated by using *Trajectory Statistics* method. One of this technique is called as *Potential Source Contribution Function* (PSCF) and will be discussed in the following sections.

In the following chapter of this thesis one can find a survey of existing works relevant to the global atmosphere, and specific to the Black Sea Coastal Zones after a brief review of sources of trace elements in the atmosphere. This chapter reviews the receptor modelling techniques also that are commonly used for source apportionment purposes and climatology and meteorology of the Western Black Sea Basin.

Sampling techniques, instrumentation and the analytical techniques were discussed in the third chapter of this study. Within this study, a total of 350 daily aerosol samples were analyzed with combination of Instrumental Neutron Activation Analysis (INAA), Atomic Absorption Spectrometry (AAS), Ion Chromatography (IC) and VIS Spectrometry techniques. The results of data quality assurance, blank values, detection limits of the analytical techniques used are also given in the third chapter.

The results obtained are extensively discussed in the fourth chapter. A discussion on the source regions and signatures of pollutants which were determined through application of various receptor modelling techniques are also included.

In the fifth chapter of this study, concluding remarks, some suggestions for further research on this subject were given.

CHAPTER 2

BACKGROUND

2.1. Atmospheric Trace Elements and Ionic Species

Aerosols in the atmosphere originate from both natural and anthropogenic sources. Ambient air pollution consists of a complex mixture of gases, vapors, and aerosols (solid and liquid particles) which vary in concentration, chemical composition and physical characteristics with source, time and location. The latter is also called as particulate matter which is a collective term used to describe very small solid and/or liquid particles. They may be produced by natural processes (pollen, salt spray, soil erosion) and by human activity (soot, flyash, metal oxides). Their presence as aerosols in the atmosphere may contribute the visibility reduction and pose a threat to public health.

One of the major characteristics of aerosol in the ambient atmosphere is particle size. Particles range in size from approximately 0.005 to 500 µm. The smallest are molecular clusters and the largest are visible to the unaided eye. Small particles which has aerodynamic diameters less than 1 µm behave as gases; that is, they are subject to Brownian motion, follow fluid stream lines around obstacles, and are capable of coagulation. Larger particles are more characteristic of solid matter, as they are strongly affected by gravity (Godish, 1991 and Finlayson-Pitts, 1986).

The expression of particle size is usually based on particle behavior in the earth's gravitational field. The so-called aerodynamic equivalent diameter refers to a spherical particle of unit density (1 g/cm^3) that falls at the same velocity. It does not refer to the actual dimensions of the particle. The size distribution of particles in the atmosphere has been characterized a being trimodal. In the idealized diagram in Figure 2.1, three peaks are seen. Two of the peaks characterize the fine particle fraction (< 2 μm), the third the coarse fraction (> 2μm). The fine particle fraction consists of a nuclei and an accumulation mode.

The coarse particles are usually produced by mechanical processes and are either natural or anthropogenic. Sources, atmospheric behavior, and deposition of coarse particles are mostly independent of those characteristics of fine particles. In urban areas, particulate aerosols are about evenly divided between fine and coarse particles. Under calm atmospheric conditions, the fine particle mass begins to exceed the mass of coarse particles with increasing downwind distance from urban areas. Because of their low settling velocities, fine particles may be transported 1000 km or more from their source region.

Major and minor elemental composition of particles are used as a tracer to determine sources of particles in ambient aerosols (Hopke et al. 1976; Thurston and Spengler, 1985). Trace elements which sources are well documented would be the ideal tracers.

2.1.1. Sources of Trace Elements

Trace elements are introduced into the atmosphere from both natural and man-made sources. Crustal material from wind-blown dust, buble bursting over the ocean, forest fires, volcanoes and biogenic emissions are the most common natural sources of the particles in the atmosphere. Among these, wind-blown crustal dust is particularly important. Arid and semi-arid areas are the major continuous sources of the crustal material and volcanoes seem to be dominant natural source of chalchophilic elements at remote locations (Cunningham and Zoller, 1981).

The atmospheric aerosols are divided into two classes according to their generation as low- and high-temperature generation processes (Chester, 1990a). This division is stressed since the forms in which elements are present in the atmosphere

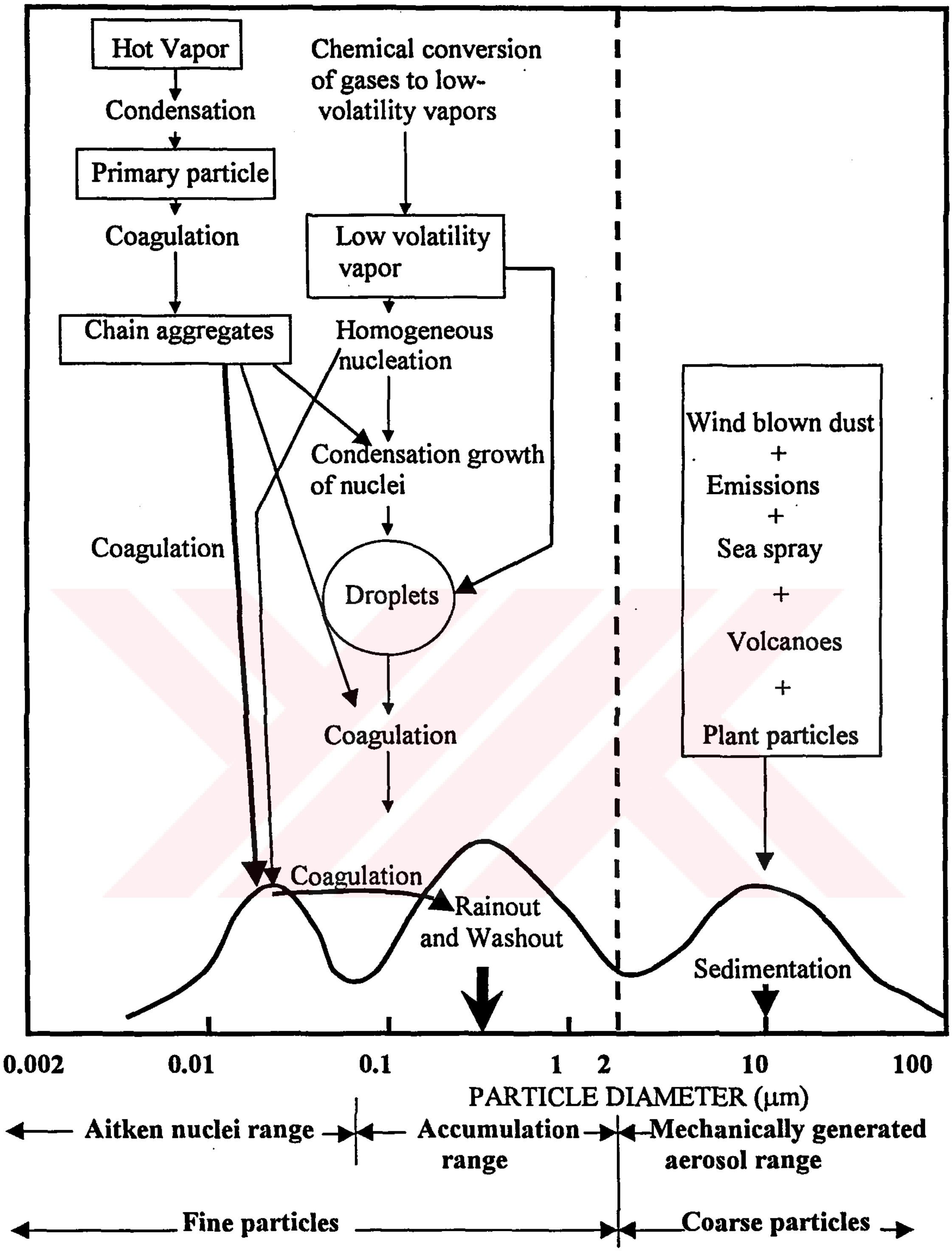


Figure 2.1. Schematic of an atmospheric aerosol size distribution showing the three modes, the main source of mass for each mode, and the principle processes involved in inserting mass into and removing mass from each mode (Finlayson-Pitts, 1986).

i.e., their speciation can be strongly dependent on the temperature at which they were released from their parent host. Following this broad classification of the generation of the atmospheric particulate material, it has long been identified that they are produced both by natural and anthropogenic sources as explained below.

2.1.1.a. Natural Sources

The surfaces of the earth and the oceans can supply material to the atmosphere both in particulate and gaseous forms. The generation of particulate material from these widespread sources occurs during the low temperature mechanical mobilization of surface deposits and sea salts. Emissions from volcanoes and forest fires are other major natural sources of trace metals in the atmosphere formed from high-temperature processes (Chester, 1990a). These two types of source can release particulate material, e.g. ash, together with gaseous phases that may undergo condensation reactions and can result in the enrichment of particulate material. The high temperature burning of vegetation and the consequent emission into the atmosphere of particulate and vaporized elements from plant surfaces and soils are counted as natural sources.

2.1.1.b. Anthropogenic Sources

A variety of anthropogenic sources release both particulate and gaseous material into the atmosphere. These include the combustion of fossil fuels, including such additives as the lead in gasoline, the roasting of ores for refining metals, waste incineration, the processing of crustal materials for manufacturing cements, the production of chemicals, agricultural utilization and numerous other industrial and social activities.

Combustion of fossil fuels to produce electricity and heat is the main source for the anthropogenic emissions of Be, Co, Hg, Ni, Mo, Se, Sb, Sn and V (Güllü, 1996 and Ölmez et al., 1997). Combustion processes are also important sources of atmospheric As, Cr, Cu, Mn and Zn. Sources of atmospheric particulates and their elemental markers were tabulated by Ölmez et al., 1997 and it is given in Table 2.1. The elements like Zr, Mo, In, Zn, Cl, As, Au, Cd, Hg, Br, Sb, and Se are mostly volatile and are found in the atmosphere at elevated concentration levels due to anthropogenic activities. The impact area ranges from regional to global. Depending upon the type and the characteristics of their emission sources, most of the gasses' and some of the elements' atmospheric residence times may be an order of several years. Particulate forms of these elements have much shorter atmospheric residence times, but are useful as conservative markers for various industrial processes as listed in Table 2.1.

Table 2.1. Marker elements and their possible sources

Source	Element
Crustal material	Al, Sc, Mn, Fe, REE, Th, U
Marine aerosols	Na, Cl
Coal Combustion	As, Se, Hg
Oil Combustion	V, La, La/Sm
Refineries	REE
Motor vehicles	Br, Zn, Sb
Wood burning	K
Incinerators	Na, K, Cl, In, Hg
Chlor-alkali plants	Cl, Hg
Precious and other metal works	Co, Zn, Au
Aluminum plant	Al, Mg
Industrial urban areas	V, Zn, As, Se, Br, Sb
Iron/Steel works	Fe, Zn, Se, Mo, Sb
Regional transport	Fine mass, As, Se, Hg
Zn, Cd, Pb smelters	In, Zn, Cd, Sb, Pb
Ni, Cu smelters	Ni, Cu, Hg, As, As/Se

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

2.2. Long Range Transport of the Pollutants to the Black Sea Basin

The long range transport of materials through the atmosphere has long been known. Through out the earth's geological history materials have been atmospherically transported from continent to ocean; this long range atmospheric transport is now recognized as an important mode of global transport for a variety of trace substances. Trace elements are of interest in studies of long range atmospheric transport because of their importance in biogeochemical processes, including global oceanic fluxes. Tracers from a particular source region including various metals with characteristic origins, have been used to document the dispersal caused by atmospheric transport. Trace elements with magnitudes and sources well documented over geologic time would be the ideal tracers. Tuncel et al., 1985 have demonstrated that the fine fractions of atmospheric particulate samples that were collected at Shenandoah Valley contained a sulfate component that originates from distant sources. They used regional scale receptor modeling in which back trajectories of air masses for each sampling period were calculated and the results were combined with the factor analysis results and the observed sulfate peaks were interpreted as regional sulfate if the high sulfate concentration comes from the same directions as the trajectories. Kubilay et al., 1995 and Kubilay and Saydam, 1995 reported that the chemical composition of the Black Sea aerosols can change very rapidly in accordance with changes in the wind regime. The results of the first long term land based sampling of the atmosphere above the Turkish coast of the north eastern Mediterranean Sea has demonstrated the dominance of Sahara Desert particles over the eastern Mediterranean Basin. During such pulses they observed order of magnitude increases in the concentration of the elements like aluminum (Al) and iron (Fe). They also reported that any stagnant air mass over the Western Black Sea tends to increase the concentration of the elements associated with heavy fuel burning due to the increase in the number of ships through the Bosphorous.

Dulac et al., 1995 presented a number of quantitative results on atmospheric transport of African dust to the Mediterranean basin on the analysis of spaceborne observations from Meteosat and CZCS. They compared these observations with the coincident meteorological or chemical measurements and reported that most of the dust particles are confined in the dust-loaded African air layer which is uplifted over the boundary layer in the Western Mediterranean. In addition, their results showed that similar high dust years are found in the Atlantic and the Mediterranean which indicate that African dust transport is mainly driven by climatic conditions in the source regions.

A previous study carried out by Kubilay et al., 1995 showed that there are four types of air mass trajectories and the aerosols from each trajectory were named as A, B, C, and D type aerosols. Type A aerosols are influenced by Saharan dust; Type B aerosols are from mixing of air masses from Anatolia and local marine sources; Type C aerosols are the atmospheric input of Eastern Europe; and Type D aerosols are from atmospheric input of Russian Federation.

As will be discussed in the fourth chapter, in our study we also observed very high concentrations for crustal elements that may originate from Saharan dust pulses. The chemical compositions of the aerosols in this study changes in short term periods which may indicate the long range transport to the Black Sea basin. These will be understood very clearly after calculating the back trajectories for every sampling day and combining the results with the results obtained from factor analysis.

2.3. Receptor Models

Two statistical receptor modelling techniques namely Factor Analysis (FA) and Chemical Mass Balance (CMB) have been extensively applied in atmospheric studies (Hopke, 1991; Dzubay et al., 1988 and Ölmez et al., 1997) to identify potential sources and to estimate the source contributions affecting the chemical compositions of the aerosols at a sampling site. Factor analysis does not require a priory knowledge of the types or number of the sources influencing the aerosol samples. Some smearing of multiple sources which may be collinear in time or space may be observed. The number of samples for a reliable FA should be statistically significant (100 samples or more is generally acceptable) with large numbers of species that can be used as source markers. The data set (230 of 354 samples and around 25 variables) used in this study qualifies very well for FA methodology.

Chemical Mass Balance Techniques can be applied even to a single sample, although all of the potential sources and source profiles must be well defined prior to the analysis. The CMB is generally considered to be free of smearing effects from multiple sources since the individual source profiles are used to apportion average compositions observed at the receptor site. However, Ölmez et al., 1997 showed that application of CMB as currently used for source apportionment is misleading and requires major improvements, even in regions with relatively well defined boundaries. Based on these limitations we decided not to use the CMB approach, because our sampling site was set up at a rural site and there is no any pollution source which may affect the aerosol composition. In this study, our main objective was to determine the long range transport of pollutants from remote pollution sources. Therefore, the sampling station must be installed at a rural site which is not affected by local sources.

The source identifications made by FA are supplemented by examining the back projected, three dimensional upper atmospheric wind trajectories using the ECMWF trajectory model which was discussed in Section 2.4.

This serves both to confirm the source types indicated in the factor analysis (by matching source types identified through their elemental signatures with wind patterns coming from known sources of those types) and to separate the influences of sources of the same type but in different locations.

The receptor models mentioned above use the chemical measurements of the aerosol samples collected from a receptor site and identify the possible sources in terms of their chemical nature and estimate the importance of contribution of these sources. First generated receptor models like PCA, FA and CMB have limited abilities to locate the regional sources of air pollutants because only chemical information is used and the regional pollutants are generally secondary in their chemical nature and these receptor models can not determine the specific locations of the sources. To overcome these shortcomings, meteorological information is needed to be incorporated into these receptor models.

A brief definitions and applications of some of mostly used multivariate statistical methods which will also be used in this study are discussed in the following sections.

2.3.1. Factor Analysis

In mathematical terms the goal of FA is to reduce the dimensionality of the data set from the number of different measured variables to the number of actual factors influencing the system. When applied to the receptor modelling of environmental samples FA allows the various sources influencing each sample and site to be separated and identified. As an example, atmospheric particulate samples almost always contain some amount of crustal material which contains large relative concentrations of Al, Sc, and rare earth elements. Rather than simply reporting the concentrations of these elements, it is much more useful to present the amount of crustal material in the sample from which the concentrations arose (Ölmez et al., 1997).

Difficulty in performing the analysis is due to the fact that concentrations of most elements found in a sample are the result of the combined influences of several sources. The method relies on observing the communalities of the variation of the variables in order to separate the effects of different sources.

A large data set, however, is not always sufficient for separation of the sources. Because the use of FA to identify sources from receptor samples is entirely dependent on the transport of the species, it is very difficult to distinguish between two sources located close to each other even if they have very different types of emissions. Thus, sources which are far from the sampling site tend to get smeared together, and local wind patterns can greatly affect the results by mixing air from different directions. Sampling durations which are longer than the temporal changes in the wind patterns can also result in the smearing of different sources into one factor. Since prevailing winds are often a function of season, it is important and beneficial to have samples covering at least one year before performing the analysis. Also, if there is a force which is not measured but which affects two or more of the elements equally (e.g. some atmospheric transformation dependent on humidity) then this might cause the elements to be linked as if they were from a common source.

There are several reasons why FA results are useful. First, FA represents data as a summation of influences rather than effects, which is often more useful. From this representation the relative impact of the causal factors or sources can be detected. This is important in environmental work where several different sources may be partially responsible for some unwanted effect. The unknown source of a measured element can be found by its inclusion in a factor of known origin. Finally, a source may be found which had not been previously identified. This is a result of the fact that no a priory knowledge of the source is needed for FA, the only input is the sample data.

When FA is applied to a data set the first result obtained is a factor matrix which relates each of the elements or variables. The numbers in the matrix are referred to as the factor loadings and indicate how much of the variance of the given element can be explained by the given factor. Though the complete square matrix would exactly transform the data points between the two representations, the factors in the matrix are given in order of decreasing ability to describe the variance of the whole system. Usually only the higher order factors are retained for further analysis (generally factors having eigen values greater and equal to 1.0). The physical meaning of the factors must be interpreted by observing which elements or variables display high ($\geq$ 0.25) loading within the factor. Although many elements may display high loadings, a particular source type is usually identified with a factor by the presence of high loadings of a few marker species which are characteristics of that source type. These markers will be discussed extensively in the discussion part of the thesis.

The next step is to plot data using the factor scores rather than the elemental concentrations as the dependent variables. The magnitude of a factor's (or a source's) influence on a specific sample is given by a factor score for that sample. The factor score is the number of standard deviations from the mean of that factor as averaged over all the samples. An average contribution from the factor gives a score of zero, a greater than average contribution (i.e. zero) gives a positive score, a less than average contribution gives a negative score. Factor scores greater than one indicate a strong influence of that source or factor on that individual sample.

2.3.2. PSCF Analysis

PSCF is a new receptor oriented method which is able to incorporate the meteorological information into an analysis. The concept of PSCF was introduced to identify geographical regions that may have a higher probability of being source areas of potential harmful substances like sulfate in the study area. The results of the PSCF analysis may then be useful in tracing atmospheric constituents (Malm et al., 1986).

Trajectories are related to the composition of collected material by selectively matching the time of arrival of each trajectory at the receptor site to sampling interval of filter sample. The value of PSCF for a single grid cell of 5° long by 5° latitude is calculated by counting each 1-hour trajectory segment end point that terminates within that grid cell. Suppose N represents the total number of trajectory segment end points for the whole study period, T. If the number of end points that fall in the ij^{th} cell is n_{ij}, the probability of an event at the receptor site is related to that cell, A_{ij}, over entire study period T is given by;

$$P[A_{ij}] = \frac{n_{ij}}{N} \qquad \text{.....................2.1}$$

If, for the same cell, there are m_{ij} end points whose arrival times of air parcels correspond the events with pollutant concentrations higher than an arbitrarily given value, the probability of this "matched" event, B_{ij} is given by;

$$P[B_{ij}] = \frac{m_{ij}}{N} \qquad \text{...................2.2}$$

The PSCF for the ij^{th} cell is then defined as:

$$PSCF_{ij} = \frac{P[B_{ij}]}{P[A_{ij}]} = \frac{m_{ij}}{n_{ij}} \text{.........2.3}$$

The PSCF value can be interpreted as the conditional probability that concentrations larger than a given criterion value are related to passage of air parcels through the ij^{th} cell during transport to the receptor site.

Cells for which high PSCF values are calculated result from the arrival of air parcels at a receptor site with pollutant concentration higher than a given value observed at the site. These cells are indication of areas of "high potential" contributions to the pollution at a receptor site. It is important to note that the exact location of the source(s) within the high potential areas is unknown in the present analysis because of (1) the fundamental limitation of the PSCF methodology that cells must be large enough to have a reasonable number of counts in them, and (2) the uncertainty involved in calculating the backward air parcel trajectories (Güllü, 1996).

2.3.3. Enrichment Factor

Enrichment factor is a simple statistical approach which is calculated using double normalization of the variable. First the ratio R_{sample} is calculated by dividing the concentration of an element X in a sample (e.g. Zn) by the concentration of a normalizing element Y from the same sample. The normalizing element is the one whose presence is attributed to a known and single source. In atmospheric aerosol samples Al, Sc, Fe or Ca are usually chosen, their source is wind blown crustal material or dust, and concentrations do not vary greatly with geographic location. In this study Al was selected as a normalizing element. The normalization eliminates any sample-to-sample variation in crustal material loading. Next, R_{sample} is divided by the average natural crustal ratio of the same two elements, $R_{crustal}$:

$$(EF_X)_{sample} = \frac{R_{sample}}{R_{crustalaverage}} = \frac{(X/Y)_{sample}}{(X/Y)_{crustalaverage}} \quad \text{....................2.4}$$

This ratio is the enrichment factor (EF) for element X and should be unity if the element X originates only from crustal material. A high value for EF indicates that additional sources exist for element X in that sample. The EF calculation is applied to every sample for every element determined. The EF results obtained for in this study will be discussed in the fourth chapter.

2.4. Back-trajectory Analysis

One of the most commonly used method for the interpretation of measurements and evaluation of the transport of chemical constituents in the atmosphere is the atmospheric trajectory models. The backward trajectory models were developed to study the origin and history of air parcels during their travel over the previous three or four days before arriving at the receptor site.

To obtain the three dimensional (3-D), three days backward air mass trajectories, the publicly available operational model on the CRAY C90/UNICOS super computer at the European Center for Medium-Range Weather Forecast center (ECMWF, Reading, U.K.) was utilized. In order to run this model from a remote site and obtain trajectory data for a specified region and date, the job (a request file for a trajectory) given in the Appendix (Table A1) was initialized via internet.

The model uses analyzed wind field components; *u* and *v*, zonal and meridional, respectively, plus the vertical velocities available in the archieve of the center (MARS) in the form of a special, on-line data base gridded every 6h (00, 06, 12, 18 UT) for standard pressure levels (Kubilay, 1996). The grid space is equal to 1.875° for both latitude and longitude. The model recalculates the new position of the air parcel at each 15-min. time step by utilizing linear spatial and temporal interpolations. All calculations are carried out on a regular latitude-longitude grid, with a resolution selected by the user. In this study a resolution of 1.5x1.5 degrees has been used. A coarser resolution may be selected, in order to reduce computer time. The resulting parcel positions (expressed as latitudes and longitudes) together with wind components and pressures have been entered hourly as characters to a resultant file.

After sending a request job to the center, a data matrix is sent back to the user. The data matrix contains 8 colums and each column gives the following information about the air parcel:

The first and second columns show time steps for back tracking, the third, fourth and fifth columns show *u*, *v*, and *w* components of the wind in every time step. The sixth and seventh columns show the position of the air parcel in latitude and longitude, respectively at each time step whilst the last column gives the pressure of the tracked air parcel at its new position (an example of such a result file is given in Appendix, Table A2).

The data for trajectories arriving at four different barometric levels (900, 850, 700 and 500 hPa or mbar) were obtained daily throughout this study. The hourly longitude and latitude of air parcels have been plotted on horizantal mercator projection maps. Such plots are known as air mass back trajectories, the actual 3-D paths that air parcels follow as they move through space.

Calculated air mass back trajectories provide information only about the source regions of the air masses arriving at the sampling zone. They do not give information on precipitation that the air mass might have experienced during its travel to receptor site-which would be a useful parameter in explaining the varience in the atmospheric concentrations of the measured species. Local precipitation data at the atmospheric sampling site has been used both for the assessment of its effect on the variability of the elemental concentrations in the aerosols and in wet-deposition calculations. The daily amount of local precipitation at the sampling site was obtained from a rain gauge which was installed to station together with the aerosol sampler and gas phase autoanalyzers. The data obtained from the rain gauge was stored in the data logger, automatically for each day throughout the sampling period. The rain gauge results were also compared with the wet deposition amounts obtained from Andersen Wet only collector which was also installed to our monitoring station at the same time.

2.5. Statistical Treatment of Data Set

The arithmethic and geometric means of the measured parameters are the mostly used statistical tools in order to understand the distribution types of the measured elemental concentrations in a time period. Statistically, if there is a significant differences between the arithmetic and geometric means for an element and if the geometric mean and the median of the elemental concentration are very close to each other, then the distribution is accepted as log-normal distribution. Log-normally distributed data set can be better described by the geometric mean and standard deviations. The geometric mean is defined as:

$$\bar{x}_g = \exp\left[\frac{\sum_{i=1}^{N} \ln x_i}{N}\right] \quad \ldots\ldots\ldots\ldots\ldots 2.5$$

where, x_i is the concentration of the element measured.

The dimensionless geometric standard deviation (σ_g) for each chemical component represents the spread in the data around the geometric mean. The geometric standard deviation reflects the different levels of stochastic processes that influence the chemical component. The geometric standard deviation representing the slope of a log-probability plot is calculated by using the following definition:

$$\sigma_g = \exp\left[\frac{\sum_{i=1}^{N} (\ln x - \ln \bar{x}_g)^2}{N-1}\right]^{1/2} \quad \ldots\ldots\ldots\ldots\ldots 2.6$$

where, σ_g and x_g are geometric standard deviation and geometric mean, respectively and N is the number of samples.

CHAPTER 3

MATERIAL AND METHODS

3.1. Sampling Site Description

Site selection is the most important and critical step in establishing reference stations where sampling is performed to study trace amounts of pollutants from long range transports and in order to separate local contributions. The sampling site should not be under the influence of any local pollution source. There are two important objectives in site selection criteria. These are; (1) the generated data should give information about fluxes of pollutants to the Black Sea Basin, and (2) the generated data should supply information about the source regions. The second objective requires that samples should not be influenced from local sources. Based on above requirements a monitoring station should fulfil the following criteria;

Major pollution sources like power plants, cities with a population of greater than 10,000 etc..., must be at distances greater than 10 km; the sampling site should be at least 1 km away from major roads and small towns with a population of around 1,000; electricity should be available at the site in order to operate the instruments; and the aerosol and precipitation samples that are collected at the site have low concentrations of metals and ions, so extreme care should be taken in order not to contaminate the samples. In this work, an atmospheric sampling and pollution monitoring station was implemented at the Western Black Sea Coastal site of Turkey. The station is at 20 km east of Amasra town (Figure 3.1.a and Figure 3.1.b) and 3.5 km far from the Black Sea (41° 47' N and 32° 29'E). The altitude of the station from the sea level is approximately 150 m. In this work we could not obtain the digital map for the sampling site in order to get the 3-D map of receptor site.

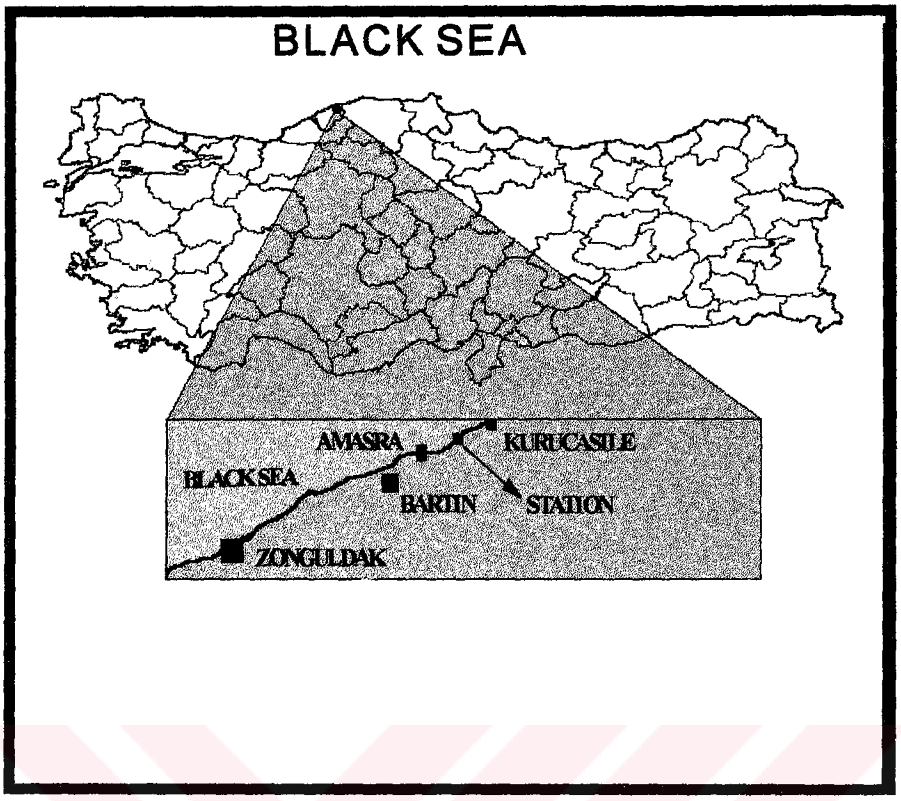


Figure 3.1.a. Sampling site.

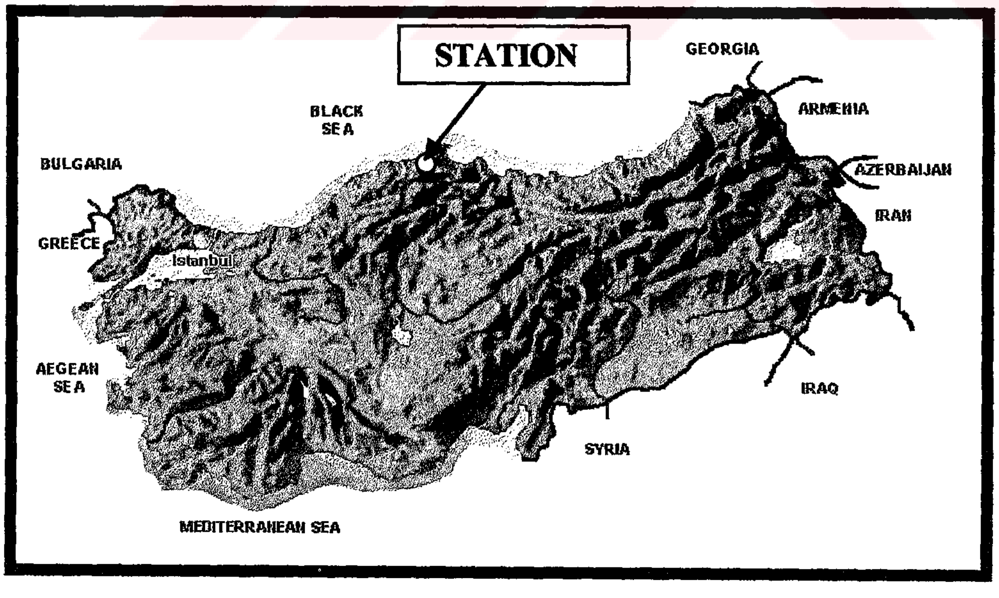


Figure 3.1.b. Topographic view of the sampling site

The receptor site belongs to military zone and it is impossible to obtain a map in 1:25,000 scale. Instead, a less detailed map showing the sampling site was inserted (Figure 3.1.b). The station was located in a platform whose ground was filled with large sand stones. This platform contains Hi-Vol PM-10 aerosol sampler and a wet and dry deposition collector. There is a field laboratory connected to the platform which contains automated; sulfur dioxide, nitrogen oxides (NO, NO_2 or NOx), ozone, rain gauge, PM-10 suspended particulate matter (SPM) analyzers. The field laboratory consisted of a container with dimensions of 3mx2mx2m. The container was equipped with electrical power lines and the electricity was distributed to the instruments from the container. The sample change area consists of a table where precautions were taken to minimize the sample contamination during the changes of filters. The table was lined with a sheet of polyethylene and a small plate of plexiglass with dimensions of 50 cm x 40 cm was placed on the polyethylene sheet. The entire sample handling in the field laboratory was carried out on this plate. The plate is covered with nylon bags if it is not used.

3.2. PM-10 High Volume (Hi-Vol) Sampler

High volume samplers, in general, consists of three basic components; a filter holder, a blower (pump) which generate vacuum through the filter and a housing which protects the sampler from any external impact. Most of the high volume samplers contains a roof on the housing which serves as a preimpactor to limit the particle sizes reaching the filter. The motor (pump) is adjusted to maintain a constant air flow through filter between 1.13 and 1.7 m^3/min. Sampler collects particles over a wide range of particle sizes, but generally smaller than 100 µm. A size selective inlet is added to restrict the upper size range of the collected particles to less than 10 µm.

The most widely used airborne particle sampler in rural studies is the high volume samplers. In this study, PM-10 aerosol sampling was done with a Sierra-Andersen Model SAUV-10H PM-10 High Volume sampler. The filters used for the aerosol collection was 20.3x25.5 cm Whatman 41 cellulose filters. The size selective inlet attached to the Hi-Vol sampler (Figure 3.2) separates particles smaller than 10 μm aerodynamic diameter from the larger particles. Particles with sizes less than 10 μm are collected on the filter and the larger particles are precipitated to the collection shim of the inlet or preimpacted before reaching to the nozzles.

The atmospheric aerosols were sampled with flow rates in the range of 1.4 to 1.7 m^3/min. The symmetrical design of the sampler makes it insensitive to wind direction, and the inlet design and the internal configuration make the collection efficiency independent of wind speed from 0 to 36 km/h. Particles are accelerated through multiple circular impactor nozzles. By virtue of their larger momentum, particles greater than the 10 μm impactor cut point impact onto the greased impaction surface. The particles having sizes 10 μm and below are carried vertically upward by the air flow and then downward through multiple vent tubes on the filter holder, where they are collected on the filter. The larger particles collected in the impaction chamber on the collection shim are removed during maintenance periods.

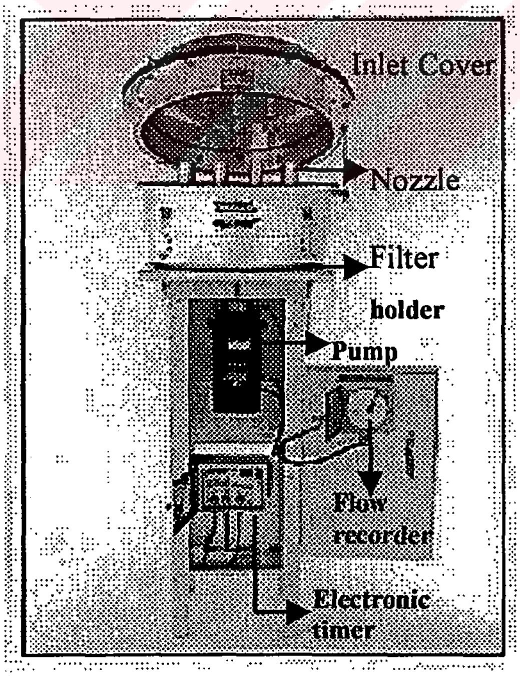


Figure 3.2. Picture of PM-10 Hi-Vol aerosol sampler.

The Whatman 41 filters were used for the collection of atmospheric aerosols. This filter is strong enough to stand for high flow rates and does not cause significant pressure drop due to the particle load. It has also advantage of less background levels for most of the elements determined. The volume of sample air was determined from a dry gas meter connected to the sample air outlet of the sampler. The sampler was operational for 24-hour periods during sampling.

3.3. Sample Handling and Analyses

All persons responsible for the collection and handling of samples were thoroughly familiar with precautions to be taken. Whatman 41 cellulose filters for the collection of aerosol samples were first weighed at the central laboratory, Class-100 clean laboratory, Environmental Engineering Department, METU. After putting the weighed samples in pre-washed (nylon bags washing was done with 5 (v/v)% HNO_3 solution and subsequent washings with distilled deionized water until the pH of wash water becomes 5.5) nylon bags, they were given an ID number and heat sealed. Then the filters were sent to the field laboratory with sampling information sheet. Following the sample collection, the aerosol loaded filters were sent back to the central laboratory and were reweighed to determine the mass of the aerosol sample collected.

Filters were changed at around 9:00 am every day. To change the filter, the sampler was stopped, and the final volume of the sample air was recorded on the sampling information sheet from the dry gas meter. Then the filter cartridge on the PM-10 sampler was opened and put in a nylon bag and carried to the container. The cartridge was opened on the plate mentioned above and the filter was folded into two and put in the acid washed nylon bag and heat sealed and placed in a paper box to sent to central laboratory in Ankara. The filter cartridge was wiped with damp tissue paper, an unused Whatman 41 filter was placed in the cartridge and carried too the sampling platform in a polyethylene bag. The nylon bag and the cartridge cover were removed and placed on the sampler. The initial volume was recorded on the information sheet of new sample and the sampler was started for 24 hours until the next day around 9:00 am.

To obtain field blanks, all manipulations carried out for the real samples were performed except air was passed through the filter for only a few seconds. The loaded filters and field blank samples were sent to the central laboratory at approximately 3 months prior to the analysis. The samples were kept in the refrigerator at 4°C until analysis. During sample handling processes, all sample manipulations were done using Teflon coated tweezers and polyethylene gloves.

The sample handling and preparation manipulations were carried out in a clean area in the Environmental Engineering department. The clean room consisted of two parts connected to each other with a door. The outer part of the room was used as a laboratory for storage of samples in the refrigerator. It also contains Ion Chromatography, pH meters and deionized water preparation unit. The pH measurements of wet and dry deposition samples and ion chromatography analysis of the samples were carried out at this part of the clean laboratory. The inner part of the room was used to prepare sample filters and to filter the wet and dry samples. There are five high efficiency particulate (HEPA) filters in the inner room to remove particles (particles having sizes smaller than 0.1 mm) in the indoor air.

For each set of aerosol samples to be digested an acid blank and a filter blank were prepared and digested at the same time with the samples. Each digestion set contained 20 samples including the blanks. Acid blank was prepared by adding only the same amounts of reagents (subboiled nitric acid and concentrated HF) used for the samples, however, filter blanks were prepared by cutting one fourth of an empty filter and adding again the same amounts of the reagents required for the digestion. The acid blanks were used for the purpose of checking the contamination possibilities. But filter blanks were used for the corrections of background contributions from both reagents and substrate (filter paper). The concentrations of all the measured species from the filter blank were subtracted from the samples corresponding to the same digestion set.

The loaded filters came from the field laboratory were prepared for the analysis in the clean room. The filters were weighed and divided into four equal parts by using a lancet and these parts were also weighed separately in order to calculate the volume of sample air passed through the one fourth of the filter. The first part of the filter was used for IC analysis for major anions, Cl^-, NO_3^-, SO_4^{2-} and for NH_4^+ by VIS spectrometry; the second part was used for the determination of heavy elements using Atomic Absorption Spectrometer; the third part of the filter was used again to determine the tarce elements using Instrumental Neutron Activation Analysis. The fourth parts of the filters were archived for any potential future use.

3.3.1. Preparation of DDD-Water and Pure Nitric Acid

In the sample preparations for the analysis only nitric acid, hydrofluoric acid and double distilled deionized water were used. The monodistilled water was redistilled using CORNING ag-11 Model water distillation unit which contains four electrical resistances in quartz tubings. All parts of the instrument is made up from glass and there is no any metallic part touching to the water. The double distilled water obtained from this instrument was then carried to the clean laboratory and purified further with a Millipore Model 2010 deionizer equipped with two ion exchange cartridges to remove ions and a third cartridge removing the organic and particulate matter. The produced deionized water finally has a resistance of 18 MΩ.

In the digestion of aerosol samples for AAS analysis, pure nitric acid was prepared using subboiling distillation unit. The subboiling system was made up of quartz and the electrical resistances were also enclosed in quartz tubings. The reagent used for the purification was analytical grade Nitric Acid (MERCK and 65 % pure). The commercial analytical grade nitric acid was heated slowly with two quartz rods equipped with an electrical heater. Then the vapor of nitric acid was condensed on a cooled quartz rod and collected in quartz flasks. This purification technique was used in order to avoid the high cost of large volumes of commercial suprapure grade nitric acid. The Hydrofluoric acid used in the digestion of samples together with pure nitric acid was commercial suprapure grade (MERCK) reagent.

3.4. Analytical Techniques

In the analysis of the aerosol samples, Atomic Absorption Spectrometer (AAS), Instrumental Neutron Activation Analysis (INAA), Ion Chromatography (IC) and VIS-Spectrometer were used. For the determination of trace and heavy elements INAA and AAS were used. For the determinations of major anions like chloride, sulfate and nitrate IC was used and for the determination of ammonium ion a visible spectrometer was used. Brief summaries of the analytical techniques used are given in Table 3.1.

Table 3.1. Analytical techniques and measured species.

Measured parameter	Analytical technique
Pb, Ni, Cr, Cd and V	GF-AAS (Perkin Elmer 1100B Spectrometer coupled with HGA 700 Atomization unit.
Al, Mg, Fe, Zn, Cu and Ca	Flame-AAS (Perkin Elmer 1100B Spectrometer (Air/Acetylene Flame and Nitrous oxide/Acetylene flame for Al).
Na and K	Flame-AES (Perkin Elmer 1100B Spectrometer (Air/Acetylene Flame).
Cl^-, NO_3^- and SO_4^{2-}	HPLC – Varian 2010 (Vydac column with Jasco 875 UV/VIS detector
NH_4^+	VIS spectrometer (Nessler's Method)
Na, Mg, Al, Ca, Cl, K, Sc, Ti, V, Cr, Mn, Fe, Co, Zn, As, Se, Br, Mo, Cd, In, Sb, Ba, Cs, La, Ce, Nd, Sm, Yb, Lu, Hf, Au, Th, U, and Hg	Instrumental Neutron Activation Analysis. **Short-1:** Al, Mg, Ti, and V. **Short-2:** Na, K, Cl, Mn, In, Ba, and Yb. **Longs** : Ca, Sc, Cr, Fe, Co, Zn, As, Se, Br, Mo, d, Sb, Cs, La, Ce, Nd, Sm, Lu, Hf, Au, Th, U, and Hg.

3.4.1. Ion Chromatography

Ion chromatography (IC) is a versatile, selective and sensitive method for the determination of a variety of anions and cations at trace and ultra-trace levels (Frankenberger et al., 1990). It has been applied to hundreds of problems in various fields involving ionic analysis in clinical, food, pharmaceutical, industrial, plating solution and environmental samples. The major reason for the rapid growth in popularity of IC is its usefulness in the environmental field. Due to the general complexity of the environmental samples, IC has become an integral part in environmental analysis. IC is a valuable tool for the determination of ions of various airborne samples such as ambient air, aerosol and dust. An airborne sample must first be dissolved in a solvent before it can be analyzed using IC. But this is not always so straightforward. For example, if SO_2 is collected, it must first be converted to an ionic form such as SO_4^{2-} before the IC sample analysis can be performed.

The aerosol samples in this work were analyzed for Cl^-, NO_3^- and SO_4^{2-} by using a Varian model 2010 HPLC coupled with a VYDAC 302 IC anion exchange column and a JASCO UV/VIS 875 detector. The IC system was connected to a PC and PEAK 2 software was used to run the system. The operation conditions of the ion chromatography are given in Table 3.2. The concentrations of anions are determined indirectly. In this technique, the mobile phase absorbs the UV light coming from the UV source (254 nm) and when the anions like chloride, nitrate or sulfate come to the measuring cell, the absorbance of the mobile phase decreases proportionally as the concentrations of the anions increase. The decrease in the absorbance of the mobile phase is converted to the concentrations of anions by using the calibration plot which was stored to PC before. This type of detection is called indirect or absence UV detections.

The first, one-fourth of the each filter sample was placed into 100 mL glass beaker containing 50 mL of double distilled deionized water. Then the beaker was placed into an ultrasonic shaker and sonicated for 40 minutes. The extract was filtered through 0.22 μm pore size cellulose acetate filter. For the analysis of major ions a 100 μL of aliquot was injected to the IC.

The mobile phase was 1.0 mM phthalic acid buffered to pH of 4.95 with the additions of saturated sodium tetraborate solution. The mobile phase was degassed for approximately 30 minutes to expel the dissolved air. Calibration curves were prepared with 0.50, 1.00, 3.00, 5.00, 10.00 and 15.00 ppm (mg anion/L solution) standard solutions of Cl^- (from NaCl), NO_3^- (from $NaNO_3$), and SO_4^{2-} (from K_2SO_4).

Table 3.2. Parameters for ion chromatography analysis of major anions

Eluent (mobile phase)	1.0 mM phthalic acid
Separator column	302 IC
Sample injection volume	100 μL
PH of the mobile phase	4.95
Mobile phase flow rate	3.0 mL/min.

3.4.2. Determination of NH_4^+ by VIS-Spectrometer

Ammonium ion in the aerosol samples was determined using UNICAM 8625 UV-VIS Spectrometer. Direct Nesslerization method was used (Standard Methods, 1990). In this method, Nessler's reagent which is an alkaline solution of mercuric iodide (K_2HgI_4) combines with NH_3 to form a yellowish-brown colloidal dispersion which the intensity is directly proportional to the amount of NH_3 originally present. The following reaction takes place in Nesslerization;

$$2HgI_4^{2-} + 2NH_3 \rightarrow NH_2Hg_2I_3 + NH_4^+ + 5I^-$$

The absorbance of the colored solution was measured at 425 nm in a 1 cm path length glass cell. Standard ammonium samples were prepared from ammonium sulfate after drying the solid reagent at 100°C for about 1 hour. A new calibration curve was prepared each time when Nessler's reagent was changed. The filtered samples that were used for the IC analysis were used for the determination of NH_4^+.

3.4.3. Preparation and Analysis of Aerosol Samples for Trace Elements Using Atomic Absorption and Emission Spectrometers

The 354 daily aerosol samples collected with PM-10 aerosol sampler were analyzed for trace elements using Graphite Furnace Atomic Absorption Spectrometer (GF-AAS), Flame Atomic Absorption Spectrometer (FAAS) and Flame Atomic Emission Spectrometer (FAES). Concentrations of 13 elements were determined with these techniques. The data quality assurance of AAS results were performed using SRM 2704 (Buffalo River Sediment, NIST), GSP-1 (U.S. Geological Survey) and SRM 1646 (Estuarine Sediment, NBS). Before performing the calibration curve for the samples, standard addition method was applied to these standards and if certified values were observed with the error range of less than ± 10%, standard addition calibration was prepared for the samples. The standards were added to the *zero sample* (sample matrix) which was prepared by combining 2 mL's of each sample.

In order to determine the elemental concentrations of trace metals in atmospheric aerosol samples by atomic absorption spectrometer, it is necessary to bring the materials into a solution that can be accomplished by acid digestion. For the digestion and handling of aerosol loaded filter samples, procedures developed in the WMO/UNEP Expert Meeting on Quality Assurance for the MED POL Airborne Pollution Measurements (27-30 May, 1993) were followed. The procedure used in this work was partially modified and full procedure that we used is given as follows;

One fourth of the aerosol filters (2nd part of the aerosol loaded Whatman 41 filter, in this work) were transferred into 250 mL Teflon beakers and 40 mL's of subboiled nitric acid (15.6 M after subboiling process) was put. Then the Teflon lids were inserted on the beakers and the samples were digested for 12-14 hours on a hot plate at 140±10 °C. In one set of this procedure there were 18 aerosol samples, 1 acid blank and 1 filter blank. The clearness of the filter blank shows the complete dissolution of the sample. If there were undissolved filter material, 10 mL of additional nitric acid was added to each of the samples and refluxed for 4-6 hours to complete the dissolution. After complete dissolutions of the samples, the covers were removed and the aliquots were vaporized until approximately 1-2 mL's left. Then 5 mL's of supra pure hydrofluoric acid (HF) was added to all of the samples including acid and filter blank samples. The beakers were covered with their lids again and refluxed again for 6-8 hours. The purpose of adding the HF is to dissolve the silicate matrices such as alumina silicates. When the refluxing of samples were completed, the lids were removed and the aliquots were evaporated near dryness. In order to remove all the HF in the solution 5 mL's of HNO_3 were added and evaporated. This step was repeated several times until no white fume of HF was seen. If HF is not removed completely from the sample solution, it will give damages to the nebulizer and other glass parts of the instrument. After evaporating all of the HF, samples were removed from the hot plate and diluted to 50 mL with 1(w/w)% HNO_3 solution which can be prepared by diluting 1.5 mL of subboiled nitric acid to 100 mL with double distilled deionized water.

3.4.3.1. Flame Atomic Absorption and Emission Spectrometers

Atomic absorption is a standard laboratory analytical tool for the metals. The metal is extracted into solution and then vaporized in a flame. A light beam with a wavelength absorbed by the metal of interest passes through the vaporized sample. The emission and absorption wavelengths of any metal (atomic vapor) perfectly match and that's why Hollow Cathode Lamps (HCL's) are used as a source in FAAS technique. The monochromatic light intensity is attenuated by the analyte atoms at the flame proportional to its amount and the attenuation is monitored by a photomultiplier tube and Beer's Law applies (Finlayson-Pitts, 1986).

In flame emission spectrometry, an element is excited to an upper electronically excited state, from which it returns to the ground state by the emission of radiation. The wavelength emitted is a characteristic of that species and under the appropriate conditions the emission intensity is proportional to the its concentration. But in flame emission spectroscopy (FES), the analyte is excited thermally after aspirating the liquid sample into the flame.

The aerosol samples were analyzed for Ca, Mg, Fe, Cu, Zn (with FAAS), Na, K (FAES) and Al (Flame AAS, nitrous oxide/acetylene flame). A Perkin Elmer 1100B Model atomic absorption spectrometer connected to an Epson L-850 printer was used for FAAS and FAES analysis. The instrumental parameters optimized for the environmental samples are given in Tables 3.2 to 3.5. Aluminium was determined with nitrous oxide/acetylene flame and the others were determined by using air/acetylene flame.

Before starting to the analysis, instrument was allowed to warm and then the light path length was adjusted until obtaining maximum sensitivity. As a source in the FAAS, Hollow Cathode Lamps (HCL's) were used. The sample aspiration flow rate was 6 to 8 mL/min. The standard solutions used in these analyses were commercial 1000 ppm multi element standard (11355 ICP Multi Element Standard IV, MERCK) and 1000 ppm single element standards of Aldrich were used. For all of the analysis, method of standard addition was applied.

3.4.3.2. Graphite Furnace Atomic Absorption Spectrometer

Graphite furnace atomic absorption spectrometer (Perkin Elmer 1100B Model, with HGA 700 electrothermal atomizer) was used to determine the concentrations of five trace elements in this work. The concentration levels of the elements were not high enough to be determined using FAAS or FAES techniques. GF-AAS is a very sensitive technique and trace elements with concentrations at ppb levels can be determined accurately. For this reason, Pb, Cr, Cd, Ni and V were determined using GF-AAS. The carrier gas used in this analysis was Ar and a deuterium lamb was used to correct the non specific background absorption. During the drying and preashing periods the internal gas flow rate was 300 mL/min and it was zero during atomization period. During the last step of temperature program (cleaning step) the gas flow rate was again 300 mL/min. Instrumental settings and the temperature programs for each element are listed in Table 3.3, Table 3.4 and Table 3.5.

Table 3.3. Analytical parameters for the major elements

Element	Na	K	Ca	Mg	Fe	Zn	Al
Technique	FAES	FAES	FAAS	FAAS	FAAS	FAAS	FAAS
Flame	A/Ac	A/Ac	A/Ac	A/Ac	A/Ac	A/Ac	N/Ac
λ, nm	589.1	766.5	422.7	285.2	248.2	213.9	309.2
Slit Width, nm	0.2	0.7	0.7	0.7	0.2	0.7	0.7

A: Air; Ac: Acetylene; N: Nitrous oxide.

Table 3.4. Parameters used in GF-AAS analysis

Element	Cd	Pb	Ni	Cr	V
GF-tube type	uncoated	uncoated	p-coated	p-coated	p-coated
λ, nm	228.7	283.3	232.0	357.8	318.4
Slit Width, nm	0.7	0.7	0.2	0.7	0.7
Sample Volume, µL	30	20	20	20	40
Lamp Current, mA	3	7	30	16	20

Table 3.5. GF-AAS temperature program for the trace element determination in aerosol samples

Element	Step No.	1	2	3	4	5
Cd	Furnace temp., °C	90	130	700	1600	2000
	Ramp time, sec.	5	10	10	0	2
	Hold time, sec.	15	10	25	6	5
Cr	Furnace temp., °C	90	130	1600	2500	2650
	Ramp time, sec.	5	10	15	0	2
	Hold time, sec.	15	20	20	5	8
Ni	Furnace temp., °C	90	130	1400	2500	2650
	Ramp time, sec.	5	10	10	0	2
	Hold time, sec.	15	15	25	5	6
Pb	Furnace temp., °C	90	130	750	1800	2100
	Ramp time, sec.	5	10	10	0	2
	Hold time, sec.	15	15	25	5	8
V	Furnace temp., °C	90	130	1200	2650	2650
	Ramp time, sec.	5	10	10	0	2
	Hold time, sec.	15	15	25	7	10

During the analysis of refractory elements like Ni and Cr, memory effects from the graphite tube were observed. When the concentrations of Ni or Cr is high, they are deposited at the colder regions of the graphite tube and appear as a memory effect during next injections. Using the manual temperature program of the instrument for about 10 seconds after the completion of all temperature program steps solved this problem. New pyrocoated graphite furnaces were installed to the instrument after conditioning with the procedure given by the manufacturer. The temperature program for conditioning a new pyrocoated graphite tube is given in Table 3.6. The conditioning of the pyrocoated graphite tube is done to obtain maximum analytical and mechanical life time. During the each step given in table, the Ar was passed through the furnace with a flow rate of 300 mL/min.

Sample volumes, ashing and atomization temperatures and ramp-hold times were optimized for each of the element before starting to the sample analysis to obtain maximum sensitivity.

Table 3.6. Temperature program for the conditioning of pyrocoated GF.

Step	Furnace temp., °C	Ramp time, sec.	Hold time, sec.
1	2650	60	2
2	20	1	20
3	2650	10	10
4	20	1	20
5	2650	10	10
6	20	1	20
7	2650	10	10

3.4.4. Analysis of Aerosol Samples for Trace Elements Using Instrumental Neutron Activation Analysis (INAA)

In this technique, the sample is bombarded with neutrons and the radioactivity induced in the sample is then measured. Both beta and gamma radiation can be monitored, but gamma radiation is more frequently used because of the discrete wavelengths associated with emission which can be used to identify the emitter (Finlayson-Pitts, 1986). Trace elements on particles in the atmosphere or in any other environmental sample are becoming extremely important because of their effects as being toxic or catalyzer to many biological reactions. Therefore, nuclear techniques are very important for the study of environmental problems as the sensitivity of these techniques allows detection limits of nanogram or less for a large proportion of the elements in the periodic table (Ölmez and Aras, 1977).

Instrumental neutron activation analysis is the most common variant. Most often thermal neutrons in a nuclear reactor are used to irradiate the sample, but neutrons produced by a neutron generator, by irradiation of a berillium target with cyclotron accelerated deuterons or from a ^{252}Cf source can also be used. The neutron fluxes obtained there are much lower than in a nuclear reactor, so that for trace element determination these techniques are not of much use apart from some special applications (Vandecasteele and Block, 1995).

Almost all of applications to date, and certainly those of instrumental multi-element determination, are based on the measurement of the emitted γ-rays using high-resolution γ-ray spectrometers with semiconductor detectors. The elements (radionuclides) present are identified by the energies and relative intensities of the γ-ray lines in the spectrum, and the area of the appropriate photopeak is related to the amount of the element. When the measurement is carried out without prior chemical separation, the method is called instrumental neutron activation analysis (INAA). If it is necessary chemically to separate the radionuclide produced, the term radiochemical neutron activation analysis (RNAA) is used.

When the aerosol samples are irradiated with thermal neutrons in a nuclear reactor, nuclear reactions take place like (n, γ). Thermal neutron and stable isotope of an element produce a radionuclide. The radiation emitted by the decaying radionuclide is measured with a γ-ray detector, as explained above. Then the decay corrected activity can be calculated with the following formula;

$$A_0 = \frac{A\lambda e^{-\lambda t_1}}{1 - e^{-\lambda(t_2 - t_1)}} \quad \text{....................3.1}$$

where, A_0 is the decay corrected count rate at the end of the irradiation, A is the measured activity, t_1 is the time out of the reactor to beginning of counting and t_2 is the time out of the reactor to end of counting.

Concentrations of the elements in the aerosol samples are determined by comparing the isotope activities with the activities of same isotopes in the standards which are irradiated together with the samples. The mass of the unknown element can be calculated with the following formula;

$$m_x = m_s \cdot \frac{A_x}{A_s} \quad \text{....................3.2}$$

where, m_x is the mass of analyte element, m_s is the mass of the same element in the standard, A_x is the decay corrected activity of analyte element, and A_s is the decay corrected activity of the standard.

A total of 251 aerosol samples which were collected at Amasra Air Pollution Monitoring Station in 1996 and 1997 were analyzed by using Instrumental Neutron Activation Analysis (INAA) in which the procedure developed by Ölmez (1989) was used. There were 14 field blank samples and 6 parallel samples included in the 251 samples. The INAA facilities at Massachusetts Institute of Technology, Nuclear Reactor Laboratory (MITR- II) were used in this work. Approximately one sixteenth of the aerosol filter sample was weighed and irradiated twice in the 4.9 MW MITR-II research reactor at a neutron flux of 8×10^{12} $n.cm^{-2}.s^{-1}$. For the analysis of samples for short lived isotopes, samples were irradiated for 1 minute with no decay and immediately counted with high purity germanium detectors for 7 minutes (Al, Mg, Ti, and V). At the end of this Short-1 count, samples were recounted for 20 minutes to determine the gamma ray activities of the isotopes with half lives in the range of 37.3 min (Cl) to 15 hours (Na). Samples were then allowed to decay for about three weeks in order to decrease the activities of the isotopes to an insignificant level. The cooled samples were re-irradiated at the same neutron flux for 6 hours and counted for 6 to 10 hours for the determination of the activities of the long lived isotopes.

Gamma rays emitted from the irradiated samples were counted with high purity germanium detectors coupled to a 8192-channel pulse-height analyzers (Canberra, CT). The spectra were analyzed using software ND 9900 Genie System run on VMS 200, Canberra, CT, to search for the γ-peaks of each isotope. The masses of elements were determined by comparing the activities of the sample elements with that of standards (SRM-1633, Coal Flyash). Then the masses of the elements found were first corrected for the field blanks and divided by the sample air volume corresponding to the one-sixteenth of the aerosol filter sample and final result was expressed as ng/m^3. Accuracy of the analytical technique was checked by analyzing NIST SRM-1571 (Orchard Leaves) which were irradiated and counted at the same time with the samples and standards. The gamma ray energies, half-lives and the scanning stages of the isotopes are given in Table 3.7.

Table 3.7. Half-lives, γ-ray energies and counting stages of the elements determined.

Element	Half-life	Energy keV	Scanning Stage	Element	Half-life	Energy keV	Scanning Stage
Al	2.31 m	1778.9	Short-1	U	2.36 d	106.4	Long
Mg	9.45 m	843.8	Short-1	Yb	101 h	396.3	Long
Ti	5.79 m	320.1	Short-1	Ce	32.5 d	145.4	Long
V	3.76 m	1434.2	Short-1	Cs	2.07 y	795.8	Long
Ba	83 m	165.8	Short-2	Cr	27.8 d	320.0	Long
Cl	37.29 m	1642.0	Short-2	Co	5.27 y	1332.5	Long
Dy	2.36 h	94.7	Short-2	Hf	44.6 d	482.2	Long
In	54 m	417.0	Short-2	Fe	45.1 d	1099.2	Long
Mn	2.58 h	846.7	Short-2	Lu	155 d	208.4	Long
Na	15 h	1368.5	Short-2	Nd	11.1 d	91.0	Long
K	12.52 h	1524.7	Short-2	Sc	83.9 d	889.3	Long
Sb	2.75 d	564.1	Long	Se	121 d	264.5	Long
As	26.3 h	559.5	Long	Th	0.07 y	311.9	Long
Br	35.87 h	554.3	Long	Zn	245 d	1115.5	Long
Cd	53 h	335.0	Long	Mo	66 h	140.5	Long
Au	2.70 d	411.8	Long	Sm	47.1 h	103.2	Long
La	40.27 h	1596.0	Long				

Pneumatic tube facility in the MITR-II research laboratory shortened the sample transfer time down to 3-4 seconds which was very crucial in this study, particularly in the analysis of short lived isotopes, like Al and V. Since the irradiation time was only 1 minute and the decay time would be significant for very short lived isotopes if the transfer time between reactor and counting system were long.

Sample handlings prior to the irradiation were done in a clean laminar flow hood in the Massachusetts Institute of Technology, Nuclear Reactor Laboratory. The one-fourths of the filters brought from Ankara was reopened from their polyethylene bags and divided into four, again (i.e. 1/16 of the whole filter). All the equipments used for the preparation of the samples were prewashed with dilute nitric acid and rinsed a few times with double distilled deionized water and dried in the clean hood. Using these tools, filters were cut and folded with the sample side facing inward. Since the geometry of the samples are very important in INAA, all of the samples and blanks were placed in ultra-thin, acid washed polyethylene bags and each bag was clearly labelled according to the sample's ID number. After irradiation, filters were removed from their thin poly ethylene bags and placed in an unirradiated, acid washed clean bag, heat sealed and relabelled and counted.

For the determination of background contributions from Whatman 41 filters, 14 field blank samples were also analyzed for the same elements as in the case of aerosol samples. These field blank samples were prepared in the Amasra Air Pollution Monitoring Station and handled as other samples. Air was passed through the filters for about 15 seconds in order to get the maximum probable contamination level during changing and handling the filters. In order to test the reproducibility of the technique used, six samples were prepared from the same aerosol sample filter (BAW 265) and analyzed as different samples. The results of all these analysis will be discussed extensively in Chapter 4.

3.4.4.1. Irradiation and Counting of Short Lived Isotopes

In MITR-II Research laboratory, there are four high purity Germanium γ-ray detectors. Four filters, one for each detector, were placed into prewashed pneumatic tube carrier that is called as “rabbit”. Using the pneumatic tube system available in the MITR-II laboratory, rabbits were transferred to the reactor and irradiated with thermal neutrons for 1 minute. After irradiation, rabbit was sent back through the

3.4.4.2. Irradiation and Counting of Long Lived Isotopes

When the short experiments completed, the samples were cooled for about 3 weeks. Then these 40 samples and one mercury standard which was encapsulated in a quartz tube were placed in a rabbit and sent for the long irradiation. They were irradiated for 6 hours and cooled for three days. The rabbit containing standards and samples was opened behind the lead shield in the hot laboratory and the irradiated polyethylene bags were changed with new ones, relabelled and carried to the counting room with a pig. The samples were counted for 6 to 10 hours.

Mercury standard was encapsulated in a clean quartz tube in order to prevent the mercury loss and consequent contamination of other samples. However, the irradiation port of the reactor is cooled to room temperature, therefore, the fast neutron flux was kept minimum. This unique property of the reactor overcame the mercury loss due to the heating problem during irradiation.

The gamma-ray emissions from the isotopes in the samples were measured by means of high purity germanium detectors with FWHM of about 1.75 keV for the 1332 keV line of ^{60}Co. The elements determined in long countings are given in both Table 3.1 and Table 3.7. The spectra obtained after short and long countings were analyzed using software ND 9900 Genie System run on VMS 200 to search for the γ-peak of each isotope.

Before starting to the counting of samples, the detectors were calibrated by using isotopes with known gamma peak energies. The isotopes that we used for the calibration are ^{60}Co (1173.2 and 1332.5 keV) and ^{137}Cs (661.6 keV). The software uses an available library which includes the each nuclide, its symbol, proton and neutron numbers, half-life, number of gamma lines and energies and branching ratio.

3.5. Data Quality Assurance

3.5.1. Blanks

There are three kinds of blank samples in this work. These are acid blanks, filter blanks and field blanks. The acid blanks and filter blanks were prepared during the digestion of samples for the AAS analysis. The field blanks were prepared at the monitoring station and handled and treated as aerosol samples. In INAA analysis, only field blanks were analyzed but in the AAS analysis of the aerosol samples both acid and filter blanks were analyzed.

Acid blanks and filter blanks contained the digestion reagents used for the dissolution of aerosol samples. After the digestion the blanks also treated as samples and diluted to 50 mL with 1 (w/w)% HNO_3 solution. They were injected to the AAS before the samples following the calibration and SRM certified value checks. Each set of digestion had an acid and a filter blank and the each set was corrected by using their filter blanks in the AAS analysis.

Field blanks were prepared in each tour to the monitoring station and sample air was passed through the filters about 15 seconds considering the maximum contamination cases. The filter installations and handling were done similar to the samples. The field blanks were analyzed using INAA, AAS and IC techniques. The average concentrations of field blanks in ng/g are given in Table 3.8 and 3.9, respectively.

Table 3.8. The average concentrations and ± standard deviations (STD) of species determined from the field blanks by using INAA technique. The numbers in parentheses are the numbers of field blanks used to calculate the averages.

Element	Avg.conc.± STD (N) (ng/g-filter)	Element	Avg.conc.± STD (N) (ng/g-filter)
Na	13000±2800 (12)	Br	720±39 (8)
Mg	10000±3700 (8)	Mo	21±6.6 (11)
Al	2600±340 (13)	Cd	28±5.2 (4)
Ca	150000±17000 (4)	Sb	13±7.2 (10)
Cl	71000±14000 (14)	Ba	3700 (1)
K	81000±19000 (3)	Cs	36±16 (3)
Sc	1.1±0.4 (3)	La	1.7±0.8 (10)
Ti	3900±1300 (3)	Ce	39±7.1 (3)
V	17±6 (5)	Nd	660±100 (13)
Cr	1200±570 (13)	Sm	0.3±0.1 (11)
Mn	64±19 (12)	Lu	0.5±0.2 (3)
Fe	16000±7400 (8)	Au*	120±37 (7)
Co	59±13 (10)	Th	9.6 (1)
Zn	1700±420 (9)	U	3.2±0.7 (3)
As	2±2 (6)	Hg	2.9±0.9 (6)
Se	120±3 (3)		

*pg/g-filter

Table 3.9. Average concentrations (ng/g-filter) and standard deviations (STD) of species determined from field blanks using atomic absorption and emission spectrometers and ion chromatography. Numbers in parentheses are the numbers of observation of measured specie on that filter sample.

Element	Average±STD (N)	Element	Average±STD (N)
Na	17200±1160 (15)	Ca	11100±3710 (15)
Mg	3710±1100 (15)	Zn	780±520 (13)
Al	34900±15400 (15)	Ni	132±51 (12)
K	1540±970 (15)	Cr	155±24 (11)
Fe	715±600 (4)	Pb	60±57 (2)
Cu	390±100 (15)	Cd	46±37 (5)
Cl^{-*}	28800±17500 (15)	V	38±24 (12)
NO_3^{-*}	17700±9500 (15)	NH_4^{+**}	Not Detected (15)
SO_4^{2-*}	7870±4760 (15)		

* Ion chromatography results.
**UV/VIS spectrometry results.

3.5.2. Detection Limits

The concentration levels of most of the species monitored in air pollution studies are too low to be detected reliably. Therefore, for such data sets with some of the values are at below detection limits of the analytical technique, one should first determine the detection limit of the analytical technique before starting to analysis. The detection limits change with the nature of the samples and sensitivity of the instrument used.

In INAA technique, the detection limit is controlled by several factors like, intensity of the neutron flux, the background in the γ-ray spectrum, composition and geometry of the sample and experimental parameters. Therefore, the detection limit in the INAA is unique to each sample and determined by both the element under consideration and the presence of other elements. If the concentration of an element is too high, it yields a very high background levels (compton peak of that element overlaps with the peak of other elements with small concentrations) in the spectra and results in poor signal-to-noise ratio. In this case the detection limits are higher values than actual value in that sample for other elements. Because of the factors explained here, generally valid detection limits can not be provided for INAA technique. Further explanations to this problem are given in section 3.5.5. The averages of several detection limit calculations for the elements are given in Table 3.10 (Güllü, 1996).

In AAS analysis, the detection limits of the measured elements in this work were defined as the concentration of an element which will give a signal three times higher than the standard deviation of 10-replicate analysis for one of the laboratory filter blank. The detection limits for the elements determined are given in Table 3.11 as ng/g- filter blank).

The detection limit of ion chromatography was defined in a way similar to those for the AAS. The detection limits of the IC results calculated with in these criteria are also included in Table 3.11. All the detection limits calculated from these analytical techniques are much more smaller than corresponding observed concentrations of the elements in the samples.

Table 3.10. Calculated detection limits for the elements observed by the INAA (ng element/g-filter)* and average concentration and standard deviations of the elements determined from the samples (ng element/g-sample filter).

Element	Detection limit	Average conc.	Element	Detection limit	Average conc.
Na	15000	180000±15000	Cd	35	84±66
Mg	7900	96000±99000	In	1.0	5.8±4.0
Al	5500	150000±170000	Sb	1.2	160±140
Ca	110000	400000±350000	Ba	1200	6300±3600
Cl	16000	190000±130000	Dy	1.6	36±24
K	9400	160000±80000	Cs	2.1	88±78
Sc	0.31	30±37	La	3.1	92±120
Ti	730	15000±11000	Ce	5.2	150±190
V	20	1300±1200	Nd	17	840±600
Cr	730	2600±2400	Sm	0.1	13±19
Mn	84	4500±3300	Eu	0.5	20±24
Ga	520	2100±1700	Tb	0.2	12±14
Sr	52	11000±48000	Yb	0.3	6.7±6.5
Fe	1500	150000±130000	Lu	0.08	1.5±1.3
Co	3.1	140±100	Hf	0.8	17±15
Zn	220	8100±8300	Ta	1.8	130±130
As	4.2	690±710	Au	0.8	0.45±0.73
Se	2.1	290±200	Th	0.3	40±78
Br	210	3700±1700	U	7.3	14±9.4
Rb	5.2	1800±2200	Hg	2.1	31±27
Mo	21	340±500			

*Detection limits in ng/27 cm^2 (Güllü, 1996) were converted to ng/g-sample filter.

Table 3.11. Detection limits of the elements and ions (ng/g-filter blank).

Element (technique)	Detection limit	Element (technique)	Detection limit
Al (FAAS)*	16000	Cd (GF-AAS)	320
Na (FAES)	37000	Cr (GF-AAS)	140
K (FAES)	8500	Ni (GF-AAS)	470
Ca (FAAS)	97000	V (GF-AAS)	260
Mg (FAAS)	17000	Cl^- (IC)	580
Fe (FAAS)	30000	NO_3^- (IC)	580
Pb (GF-AAS)	7900	SO_4^{2-} (IC)	690
Zn (FAAS)	6300	NH_4^+ (VIS)	580
Cu (FAAS)	4100		

*N_2O/C_2H_2 flame was used.

3.5.3. Quality Control

The accuracy of the daily AAS analyses throughout this work were tested continuously by the analyses of the standard reference materials. Three different SRMs from NIST (USGS (GSP-1), Estuarine sediment (SRM-1646) and Buffalo river sediment (SRM-2704)) were digested and analyzed with the samples. For the preparations of SRM samples, 0.10 g of SRM was weighed and put in the Teflon beaker. Then 4.5 mL of subboiled nitric acid (15.6 M) and 1.0 mL of concentrated HF were added. After closing the lid, the Teflon beakers were inserted in Acid bombs and digested for 6 hours at 150±10 °C. After cooling, the lids were opened and the aliquots were evoparated and the HF in the solution was removed by adding 2 mLs of subboiled nitric acid and evaporated near dryness. This step was repeated at least three times. Then, the remaining residue was diluted to 50 mL with 1.0 (w/w)% nitric acid solution. An acid blank was also prepared with the SRM standards to correct the elemental contributions from the reagents used.

Each day before starting to analyses of samples a standard addition calibration was prepared for SRMs and the concentration of element to be determined was found. If the concentration found was around the certified value (that is, the concentration found was10% less than or equal to the certified value) a new standard addition calibration for the aerosol samples was prepared and the elemental concentrations were determined by using this new calibration plot. The elemental concentration ranges determined in SRM samples by using AAS and the certified values are given in Table 3.12. These ranges were obtained from 35 different experimental works.

Table 3.12. Concentrations of the elements observed in NIST-SRMs, SRM-GSP-1, SRM-2704 and SRM-1646; Comparision with the certified values.

Element	Found			Certified		
	GSP-1	2704	1646	GSP-1	2704	1646
Na*	2.04±0.17	0.68±0.10	1.95±0.13	2.08	0.76	2
K*	4.54±0.14	1.97±0.10	1.79±0.13	4.57	2	1.63
Ca*	1.56±0.18	2.40±0.12	0.73±0.16	1.46	2.6	0.83
Mg*	0.61±0.04	1.17±0.15	1.05±0.10	0.596	1.2	1.09
Al*	8.31±0.21	6.44±0.26	6.48±0.22	8.2	6.11	6.25
Fe*	3.0±0.10	3.9±0.30	3.3±0.10	3.01	4.11	3.35
Mn	308±0.30	554±0.13	373±0.35	310	555	375
Zn	115±6.0	464±15	152±10	103	438	138
Cr	12±3.0	129±2.0	80±3.0	13	135	76
Ni	11±3.0	38±7.0	27±6.0	9.8	44.1	32
V	51±3.0	94±6.0	95±2.0	53	95	94
Cd	55±4.0	3.4±0.8	0.34±0.10	56	3.45	0.36
Pb		163±0.30	30±3.0		161	28.2

*Units are in (w/w)% the others are in (w/w) ppb.

3.5.4. Parallel Analysis

To test the reproducibility of the results obtained from INAA technique, one fourth of the aerosol sample with ID number of BAW-265 was divided into six parts and each part was weighed and analyzed as different samples. In addition, three of these six samples were enclosed in polyethylene vials in order to check the loss of mercury from the samples during irradiation.

The results of this experiment are given in Table 3.13. Table includes average concentrations and standard deviations in ng/m^3. Results showed that there was no significant amount of mercury loss during the irradiations of samples. This result was expected because of room temperature irradiation at MIT Reactor. Almost same results were obtained from these parallel samples for the trace and major elements determined with in 10% range.

There are small differences among the subsamples of the original sample for the same elements determined. This may be caused by both uncertainties in the sample preparation procedures (weighing) and inhomogenities of the aerosol samples on the filter paper. However, for most of the elements these two factors are not so effective, they are effective in some of the trace elements determined because of the very low concentrations in the aerosol samples and the sensitivities of the analytical instruments used. This can easily be understood if the standard deviations for each element are compared with the its average concentration.

Table 3.13. The concentrations of elements determined from 6-parallel samples.

Element	No of observation	Average±STD	Element	No of observation	Average±STD
Na	6	100±7.3	Br	6	8.1±2.3
Mg	5	120±33	Mo	5	0.2±0.09
Al	6	350±17	Cd	6	0.3±0.09
Ca	1	730	In	4	0.01±0.01
Cl	6	130±53	Sb	6	0.8±0.2
K	3	190±120	Ba	2	5.1±2.5
Sc	6	0.07±0.01	Cs	4	0.05±0.03
Ti	5	17±11	La	6	0.24±0.02
V	6	3.5±1.1	Ce	4	0.1±0.1
Cr	5	9.3±7.9	Nd	6	2.1±0.9
Mn	6	10±1.0	Sm	6	0.03±0.0
Fe	6	320±58	Yb	5	0.01±0.001
Co	5	0.16±0.13	Hf	2	0.02±0.02
Zn	6	24±12	Au	5	0.002±0.003
As	6	2.8±0.2	Th	4	0.02±0.01
Se	6	0.6±0.5	U	3	0.03±0.01
Hg	6	0.02±0.01			

3.5.5. INAA and Comparison with Other Analytical Techniques

Despite the high resolution of germanium semiconductor detectors, the detectability of a γ-line in the spectrum of an activated sample depends strongly on the presence of other radionuclides. The "Compton Background" of an intense high energy γ-ray emitter will mask weak low energy γ-lines and will thus severely impair the detection limits for the corresponding elements. Instrumental NAA is therefore only feasible when the activity induced in the matrix is not prohibitively high and when no major activity is produced that overshadows the other radionuclides. Atmospheric aerosols collected on an organic filter are very well suited for INAA, as the major elements of the sample and of the filter –C, O, H, S, N- do not give significant γ-activities. In addition the most abundant elements in the inorganic fraction, Si, Fe, Ca, Mg, and Cl have relatively low cross-sections for neutron induced reactions and/or yield radionuclides with low abundances of their γ-ray transitions (C. Vandecasteele and C. B. Block, 1995).

Activation analysis is best suited for the analysis of solid samples. Water samples can also be analyzed, but usually preconcentration is then required, for example, by freeze-drying or bay fixation on an ion exchange resin.

Sensitivities and detection limits in INAA are determined by several factors, including nuclear constants, experimental parameters and presence of easily activable elements in the sample. The sensitivities and detection limits vary in an irregular way from element to element and several elements are difficult or impossible to determine by standard instrumental NAA, e.g. Li, Be, B, C, N, O, Si, P, S, Sn, Tl and Pb.

In principle, INAA can provide very accurate results. In general, neutrons and γ-rays are not strongly absorbed by matter, and corrections for absorption effects are therefore small and often negligible.

A further and extremely important advantage is that contamination can occur only before or during irradiation. Usually the amount of sample handling required before or during the irradiation can be limited. When a post-irradiation radiochemical separation is required, the separation can be carried out without danger of contamination. In addition the separation does not need to be quantitative, as a yield determination can be carried out.

Activation analysis has some drawbacks, however. For many elements the turn-around time is long, which may be a serious drawback for routine analysis; a nuclear reactor or other source of activating particles is required.

When compared with other sensitive analytical multi-element methods like ICP-MS and single element technique GF-AAS, the INAA has the following advantages.

(1) For solid samples INAA has the definite advantages of not requiring sample dissolution, with the attendant problems of difficult or incomplete dissolution of some matrices, possible losses of some elements such as As, Se or Hg by volatilization, precipitation or adsorption losses.

(2) No blank is introduced from acids or other reagents, which is a common major source of contamination. This advantage is very important for materials with low analyte levels that require considerable effort for contamination-free dissolution.

(3) Probably the most important advantage of the activation analysis is that, whenever interferences occur-for instance in the analysis of biological materials, where the γ-ray radioactivity of ^{24}Na, ^{38}Cl, ^{42}K, ^{80}Br and ^{82}Br and Bremsstrahlung from ^{32}P are the main matrix activities- the radionuclide of interest can be carried through even complex radiochemical separations without the danger of contamination and with addition of non-radioactive carriers to ease the separation. In ICP-MS and/or GF-AAS, to improve detection limits for elements subject to interference by polyatomic species, a chemical separation (or inactivation of interfering species) can of course also be carried out, but always with contamination risk and in addition, the separation must be carried out at the trace element level.

(4) Another advantage of INAA is specific to the analysis of reference materials. Activation analysis is based on a principle different from that of other analytical techniques and is subject to other types of systematic error.

(5) INAA is a multi-element and a non-destructive technique. ICP-MS is also multi-element technique but a destructive technique and needs large amounts of samples compared to INAA. GF-AAS is a single element technique and needs specific light sources for each element to be determined and is a destructive technique.

3.5.5.1. Comparison of INAA Results for the Common Elements Measured with AAS and AES Techniques

As mentioned before, 230 samples were analyzed for more than 35 trace and major elements by using INAA and about 354 samples were analyzed for 13 elements by using AAS. The 230 samples analyzed with INAA were also analyzed by using GF-AAS, FAAS and FAES techniques and chloride was determined by using ion chromatography. The common elements which were measured by using the mentioned techniques are Na, K, Ca, Mg, Al, Cr, Pb, Cd, V, Fe, Cl, and Zn. The results obtained from each sample for the same elements were blank corrected and illustrated as scatter plots of each technique. The plots are given in Figure 3.3.

As can be seen from the figure, most of the elements determined by using different techniques are in good agreement. These elements are; Mn, Al, Cl, Zn, V, Fe and Na. The agreement between the results obtained for Mg, Cd and K are fairly well but there is a little agreement in the results of Ca and Cr which can be measured more accurately by using AAS techniques. Although, the INAA technique can give reliable results as AAS techniques do, there are some requirements that must be supplied in the case of INAA like enough cooling and counting times. In this work, we could not supply enough cooling times for the long lived isotopes which require at least 20 days of cooling time. The reason of this disagreement between the results of these two elements may be the inefficient cooling time required for chromium (half life is approximately 1 month) and excess cooling for calcium (half life is 4.7 days).

In this study we used chromium results obtained from AAS because we could see chromium only in 70% of the samples and the results were not very accurate when compared to control standard SRM 1571 (Orchard Leaves). The observation statistics for Mg, K, and Ca were less than 80 % in INAA results, therefore, for these elements the missing values were computed with the results obtained from AAS analyses.

The chlorine concentrations determined both by INAA and ion chromatography are almost similar as in the case of other elements which have very close average values for both techniques. The INAA-AAS scatter plots of the elements are fairly different from unity slope and zero intercept which may be caused from the uncertainties in the analyses procedures and inhomogenities in the filter samples.

Consequently, most of the elements measured by using both techniques have very large correlation coefficients and low intercept values when compared to their concentrations, the results tells us that both techniques can be applied efficiently in the analysis of environmental samples. Non of these two techniques are superior to other in most cases (like detection limit and sensitivity and also capability of determining all the elements found in the samples) but they are generally complementary techniques to each other and both techniques are necessary for environmental studies.

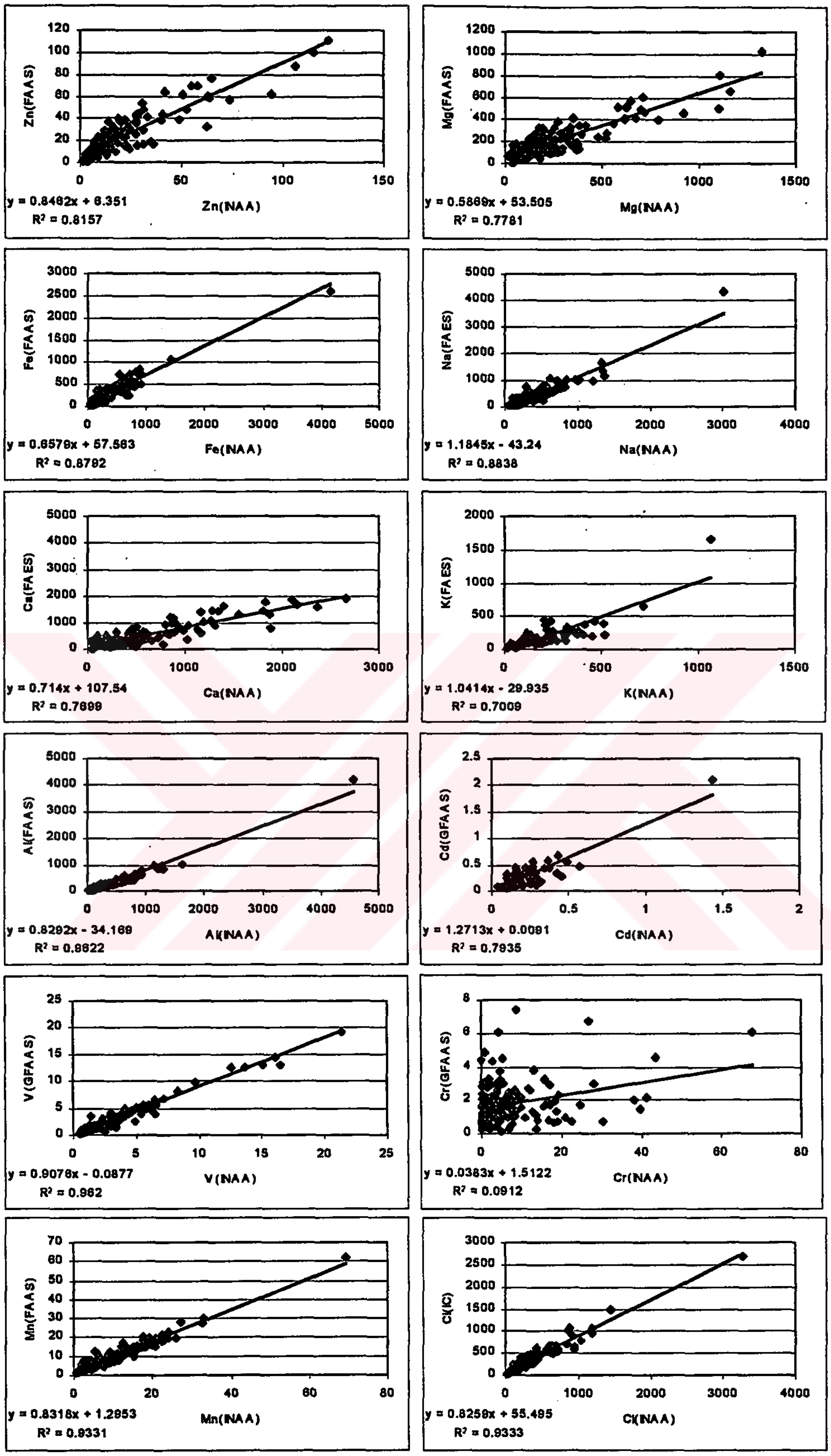


Figure 3.3. Scatter plots for the concentrations of commonly measured elements by using INAA, AAS and IC.

CHAPTER 4

RESULTS AND DISCUSSION

4.1.1. General Characteristics of Data

Statistical summary of elemental concentrations obtained from 354 daily aerosol samples which were collected in the Western Black Sea cost of Turkey from April 1995 to July1997 is given in Table 4.1., which includes arithmetic and geometric mean concentrations with associated standard deviations, number of samples, median and mode values. The arithmetic standard deviations of the measured parameters listed in Table 4.1 are comparable to their mean concentrations. High standard deviations are not unusual in environmental data sets and do not necessarily incorrect use of sampling and analysis procedures. The observed high standard deviations are due to large variability of the atmospheric concentrations of the elements over short periods of time, which are caused by the variations in the meteorological conditions, physical and chemical transformations, air mass transport patterns and the variations in emissions affecting the receptor site.

Mean concentrations of anions change between 4.9 $\mu g.m^{-3}$ (SO_4^{2-}) and 0.92 $\mu g.m^{-3}$ (NO_3^-) for the whole data set. The mean concentrations of the trace and major elements change between 410 $ng.m^{-3}$ (Ca) and 0.014 $ng.m^{-3}$ (In and Yb). Major elements in the aerosol samples have mean concentrations (expressed as $ng.m^{-3}$) of 380 (Na), 150 (Mg), 320 (Al), 180 (K) and 280 (Fe) for the whole data matrix. Trace elements like Pb, Zn and Br have the highest mean concentrations in the data set as shown in Table 4.1. and are 17.0, 16.0 and 7.2 $ng.m^{-3}$, respectively.

4.1.2. Distribution Characteristics of the Concentrations in the Aerosols of Turkish Western Black Sea Basin

In general, a data matrix is generally treated as normally distributed values and described with arithmetic mean and standard deviation in which it is assumed that there is a symmetric gaussian distribution. However, in a data set affected by different pollution sources, elements generally follow a log-normal distribution. The distribution type of aerosol composition over a long period of time is dependent on the fluctuations in the meteorological conditions and source strength variations. Frequency distributions of pollutants are useful to search for similarities and differences among the components which may help to understand processes that influence the ambient levels. For a symmetric gaussian distribution, the values of the arithmetic mean, median and mode are identical. If the mode<median<arithmetic mean, then the upper tail of the distribution extends toward larger values and called as positively skewed. If the order is reversed, the distribution is called as negatively skewed. As it is seen from Table 4.1, the arithmetic mean, median and mode values for almost all the measured species are in the order of mode<median<arithmetic mean indicating that the distribution of all variables are positively skewed. The skewness indices and distribution types of elements obtained are given in Table 4.2. The values of skewness for all the variables in this study are positive indicating that the distribution of elemental concentrations are positively skewed. The arithmetic mean to geometric mean ratios of the elements given in Table 4.2, column 2 is also a measure of skewness. As this ratio becomes greater than unity the distribution type deviates more from normal distribution. The arithmetic to geometric mean ratios of the elements show that almost all of the measured parameters show lognormal distribution resulting from ratios greater than one.

Skewness is a value used to measure the symmetry or shape of the data. In a frequency polygon, histogram, or density trace that shows the distribution of the data, the right end of the plot has a longer tail; therefore, the mean is greater than the median and is called *skewed right*, and when the left end of the plot has a longer tail; then the median is greater than the mean and is called *skewed left*. Skewness index or skewness coefficient is a measurement of the symmetry, or shape, of the data. A skewness of 0 indicates that the data are symmetrically distributed. Positive values of skewness tell us that the upper tail of the curve is longer than the lower tail; negative values tell us that the lower tail is longer (Statgraphics for Windows 3.1 Manual, 1997). These criteria can be classified as follows:

S=0 symmetric,
S>0 left sided asymmetry (positively skewed), and
S<0 right sided asymmetry (negatively skewed).

In describing the positively skewed data set, log-normal and Weibull distributions can be used. In the Weibull distribution model, statgraphics software performs a Chi-Square test which divides the range of variable into nonoverlapping intervals and compares the number of observations in each class to the number expected to based on the fitted distribution. Then Kolmogorov-Smirnov test computes the maximum distance between the cumulative distribution of variable and the cumulative distribution function (CDF) of the fitted Weibull distribution. If the p-value amongst the test performed is less than 0.05 (at 95% confidence) then the hypothesis that the variable comes from a Weibull distribution is rejected. In the case of a log-normal distribution again the same steps are followed by the statgraphics software to test the distribution model.

The Kolmogorov-Smirnov (K-S DN) statistics is used to test the goodness-of-fit of the data to log-normal distribution. The K-S test involves the entire distribution of the examined variable, but not just its central value, and compares the emprical cumulative distribution function to that of the hypothesized distribution. In the case of the log-normal distribution, the maximum absolute distance between the data and the hypothesized distribution is calculated to test the conformance of the two cumulative distribution functions (Statgraphics for Windows 3.1 Manual, 1997).

The observed significance level for the Kolmogorov-Smirnov DN statistics is represented by a value of ALPHA in Table 4.2. The significance level of an observed value of DN, that is ALPHA, (as a disproof of the null hypothesis that the distribution is log-normal) is given by:

$$ALPHA = \left(\sqrt{N} + 0.12 + \frac{0.11}{\sqrt{N}} \right) DN \ldots\ldots\ldots\ldots\ldots 4.1$$

The nature of approximation in Equation (1) is that it becomes asymptotically accurate as N becomes large. The sample size for each measured variable in this study has adequate degrees of freedom to use the DN statistics. Thus an ALPHA greater than 1.358 as given in Table 4.2 indicates that the cumulative distribution function of a composition variable is significantly different from the log-normal function at a 95% confidence level

While the emissions from sources may be approximately constant, the successive mixing and dilution of pollutants as they are transported from source to receptor results in a log-normal frequency distribution for the ambient concentrations measured at the receptor (Hacısalihoğlu et al., 1992 and Güllü,1996).

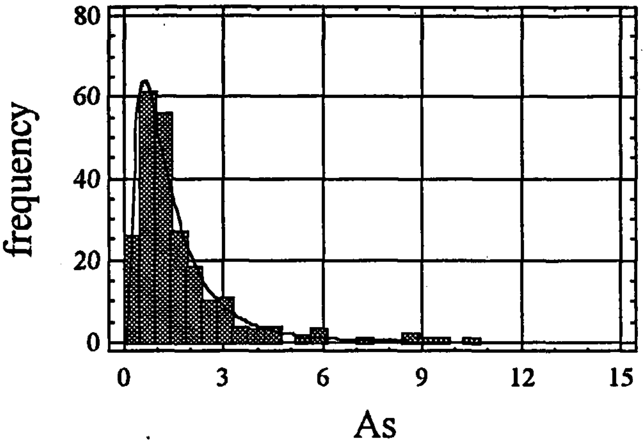
As it is shown in Table 4.2, ALPHA values for all elements (except for Ca, NH_4^+ and SPM) are smaller than 1.358, indicating that the data fits the hypothesized distribution (that is, log-normal distribution). The distribution of ammonium is very close to normal distribution when examined visially and also after applying the distribution tests. The parameters like Ca, NH_4^+ and SPM (suspended particulate matter) do not fit the hypothesized distribution may be because they are affected heavily from the local sources. Since these parameters are mainly originated from local sources, there will be minimum mixing and dilution for these variables thus, causing less skewed distribution. Aluminum and Sc may also come from local soil and should show similar distribution patterns with Ca, however, they do not show similar distribution type may be because of an additional source of Ca in the aerosol samples which is sea salt. The frequency histograms and associated distribution curves for a crustal (Al), marine (Na) and pollution derived elements (As and Cd) are given in Figure 4.1.

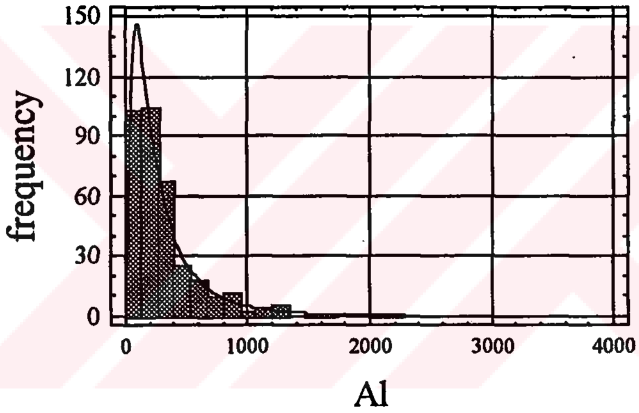
Table 4.1. Summary Statistics of Turkish Western Black sea basin aerosols: Arithmetic and geometric means, standard deviations, median and mode values.

Element (unit)	Number of samples	Arithmetic mean (STD)	Geometric mean (STD)	Median	Mode
Na (ng.m^{-3})	340	380(300)	300(2.0)	300	200
Mg (ng.m^{-3})	302	150(130)	110(2.2)	120	50
Al (ng.m^{-3})	354	320(380)	210(2.6)	230	200
Cl (ng.m^{-3})	354	310(330)	220(2.3)	230	200
K (ng.m^{-3})	354	180(180)	140(2.1)	140	140
Ca (ng.m^{-3})	279	410(450)	270(2.8)	290	200
Sc (ng.m^{-3})	229	0.071(0.11)	0.045(2.6)	0.047	0.030
Ti (ng.m^{-3})	152	32(38)	20(2.7)	22	20
V (ng.m^{-3})	354	2.7(2.3)	2.1(1.9)	2.0	1.8
Cr (ng.m^{-3})	354	1.3(1.1)	0.87(2.7)	0.98	0.90
Mn (ng.m^{-3})	230	11(7.6)	8.7(2.0)	9.3	9.0
Fe (ng.m^{-3})	354	280(300)	200(2.4)	230	200
Ni (ng.m^{-3})	354	1.6(1.4)	1.1(2.4)	1.1	1.0
Cu (ng.m^{-3})	354	170(350)	41(4.2)	27	100
Co (ng.m^{-3})	195	0.23(0.26)	0.13(3.3)	0.14	0.10
Zn (ng.m^{-3})	353	16(18)	10(2.8)	10	12
As (ng.m^{-3})	230	1.6(1.6)	1.2(2.2)	1.1	1.3
Se (ng.m^{-3})	193	0.46(0.49)	0.30(2.9)	0.33	0.20
Br (ng.m^{-3})	230	7.2(3.4)	6.4(1.6)	6.5	6.4
Mo (ng.m^{-3})	194	0.44(0.28)	0.35(2.1)	0.39	0.30
Cd (ng.m^{-3})	354	0.28(0.30)	0.21(2.0)	0.22	0.20
Sb (ng.m^{-3})	230	0.37(0.30)	0.30(1.8)	0.30	0.25
La (ng.m^{-3})	230	0.23(0.36)	0.15(2.3)	0.15	0.15
Ce (ng.m^{-3})	179	0.32(0.64)	0.17(3.1)	0.18	0.18
Sm (ng.m^{-3})	230	0.032(0.055)	0.020(2.5)	0.021	0.020
Au (pg.m^{-3})	204	1.3(2.8)	0.43(4.1)	0.41	0.1
Hg (ng.m^{-3})	166	0.046(0.030)	0.037(2.1)	0.040	0.037
Pb (ng.m^{-3})	354	17(14)	12(2.5)	13	10
In (ng.m^{-3})	89	0.014(0.010)	0.012(1.8)	0.012	0.010
Cs (ng.m^{-3})	153	0.14(0.14)	0.090(3.1)	0.10	0.10
Nd (ng.m^{-3})	136	1.4(1.3)	0.84(3.2)	0.88	0.45
Yb (ng.m^{-3})	144	0.014(0.022)	0.010(2.6)	0.010	0.0090
Lu (pg.m^{-3})	108	2.6(4.3)	1.3(3.4)	1.5	1.5
Th (ng.m^{-3})	163	0.074(0.13)	0.040(3.2)	0.047	0.10
SPM (μg.m^{-3})	183	49(34)	37(2.6)	45	69
NO_3^-(μg.m^{-3})	354	0.92(0.51)	0.79(1.7)	0.81	1.00
SO_4^{2-}(μg.m^{-3})	354	4.9(2.9)	4.2(1.8)	4.1	3.2
NH_4^+(μg.m^{-3})	354	1.4(0.72)	1.2(1.7)	1.3	1.4

Table 4.2. Kolmogorov-Simornov statistics (K-S DN), skewness, arithmetic mean to geometric mean ratios and the distribution types of the fitted variables

Element	A.mean/G.mean	K-S DN	Skewness	ALPHA	Distrib. type
Br	1.113	0.052	1.36	0.795	Log-normal
NH_4^+	1.145	0.076	2.05	1.439	Normal
NO_3^-	1.155	0.052	1.75	0.985	Log-normal
SO_4^{2-}	1.169	0.022	1.80	0.417	Log-normal
In	1.187	0.063	2.21	0.603	Log-normal
Sb	1.220	0.045	3.91	0.688	Log-normal
Mo	1.246	0.078	1.00	1.096	Log-normal
Mn	1.256	0.073	2.56	1.116	Log-normal
V	1.258	0.036	3.89	0.682	Log-normal
Hg	1.261	0.071	1.27	0.924	Log-normal
Na	1.270	0.046	3.21	0.854	Log-normal
K	1.307	0.041	5.93	0.771	Log-normal
SPM	1.313	0.138	2.62	1.885	Log-normal
Cd	1.327	0.033	5.64	0.625	Log-normal
Mg	1.348	0.038	2.58	0.658	Log-normal
Ni	1.389	0.062	3.18	1.174	Log-normal
As	1.399	0.043	2.92	0.658	Log-normal
Pb	1.413	0.057	1.56	1.080	Log-normal
Fe	1.414	0.071	6.79	1.345	Log-normal
Cl	1.428	0.053	3.97	1.011	Log-normal
Cr	1.437	0.064	2.13	1.212	Log-normal
La	1.507	0.035	9.10	0.535	Log-normal
Ca	1.528	0.103	4.37	1.733	Log-normal
Al	1.529	0.047	5.20	0.881	Log-normal
Ti	1.563	0.066	5.05	0.822	Log-normal
Zn	1.569	0.046	2.64	0.870	Log-normal
Se	1.569	0.076	3.18	1.066	Log-normal
Sm	1.576	0.042	9.27	0.642	Log-normal
Sc	1.580	0.061	8.38	0.931	Log-normal
Cs	1.596	0.081	2.47	1.012	Log-normal
Yb	1.625	0.067	7.32	0.813	Log-normal
Nd	1.651	0.098	1.23	1.156	Log-normal
Co	1.769	0.068	2.46	0.958	Log-normal
Th	1.819	0.076	8.10	0.980	Log-normal
Ce	1.917	0.056	8.04	0.756	Log-normal
Lu	1.992	0.069	5.70	0.726	Log-normal





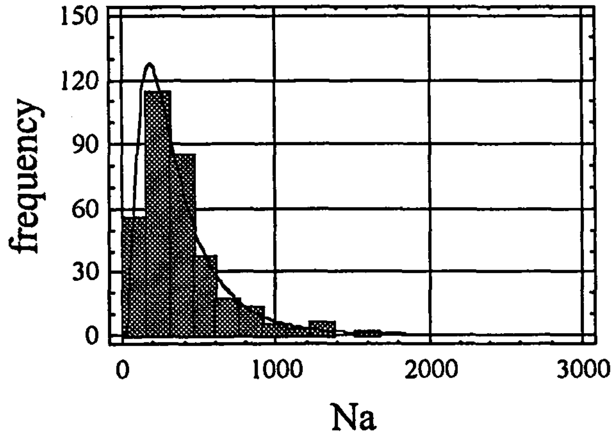


Figure 4.1. Frequency histograms and associated distribution curves for an anthropogenic (As), crustal (Al) and marine (Na) elements

4.1.3. Comparison of Data with Other Studies

The mean concentrations of the elements in atmospheric particulate matters exhibit substential spatial variations, which differ markedly from element to element. In urban areas concentrations are compared with the regulatory standards. But in rural areas concentrations are too low to be compared with the regulatory standards. Current state of pollution can be assessed by comparing with the data sets obtained from comparable rural sites.

In order to validate the level of pollution at the Turkish Western Black Sea Basin, the results obtained in this study were compared with the comparable sites in the Europe. For comparison of the data obtained in this study with those reported for other comparable sites, arithmetic mean values of elements have been preferred because most of the previous results were reported as arithmetic means. Since the sampling site in this study was located at a rural area, the literature data were also selected from rural sites in the Mediterranean and Black Sea Basins. The selected sites for the comparison are Western Black Sea (Hacısalihoğlu et al., 1992), Eastern Black Sea (Dzubay and Stevens, 1984), Black Sea (Kubilay et al., 1995), Eastern Mediterranean (Güllü et al., 1998; Kubilay, 1996), Western Mediterranean (Dulac et al., 1987; Mateu et al., 1996), Italian Alps (Braga Marcazzan et al., 1993), and Northwestern Mediterranean (Guieu et al., 1997).

Short descriptions of the sampling sites and the measurement techniques are given below.

1) Western Black Sea (Hacısalihoğlu et al., 1992)

Limited shipborne samples were collected during the summer of 1989 from the Black Sea atmosphere and samples were analyzed by instrumental neutron activation analysis, atomic absorption spectrometry and ion chromatography for approximately 40 elements and ions. The results were reported as arithmetic means for both Western and Eastern Black Sea.

2) Eastern Black Sea (Dzubay and Stevens, 1984)

Ambient air aerosol particles were collected by means of dichotomous samplers equipped with inlets at d_{50} = 15, 2.5 and 3.5 μm's, at Abastumani Astrophysical Observatory (Georgia), in July 1979 for 21 days. Samples were analyzed for mass, elemental, crystalline, and ionic species concentrations and for size and composition of individual particles. The analytical techniques used for the analysis of samples are β-gauge, XRF, XRD, IC, and SEM. The obtained results were reported as arithmetic means for each ultrafine, fine and coarse fractions of the aerosols collected.

3) Black Sea (Kubilay et al., 1995)

The chemical composition of the Black Sea aerosol was studied during the July 1992, CoMSBLACK 92 cruise on board research vessel R/V Bilim. A hi-vol sampler was used to collect aerosol samples and the collected samples were analyzed for trace elements by atomic absorption spectrometry and the results were reported as both arithmetic and geometric means.

4) Eastern Mediterranean (Güllü et al., 1998)

Concentrations of trace elements and major ions were measured in aerosol samples which were collected at a rural site on the Mediterranean coast of Turkey, 20 km to the west of Antalya. Samples were collected by means of a PM-10 hi-vol sampler and collected samples were analyzed using the instrumental neutron activation analysis, atomic absorption spectrometer, ion chromatography and UV/VIS spectrometry for more than 35 trace elements and ions. The results were reported both as arithmetic and geometric mean. The median and mode values were also reported in this study.

5) Western Mediterranean (Dulac et al., 1987)

The factors controlling the variability of atmospheric trace metal concentrations over the Western Mediterranean Sea were investigated. For this purpose, Al, Br, Cd, Na, Pb and ^{210}Po were determined in the aerosols. The samples were collected from a bow tower extending forward of the ship 8 m above the sea level. The samples were analyzed by using instrumental neutron activation analysis and atomic absorption spectrometer. Arithmetic mean values of elements were reported for 5 different regions at the Western Mediterranean basin.

6) Italian Alps (Braga Marcazzan et al., 1993)

Daily aerosol samples were collected at Stelvio National park in the Italian Alps. The airborne particulate matters were collected on nucleopore filters by means of a low volume standard automatic air sampler with an upper cut point of about 50 μm. Mass of the total suspended particulate matter (TSPM) was determined gravimetrically and the elements were determined by using PIXE (Particle Induced X-ray Emission) technique. The results were reported for two periods, summer and spring as arithmetic means.

7) Alfabia-Spain (Mateu et al., 1996)

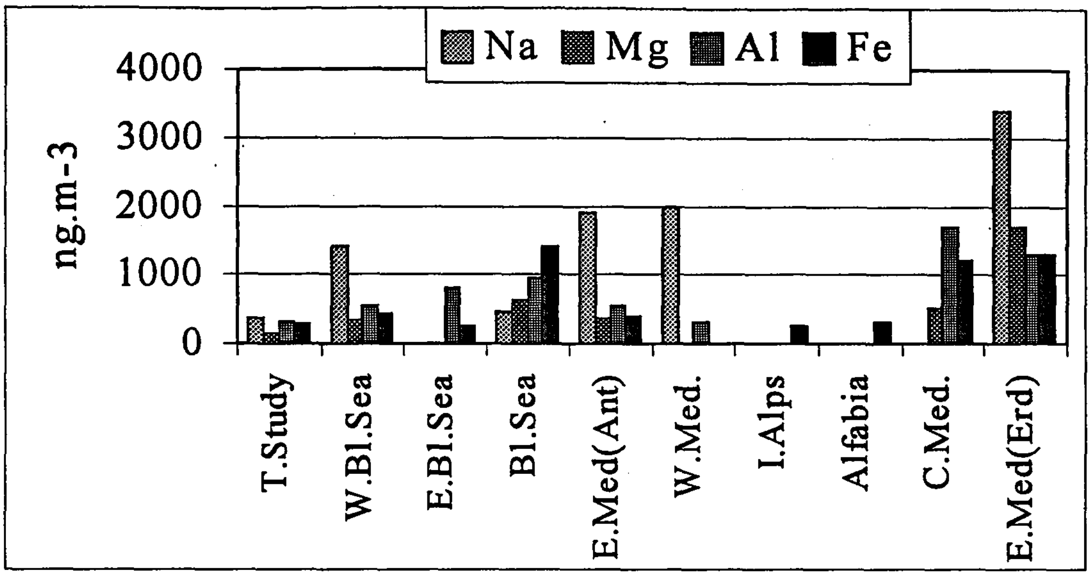
In this study, atmospheric aerosols were collected by using a cascade impaction system at the Alfabia station in Majorca, Spain. The collected samples were analyzed for 13 elements by using inductively coupled plasma-atomic emission spectrometry (ICP-AES). The results were reported as arithmetic means.

8) Northwestern Mediterranean (Guieu et al., 1989)

Concentrations of trace elements (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were determined in aerosol, dry deposition, total deposition and precipitation samples collected from five stations on islands and coastal zone of the Northwestern Mediterranean. Aerosol samples were collected at all the sites which are Tour Du Valat, Cap Ferrat, Blanes, Corsica, Sardinia, Mallorca and Baleares Islands. For comparison with our data the results reported for Cap Ferrat was selected because the site is resemling our sampling site which is also on a coastal zone. They reported that average aerosol compositions for all the sites are very homogeneous especially at the coastal sites.

9) Eastern Mediterranean (Kubilay, 1996)

Aerosol samples at a rural site (Erdemli, İçel) were collected by means of a hi-vol aerosol sampler without a preimpactor. The aerosol samples were analyzed by using flame and flameless modes of atomic absorption spectrometer for 13 elements.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Al
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3000
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T.Study
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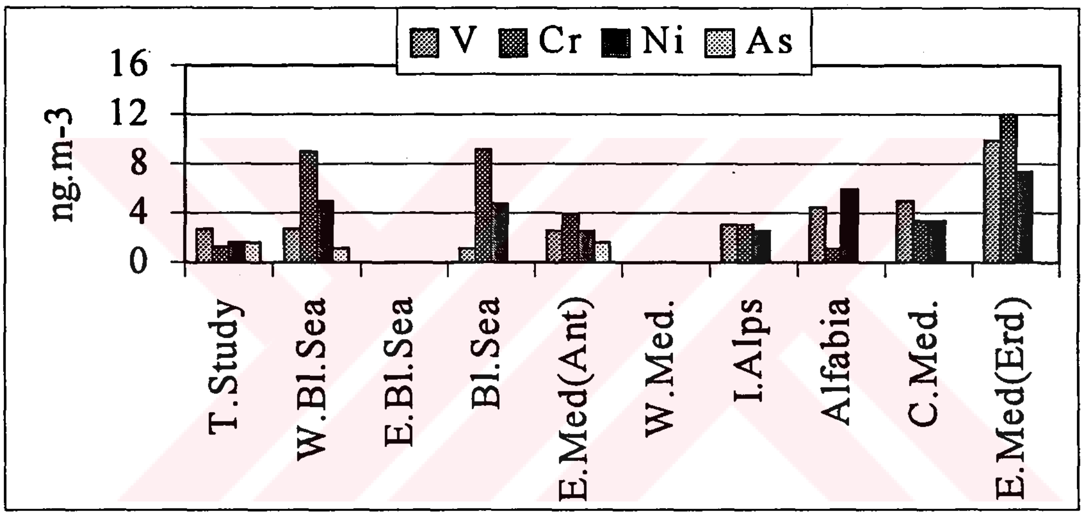
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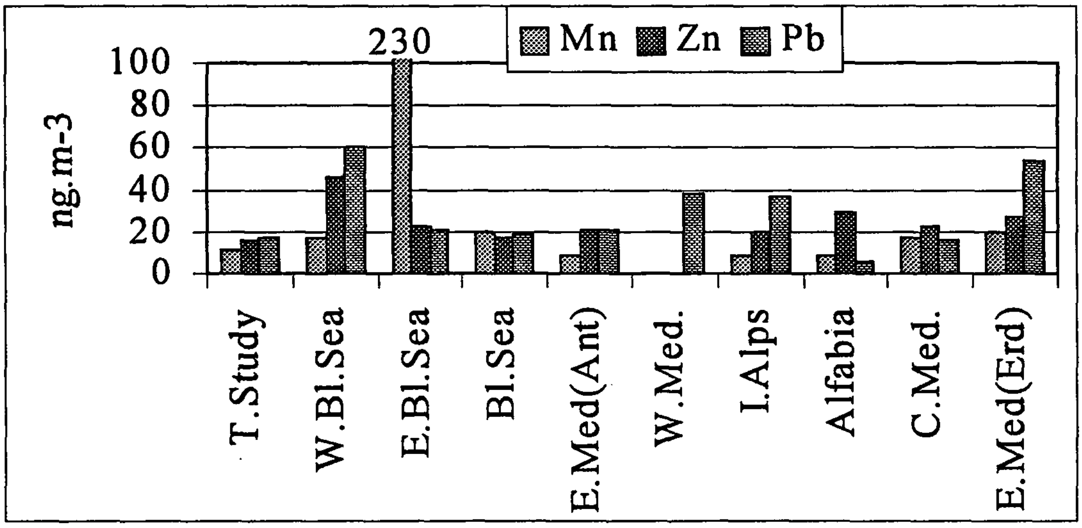
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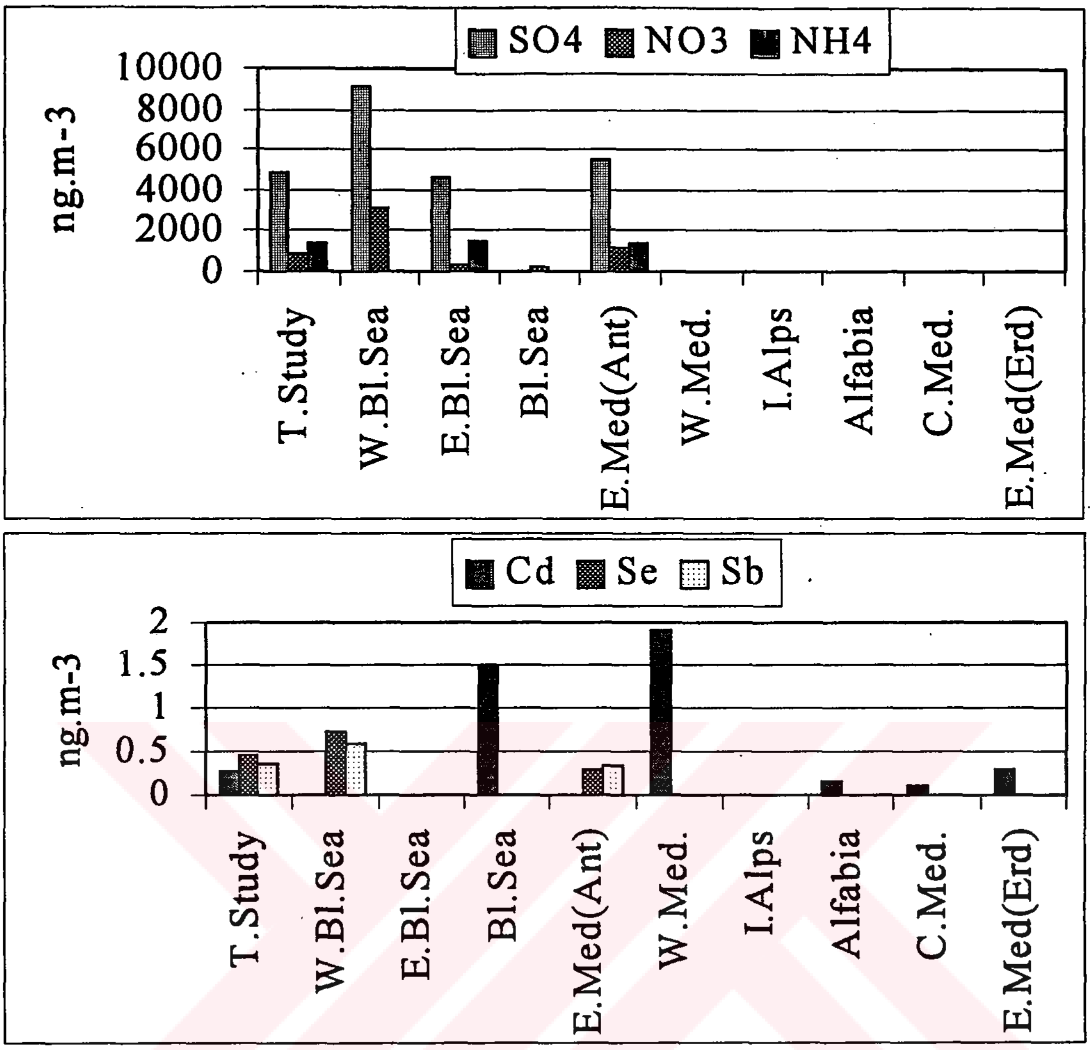


Figure 4.2. Comparison of mean concentrations of common elements and ions measured with other rural sites

The data comparison with measured species are depicted in Figure 4.2. Concentrations of elements and ions measured at the Turkish Western Black Sea Basin with those measured in other rural sites in Europe showed that our results are not significantly different from the other sites for most of the parameters measured. The sulfate and ammonium ion concentration levels in our site are similar to values reported by Güllü et al., 1998 for Eastern Mediterranean and Dzubay and Stevens, 1984 for Eastern Black Sea region both of which fairly clean sites. Concentrations of marine elements like Na, Cl, Br and Mg measured in this study are the lowest reported for the Mediterranean and Black Sea regions. Marine elements are associated with sea salt particles which are generated by the bubble bursting on the sea surface. The bubble bursting process is known to produce large particles. Since these coarse particles rapidly settle out from atmosphere, concentrations of marine elements measured at all sites depends strongly on the distance between the sampling site and the sea.

Concentrations of crustal elements, such as Al, and Fe measured in this study are low compared to the corresponding concentrations reported for other Mediterranean and Black Sea sites. Concentrations measured in this study was lower than those reported for other Black Sea sites due to different sampling techniques. In all aerosol studies in the Black Sea hi-vol samplers were used without any size segregation. However, sampler used in this study was equipped with a preimpactor which prevents particles larger than 10 μm from entering the sampler. Simultaneous sampling of atmospheric particles with and without such preimpactor in the Mediterranean region have demonstrated that approximately 30% of the crustal mass is removed from the sampling stream by the PM-10 preimpactor (Kuloğlu, 1997), which explains smaller concentrations of crustal elements in this study compared to other studies in the Black Sea atmosphere.

The difference in between the concentrations measured in this study and those measured in the Mediterranean sites can be partly due to the same reason and partly due to the more extensive aridity in the Mediterranean region where resuspension of soil is easier than in the plant covered Black Sea coast. Observed concentrations of elements Ca and K are contributed by marine and crustal sources. Since concentrations of both marine and crustal elements are low at our site, comparison of Ca and K also followed a similar trend.

Concentrations of anthropogenic species, Cd, Zn, As, Se, Sb, Pb, SO_4^{2-}, and NO_3^- are comparable with the concentrations reported for other Black Sea and Eastern Mediterranean sites. However, concentrations of these pollution derived elements and ions are generally high in the Western Black Sea and Western Mediterranean compared to the concentrations measured in our site. Atmospheric levels of anthropogenic elements are determined by distances of sampling sites to source regions of these particles which are in Europe, and the extend of particle scavenging during transport (Güllü et al., 1998). The difference between the concentrations measured in this study and western Black Sea and Mediterranean is due to closer proximity of the latter to strong emission sources in Europe and Balkans. Concentrations of anthropogenic elements and ions measured in the central Black Sea (this work) are fairly similar to those reported for the Eastern Mediterranean. The lead levels in the Eastern Mediterranean which are expected to be comparable to the concentrations measured in the Central Black Sea, are actually a factor of three higher than Pb concentrations measured in this study. The stations in the eastern Mediterranean stations are located fairly close to roads with heavy traffic, particularly during summer season, and observed differences in Pb concentrations is probaly due to the influence of local vehicular activity. Similarly, the Pb levels reported for Western Black Sea (Hacısalihoğlu et al., 1992) are about four times higher than the levels we have found. Western Black Sea study was a preliminary work for this study so it covered about 20 days of sampling period in 1992 summer. In such a short term sampling period it is very difficult to decide the pollutant level. Because the levels of pollutants change with changes in meteorologic conditions, therefore, the high levels of Pb in that study may be because of transports from NW Black Sea region (i.e. through Istanbul or Europe).

Although concentrations of elements measured in the Black Sea atmosphere are smaller than the concentrations reported for the Mediterranean and western Black Sea, comparison of enrichment factors calculated from the same data sets points different pollution characteristics of these regions.

Enrichment factors of selected elements in various Black Sea, eastern and western Mediterranean data sets are depicted in Figure 4.3. Crustal and marine elements are not included in the EF_c comparison as the aim is to understand different pollution characteristics of these regions. Crustal elements are not enriched in any of the data sets and marine elements are enriched to different levels due to different sea salt concentrations at different sites, which depends on the meteorological parameters such as surface wind speed and has nothing to do with the incursion of pollutants to the regions.

The figure reveals two fairly interesting features. With the exception of Mn, enrichments of elements in different Black Sea data sets are fairly close to each other. This is particularly obvious in the EF_c's of Cd, Zn, Se and Sb. Manganese is not an exception, but its EF_c in the Georgia site is much higher than its EF_c in all other sites due to close proximity of that site to a Ferromanganese industry (Dzubay and Stevens, 1984). One would normally expect the EF_c's of pollution-derived elements to be significantly different in coastal and ship-borne samples, because of the different sizes and settling velocities of Al (which is used as reference element in EF_c calculations) and anthropogenic elements. Hovewer, such difference is not observed, indicating that although concentrations of elements show spatial changes in the Black Sea, pollution nature of the aerosols do not seem to change.

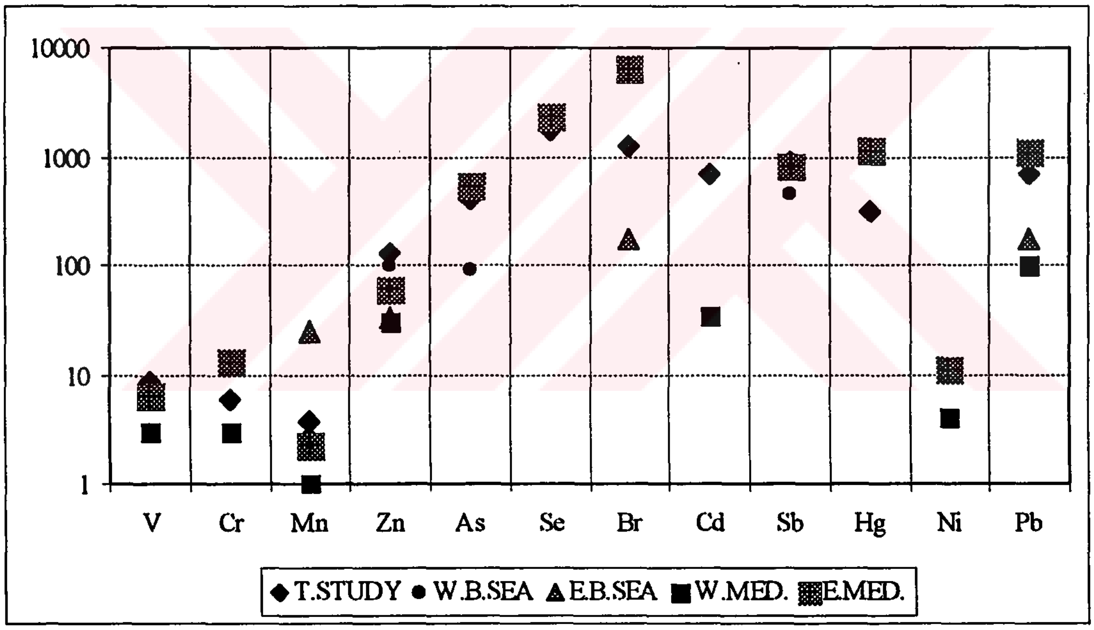


Figure 4.3. Comparison of crustal EF of selected anthropogenic elements with the W. Mediterranean (Guerzoni et al., 1989),E. Mediterranean (Güllü, 1996), E. Black Sea (Dzubay and Stevens, 1984) and W. Black Sea (Hacısalihoğlu et al., 1992) Sites.

For most of the elements, enricment factors in Black Sea data sets are higher than their EF_c's in the Mediterranean data sets. This is a significant observation, becasue although concentrations of elements in some of the Mediterranean sites are higher than corresponding concentrations measured in the Black Sea atmosphere, higher EF_c values in the Black Sea aerosols suggests that, pollution derived particles in the Mediterranean atmosphere is diluted by natural crustal particles, and contribution of pollution derived particles to total aerosol mass is higher in the Black Sea region.

To demonstrate the possible existences of differences in the concentrations of the elements in the atmosphere over the Black Sea and to determine the general feature of the aerosols from the Western Black Sea Coast of Turkey, the data obtained from present study were compared with the other results obtained from literature as given above. The locations of these sampling sites are shown in Figure 4.4.

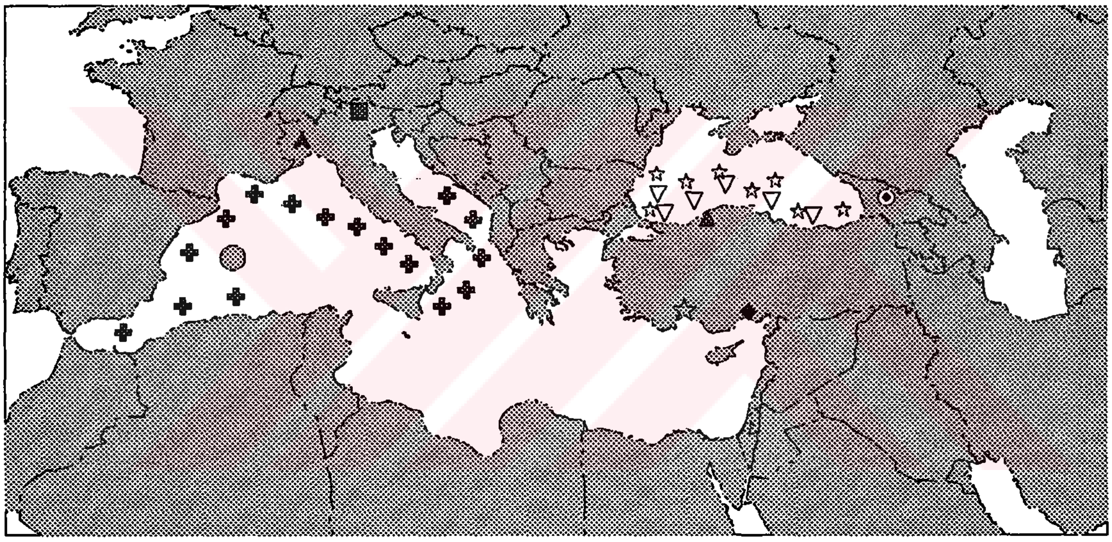


Figure 4.4. Locations of the sampling sites which were used in comparison.

⊙Eastern Black Sea (Dzubay and Stevens, 1984), ■ Italian Alps (Marcazzan et al., 1993), ✫ Eastern Mediterranean (Güllü et al., 1998), ∇ Western Black Sea (Hacısalihoğlu et al., 1992), ★ Black Sea (Kubilay et al., 1995), ✙ Western Mediterranean (Dulac et al., 1987), ⩓ Northwestern Mediterranean (Guieu et al., 1997), ● Alfabia-Spain (Mateu et al., 1996), Δ Western Black Sea Coast of Turkey (This Study) and ◆ Eastern Mediterranean (Kubilay, 1996).

4.2. Analysis of 3-D Back-trajectories of the Western Black Sea

Variability of the elemental concentrations in the atmosphere depends on both local sources and the origins of the air masses arriving at the sampling site. Three-D back trajectories are the most widely used tools to study the effects of different source regions.

In this study, the upper atmospheric 3-D back trajectories at three final barometric levels of 700 hPa (3000 m), 850 hPa (1460 m) and 900 hPa (990 m) were calculated for each sampling day and the trajectories were retrieved for 12 00 UT from April 1995 to July 1997. In order to see the mean air flow pattern at the sampling site throughout the duration of study, the air mass back trajectories have been classified according to the air flow directions. To do this, the possible regions affecting our sampling site was divided into 5 subregions as shown in Figure 4.5. We called western Europe as Region1, eastern Europe as Region 2, Black Sea and Russian Federation as Region 3, Turkey itself as Region 4 and Mediterranean Sea and Africa as Region 5. Each trajectory was assigned to the region on which it spends the most of its four days of travel.

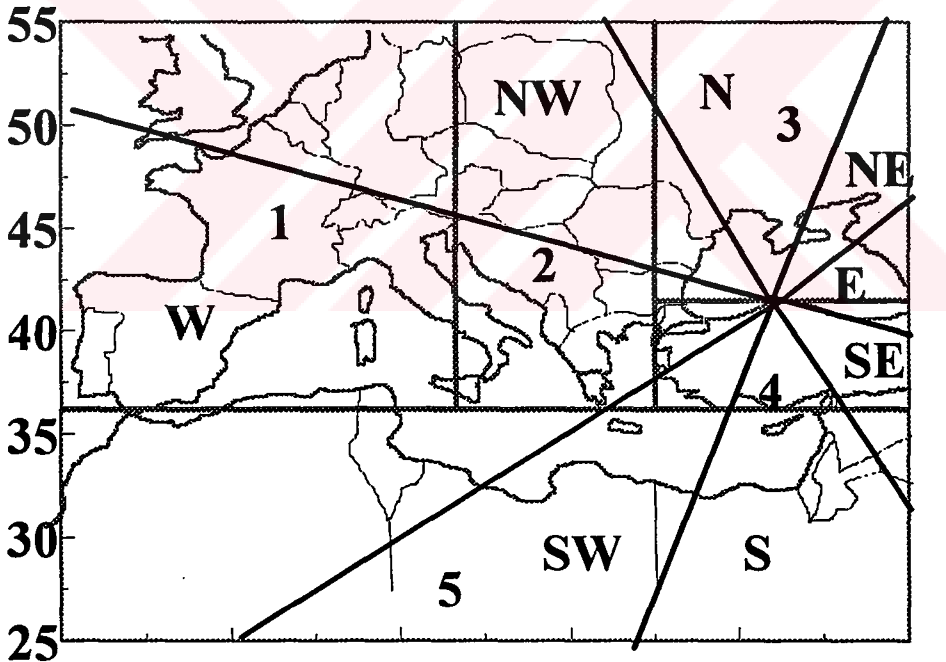


Figure 4.5. Sectoring technique for the grouping of back trajectories according to their originating geographic regions

Transports from different wind sectors are expected to bring different types of aerosols to the sampling site. After grouping the back trajectories, four main source areas were identified and related to trajectory sectors. These areas are; western Europe (W sector), eastern Europe (NW sector), Mediterranean Sea and Africa (S and SW sectors) and Russian Federation countries (N and NE sectors). The percent frequencies of back trajectories coming from these regions are presented in Figure 4.6. Each trajectory was first grouped for their barometric levels and co-existence and then regrouped according to the regions where they spent the most of their 4 day travel to receptor site. Figure 4.6. shows that the most dominant regions are Europe and Russian Federation countries, the other regions do not play significant role as aerosol source regions. North Africa seem to have significant effect on aerosol compositions at two barometric levels, 700 and 850 hPa, which can contribute the concentrations of crustal elements at the sampling site. An air mass trajectory originating from North African region can increase the crustal elemental concentrations in the aerosol samples up to an order of magnitude. Therefore, lower percent frequency of trajectories for North African region does not mean that the region is ineffective in contributions to aerosol mass and elemental concentrations. For example, trajectories corresponding to 22-23 April 1997 samples brought huge amounts of Saharan dust and increased the concentrations of crustal elements about an order of magnitude as shown in Figure 4.7.a (Al as an example of crustal elements). This episodes were also observed in other studies like Kubilay, 1996; Güllü, 1996; Guerzoni and Chester, 1996; Hacısalihoğlu et al., 1992 and 1998; Al-Momani, 1995; and Dulac et al., 1996.

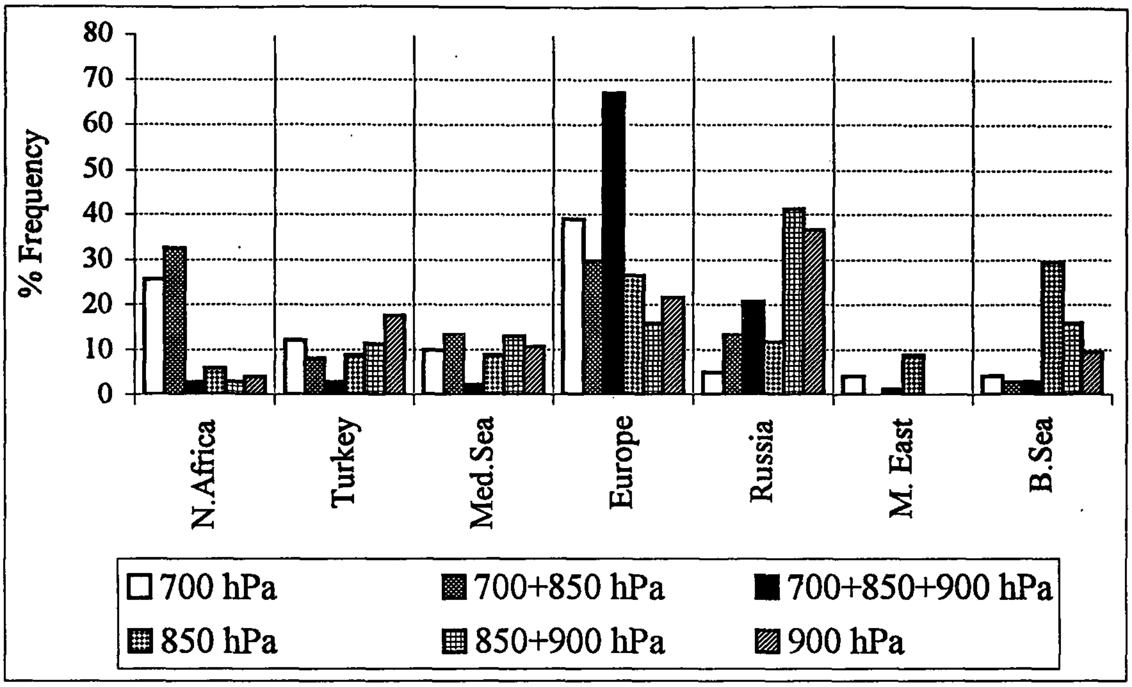


Figure 4.6. Percent frequencies of trajectory groups arriving at Amasra station from regions where they spent the most of their time during travel

Therefore, with this kind of classifications it would be possible to evaluate the role of long and short range transports on the trace metal distributions in atmospheric particulates over the Black Sea region. Short trajectories may be assumed to include aerosol transports from Anatolia, eastern Mediterranean Sea and Middle East countries. However, long trajectories may bear aerosols from the Eurasian mainland, North Africa, Commonwealth of Independent States and the Arabic Peninsula as well as from the corresponding regions covered by short range trajectories.

4.3. Temporal Variations of Elemental Concentrations in the Black Sea Aerosols

Short and long-term temporal variations in the concentrations of elements and ions can provide information on the mechanisms of particle transport from source regions to receptor sites and factors affecting transport. Temporal variations of elemental concentrations are generally studied for two different time-scales. Short-term variations are the episodic changes in concentrations, whereas long-term variations are the average changes in time-scales of at least a season. Concentrations of elements, in this study and elsewhere show large variations from one day to another due to daily changes in emission strengths, local meteorology and transport patterns. One-to-two orders-of-magnitude difference in the concentrations of elements and ions from one day to another are reported for eastern and western Mediterranean (Güllü et al., 1998; Bergametti et al., 1989). Episodic changes are more pronounced for soil and sea salt related elements compared to those observed in anthropogenic elements. Investigation of short-term variations can provide useful information on the point sources, source regions and transport patterns affecting anthropogenic element content of aerosols in the study area and specific meteorological patterns that give rise to elevated levels of natural crustal and sea salt particles.

Long-term variations in the concentrations of elements and ions can, on the other hand provide information on factor affecting aerosol population in the receptor site. Such variations are shown to be due to factors such as, seasonal variations in the emissions (particularly for crustal and sea salt particles in rural areas and for anthropogenic elements in urban areas), seasonal changes in transport patterns, and seasonal changes in particle scavenging in the atmosphere (Güllü et al., 1998). Study of annual variations in the concetrations can also provide information on trends in the concentrations of elements and ions. The short and long term variations in the concentrations of species are discussed in sections 4.3.1 and 4.3.2, respectively.

4.3.1. Short-term Variations of the Elemental Concentrations in the Western Black Sea Atmosphere

Short term variations in the concentration of a crustal element Al is depicted in Figure 4.7.a. as an example. Concentration of Al (and all other soil-related elements) show strong short term variations. Some of the episodes shown in Figure 4.7.a, indicated that the concentratins of soil-related elements change by approximately an order of magnitude within few days. The scavenging of soil particles from atmosphere in the study area is responsible for minimum measured concentrations in the figure. Each rain shown in the figure corresponds to a minimum in the temporal variations of elements. The rain-to-non rain concentration ratio which is obtained by taking average concentarions of elements measured in all rainy days to those measured 2 days prior to each rain is depicted in Figure 4.8 for all the measured parameters.

The rain events have a significant influence on observed minimum concentrations of crustal elements, because atmospheric concentrations of crustal elements are determined by resuspension of surface soil in the vicinity of the station. Such particles are large and scavenged effectively from atmosphere during rain events. Consequently, atmosphere is washed from soil particles during early stages of each rain, which results in lower concentrations during or immediately after rain events.

Although, wet removal of particles from atmosphere can explain minima in Figures 4.7.a and 4.8, it can not explain observed episodic high concentrations in crustal elements. The main source of crustal elements in the atmosphere is the resuspension of local soil particles as mentioned previously. The resuspension process depends (a) on the moisture of surface soil and (b) surface wind speed. The observed episodes in crustal elements occur generally during summer season when the surface soil is dry, and at high wind speeds which enhances the crustal aerosol formation.

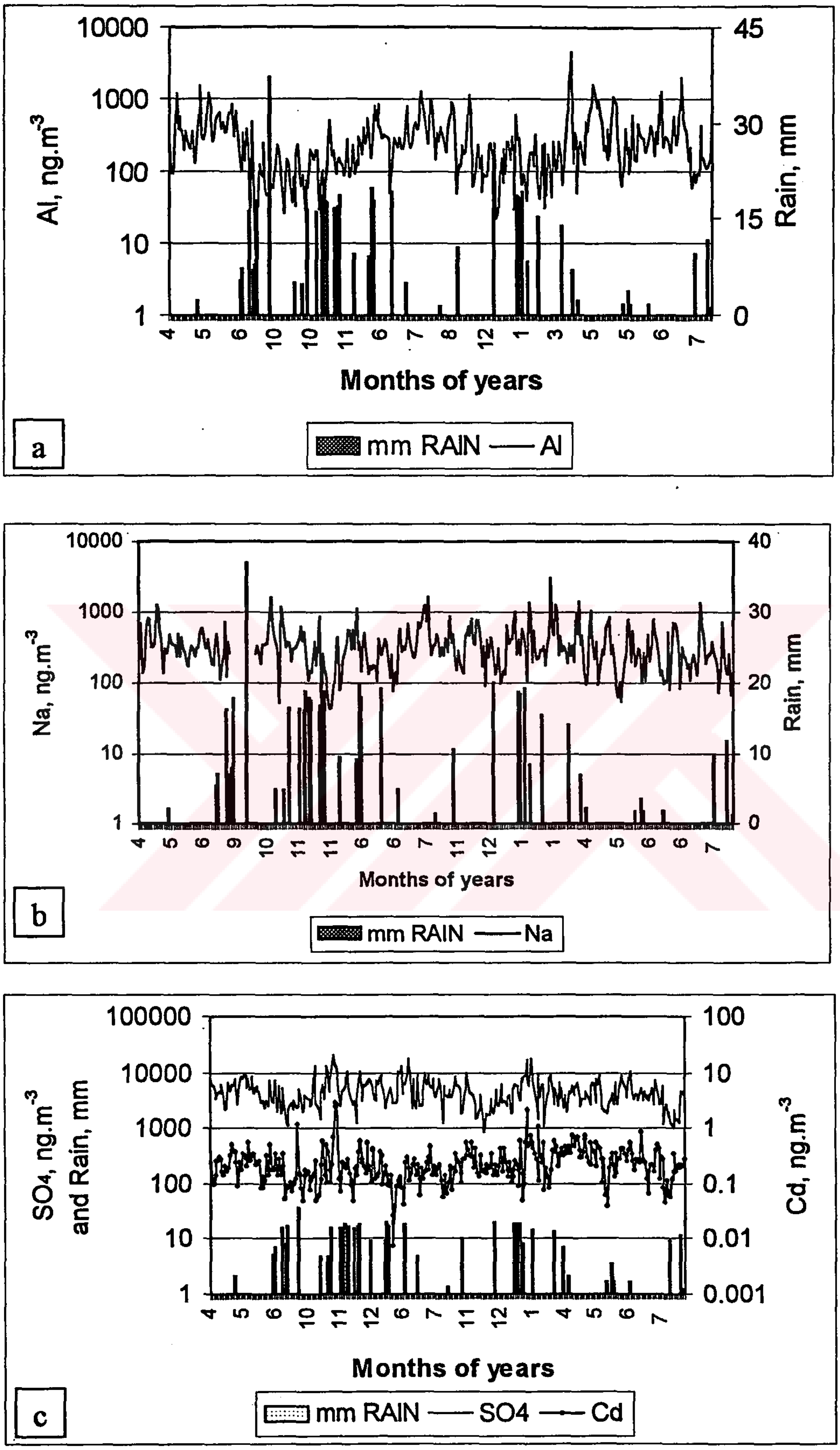


Figure 4.7. Short term variations in the concentrations of a)crustal, b) marine and c) anthropogenic elements.

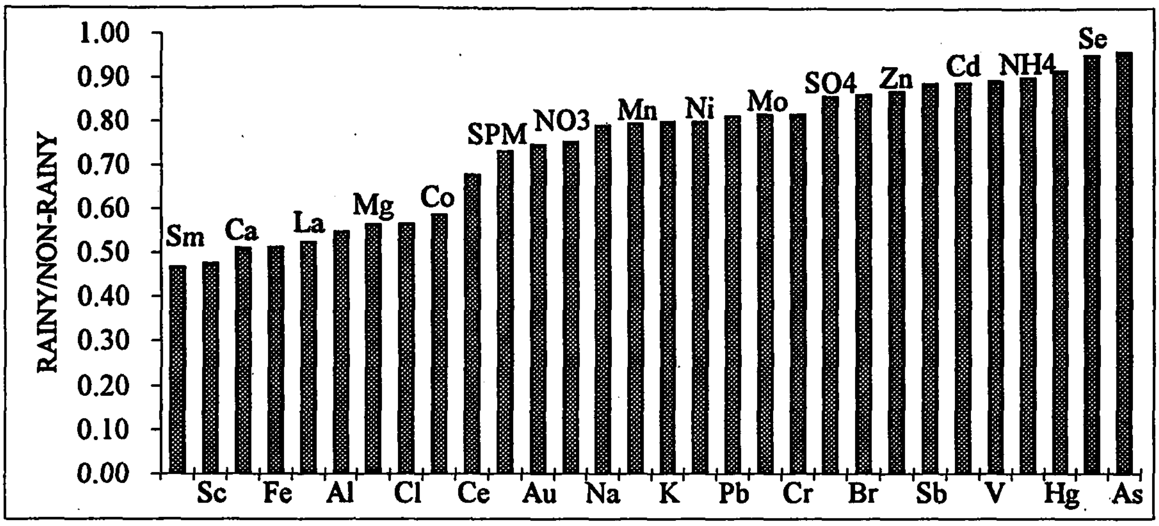


Figure 4.8. Average concentration ratios of the measured species in rainy to non-rainy days.

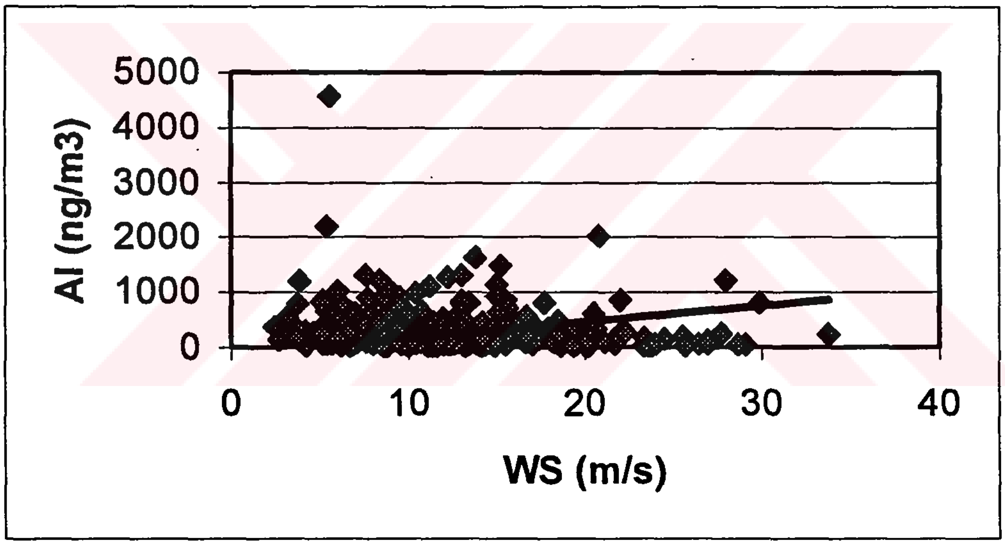


Figure 4.9. Effect of surface wind speed on the concentration of Aluminum.

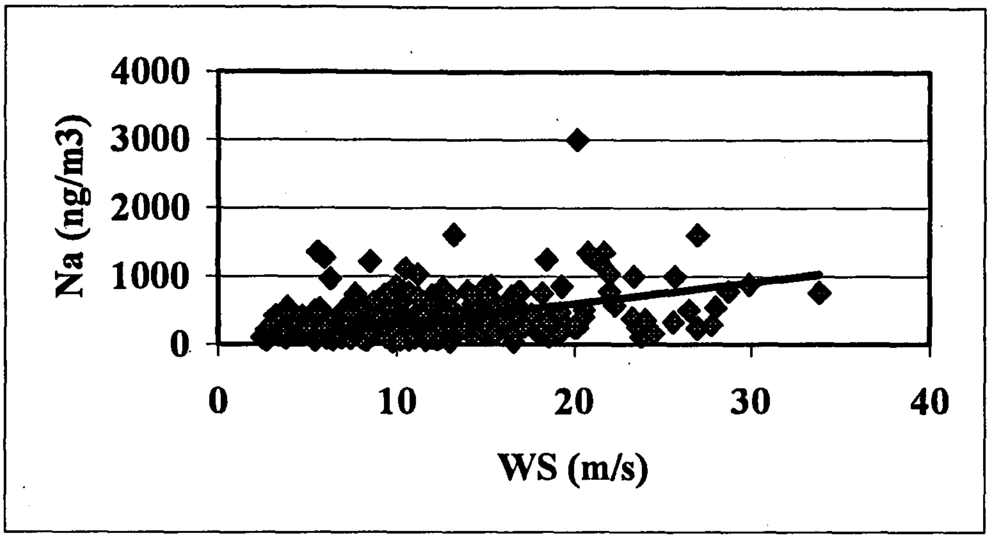


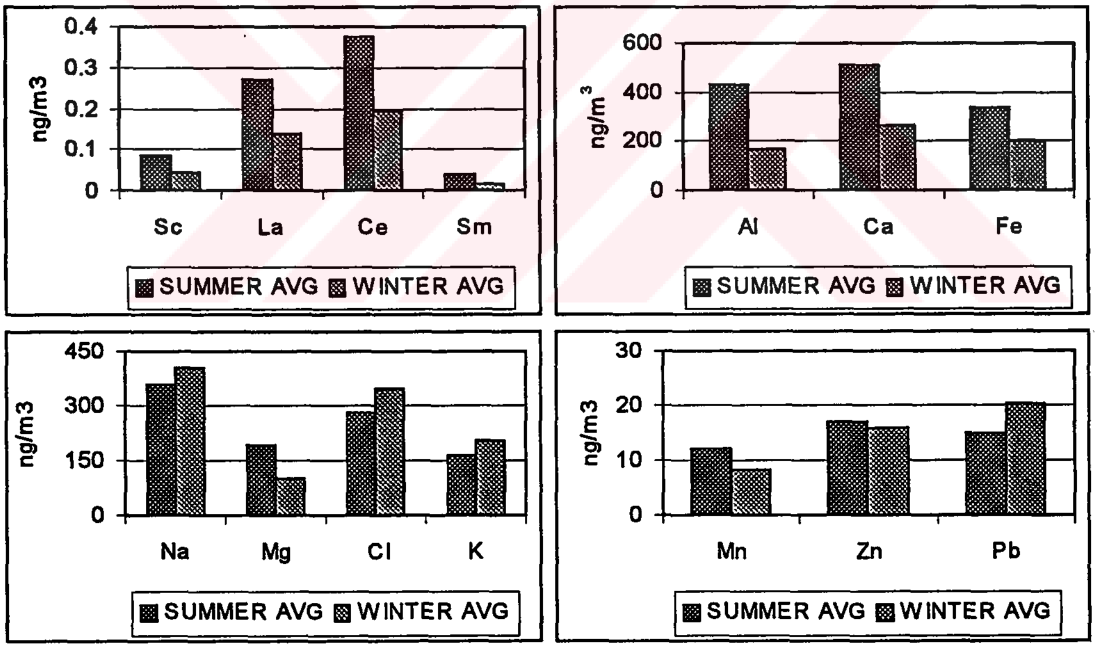
Figure 4.10. Effect of surface wind speed on the concentration of sodium.

Concentrations of marine elements also show short-term variations as depicted in Figure 4.7.b for Na and Figure 4.8 for all the elements. The episodes in the concentrations of sea salt elements are due to storm activity in the proximity of the station, because sea salt particles are generated by bubble bursting process over the sea, which depends on the surface wind speed. The role of surface wind speed on Na concentrations is given in Figure 4.10.

Temporal variations of pollution elements (Cd and SO_4^{-2}) are shown in Figure 4.7.c. As shown in the figure, the pollution elements also show short term variations. However, the local rain effect is not so much significant in this case when compared with the crustal elements. Therefore, effect of local rain event is very severe in crustal and marine elemental concentrations. On the other hand, pollution elements have small sizes and therefore they are brought to receptor site from distant sources by the upper atmospheric air masses that may contribute the concentrations of pollution elements via the rain out process.

4.3.2. Long-term Variations of the Elemental Concentrations in the Western Black Sea Atmosphere

Long-term variations in this study refer to seasonal changes in the concentrations of elements and ions, as data is not long enough (for the time being) to assess annual variations. Each year is divided into two seasons, as summer and winter and average concentrations of elements and ions in each season is investigated. Division of each year into seasons is tentative and based on the precipitation amount and frequency, because it was shown that the particle scavenging is the most important factor affecting seasonality of elemental concentrtions at rural Mediterranean sites (Güllü et al., 1998; Al-Momani et al., 1998; Bergametti et al., 1989; Kubilay and Saydam, 1995). The seasonal variations of crustal, marine and pollution derived species for this study are given in Figure 4.11.



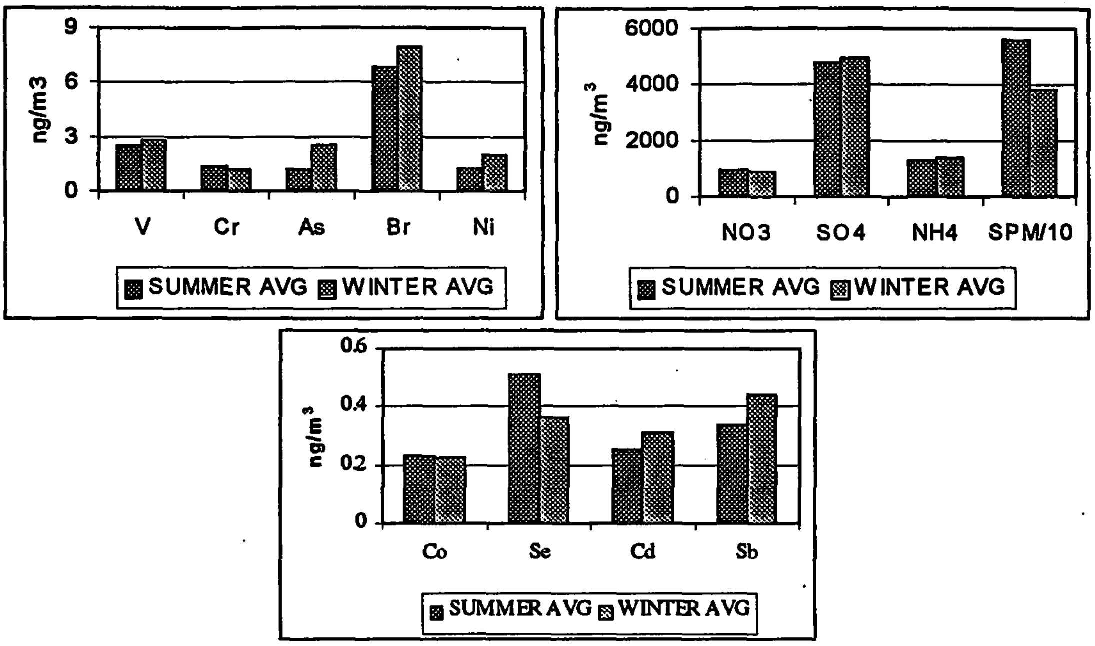


Figure 4.11. Seasonal variations in the concentrations of elements.

The crustal elements, Al,Ca, Fe, Mg, K, Mn, Sc, La and Sm are the elements having summer peaks. Sodium, Cl, NO_3^-, and Br have winter peaks because they are produced more in winter, as discussed above. The seasonal difference in average Cl concentration is less than that of marine Na and the seasonal change in the average concentrations of total sodium is also less than marine sodium. As will be discussed in enrichment factors of the elements, Na is also contributed by the earth crust and so its marine concentration must be calculated.

Among the anthropogenic species only As, Ni and Pb showed seasonal changes and the others did not change significantly with changes in the meteorologic conditions in different seasons. These three elements have winter peaks like marine elements. However, the generation processes for these two kinds of element groups are very different. Sea salt elements are natural in origin and As, Ni and Pb are mainly produced via human activities. Arsenic showed similar behavior in our previos study (Güllü, 1996). The reason of such seasonal behaviors of these elements will be discussed extensively in the following sections after applying receptor models and air mass back trajectory informations.

In addition to short and long-term variations in the concentrations of elements and ions, we have also investigated variations in the "regional background" concentrations of elements and ions. Generally it is assumed that the aerosol population in a given region consists of a uniform concentration of background levels on which spikes due to individual transport episodes are superimposed. Seasonal and annual concentrations of elements and ions at a given site is determined by the combined influence of background levels and transport events. In this sense background levels of elements and ions are expected to be fairly uniform throughout the Black Sea region and is not expected to show dramatic changes from one part of the region to another. Understanding the composition of the background aerosols is more important because, it influences the whole region more or less permanently.

4.3.3. Regional Background Concentrations of the Elements in the Black Sea Atmosphere

Source attribution and apportionment studies are very difficult because of the uncertainties in the assessment of elemental background concentrations at the receptor sites. Centuries of human activities have altered the availability of chemicals above what would be due to natural processes alone. The consequence of this activity is that a natural background does not exist anymore, almost anywhere in the globe (Ölmez et al., 1997). In this study we will use the concept of Receptor Background Concentrations of the elements reported by Ölmez et al., 1997. Receptor background elemental concentrations are calculated by plotting frequency distribution of the elemental concentrations. The receptor background concentrations were assumed to be equal to the most frequently occurring values (MFOV). Since 354 daily samples over two and half years are available in this study, the assumption that the receptor background is equal to the most frequently occurring value is a valid approximation. The frequency distributions for the measured specie are also useful in searching for similarities and differences among the elements, which aids in identification of the sources that influence ambient levels as also mentioned in section 4.1.1. As shown in Figure 4.12, the most frequently occurring point is the peak point of a best-fitted distribution.

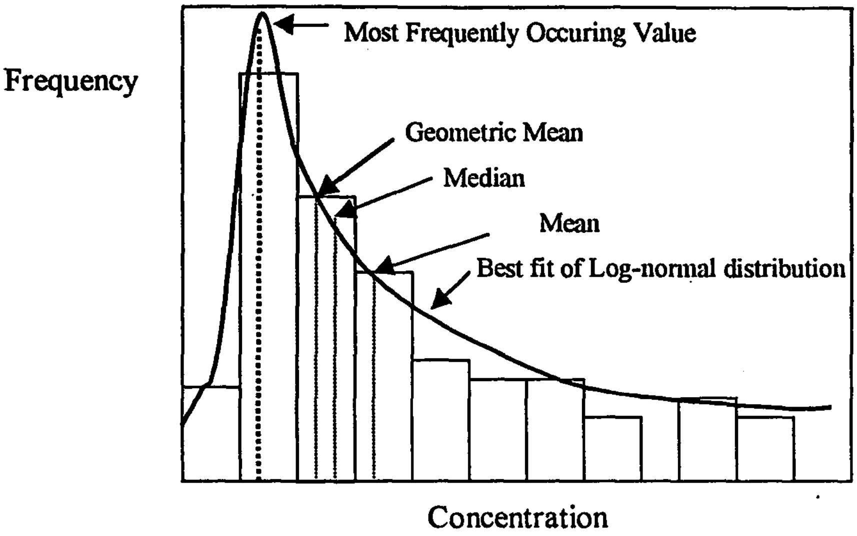


Figure 4.12. Histogram for calculation of the most frequently occurring value

In order to calculate the receptor background concentrations, the first step is to find the best-fitted distribution. Again in section 4.1.1. we showed that concentrations resulting from a series of independent random dilutions tend to be log-normally distributed. Hence, even if emission from sources are constant, the mixing and dilution of pollutants as they are transported from source to receptor results in a log-normal distribution of the ambient concentrations.

The receptor background concentrations for our sampling site is given in Table 4.3. Ideally, if regional natural abundances were not altered, there should be no large variations in the elemental background concentrations from one site to another.

4.3.4. Factors Affecting the Temporal Variations of Elemental Concentrations

There are several factors which affect the aerosol compositions in the ambient air. Some of these factors are source strengths, and source distances, transport patterns, local rain events and the elemental scavenging efficiencies. In the following section we will discuss the influence of the local rain events on the variabilities of the elemental concentrations at the our receptor site. Because, rain is the most effective removal mechanism of the elements in the ambient air through the process called washout.

Table 4.3. Receptor background elemental concentrations at the western Black Sea Basin of Turkey in ng.m^{-3}.

Element	Receptor Background Conc.	Element	Receptor Background Conc.
Na	290	La	0.15
Mg	140	Ce	0.24
Al	160	Sm	0.020
Ca	140	Au	0.00055
Cl	190	Hg	0.024
K	120	Ni	0.70
Sc	0.038	Pb	4.8
V	1.7	NO_3^-	610
Cr	0.50	SO_4^{2-}	4000
Mn	7.7	NH_4^+	980
Fe	120	Ti	0.55
Co	0.050	In	0.012
Zn	7.0	Cs	0.048
As	0.80	Nd	0.29
Se	0.24	Yb	0.0070
Br	5.3	Lu	0.0010
Mo	0.30	Th	0.040
Cd	0.20	U	0.0080
Sb	0.22		

4.3.4.1. Meteorology of the Sampling Site

Monthly average temperatures (°C) and amount of rain (mm) for 21 and 26 years average, respectively are shown in Figure 4.13 for our sampling site. Amount of wet precipitation ranges from 45 mm (for May) to 130 mm (for December). It is clearly demonstrated in the figure that our sampling site is mostly wet when compared to Antalya station in which there is almost no wet deposition during summer months (Güllü, 1996). The soil at the sampling site is generally humid because of frequent wet deposition events and therefore the local atmosphere is contributed less by the crust in terms of soil related elements.

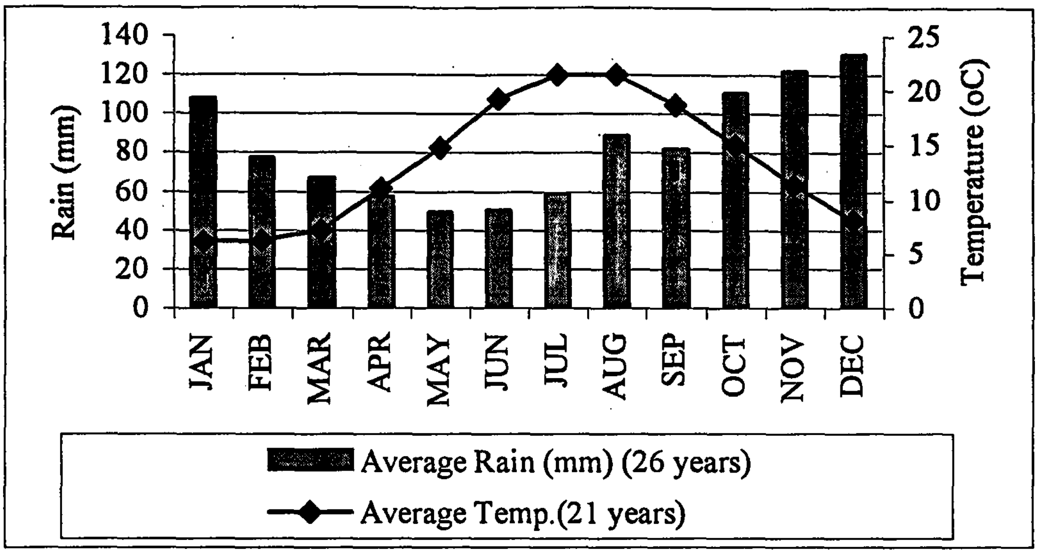


Figure 4.13. Monthly average amount of rain (26 years) and temperature (21 years) at the sampling site.

Figure 4.13 shows also that the local ambient temperature is not so high again when compared to Antalya and Erdemli stations (Güllü, 1996 and Kubilay, 1996). It ranges from 6 °C (in January) to 22 °C (in July). The atmosphere of the Black Sea region of Turkey is mostly covered by clouds which prevents occurrence of elevated temperatures. Only the summer months (Jun, July and August) have temperatures around 20 °C's and rest of the months in our sampling site have temperatures below 20 °C.

Consequently, there is no any sharp winter-summer differences in terms of rain amounts and rain event frequency and temperature differences as in other stations like Antalya and Erdemli. Therefore, it is not possible to observe a significant seasonal changes in the concentrations of elements determined from the Black Sea aerosols. This was discussed in the above sections in detail for the explanations of short term variations of the measured species.

Percent local wind pattern frequencies and average wind speeds for 12-year average and our sampling period (from 1995 to 1997) are given in Figure 4.14.a and 4.14.b, respectively. When these two figures are compared it can be seen that except NNW sector, percent wind pattern frequencies of 12 year average and our sampling period coinside. Therefore, the dominant wind sectors at the Black Sea region are

ENE (13 %), SSE (12.5 %), E (9 %), S (9 %) and W (8 %) for the 12 year average record obtained from the General Directorate of Meteorology, Ankara. During the sampling period the three year average dominant wind sectors and percent wind sector frequencies are ENE (22 %), NNW (16 %), S (9 %), SSE (12 %) and WNW (9.5 %). The figure shows that most of the local winds blew between North and West of the our sampling station and then between East and North and the third dominat sector is South and East. Therefore, local winds blows generally from Central Asia, Middle East and Western and Eastern Europe Countries. The rest of the directions were from Medirranean Sea and African countries.

The 12-year average wind speed with the corresponding wind directions observed at our station differs from the average wind speed values corresponding to our sampling period which is higher than the 12 year average. The reason of such difference is because of the wind data obtained in which the Turkish General Directorate of Meteorology reported the dominant and highest wind speed during this period. However, it is interesting that the dominant wind sectors have the highest wind speeds for both our sampling periods and the 12 year average data.

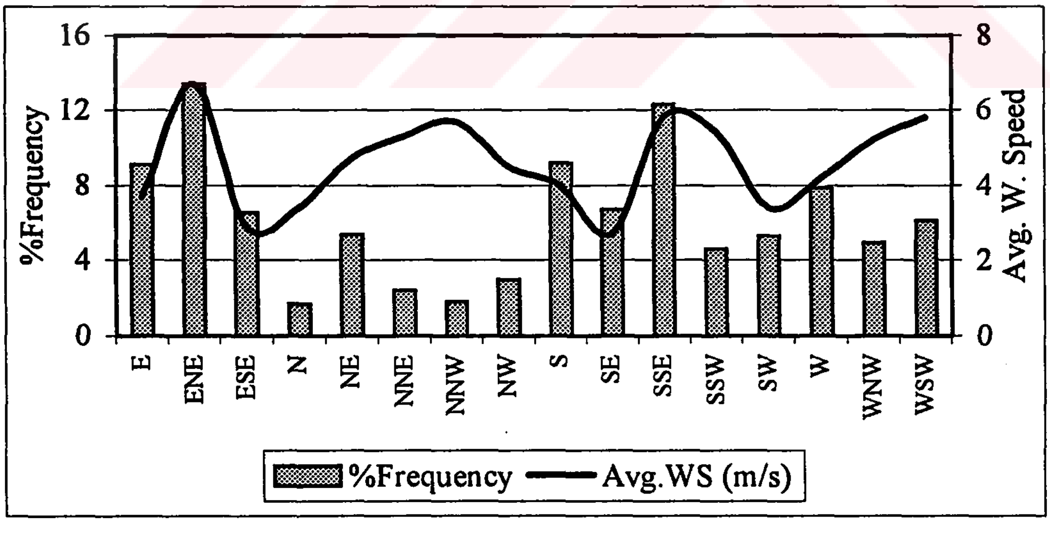


Figure 4.14.a. Twelve-year average of percent wind sector frequency and average wind speed at the sampling site.

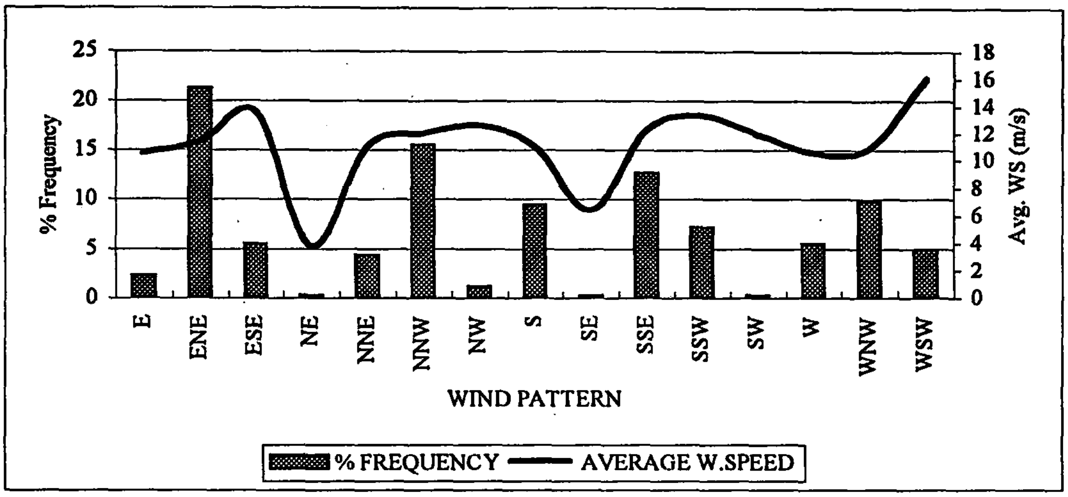


Figure 4.14.b. Percent wind sector frequency and average wind speed during the sampling period at the sampling site.

4.3.4.2. Local Wet Deposition Events

The samples were divided into two data sets as samples corresponding to rainy and non-rainy days and the changes in the average concentrations of the measured species were presented before in Figures 4.7 and 4.8. As can be seen from the figures the average concentrations of crustal elements Al, Mg, Ca, Fe and other crustal elements like Sc, La, Ce, and Sm decreases about 50% in the rainy period. The average concentrations of marine elements like Na, and Cl are decreased to about 20% which are smaller than the average concentration changes in the corresponding crustal elements. This is due to the effect of increase in the wind speed in the rainy days which enhances the sea salt formations. If the wind speed had not changed, the decrease in the average concentrations of Na and Cl should have been very close to the decreases in the concentrations of crustal elements since both crustal and marine elements are bound in coarse particles in the atmosphere so their removal by the rain event is more easy when compared with the fine particles. Because of the sea salt production with the increases in the wind speed, the variability in the marine elemental concentration is less when compared with the variations in the crustal elemental concentrations.

Some of the elements which are both antropogenic and crustal origins have slightly higher decreases in their average concentrations in the rainy periods when compared to marine elements. These elements are Co, Cr, Ni and Mn. The decreases in the average concentrations of this group of elements are in between 25 and 35 %. When these elements are emitted from an anthropogenic sources their sizes become smaller and they form opaque particles which are not soluble in rain droplets.

The pollution elements have very low concentration changes in the rainy days when compared with the non-rainy days. The decrease in the average concentrations corresponding to the rainy days are changing from 10% (e.g. Se, Mo, Cd, Br, Pb and SO_4^{2-}) to 5% (e.g. As).

A few elements have slightly higher average concentrations in the rainy periods. These are Zn, Sb, and Hg and the ammonium ion. The reason may be the rain out process and the volatilities of these elements which can alter the concentrations of these elements in the ambient air during the rain event.

4.4. Sources of Pollutants in the Western Black Sea Basin

General features of the generated data set, including levels of measured parameters in the western Black Sea region of Turkey relative to other regions, temporal variations of measured concentrations and factors affecting the temporal behaviors of elements were discussed in previous sections. Understanding the types and regions of sources are very important since this information specify the direction of regulatory actions. In order to obtain both qualitative and quantitative information about the sources some statistical techniques are needed. In the following sections these techniques and their results will be discussed in details.

4.4.1. Correlations Among the Parameters Determined

The inter-elemental correlations for the measured specie are given in Table 4.4. This kind of binary correlations are used very often in atmospheric studies to guess the types of particles in the samples. In aerosol data sets, a high inter-elemental correlation coefficient between any two measured parameter indicates that these two compounds may be generated in similar mechanisms or may come from similar sources and similar transport patterns.

When Table 4.4 is examined, it is seen that the correlation coefficients between the crustal elements are almost unity. This strong correlations between the crustal elements clearly indicates that they come from same sources which are local soil and long-range transports from the arid regions. The elements having correlation coefficients greater than 0.8 with each other are Al, Sc, La, Sm, Ce, Fe, Ca, Mg, and K. The elements like Mn and Cr have correlation coefficients around 0.5 or greater with the crustal elements given above. The elements V, Br, Ni, the nitrate ion and particulate matter (PM) slightly correlates with the crustal elements and the correlation coefficient values are changing from 0.3 to 0.4. The particulate matter has the highest correlation coefficients with the crustal elements which tells us that the aerosol mass is mainly contributed by the crustal sources.

The marine elements also correlate strongly with each other. The correlation between Na and Cl is 0.9, Na and Mg is 0.5, nitrate ion and Na is 0.6 and Br and Na is 0.6. This correlation shows that both magnesium, nitrate ion and bromine are also contributed by the Black Sea which is 3.75 km to our sampling site.

The correlations between the anthropogenic elements and secondary pollutants were found to be weak when compared with the correlation coefficients between the crustal and marine elements. Among the anthropogenic elements, Zn and Cd (0.5), and Pb(0.4), As and Br (0.5), Cd (0.6), Sb(0.5), Ni (0.5), Pb (0.6), ammonium ion (0.4) and sulfate ion (0.4) are correlates moderately. In general the anthropogenic elements are also correlated with each other however, it must be noted that the correlation coefficients found from a rural site can not be easily interpreted as in the case of an urban site. Because in the urban area the samples are collected immediately after emissions from the sources but in the rural site, there are several factors which may cause artifact correlations between the anthropogenic elements during their transport to the sampling site. Therefore, the correlations among the anthropogenic elements and the secondary pollutants do not indicate that they are from the similar sources.

Table 4.4. Binary correlations of measured species

	Na	Mg	Al	Ca	Cl	Sc	V	Cr	Mn	Fe	K	Zn	As
Na	1.0												
Mg	0.5	1.0											
Al	0.3	0.9	1.0										
Ca	0.2	0.8	0.8	1.0									
Cl	0.9	0.5	0.3	0.2	1.0								
Sc	0.3	0.8	1.0	0.8	0.3	1.0							
V	0.2	0.3	0.3	0.3	0.1	0.3	1.0						
Cr	0.3	0.5	0.5	0.4	0.2	0.5	0.4	1.0					
Mn	0.2	0.6	0.8	0.6	0.2	0.7	0.5	0.5	1.0				
Fe	0.3	0.7	0.9	0.8	0.3	1.0	0.4	0.5	0.8	1.0			
K	0.4	0.7	0.8	0.7	0.4	0.8	0.5	0.5	0.7	0.9	1.0		
Zn		0.2	0.2	0.2		0.2	0.5	0.4	0.4	0.2	0.2	1.0	
As	0.2	0.1			0.2	0.1	0.6	0.4	0.2	0.1	0.3	0.2	1.0
Se	0.1	0.1	0.1		0.1	0.1	0.2		0.3	0.1	0.1	0.1	0.1
Br	0.6	0.6	0.5	0.4	0.5	0.4	0.5	0.5	0.4	0.5	0.5	0.2	0.5
Cd	0.1	0.2	0.2	0.2	0.1	0.2	0.6	0.4	0.3	0.2	0.3	0.5	0.6
Sb		0.1	0.1	0.1		0.1	0.5	0.3	0.2	0.1	0.2	0.3	0.5
La	0.3	0.8	1.0	0.8	0.3	1.0	0.3	0.5	0.7	1.0	0.8	0.1	
Sm	0.3	0.8	1.0	0.8	0.3	1.0	0.3	0.5	0.7	1.0	0.8	0.1	
Au	0.1	0.2	0.1	0.1		0.1		0.2		0.1	0.1	0.1	
PM		0.4	0.4	0.4	0.1	0.4	0.2	0.4	0.3	0.3	0.3	0.3	0.2
Ni	0.2	0.3	0.4	0.4	0.2	0.5	0.7	0.5	0.4	0.5	0.6	0.3	0.5
Pb	0.1	0.2	0.1	0.1		0.2	0.1	0.4	0.2	0.1	0.2	0.4	0.6
NO_3	0.6	0.5	0.5	0.4	0.6	0.5	0.5	0.4	0.5	0.5	0.6	0.2	0.3
SO_4	0.1	0.1	0.1			0.1	0.5	0.1	0.3	0.1	0.2	0.2	0.4
NH_4	0.1	0.1	0.1	0.1			0.5	0.2	0.3	0.1	0.1	0.3	0.4

Table 4.4. Continued

	Se	Br	Cd	Sb	La	Sm	Au	PM	Ni	Pb	NO_3	SO_4	NH_4
Se	1.0												
Br	0.1	1.0											
Cd	0.1	0.4	1.0										
Sb		0.3	0.5	1.0									
La	0.1	0.4	0.2	0.1	1.0								
Sm	0.1	0.4	0.1	0.1	1.0	1.0							
Au		0.2			0.1	0.1	1.0						
PM		0.2	0.4	0.2	0.4	0.4		1.0					
Ni	0.1	0.5	0.5	0.4	0.5	0.5		0.3	1.0				
Pb		0.4	0.6	0.4	0.1	0.1	0.1	0.2	0.4	1.0			
NO_3	0.1	0.6	0.4	0.2	0.5	0.5		0.3	0.5	0.3	1.0		
SO_4	0.3	0.2	0.4	0.3	0.1	0.1			0.3	0.4	0.3	1.0	
NH_4	0.3	0.3	0.5	0.3			0.1	0.2	0.2	0.4	0.3	0.6	1.0

4.4.2. Enrichment Factors

As discussed in Chapter 2, section 2.3.3 the enrichment factor of an element is the ratio of the concentration of the test element to the reference element in the same sample divided by the same ratio in reference material like soil or sea water. In this study we performed two types of enrichment factor calculations in which the reference materials are earth crust and sea water. These two sources are generally the most contributing sources to the aerosol composition. In the first calculation Al was selected as a reference for soil component. Because it is very difficult to alter the composition of soil with respect to aluminum because of its high concentration. As a reference element for the sea water marine component of Na was selected. Chlorine can also be selected as a reference element for marine enrichment factor, but since our station is not very close to the sea shore, the chlorine is depleted during the transport to our station and in addition chloride has other industrial sources. However, sodium is very inert in the marine environment when compared to chlorine and the second important source for sodium is the earth crust. The crustal contribution to sodium concentration was corrected by using the Equation 4.2 to get the marine component of sodium. This equation involves an approximation in which it is assumed that sodium has only two sources, earth crust and sea water. The pollution component of the sodium is neglected in this equation.

$$[\mathrm{Na}]_{m} = [\mathrm{Na}]_{aerosol} - 0.29*[\mathrm{Al}]_{aerosol} \ldots\ldots\ldots\ldots\ldots 4.2$$

Where, $[\mathrm{Na}]_{m}$ is the marine component of sodium, $[\mathrm{Na}]_{aerosol}$ is the concentration of Na in the aerosol, 0.29 is a constant and it is the ratio of global average concentration of sodium in the earth crust to the global average concentration of aluminum in the earth crust (Taylor, 1972), and $[\mathrm{Al}]_{aerosol}$ is the concentration of aluminum in the aerosol.

The crustal enrichment factor (EF) for the measured elements are shown in Figure 4.15 and the marine EF for the same elements are shown in Figure 4.18. In ploting these figures, the median EF and the EF ranges of the elements were used, since all of the elements distribute log-normally and median or geometric mean may be best explain the elemental behaviors and they can not be altered more because of any peak values in the data set but arithmetic mean and standard deviation can be altered by any outlier value.

4.4.2.1. Crustal Enrichment Factors of the Elements

In the calculation of crustal enrichment factors of the elements aluminum was selected as normalizing element, and Taylor's average crustal composition (Taylor, 1964) was selected as the normalizing matrix for this study.

Ranges and median values of calculated enrichment factors for every element measured in this study are given in Figure 4.15. Elements in this figure are arranged according to increasing median enrichhment factors which indicate the increasing anthropogenic content. The elements were divided into three general groups with respect to their median EF values; non-enriched elements (EF < 10), moderately enriched elements (10 < EF <100), and highly enriched elements (EF >100).

The non-enriched group includes elements generally found in wind-blown dust or crustal material (from Sc to Nd) with no major additional sources. In the ideal case, since the normalizing matrix is also average crustal material, these elements should have EF values very close to unity. However, due to the possible variations in crustal compositions, analytical uncertainties, and additional but not significant other sources, etc. we considered EF = 10 as an upper limit.

Although, Mg, Na, Cr, Ni, Co and V have other sources (marine for Na and Mg and anthropogenic for Cr, Ni, Co and V), they appear in the non-enriched group of elements. However, as will be discussed later, factor analysis shows that these elements are not purely from earth crust but also from other sources like marine and anthropogenic emissions, respectively.

Among the non-enriched elements, Ce, Hf, Fe, Mg, Co, K, Ca, Cr, Na, Ni and V have very wide EF ranges. The wide range of EF values show that there are additional sources along with the crustal material contributing to its ambient concentrations. The wide ranges for the elements Ce and Hf can be caused by the uncertainties in the analysis, however, the other elements are mainly contributed by multiple sources.

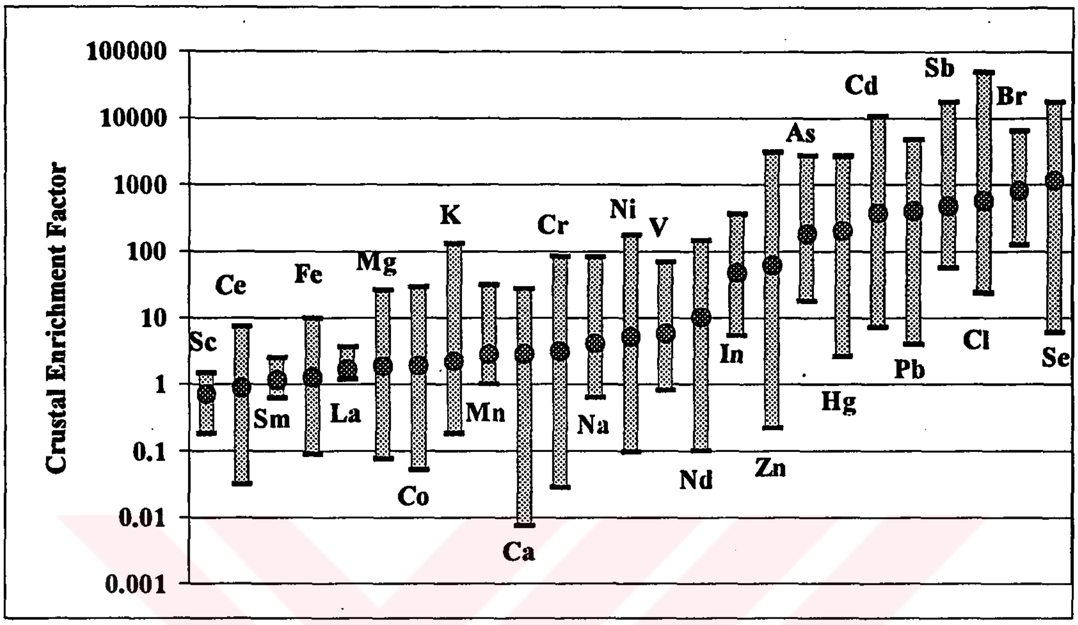


Figure 4.15. Crustal enrichment factors (EF's) of the elements

There are only four elements belonging to second group (moderately enriched) which are Au, In, Zn and Mo. Except indium, Au, Zn and Mo have wide ranges indicates that there are again additional sources for these elements. The concentration of gold in the aerosol samples was in the pg/g levels therefore, the reason for the wide range of EF values may be because of analytical uncertainties and in addition we know that gold has other sources like earth crust and precious metal works. Indium, Zn and Mo generally originate from anthropogenic sources like smelters and power plants.

Elements which are highly enriched (As, Hg, Cd, Pb, Sb, Cl, Br and Se) are mostly volatile and are found in the atmosphere at elevated concentration levels due to the anthropogenic activities. Their impact area ranges from regional to global. Depending upon the type and the characteristics of their emission sources, most of the highly enriched elements are released to atmosphere as fine particles or gases. The gaseous ones have atmospheric residence times of several months to years depending on their reactivity in the atmosphere. Particulate forms of highly enriched elements have much shorter atmospheric residence times than the gaseous ones and are useful as the conservative markers for various industrial processes.

Selenium is the most enriched element in our sampling site followed by the Br, Cl and Sb. This trend for Se and Sb are rather common and is even observed in very remote areas (Tuncel et al., 1985). Known natural and anthropogenic sources are volcanoes, fossil fuel burning and industrial activities (Ölmez et al., 1997). The selenium generally associates with aged particles and represents the long range transport however, Sb may have local sources like antimony roaster and motor vehicles (Dzubay et al., 1988; Huang et al., 1994).

The second and the third most enriched elements are Br and Cl. Generally, the major source for Br in the atmosphere is considered to be motor vehicles burning leaded gasoline. However, as leaded gasoline has been phased out, this source has became insignificant except in urban areas (Ölmez et al., 1997). There are numerous industrial uses of Br and its compounds including the production of medicinal compounds and gases used by the military. Bromine is also used in organic synthesis, and is a constituent of oxidizing and bleaching agents, and solvents. Both Cl and Br are the group 7 elements (halogens) in the periodic table of the elements and are generally used in similar processes in the industry. In addition, they both have another source which contributes Cl concentration in the ambient air more than that of Br is the sea. The rest of the highly enriched elements have been attributed to different industrial processes as will be discussed in the following sections.

In order to distinguish the natural and anthropogenic sources of the group one elements (EF < 10), enrichment factor diagrams which are the log-log plots of the crustal EF's of the elements vs Al concentrations were prepared. The crustal EF of purely crustal elements does not change with changes in the aluminum concentration (which was used as the normalizing element in the EF calculations) resulting in a horizantal line in the EF diagram. Since, concentrations of both the crustal element and aluminum change in similar manners with increasing and/or deceasing loading of crustal particles in the atmosphere, the crustal enrichment factor stays the same.

The EF diagrams of two purely crustal elements Sc and Sm are given in Figure 4.16 as an example. Enrichment factors of non-crustal elements, on the other hand are independent of the Al concentration in the aersol samples. The EFc values of such type of elements decrease with increases in the aluminum concentration and results in a negatively correlating line in the EF diagram.

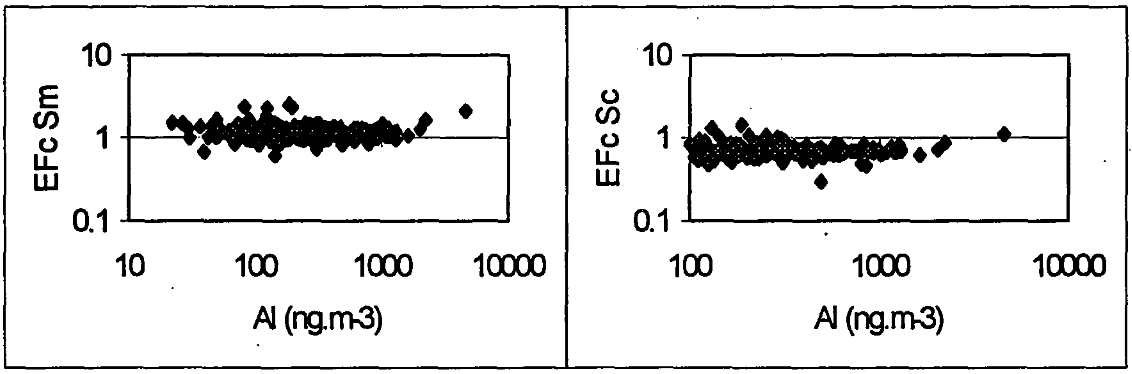


Figure 4.16. EF diagrams of Sc and Sm.

As can be seen from Figure 4.17, EFc diagrams for K, Cr, V and Ni show different pattern from that of purely crustal elements shown in Figure 4.16. Therefore, it is clear that they have additional sources other than earth crust since significant numbers of samples show high EF values for these elements when compared to median values of elemental enrichment factors. Figure 4.17 indicates that these elements are from other sources when Al concentration is around 100 ng.m^{-3}, then stays almost constant (crustal only) and then again starts to decrease with increase in Al concentration around 600 ng.m^{-3}. This observation is different from the results obtained at the eastern Mediterranean aerosols (Güllü, 1996) in which they observed that K and V behave like purely crustal elements at high Al concentrations and behave like anthropogenic elements at low Al concentrations. As can be seen in Table 4.5, except K, the winter to summer EFc ratios of these elements are greater than one which demonstrates that these elements are contributed mainly by the other sources rather than the earth crust. Consequently, slight enrichhments of these elements are due to the presence of non-crustal sources not because of the differences in the chemical compositions of the soil samples in Taylor's compilation data used in the calculations of elemental EFc values.

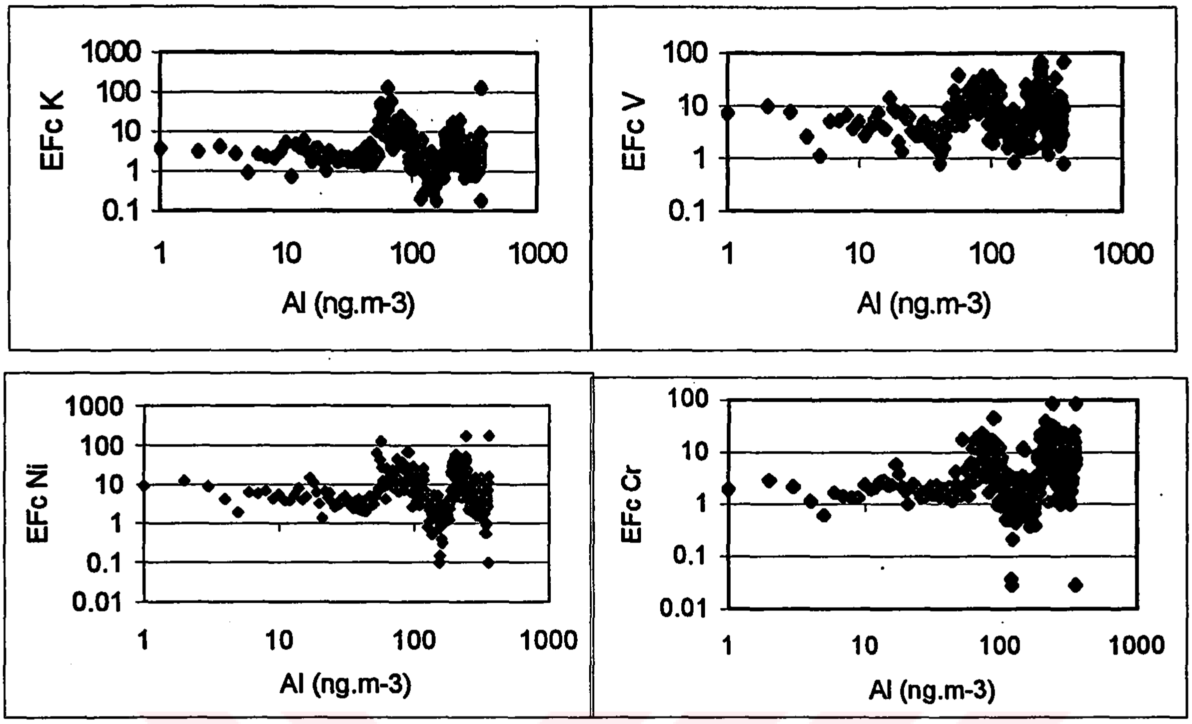


Figure 4.17. EFc Diagrams of K, V, Ni and Cr.

To determine the seasonal changes in the EF values of the elements, average enrichment factors for summer (May-October) and Winter (November-April) periods were calculated (including standard deviations and winter to summer ratios) and were given in Table 4.5.

Winter to summer EFc ratios are about unity for most of the elements which tell us that most of the elements have no seasonal change in the EFc values. But, when the standard deviations are examined, it is clear that non-crustal elements having average winter to summer EFc ratios of about unity have higher standard deviations than the pure crustal elements. The elements having almost unity ratios and small standard deviations are Sc, Ce, Sm, Fe, La, Mg, Ca, and Mn. This group of elements behave as expected because all of these elements are mainly originating from crustal materials at the receptor site.

Table 4.5. Seasonal mean crustal enrichment factors (EFc) and winter to summer EFc ratios.

Element	Winter Average (STD)	Summer Average (STD)	Winter/Summer (STD)
Sc	0.760 (0.240)	0.685 (0.100)	1.11 (0.362)
Ce	1.17 (1.02)	0.840 (0.420)	1.39 (1.00)
Sm	1.24 (0.320)	1.16 (0.200)	1.07 (0.310)
Fe	2.04 (1.51)	1.38 (0.700)	1.48 (0.900)
La	2.00 (0.470)	1.63 (0.210)	1.23 (0.268)
Mg	2.90 (2.48)	2.34 (2.22)	1.24 (1.28)
Co	4.92 (5.23)	2.28 (3.20)	2.16 (1.76)
Hf	2.24 (2.14)	3.86 (11.7)	0.580 (3.18)
Ca	4.01 (2.96)	3.42 (3.30)	1.17 (1.21)
Mn	4.70 (4.13)	3.24 (1.85)	1.45 (1.05)
K	4.43 (3.40)	4.60 (11.1)	0.963 (2.53)
Cr	8.45 (10.1)	4.55 (5.53)	1.86 (1.70)
Na	12.0 (15.0)	6.60 (10.2)	1.82 (2.00)
V	12.7 (12.2)	6.72 (6.37)	1.90 (1.35)
Ni	17.3 (20.0)	7.20 (12.3)	2.40 (2.06)
Nd	24.6 (29.0)	13.4 (13.0)	1.84 (1.53)
In	97.0 (83.6)	37.6 (27.8)	2.58 (1.14)
Zn	126 (143)	131 (305)	0.962 (2.60)
Au	140 (190)	130 (440)	1.08 (3.65)
Mo	270 (380)	100 (120)	2.70 (1.85)
Hg	380 (420)	240 (270)	1.58 (1.58)
As	830 (640)	170 (230)	4.88 (1.56)
Pb	1150 (1100)	463 (514)	2.48 (1.47)
Sb	1500 (1510)	595 (1540)	2.52 (2.78)
Cd	1050 (1170)	495 (750)	2.12 (1.88)
Br	2100 (1400)	780 (660)	2.70 (1.08)
Cl	1650 (2140)	1470 (4240)	1.12 (3.16)
Se	2150 (2520)	1610 (1950)	1.34 (1.70)

There is a second group of elements which have almost unity winter to summer EFc ratios and high standard deviations. These elements are Hf, K, Nd, Zn, Au, Cl and Se which are generally contributed by mixed sources.

When Table 4.5 is further examined one can see two additional differently behaving groups of elements. The elements in the first group have about 2 to 3 winter to summer EFc ratios and high standard deviations and the second additional group of elements have again winter to summer EFc ratios about 2 to 3 and small standard deviations. The elements having the high EFc ratios and high standard deviations are Co, Cr, Ni, Mo, As, Pb, Sb and Cd and the elements having again high seasonal EFc ratios and small standard deviations are V, In and Br. These two additional groups of elements are mostly originate from anthropogenic sources and indicate that there are seasonal differences because of changes in the emission strengths and transport patterns of these elements.

As discussed before, the concentrations of both crustal and anthropogenic elements are high in summer seasons because of lack of wet deposition events and wind blown dust. However, the difference between the summer and winter concentrations are significant for soil related elements, resulting in lower crustal enrichment factors for pollution derived elements in summer. This situation is expected for regions having very dry summer season like Eastern Mediterranean where it was observed that the winter to summer EFc ratios of the elements change from 0.8 to 25 (Güllü, 1996). In the case of our sampling area, western Black Sea Cost of Turkey, the winter to summer EFc ratios change from 0.6 to 3 and 5 for only Arsenic. This is because of significant difference in the rain fall events observed in Eastern Mediterranean and Black Sea regions. As discussed before, Black Sea region is generally humid and gets more rain fall when compared to Eastern Mediterranean in both seasons which leads to very small winter to summer EFc ratios in the Black Sea aerosols.

Consequently, the crustal enrichment factor calculations of the elements have showed that chemical compositions of Black Sea aerosols are mainly affected by three components which include:

1. The crustal component which accounts for most of the observed concentrations of Al, Sc, Mn, Fe, Ca, La, Ce, Sm, Mg, Co, K, Nd and Hf.

2. The marine component which consists of sea salt particles generated over the Black Sea throuh the bubble-bursting process. The marine component mostly contributes the observed concentrations of Na, Cl, Br, Mg and NO_3^-.

3. The third component is the anthropogenic component and is the most important one in this type of studies. This component consists of particles and gases emitted from various industrial activities. The anthropogenic

component significantly determines the concentrations of Cr, Ni, Pb, Cd, Sb, Se, As, Br, Zn, Hg, In, Mo, SO_4^{2-} and NH_4^+.

These components will also be discussed in detail with the factor analysis results which explains the sources more effectively than the enrichment factor calculations.

4.4.2.2. Marine Enrichment Factors of the Elements

The aerosol composition in the ambient air is mainly affected by earth crust and sea salt if the receptor site is at a coastal zone. In this study, the sampling site is not so far from the Black Sea so that we should also calculate the marine enrichment factors for the measured elements. Marine enrichment factors (EFm) are useful to identify the sea salt contribution on the aerosol composition. The sea water composition given by Goldberg (1963) and marine component of sodium (Na-m) concentration in the aerosol samples were used in the calculation of EFm.

Marine enrichment factors of the elements in the western Black Sea Coast of Turkey is given in Figure 4.18. Again median and ranges of elemental EFm values were used to plot the figure. Marine enrichment factors of the Cl, Na(total), Mg and Br are smaller than 10 which indicate that these elements are not enriched in the aerosol samples and are mainly contributed by the Black Sea. There are two elements which are slightly enriched in the aerosol samples. These elements are K and Ca with median EFm values in between 10 and 100. As we shown in EFc calculation, these two elements mainly originate from crustal material. Rest of the elements have median EFm values ranging from 10^3 to 10^7 which show that except marine elements all of the elements measured in this study are highly enriched in the aerosol samples with respect to sea water composition.

To discuss the sources and the fates of chlorine and bromine in the ambient atmosphere, we compared their ratios to marine sodium (Na-m) in the aerosol with their ratios to Na in the global average sea water given by Goldberg (1963). The Cl/Na-m and Br/Na-m plot is shown in Figure 4.19.

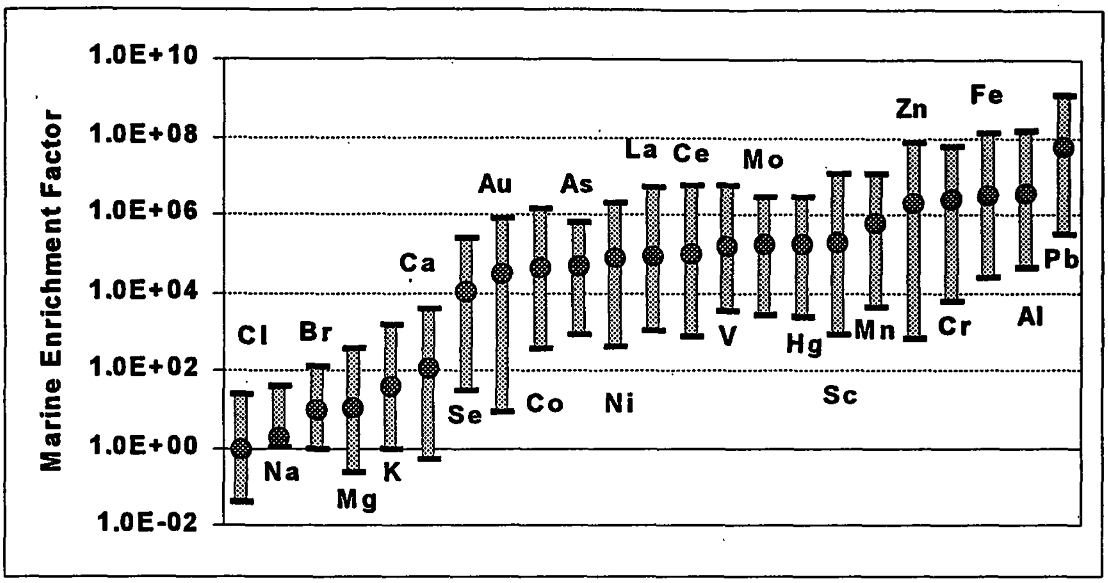


Figure 4.18. Marine enrichment factors of the elements

The average ratio of Cl to marine Na is 1.24 ± 0.87 and that of Br to Na-m is 0.061 ± 0.107 in the measured aerosol samples. The Cl ratio to marine sodium is less than the corresponding ratio in sea water (1.81) and that of Br is 10 times larger than the same ratio in the sea water in which the ratio is 0.0062. These are expected phenomena because Cl undergoes several reactions in the ambient atmosphere and so its concentration is depleted during transport from sea to receptor site. Similar processes are also valid for Br, however, Br has additional anthropogenic sources in addition to the sea salt. For that reason there is a depletion in Cl concentration and bulding up in Br concentration in the aerosol samples.

It was experimentally proved in the laboratory conditions that HCl and NaCl particles can undergo exothermic reactions with $ClONO_2$ (chlorine nitrate) and N_2O_5 (nitrogen pentoxide) producing Cl_2 and $ClNO_2$, respectively (Finlayson-Pitts et al., 1989). Similarly, Karlsson and Ljungström (1998) studied the reaction between liquid sea salt aerosol and nitrogen pentoxide and they reported that depletion in marine sea salt chloride concentration is determined by the amount of N_2O_5 present in the atmosphere.

$$NaCl\,(s) + ClONO_2\,(g) \rightarrow Cl_2(g) + NaNO_3\,(s), \quad \Delta H_{298}{}^{o} = -82.8\ kJ\ mol^{-1}$$

$$NaCl\ (s) + N_2O_5\ (g) \rightarrow ClNO_2\ (g) + NaNO_3\ (s), \quad \Delta H_{298}{}^{o} = -55.2\ kJ\ mol^{-1}$$

They suggested that the major source of NaCl in particles is as sea salt particles and therefore, in a polluted marine region, where NO_2, HNO_3 and N_2O_5 are present, production of ClNO (nitrosyl chloride), HCl and $ClNO_2$ (nitryl chloride) may occur in relative amounts that depend on the concentrations of the gas phase species and the speeds of the individual reactions.

The NaCl also undergoes reactions with HNO_3 and H_2SO_4 in the marine atmospheres and the product of these reactions, HCl, (Tuncel et al., 1989; Hacısalihoğlu, 1993; Shaw, 1991; Harkel, 1997; and Roth and Okada, 1998) can give further reactions with the chlorine nitrate and nitrogen pentoxide.

In addition to chlorine reactions, there are similar bromine reactions in the atmosphere involving in the ozone destruction processes. The sea salt bromine and its probable ozone destruction mechanism was discussed by McConnell et al., 1992. They explained the observations reported by Barrie et al.,1988 by a mechanism involving the conversion of sea salt derived bromide (Br^-) to gas phase bromine molecule ($Br_2(g)$) through photoactivated reactions on aerosols and the snow pack surface. The proposed possible mechanism for $X^- \rightarrow X_2(g)$ is given as the following pathway;

$$4Br^- + O_2 + 4H^+ + h\nu \rightarrow 2Br_2 + 2H_2O \qquad (c)$$

Recently, Oum et al., 1998 reported that chlorine molecule (Cl_2) can be generated by photolysis of ozone in the presence of aqueous sea salt particles and the subsequent photolysis of Cl_2 in the gas phase will generate atomic Cl, whose fate depends on the relative concentrations of organics and O_3.

Through the investigations done up to now, the chlorine cycle in the troposphere and stratosphere can be summarized simply by the Figure 4.20. This figure and the mechanisms given above can explain the reason why Cl and Br are depleted at rural areas.

The marine enrichment factor of Br is close to unity however, this does not mean that the Br comes only from sea salt. If this were the case, its concentration should have depleted as in the case of Cl. Since our samples are not size separated (fine and coarse), anthropogenic Br is masked by marine Br which is in the form of large sea salt particles. However, high Br/Na-m ratio tells us that anthropogenic Br do exist in the aerosol mass.

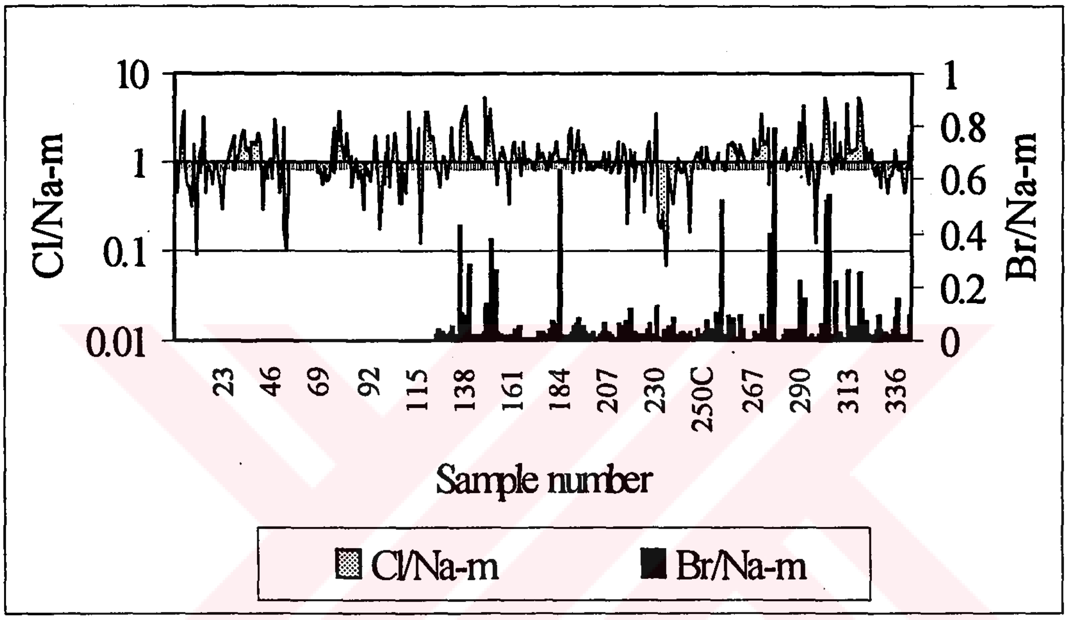


Figure 4.19. The Cl/Na-m and Br/Na-m ratios

4.4.3. Crustal and Marine Contributions to the Pollution Elements

Crustal and marine enrichment factor calculations showed that crustal and marine sources contribute to concentrations of most of the elements in the aerosols. However, EF calculation does not give a quantitative information about the relative amount of contribution on the total concentration. To get this information, we calculated percent crustal and marine contributions to individual elements and the results are given in Table 4.9.

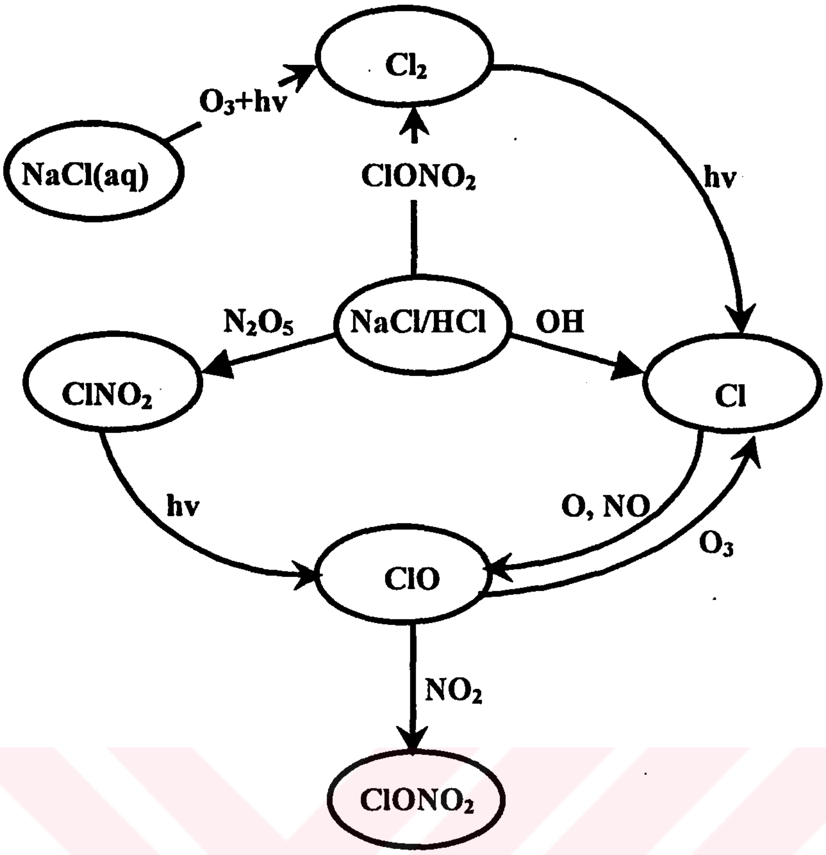


Figure 4.20. The approximate chlorine cycle in the atmosphere

The percent contribution of crustal source on the concentration of each element was calculated by assuming crustal dust is the only source of Al (which was used as normalizing element in the EFc calculations) in samples and using element-to-Al ratios given for average crustal soil in the literature (Taylor, 1972). Similarly, percent marine contributions on each elements was calculated by using Goldberg's sea water composition and marine component of sodium which was also used in the EFm calculations as a reference element. The crustal and marine components of each element were calculated by using the following equations;

$$[X]_{crustal} = [Al]_{aerosol}\{[X]/[Al]\}_{crustal} \ldots\ldots\ldots\ldots 4.3$$

$$[X]_{marine} = [Na]_{marine}\{[X]/[Na]\}_{sea\text{-}water} \ldots\ldots 4.4$$

Where, $[X]_{crustal}$ and $[X]_{marine}$ are the crustal and marine components of element under consideration, $[Al]_{aerosol}$ and $[Na]_{marine}$ are the concentrations of aluminum and sodium in aerosol samples, and $\{[X]/[Al]\}_{crustal}$ and $\{[X]/[Na]\}_{sea\text{-}water}$ are the element to reference element ratio in Taylor's crustal table and Goldberg's sea water composition table. $[Na]_{marine}$ was calculated by using Equation 4.2.

The contribution from crustal source to elemental concentrations are high for crustal elements as expected and very low for anthropogenic elements. The crustal contribution to Na concentration is 28.7 for the whole samples of Black Sea aerosols.The temporal variations of percent crustal and merine contributions to Na concentrations are given in Figure 4.21.

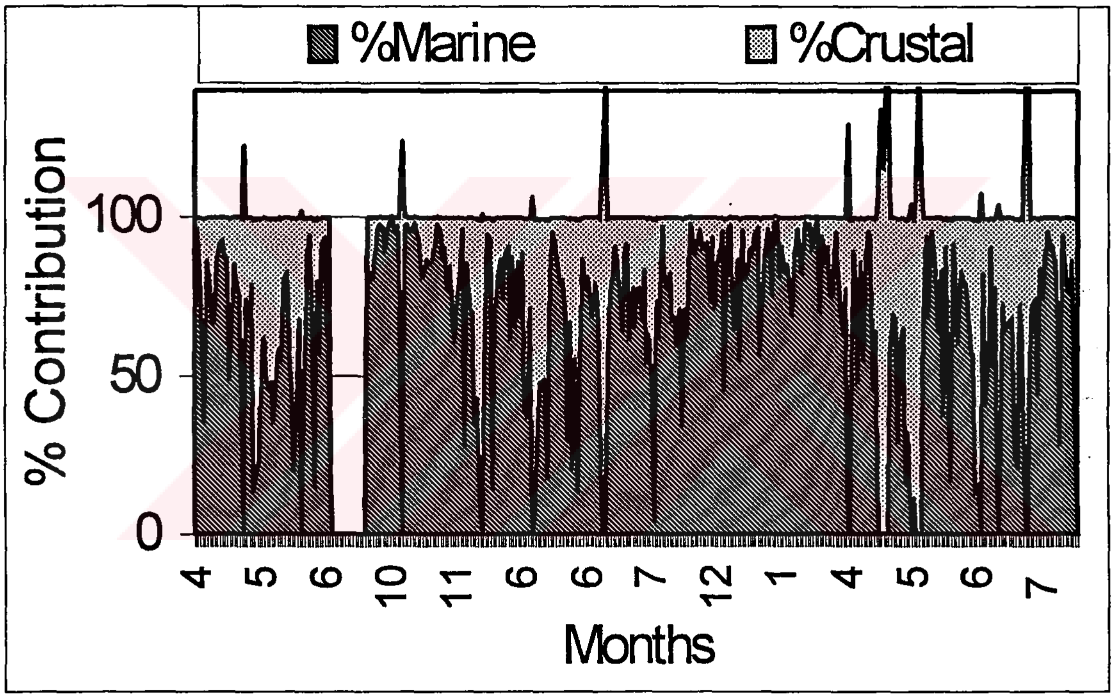


Figure 4.21. Temporal variations of crustal and marine contributions on Na.

As can be seen in Figure 4.21, some times may be because of saharan dust episodes, the loading of crustal material in the atmosphere is so high that almost all of the Na becomes crustal. In addition, the calculated crustal component of Na is larger than measured concentration in some of the aerosol samples may be results from the differences between the compositions of sampled crustal material and Taylaor's crustal abundance table.

Table 4.6 and Figure 4.22 show that the soil particles in the atmosphere make a significant contribution on observed concentrations of Sc, Ce, Al, Sm, Fe, La, Mg, Co, Ca, Mn, K, Cr, Na, V, and Ni changing from 99 % to 40 % from Sc to K and 20% to 40 % from Cr to Ni. Chromium, V and Ni generally termed as pollution elements and it is clearly seen from the table that the significant percentages of these elements can not be explained by this calculation. But Na is mainly contibuted by sea salt particles.

Marine source contributes 31.6 % for Mg, 5.8 % for Ca, 9.8 % for K, 71.2 % for Na, 84.0 % for Cl, 27.7 % for Br and only 2.1 % for SO_4^{2-} concentrations. It was observed that the sulfate is not contributed significantly by neither marine nor crustal sources which tells us that almost all of the sulfate concentration measured comes from anthropogenic sources.

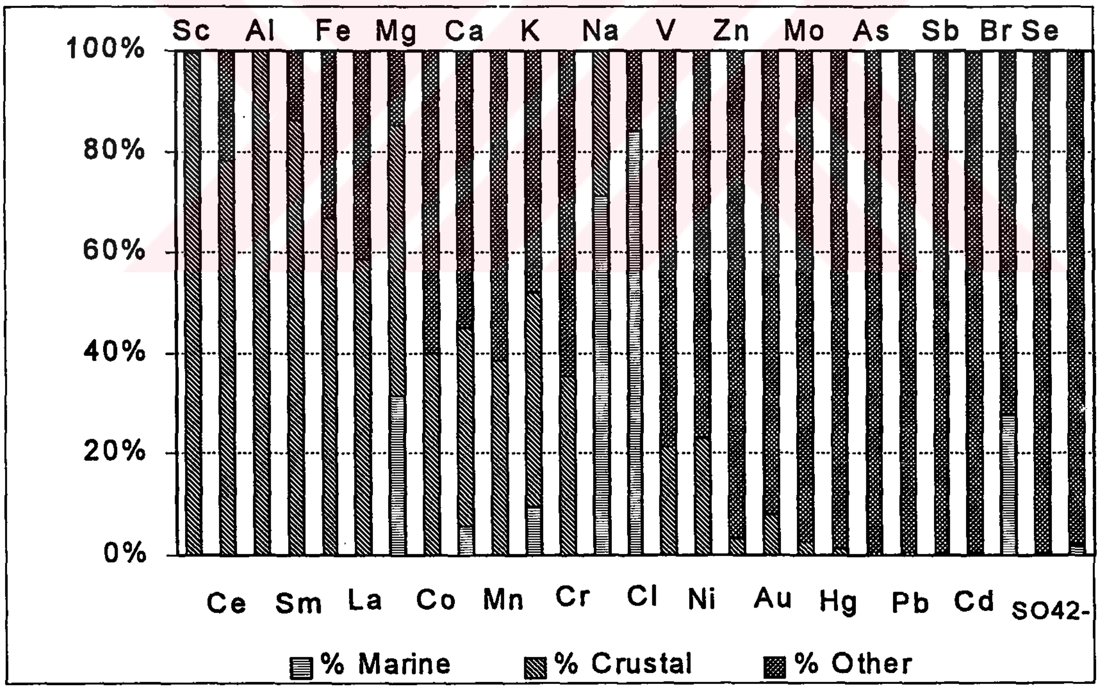


Figure 4.22. Percent contributions of sources on the aerosol composition

Most of the anthropogenic elements did not show significant loadings of both marine and crustal sources. These are, SO_4^{2-}, Se, Br, Cd, Sb, Pb, As, Hg, Mo, Au, Zn, Ni, V, Cr, and Co.

In regional scale studies, the sulfate is one of the most important parameter which represents the acidic components in precipitation and aerosols. However, although sulfate concentration is high in sea water (885 ppm as sulfur), sea salt aerosols do not contribute significantly to the observed sulfate concentration in the Black sea aerosols. Figure 4.23 shows marine contribution to sulfate and total sodium concentration as time series.

Table 4.6. Percent crustal and marine contributions to the observed concentrations

Element	% Marine	% Crustal	% Other
Sc	---	99.7	0.300
Ce	---	78.1	21.9
Al	---	100	---
Sm	---	86.4	13.6
Fe	---	66.7	33.3
La	---	58.8	41.2
Mg	31.6	53.6	14.8
Co	0.020	40.0	60.0
Ca	5.80	39.2	55.0
Mn	0.0010	38.6	61.4
K	9.80	42.1	48.1
Cr	---	35.7	64.3
Na	71.2	28.7	0.100
Cl	84.0	0.310	15.7
V	0.003	21.6	78.4
Ni	0.010	23.3	76.7
Zn	0.001	3.28	96.7
Au	0.110	7.90	92.0
Mo	0.110	2.45	97.4
Hg	0.003	1.37	98.6
As	0.010	0.750	99.2
Pb	---	0.630	99.4
Sb	0.010	0.300	99.7
Cd	0.002	0.430	99.6
Br	27.7	0.150	72.2
Se	0.100	0.160	99.7
SO_4^{2-}	2.10	0.100	97.8

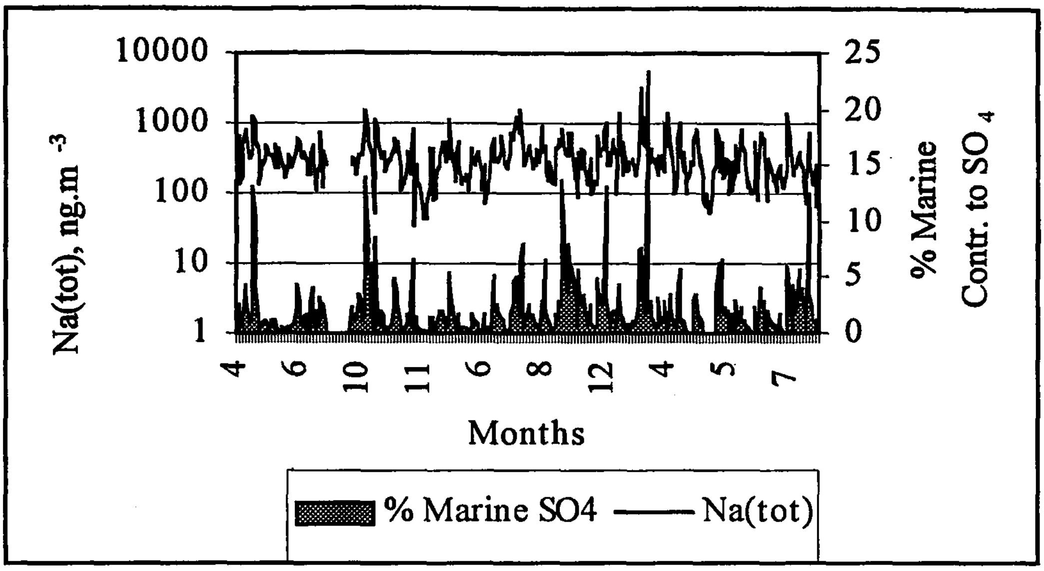


Figure 4.23. Temporal variations of total Na and percent marine contribution to SO_4^{2-} concentration.

The figure indicates that the sea salt fraction of sulfate is approximately 2 % in summer months and about 5 % during the winter months. Only in a few samples the marine contribution to sulfate concentration was exceeded 10 % in winter months because of strong winds on the Black Sea. Consequently, we can say that almost all of the sulfate measured in Black Sea aerosols come from anthropogenic and biogenic sources and it is not affected significantly by the natural sources.

4.5. Source Apportionment and Quantification

To apportion the aerosol measured at a site, several mathematical models have been developed and reported in literature. These models have been used extensively in the air pollution studies to quantify the sources of pollutants (Thurston and Lioy, 1987; Gordon, 1988, Gordon et al., 1984; Tuncel et al., 1989; Henry et al., 1984; Ehrman and Pratsinis, 1992; Sharma and Patil, 1992; and Gao et al., 1994). Most widely used mathematical models in atmospheric pollution studies are; multiple regression analysis, cluster analysis, time series analysis, chemical mass balance, and principal component analysis or factor analysis.

A basic assumption of all receptor models is mass conservation. It is hypothesized that, if p sources exist, and if there is no source emission interaction which causes mass removal or accretion, then the total pollution mass measured at a receptor (M) is the sum of all the individual source's contributions (S_j):

$$M = \sum_{j=1}^{p} S_j \quad \ldots\ldots\ldots\ldots\ldots\ldots 4.5$$

Then the concentration of aerosol property *i*, C*i*, will be:

$$C_i = \sum_{j=1}^{p} \alpha_{ij} f_{ij} S_j \quad \ldots\ldots\ldots 4.6$$

where f_{ij} is the mass fraction of source contribution *j* possessing property *I* in the source emission and α_{ij} is the coefficient of fractionation of property *i* between the source and receptor. In practice, it is not possible to discriminate between pollution from sources of the same type (e.g. between individual automobiles), so *j* usually refers to certain classes of sources (e.g. automotive emissions, residual oil combustion, etc.). The coefficient of fractionation (α_{ij}) likely varies with source type, location and time, as it accounts for the effects of pollution property loss or accretion (relative to the entire mass) in the atmosphere between source and receptor (Thurston and Lioy, 1987).

In this study, factor analysis (FA) was used as source apportionment technique. Factor analysis is applied to elemental data to characterize aerosols with respect to sources and quantify the different sources and their importance for the composition of the aerosols at the monitoring site, Amasra.

4.5.1. Factor Analysis

As discussed in Chapter 2, factor analysis provides preliminary information about the possible sources that might influence a given receptor site. In principle, factor analysis technique distinguishes groups of elements which concentrations fluctuate together from one sample to another and separates these elements into so called factors (Güllü, 1996). Each factor found from FA technique represents a source affecting the samples. In general, in the factor analysis technique, the factors having eigen values greater than unity are retained. The factors having eigen values less than one indicate that factor contribute less than a single variable. In this work, we retained the factors having eigen values greater than unity.

4.5.1.1. Treatment of Values Below Detection Limit

Concentration values below measurement detection limits are a common problems which complicates statistical analysis of measured species in environmental samples. Common methods for handling values below detection limit, such as deletion of samples or substitution of the detection limit, one half the detection limit or multiplication of detection limit with a random number between zero and one are known to produce biased estimates for means and variences and also lack statistical justification (Ölmez et al., 1997).

In this study, for the missing values in the data set, lower quartile values were used. Lower quartile means the value below which 25 percent of the data will fall; the 25th percentile (Statgraphics Manual, 1997). It was observed that treating missing values with lower quartiles or any other values did not alter the results obatined from the factor analysis when the numbers of missing values were less than 10 or 15% of the whole sample size which was the case in this study. In the factor analysis, we included the elements having percent observations greater than 85% in 354 samples. Using receptor background concentrations calculated in this study also did not changed the observed results. Consequently, for the substitution of missing values both receptor background concentrations or lower quartile values of elements can be used without altering the factor analysis results statistically.

4.5.1.2. Extraction of Factors and Treatment of Factor Scores

Factor analysis was performed using the Statgraphics software (Statgraphics Plus, version 3.1, 1997). The aerosol samples which were analyzed by INAA which results were combined with the AAS results for missing elements were used in the factor analysis to have the highest number of variables in the analysis (230 samples and 25 variables).

As shown in Figure 4.24, some of the samples have very high loadings in the factor in which they appear resulting very high factor scores. The samples having factor score values greater than 6 or 7 are generally discarded just for only FA studies in order to avoid the screening of samples having less contribution to each factor (Hopke, 1980). However, in this study, we did not discard the samples with very high factor scores because we saw that elements appearing at the same factor have high contribution to that factor resulting very high factor score. These high factor score values are very informative in the source type and strength when combined with the meteorological data. As discussed in Chapter 2, in the factor analysis, the first step in the derivation of source impacts is to calculate the factor scores for each samples. These factor scores are correlated with their respective pollution sources impacting the site. In another word, higher factor score implies a higher pollution impact and lower factor score implies a lower pollution impact by the source.

The statgraphics software first normalizes the data set before performing factor analysis. It first subtracts the mean from the individual value of any element and divides by the standard deviation of the same element in the data set. After, this normalization, the new data set is used in the FA to compute the factors. When data is normalized, the mean value becomes zero, and factor scores affected heavily by the pollution sources have positive values and the factor scores which are affected by the pollution sources less than the average contribution of sources have negative values. The software then extracts the factors having the eigen values greater than or equal to one and rotates the matrix and gives the rotation statistics. In the varimax rotation process the software simplifies the factor matrix by maximizing the variance of the squared loadings in each column (Statgraphics Manual, 1997). Final output of the software is a matrix of factors and factor loadings which are the results of correlation between original variables (measured parameters; elements and ions) and factors (sources). The factor loadings are the keys to understand the nature of a specific factor. The output includes the communality of each variable also. Communality is the amount of variance an original variable shares with all the other variables in the analysis.

The results of varimax rotated factor analysis is shown in Table 4.7. The time series plots of the factor scores corresponding to each factor are given in Figure 4.24.

Table 4.7. Varimax rotated factor loadings and probable source types

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Communality
Na			0.93		0.90
Mg	0.79		0.35		0.75
Al	0.96				0.95
Ca	0.85				0.73
Cl			0.93		0.91
K	0.82	0.26			0.80
Sc	0.98				0.98
V	0.27	0.75		0.32	0.75
Cr	0.46	0.57			0.62
Mn	0.76	0.25		0.33	0.75
Fe	0.95				0.94
Zn		0.58			0.41
As		0.76	0.29		0.68
Se				0.80	0.65
Br	0.35	0.44	0.59		0.67
Cd		0.78			0.67
Sb		0.66			0.44
La	0.97				0.97
Ce	0.95				0.93
Sm	0.97				0.97
Ni	0.44	0.61			0.58
Pb		0.80			0.65
NO_3^-	0.43	0.32	0.59		0.68
SO_4^{2-}		0.42		0.70	0.67
NH_4^+		0.51		0.59	0.61
% Variance	43.3	17.0	8.4	5.9	74.6
Probable source:	Crustal	Mixed combust.	Marine	Long range	

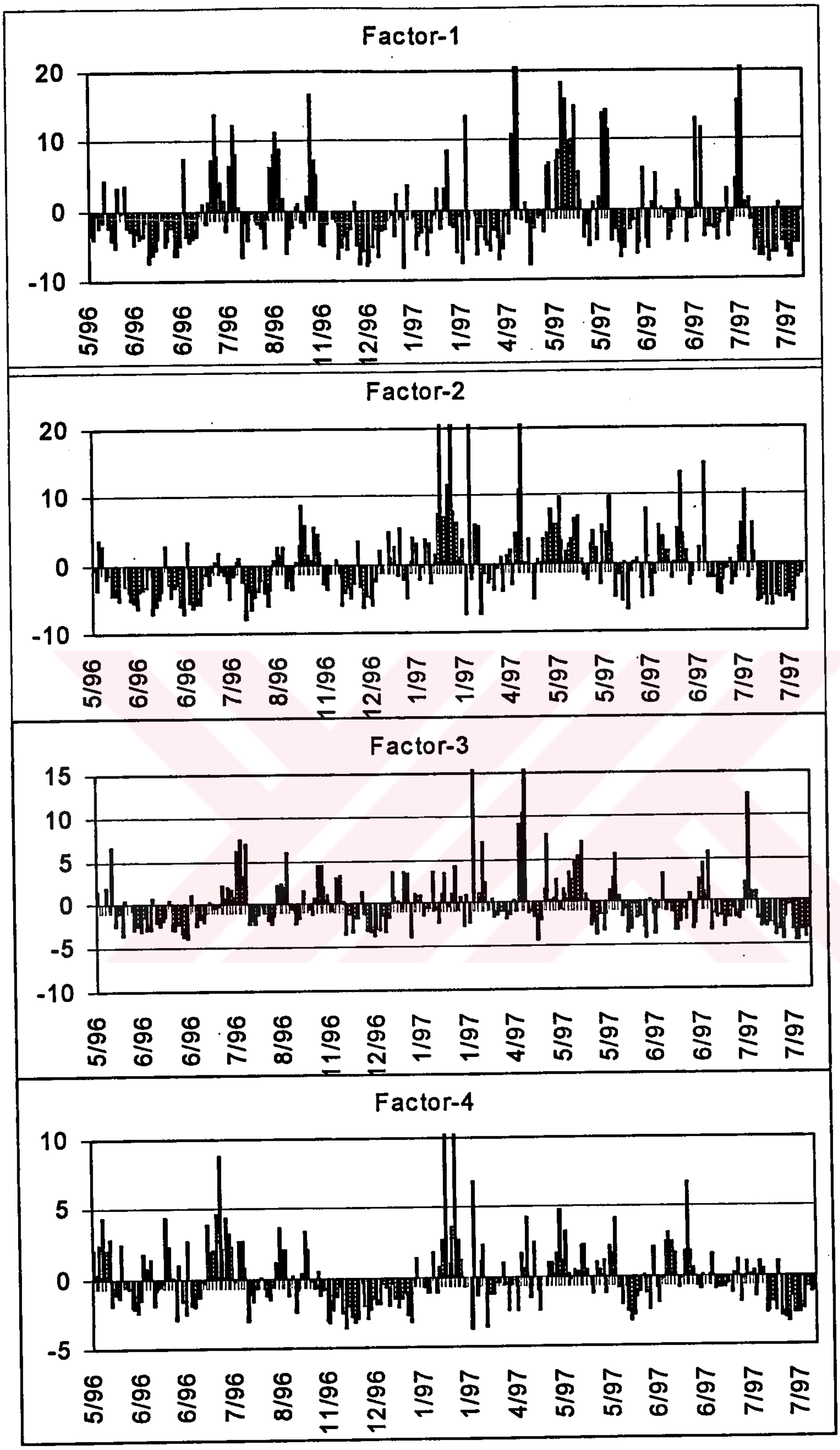


Figure 4.24. Time series plots of factor scores

Factor loadings larger than 0.25 were included in the table, because loadings smaller than this value were considered as insignificant. Four identifiable factors accounted for the 75 % of the total variance in the data set.

The first factor was identified as *crustal factor*, since all the crustal elements like Al, Sc, Mg, Ca, K, Mn, Fe and REE appeared with very high loadings. The crustal factor accounts for a 43.3 % of the system variance which is the highest percent variance in this analysis.

Factor 2 has high loadings of V, Cr, Mn, Zn, As, Br, Cd, Sb, Ni, Pb, SO_4^{2-} and NH_4^+ which are generally produced via combustion processes for example As from coal combustion and V from oil combustion. For this reason the second factor was called as mixed combustion factor. Factor 2 also includes the elements generated from industrial activities. The peaks in the factor scores (Figure 4.24) for this factor showed that the samples impacted by this particular factor coinside with north and north westerly back trajectories. Since these sectors includes industrialized countries, the air masses coming in these direction brings very high amounts of industrial pollutants. Consequently, these polluted air mass combines with the local contributions and forms a factor which is a mixture of both local and remote sources. This combustion factor accounts 17 % of the total variance explained. This factor had very high factor scores in winter months mostly which also indicates the effect of coal combustion, for example, for heating purposes in Turkey and other neighbour countries.

The third factor was again very clearly identified as a marine factor. This factor includes high loadings of marine elements only, like Na, Cl and also weak loadings of Mg, As, Br and NO_3^- which can also emitted from the Black Sea.

The last factor, factor 4, contained a few elements with high loadings like Se, sulfate and ammonium ions and two elements like V and Mn with weak loadings. The presence of Se, sulfate and ammonium ions in the same factor indicates that this factor is caused by long range transport of pollutants to our receptor site. Because, sulfate generally associates with aged particles and in addition, presence of sulfate and ammonium in the same factor shows neutralization of sulfate during long range transports. This factor has a few high factor scores (greater than 6) in winter months and a few in summer months. The fourth factor explained only 6 % of the total variance. If the samples were fine particulates this would change dramatically. In this study, PM-10 preimpaction was used during sample collection to remove the larger particles like crustal and marine aerosols. It is observed that (Güllü, 1996) this impaction can remove only 30 % of the crustal particulates which is not enough to avoid the obscurance of trace elements coming from distant sources. Therefore, because of inefficient removal of large particles by the impaction system we used, this factor became less informative when compared to first and second factors.

When the factor analysis was run for the elements appearing on the first factor (crustal) with high peaks of factor scores, two new factors were obtained with eigen values greater than unity which means that more than one element appears in each factor. This shows that the crustal aerosols in the sampling site are affected by two different sources which may be local and remote sources like Europe, Ex-USSR and Africa. The varimax rotated factor loadings of this analysis is given in Table 4.8.

Table 4.8. Varimax rotated factor loadings and probable sources for the crustal elements

Variable	Factor-1	Factor-2	Communality
Mg	0.30	0.91	0.92
Al	0.72	0.65	0.95
Ca	0.43	0.85	0.90
K	0.78	0.47	0.83
Sc	0.80	0.59	0.98
Mn	0.92		0.88
Fe	0.82	0.55	0.98
La	0.81	0.58	0.98
Ce	0.75	0.63	0.96
Sm	0.81	0.57	0.99
% Variance	87.4	6.4	93.8
Probable Source	Local	Remote sources	

When we applied PSCF to crustal elements having peak factor score values, we have seen that the element to Al ratios of Mg, Ca, K, Mn and Fe are almost constant for each source region. This result is given in Table 4.9 which also includes the average and standard deviations of same elements having no peak factor score values. In this calculation, we selected the region by looking the time spent in the region by 850 hPa trajectory. There is one difficulty in this method that is, for example, the trajectory starts at Africa, spends about 30 hours there and then passes over the Mediterranean and Turkey until arriving at our sampling site. During passage over the two additional regions, aerosol composition on that air parcel may be changed. To avoid this kind of errors, we selected the samples which was mainly represents the source region defined by counting the time spend on that region and during travel. However, this is always the case that the additional regions on the path influence the aerosol composition even in a very short time of travel depending on the concentration on the region. The standard deviations given in the table are because of these influences, otherwise, ideally they should be zero.

Table 4.9. Element to Al ratios of the regional marker elements

Source region	Mg/Al	Ca/Al	K/Al	Mn/Al	Fe/Al
Ex-USSR	0.30	0.38	0.29	0.021	0.77
(STD)	(0.046)	(0.11)	(0.056)	(0.0045)	(0.058)
TURKEY	0.51	1.26	0.28	0.022	0.83
(STD)	(0.052)	(0.33)	(0.053)	(0.0054)	(0.16)
W.EUROPE	0.38	1.31	0.24	0.020	0.72
(STD)	(0.082)	(0.46)	(0.025)	(0.0049)	(0.13)
AFRICA	0.33	0.82	0.21	0.013	0.71
(STD)	(0.025)	(0.051)	(0.026)	(0.0012)	(0.11)
M.EAST	0.55	1.1	0.35	0.016	0.84
(STD)	(0.0071)	(0.22)	(0.061)	(0.0023)	(0.11)
No peak FS	0.74	1.9	0.74	0.044	1.20
(STD)	(0.56)	(1.4)	(0.76)	(0.036)	(0.85)

The elemental ratios of these marker elements to Al can give an idea about the aerosol compositions of each source region. For example, when element to Al ratios of less contributing samples (samples having no high factor scores) are compared, the differences in the ratios become more clear. In addition to this comparison, for most of the marker elements given here have different element to Al ratios for each source region. Consequently, the element to Al ratio studied in this study can be used as a regional tracers for the regions under consideration.

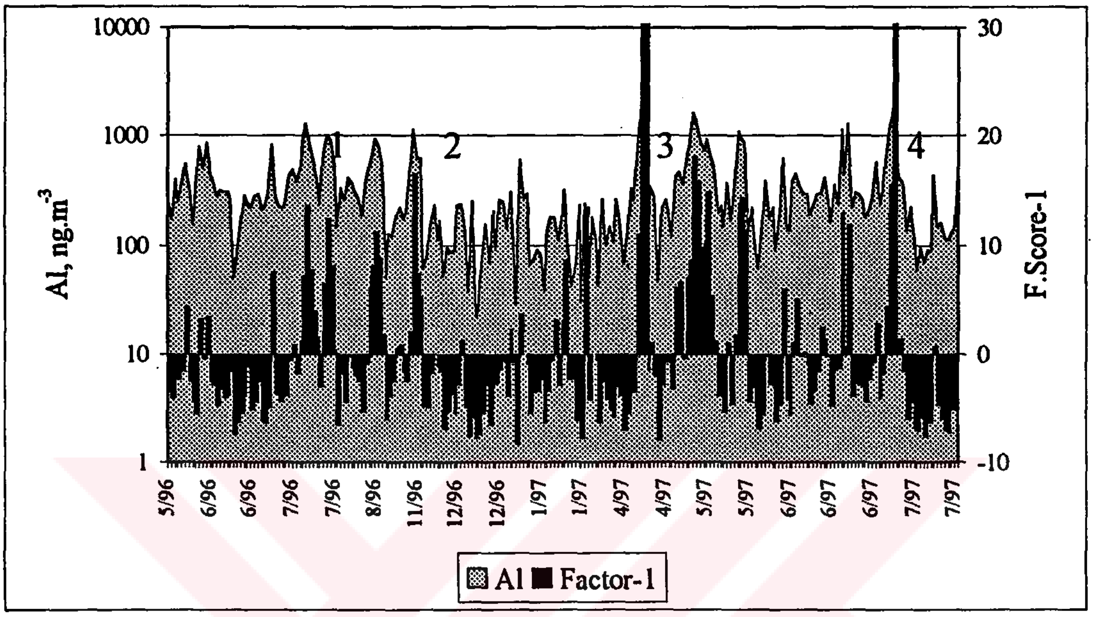
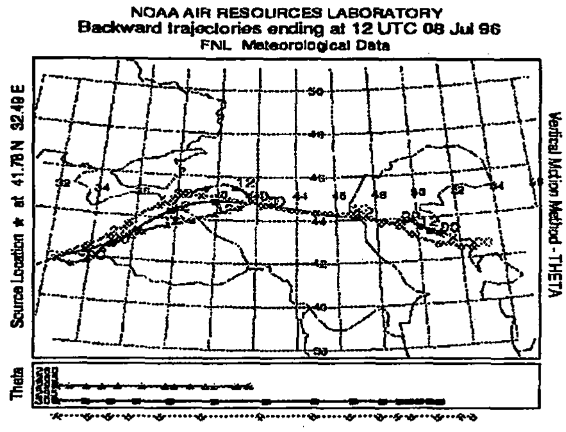


Figure 4.25. Time series plot of Al vs factor scores of crustal source


NOAA AIR RESOURCES LABORATORY
Backward trajectories ending at 12 UTC 08 Jul 96
FNL Meteorological Data
Source Location ★ at 41.78 N 32.49 E
Vertical Motion Method - THETA
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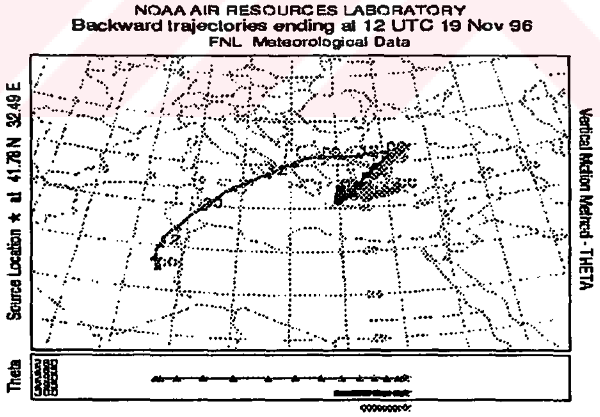
NOAA AIR RESOURCES LABORATORY
Backward trajectories ending at 12 UTC 19 Nov 96
FNL Meteorological Data
Source Location ★ at 41.78 N 32.49 E
Vertical Motion Method - THETA
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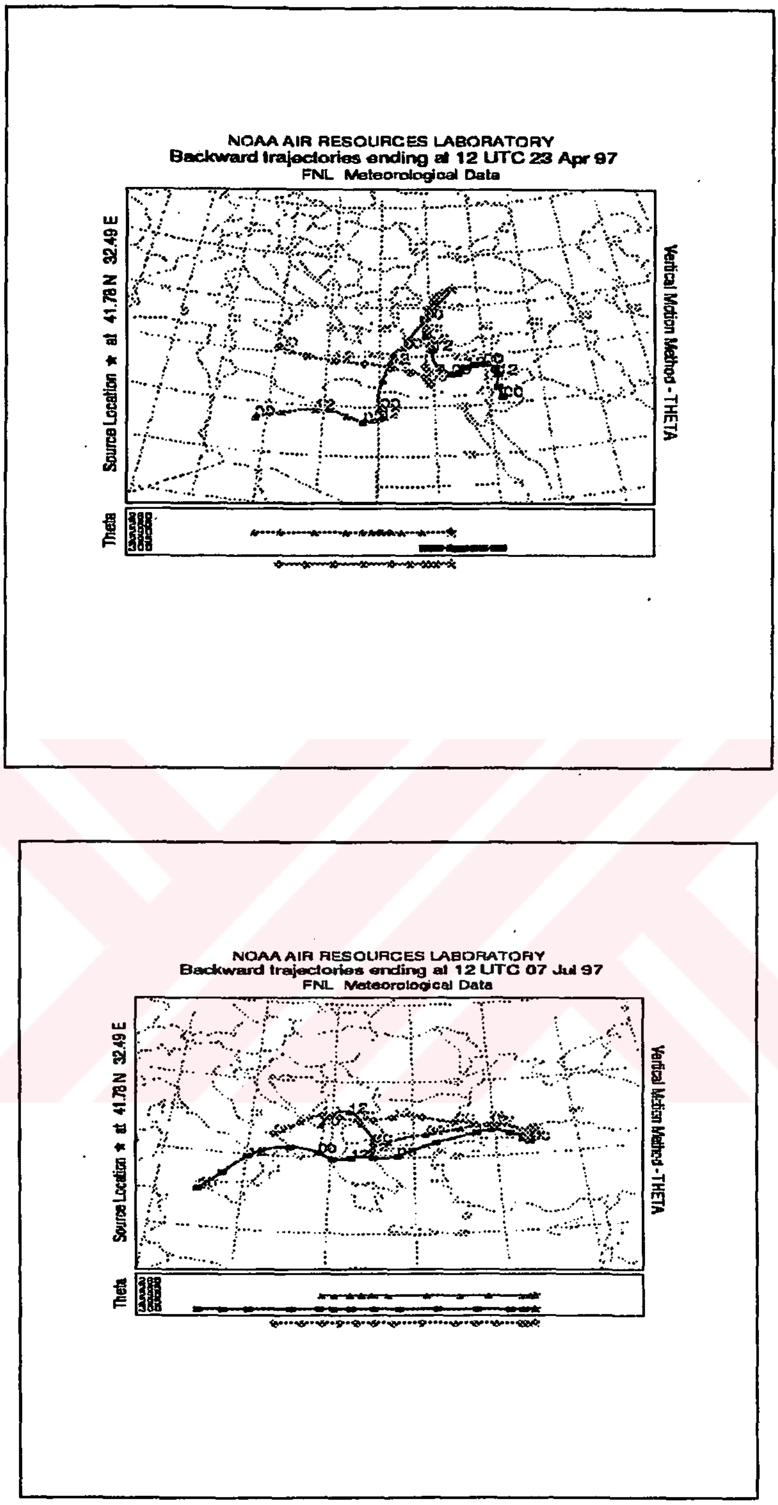

Figure 4.26. Four day back trajectories corresponding to peak values of crustal source factor scores: 1, 2, 3 and 4, respectively.

Figure 4.25 shows the temporal variations of factor scores corresponding to crustal factor and also time series plot of Al. As Al concentration increases (all the crustal elements also behave similirly) the factor score also increases which indicates that there is dust transports from arid and industrialized regions. The paths corresponding to some of high factor score values are shown by back trajectories given in Figure 4.26. It is clear that these trajectories generally originate from African, western European, Russian Federation and Middle East regions. Therefore, one should not conclude that the orders of magnitude increases in the crustal elemental concentrations are from African region, without seeing the tarnsport paths of the air masses. These figures explains this situation very clearly.

4.6. Geographical Locations of Potential Source Regions

As we discussed before factor analysis and other receptor models do not tell anything about the source regions. In order to find the locations of potential sources a source-receptor oriented methods have been developed (e.g. Malm et al., 1986). In these methods, the trajectory information is combined with the measured concentrations to determine the contributions made by each geographic region. One of the method is Potential Source Contribution Function (PSCF) which we used in this study.

4.6.1. Potential Source Contribution Function (PSCF)

The 3-D back trajectories which were ccalculated every day for every sample were segmented 1-hour time intervals and numbers of end points (1-hour segments) were counted in each subregion given in Figure 4.27.

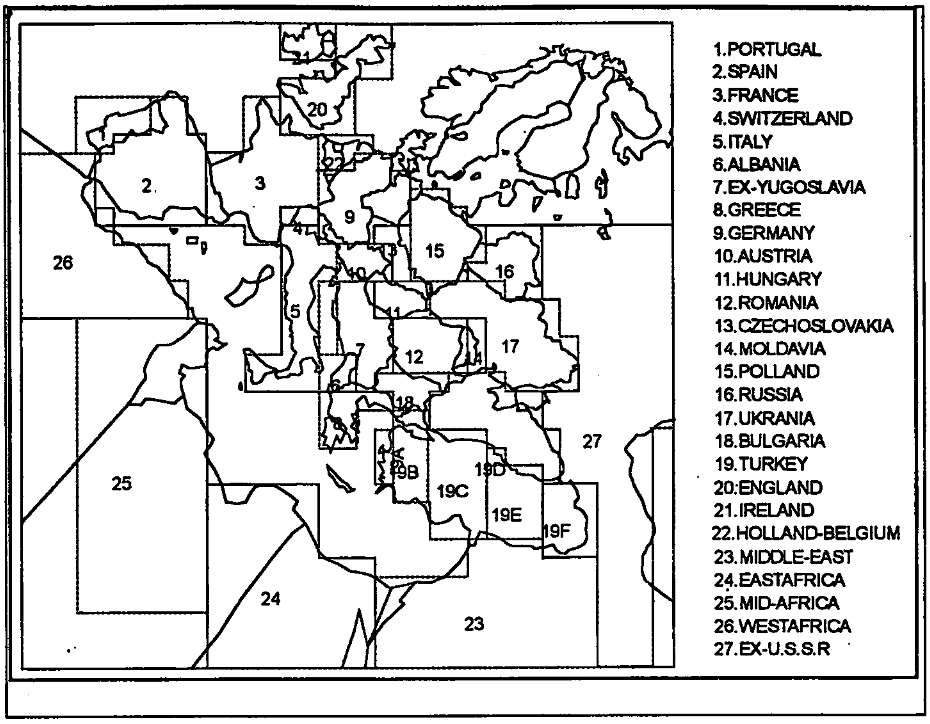

Figure 4.27. The subregions used as potential sources of aerosols

There are 27 subregions in Figure 4.27, in this work, we also included the Black Sea and the Mediterranean Sea as potential source regions so the number of regios increased to 32. We divided Black Sea into two subregions as western and eastern Black Sea. The Mediterranean Sea was divided into 3 subregions as western, central and eastern Mediterranean Sea.

For the calculation of PSCF a program was written (given in Appendix, Table A4). This program counts 1-hour segments in each subregion defined and gives an output (Table A5) which is formed by 32 columns. The first column shows the names of the subregions and the rest of the columns gives the numbers of end points in each subregions for each day of a month. In the last row of the output matrix, it gives the total number of end points accounted.

First of all the residence time of air mass on each subregion P(Aj) was calculated by dividing the number of trajectory segments in each of the defined subregion (n_j) to the total number of trajectory segments, N. Then, the trajectories which correspond to high concentrations of a specific parameter were selected and number of segments of only these polluted trajectories in each of subregions (m_j) were counted. Then PSCF is simply the ratio of m_j to n_j. The n_j is the residence time of air parcels in subregion j and m_j is the residence time of polluted air parcels in same subregion. The ratio of the two is a measure of the fraction of trajectory segments in the subregion which results in high concentrations of pollutants at the receptor site.

Calculated PSCF's for crustal elements (Al, Fe, Ca, Mg, K, La, Ce, Sm, etc...), marine elements (Na and Cl), anthropogenic elements (mixed combustion elements) (Zn, As, Se, Pb, Cd, Sb, Cr, V, Ni, NH_4^+, SO_4^{2-}, etc...), and elements transported from remote sources (Se, V, Mn, NH_4^+ and SO_4^{2-}) are presented in Figures 4.28, 4.29, 4.30 and 4.31, respectively. These plots were prepared by using the samples with highest factor scores for all factors. We assumed that the samples corresponding to high factor score values are polluted samples coming from these subregions.

The potential sources of crustal elements (Figure 4.28) are Middle and West Africa, Middle East and Ex-USSR countries. The most important source of crustal elements is West Africa with the highest mj/nj value of 0.65. Western European countries also contribute the crustal elemental concentrations at the our receptor site. As the figure shows the Western European countries have mj/nj values of about 0.10. However, we have observed that these subregions contribute to the elemental concentrations of both anthropogenic and crustal elements through industrial activities.

The PSCF's of anthropogenic elements on the other hand are very different from those of crustal and marine (Figure 4.29). For these elements the potential sources are Western and Eastern European countries, Turkey and other Black Sea countries. The mj/nj fractions calculated for these subregions change in between 0.05 and 0.12.

When the air masses reaching our receptor site after passing through the Black Sea, Aegean Sea and Mediterranean Sea bring marine aerosols which have high concentrations of Na and Cl. This is shown in Figure 4.30 in which the potential sources of Na and Cl are the subregions located around these three seas. Trajectories passes over seas during their travels from the subregions to receptor site.

In the factor analysis section we have found that Se, V, Mn, NH_4^+ and SO_4^{2-} are transported from remote source regions to our receptor site. The PSCF for these elements showed that their potential sources are germany, Moldavia, Polland, Ukraine and Ex-USSR countries. There are other potential sources appearing in Figure 4.31 like Turkey and Western and Eastern Black Sea. Turkey has mj/nj value of 0.016 and contributes locally when the air masses passes over Western Cities of Turkey. Western and Eastern Black Sea regions can not be a potential source for Mn and V, for example, however, this situation indicates that the the air masses coming from remote source areas can stop on the Black Sea and become stagnant there. So the PSCF program can not differentiate since it counts only the 1-hour segments spent in each subregions.

As a conclusion the PSCF calculations showed that there are three principle components in the Western Black Sea cost of Turkey. The main source regions of crustal, anthropogenic and marine elements are African subregions and Middle East, Western and Eastern European countries and the seas around Turkey, respectively.

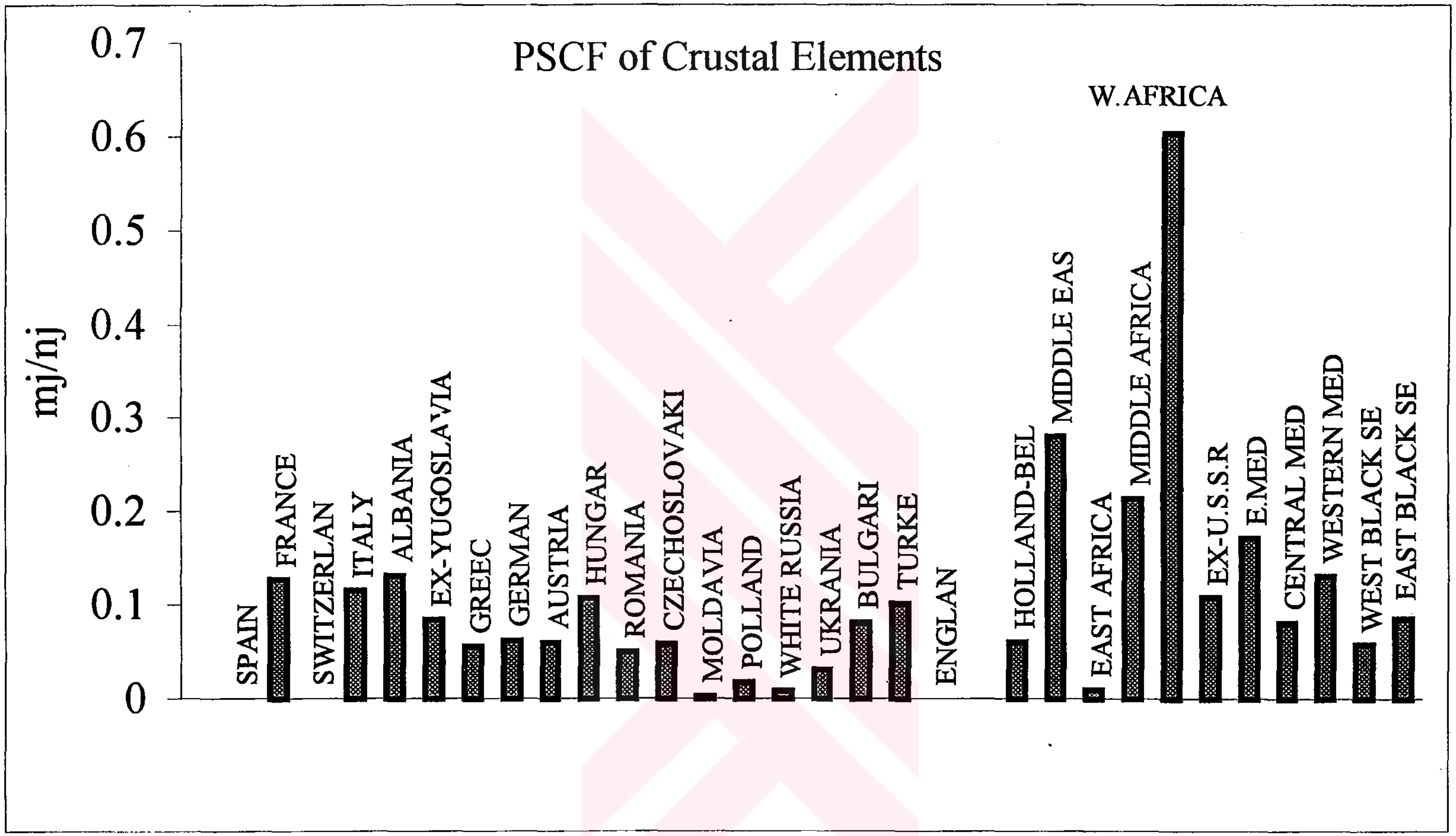

Figure 4.28. PSCF of crustal elements.

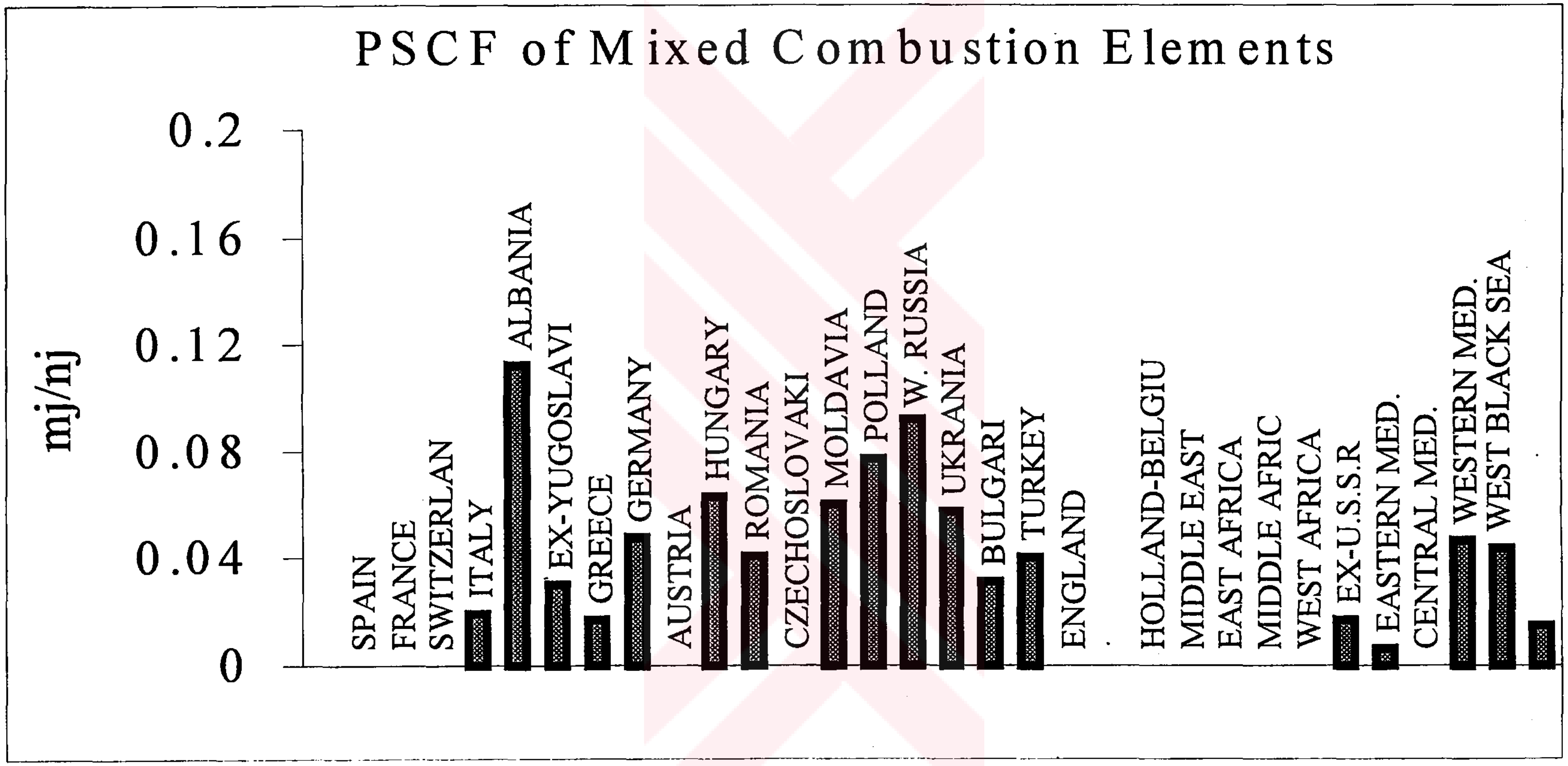

Figure 4.29. PSCF of mixed combustion elements

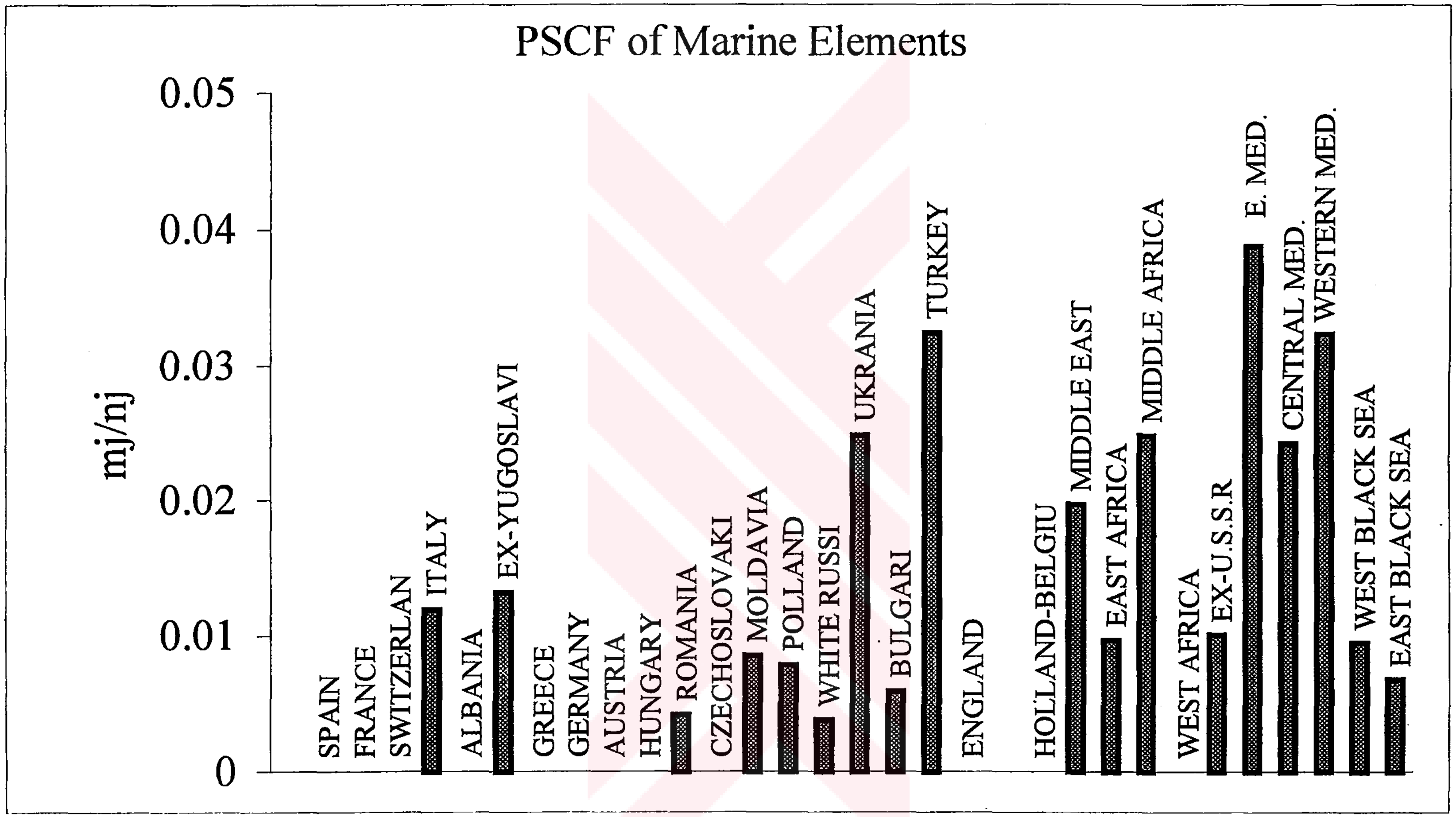

Figure 4.30. PSCF of marine elements

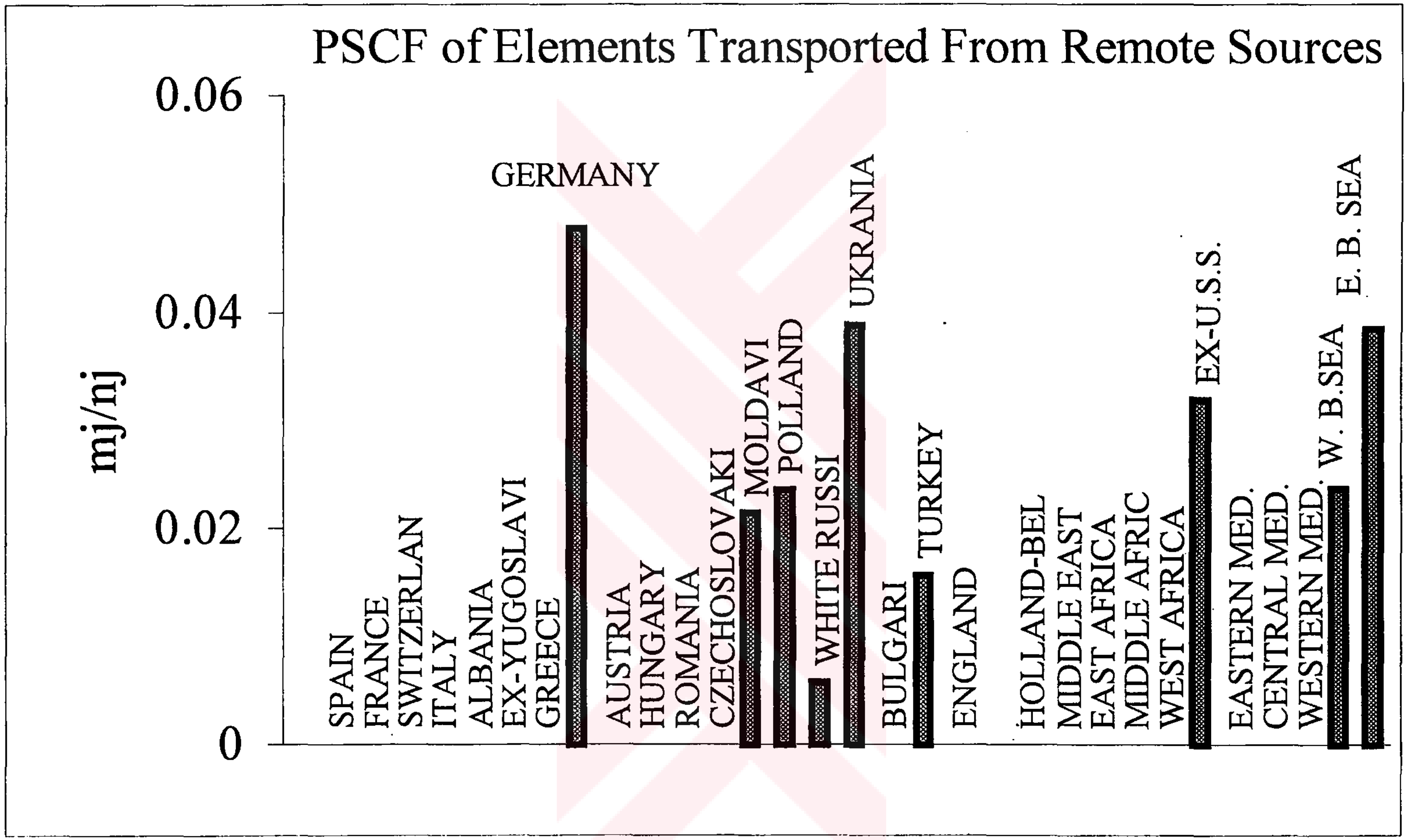

Figure 4.31. PSCF of elements transported from remote sources

CHAPTER 5

CONCLUSION

Elemental concentrations of major ions and trace elements determined by INAA, AAS, and IC in the Turkish western Black Sea region atmosphere for the years 1995 and 1997 were discussed in this study.

To be able to demonstrate the possible existence of differences in the concentrations of the elements in the atmosphere over the Black Sea region of Turkey and to determine the general features of the aerosols at the receptor site, data for aerosols from a number of different sites were compared with the results of the present study. Concentrations of crustal elements and pollution derived elements measured at the Amasra station were found to be lower than all values reported for comparable receptor sites in the Europe and Mediterranean coasts. Since the observed lower concentrations of crustal elements in this study relative to other sites is explained by the presence of preimpector on the sampler and also the frequently observed local rain events at our receptor site.

Concentrations of elements were found to be vary greatly on time scales ranging from days to seasons. In the past studies, the variability of the elemental concentrations in the Black Sea atmosphere mainly explained by the seasonal transport patterns, precipitation scavenging and source strengths. In order to understand air mass transport patterns and to explain observed seasonal variations of the measured concentrations, 4-day back trajectories (3-D), at three barometric levels ending at Amasra station were calculated daily for all of the sampling days. The classification of trajectories showed that the most frequent air mass movements occur from north, northwest and west sectors.

For the long term variations of the concentrations of marine, crustal and pollution elements, it has been found that the local rain events are the determining factor over the Black Sea atmosphere especially for the marine and crustal elements.

Studies performed to identify sources were performed in two levels. First, general source categories (or components of aerosol mass) were identified by enrichment factors and correlation analysis. Calculation of enrichment factors have revealed three general source groups, namely, a crustal source, a marine source and an anthropogenic source. Then, one of the most widely used source apportionment technique, Factor Analysis (FA), was applied to elemental data matrix to characterize the aerosol with respect to sources and quantify the different sources and their importance for the aerosol composition at the monitoring site, Amasra. Factor analysis identified four main sources, namely, a crustal source, a pollution source, a marine source and a second anthropogenic source which we identified it as a long range transport factor.

The conclusions of this study concerning the major sources of aerosol material are similar to those reported in many other similar studies, though the relative importance of sources change from site to site. The interactions of meteorological factors with emission source distributions and strengths make the Western Black Sea aerosol as a unique character. In this study, most of the afford has been spent to the understanding of these interactions which is very critical for the accurate prediction of atmospheric inputs.

Potential source contribution function identified two source regions for crustal and marine elements as African and Middle East countries. However, for anthropogenic elements the potential sources were identified as Europe, Turkey and other Black Sea countries.

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APPENDIX

Table A1. The job utilized for retrieving air mass back trajectories from ECMWF

```
#!/bin/csh/ -f

#######################################################
#QSUB -q ecgate1.normal
#
#------------------------------------------------------
# Combine the stderr and stdout
#------------------------------------------------------
#QSUB -eo
#
#------------------------------------------------------
# Run under the Korn shell (standard)
#------------------------------------------------------
#QSUB -s /bin/ksh
#
#------------------------------------------------------
# JOB-NAME
#------------------------------------------------------
#QSUB -r wstraj
#
#------------------------------------------------------
# End of QSUB parameters
#------------------------------------------------------
#QSUB
#------------------------------------------------------
# Start the executable
#------------------------------------------------------

cat >etre<<eof
41.783 32.483 900.
41.783 32.483 850.
41.783 32.483 700.
41.783 32.483 500.
eof

foreach ym (9710)
foreach dy (01 02 03 04 05 06 07 08 09 10 11 12 13 14 15 16 17 18 19
20 \
21 22 23 24 25 26 27 28 29 30 31)

set ymd="$ym""$dy"
set dats="$ymd"12
set datt=`cay<<eof \
$dats \
eof`00
/home/ms/ie/dur/traj/gettraj  -S $dats -T $datt \
-t 213 -x tre -w -b
mv scratch/trajout scratch/trajout."$dats"
mail durank@curie.chem.metu.edu.tr < scratch/trajout."$dats"
\rm -f  scratch/trajout."$dats"
\rm -f scratch/19"$datt"_19"$dats"_19"$dats"
end
end
```

Table A2. The trajectory data base obtained from the request file given in Table A.1.

```
TRAJECTORY NUMBER    1

 START:  LAT   41.8 DEG N              PRESSURE LEVEL  900 HPA
         LON   32.5 DEG E              TIME 12 UTC ON  1. 1.97

 END:                                  TIME  0 UTC ON 29.12.96

 ANALYSIS FIELDS FROM                  TIME 12 UTC ON  1. 1.97

 HOURS   LAT       LON     LEVEL  U-WIND V-WIND W-WIND    PS

     0  41.78 N   32.49 E   900.0     8.2     4.4  -0.06    970.5
     1  41.65 N   32.13 E   903.7     8.1     4.1  -0.14    972.9
     2  41.52 N   31.78 E   909.8     8.1     3.7  -0.20    977.7
     3  41.40 N   31.43 E   918.0     8.1     3.4  -0.25    983.4
     4  41.30 N   31.08 E   927.3     8.1     3.1  -0.27    988.7
     5  41.20 N   30.73 E   936.9     8.1     3.1  -0.26    992.6
     6  41.09 N   30.39 E   945.6     8.0     3.4  -0.22    994.6
     7  40.97 N   30.07 E   951.2     7.1     4.1  -0.09    993.5
     8  40.82 N   29.78 E   952.1     6.3     4.9   0.04    989.3
     9  40.65 N   29.52 E   948.6     5.7     5.7   0.16    982.6
    10  40.45 N   29.30 E   941.2     5.0     6.4   0.25    973.9
    11  40.24 N   29.10 E   931.1     4.4     6.8   0.31    964.3
    12  40.02 N   28.92 E   920.1     3.9     7.0   0.31    955.2
    13  39.78 N   28.75 E   910.2     3.8     7.2   0.24    948.6
    14  39.54 N   28.59 E   903.7     3.7     7.3   0.12    946.0
    15  39.31 N   28.43 E   901.5     3.6     7.4   0.00    947.9
    16  39.06 N   28.28 E   902.6     3.3     7.5  -0.07    953.0
    17  38.82 N   28.16 E   905.0     2.8     7.5  -0.07    959.2
    18  38.58 N   28.06 E   906.5     2.1     7.3  -0.02    964.7
    19  38.34 N   27.97 E   907.8     2.1     7.5  -0.05    969.0
    20  38.09 N   27.88 E   911.1     2.1     7.8  -0.13    972.9
    21  37.83 N   27.80 E   917.7     2.2     8.4  -0.24    977.4
    22  37.54 N   27.70 E   929.2     2.5     9.7  -0.40    984.7
    23  37.20 N   27.60 E   945.6     2.7    11.4  -0.51    996.3
    24  36.81 N   27.49 E   963.1     2.6    12.6  -0.45   1010.0
    25  36.42 N   27.41 E   974.4     1.6    11.7  -0.19   1018.8
    26  36.06 N   27.35 E   977.7     1.4    10.6   0.01   1020.3
    27  35.73 N   27.29 E   976.0     1.6     9.8   0.08   1017.8
    28  35.42 N   27.22 E   973.4     1.9     9.4   0.07   1014.7
    29  35.12 N   27.14 E   972.0     2.2     9.2   0.01   1013.5
    30  34.82 N   27.05 E   972.3     2.5     9.2  -0.03   1014.2
    31  34.53 N   26.93 E   973.6     3.3     8.9  -0.04   1015.6
    32  34.25 N   26.79 E   975.2     4.0     8.5  -0.05   1017.0
    33  33.98 N   26.62 E   976.8     4.6     8.1  -0.04   1017.9
    34  33.72 N   26.44 E   978.0     5.0     7.8  -0.03   1018.4
    35  33.48 N   26.24 E   979.0     5.2     7.5  -0.03   1018.7
    36  33.23 N   26.03 E   980.2     5.4     7.4  -0.04   1019.0
    37  32.98 N   25.83 E   981.5     5.2     8.0  -0.04   1018.9
    38  32.72 N   25.63 E   982.5     4.9     8.6  -0.02   1018.4
    39  32.43 N   25.45 E   982.2     4.7     9.4   0.03   1017.1
    40  32.10 N   25.28 E   979.6     4.4    10.4   0.11   1013.7
    41  31.75 N   25.12 E   974.6     3.9    11.3   0.17   1007.5
    42  31.38 N   24.99 E   968.7     3.0    11.8   0.16   1000.4
    43  31.01 N   24.89 E   964.4     2.2    11.0   0.08    996.2
    44  30.67 N   24.82 E   962.8     1.3    10.0   0.01    996.4
    45  30.36 N   24.79 E   962.9     0.5     9.0  -0.01    999.3
    46  30.08 N   24.79 E   963.5    -0.4     8.1  -0.02   1002.6
```

Table A2(continued)

47	29.83 N	24.82 E	964.3	-1.3	7.3	-0.02	1005.2
48	29.61 N	24.89 E	965.0	-2.2	6.6	-0.02	1006.9
49	29.40 N	24.97 E	965.6	-2.0	6.1	-0.01	1008.2
50	29.21 N	25.04 E	965.7	-1.6	5.7	0.00	1008.7
51	29.04 N	25.09 E	965.3	-1.3	5.3	0.02	1008.9
52	28.87 N	25.13 E	964.5	-0.9	4.9	0.03	1008.5
53	28.72 N	25.16 E	963.4	-0.6	4.5	0.04	1007.9
54	28.58 N	25.17 E	962.1	-0.2	4.2	0.04	1007.3
55	28.44 N	25.18 E	960.6	-0.3	4.1	0.04	1006.5
56	28.32 N	25.20 E	959.0	-0.4	3.8	0.05	1005.7
57	28.19 N	25.22 E	957.3	-0.6	3.6	0.05	1005.1
58	28.08 N	25.24 E	955.6	-0.8	3.3	0.05	1004.5
59	27.98 N	25.27 E	953.8	-1.0	3.1	0.05	1004.0
60	27.88 N	25.31 E	952.0	-1.2	2.8	0.05	1003.5
61	27.80 N	25.36 E	950.2	-1.3	2.5	0.05	1003.3
62	27.72 N	25.41 E	948.4	-1.4	2.3	0.05	1003.0
63	27.65 N	25.46 E	946.7	-1.4	2.0	0.05	1002.8
64	27.59 N	25.51 E	944.9	-1.4	1.7	0.05	1002.6
65	27.54 N	25.56 E	943.0	-1.4	1.4	0.05	1002.5
66	27.50 N	25.62 E	941.0	-1.5	1.1	0.06	1002.3
67	27.46 N	25.67 E	939.0	-1.3	1.2	0.05	1001.9
68	27.42 N	25.71 E	937.1	-1.2	1.3	0.05	1001.5
69	27.38 N	25.75 E	935.3	-1.0	1.4	0.05	1001.0
70	27.33 N	25.79 E	933.6	-0.9	1.6	0.05	1000.4
71	27.28 N	25.82 E	932.1	-0.8	1.7	0.04	999.9
72	27.22 N	25.85 E	930.6	-0.7	1.8	0.04	999.2
73	27.17 N	25.87 E	928.8	-0.6	1.2	0.06	998.7
74	27.14 N	25.89 E	926.4	-0.6	0.6	0.07	998.5
75	27.13 N	25.92 E	923.5	-0.5	0.1	0.09	998.5
76	27.13 N	25.93 E	919.9	-0.5	-0.4	0.11	998.6
77	27.15 N	25.95 E	915.6	-0.5	-0.8	0.13	999.0
78	27.19 N	25.97 E	910.4	-0.6	-1.2	0.16	999.4
79	27.22 N	25.99 E	904.9	-0.5	-1.2	0.15	999.5
80	27.26 N	26.01 E	899.6	-0.5	-1.3	0.14	999.5
81	27.31 N	26.03 E	894.7	-0.5	-1.5	0.13	999.7
82	27.36 N	26.04 E	890.3	-0.4	-1.8	0.12	999.9
83	27.42 N	26.06 E	886.5	-0.2	-2.0	0.10	1000.2
84	27.49 N	26.06 E	883.5	-0.2	-2.2	0.08	1000.3

TRAJECTORY NUMBER 2

START: LAT 41.8 DEG N PRESSURE LEVEL 850 HPA
LON 32.5 DEG E TIME 12 UTC ON 1. 1.97

END: TIME 0 UTC ON 29.12.96

ANALYSIS FIELDS FROM TIME 12 UTC ON 1. 1.97

HOURS	LAT	LON	LEVEL	U-WIND	V-WIND	W-WIND	PS
0	41.78 N	32.49 E	850.0	9.6	4.8	0.00	970.5
1	41.64 N	32.07 E	852.3	9.6	4.3	-0.13	975.2
2	41.51 N	31.65 E	859.1	9.6	3.6	-0.25	983.0
3	41.40 N	31.23 E	870.1	9.9	3.1	-0.36	991.7
4	41.31 N	30.80 E	884.3	10.2	2.9	-0.43	999.3
5	41.21 N	30.35 E	900.5	10.3	3.0	-0.46	1004.1
6	41.10 N	29.91 E	917.0	10.1	3.5	-0.46	1006.2
7	40.97 N	29.51 E	930.8	9.1	4.6	-0.30	1005.0

Table A2(continued)

8	40.80 N	29.13 E	939.2	8.1	5.8	-0.13	1001.2
9	40.59 N	28.80 E	941.1	7.4	7.1	0.03	995.4
10	40.35 N	28.51 E	937.6	6.6	8.1	0.17	987.7
11	40.08 N	28.25 E	930.3	5.6	8.6	0.24	979.6
12	39.80 N	28.03 E	922.6	4.7	8.9	0.19	973.4
13	39.50 N	27.84 E	918.4	4.0	8.9	0.05	971.4
14	39.21 N	27.68 E	919.1	3.3	8.8	-0.08	974.2
15	38.93 N	27.55 E	923.2	2.5	8.7	-0.14	979.6
16	38.66 N	27.47 E	927.6	1.7	8.3	-0.11	985.1
17	38.39 N	27.41 E	930.3	1.0	7.9	-0.04	989.2
18	38.15 N	27.38 E	931.0	0.4	7.3	0.00	991.5
19	37.90 N	27.36 E	932.5	0.8	7.7	-0.08	993.5
20	37.64 N	27.31 E	937.4	1.2	8.3	-0.19	996.8
21	37.36 N	27.26 E	945.8	1.6	9.2	-0.28	1002.3
22	37.05 N	27.19 E	956.4	1.9	10.1	-0.31	1009.5
23	36.71 N	27.11 E	965.8	2.0	10.7	-0.21	1015.9
24	36.36 N	27.02 E	970.1	2.2	11.1	-0.02	1018.5
25	36.01 N	26.94 E	968.5	2.0	10.1	0.12	1017.2
26	35.70 N	26.86 E	963.8	2.0	9.6	0.14	1014.2
27	35.39 N	26.78 E	959.6	2.2	9.3	0.09	1012.0
28	35.09 N	26.69 E	957.6	2.5	9.2	0.02	1011.4
29	34.80 N	26.58 E	957.7	2.8	9.0	-0.03	1012.4
30	34.51 N	26.46 E	959.3	3.2	8.9	-0.06	1014.1
31	34.22 N	26.32 E	961.5	3.9	8.6	-0.06	1015.9
32	33.95 N	26.16 E	963.6	4.5	8.3	-0.05	1017.3
33	33.69 N	25.97 E	965.3	5.0	8.0	-0.04	1018.5
34	33.43 N	25.77 E	966.7	5.4	7.9	-0.04	1019.1
35	33.17 N	25.56 E	968.4	5.7	7.9	-0.05	1019.1
36	32.91 N	25.33 E	970.2	5.9	8.1	-0.05	1018.6
37	32.63 N	25.11 E	971.4	5.8	9.2	-0.01	1017.4
38	32.31 N	24.89 E	970.6	5.7	10.6	0.06	1014.5
39	31.94 N	24.68 E	967.0	5.2	12.0	0.14	1008.5
40	31.54 N	24.50 E	961.7	4.1	12.7	0.15	1001.0
41	31.13 N	24.36 E	957.7	2.8	12.6	0.08	996.9
42	30.72 N	24.27 E	956.4	2.0	12.3	0.00	997.7
43	30.34 N	24.21 E	957.0	1.3	11.1	-0.03	1001.2
44	30.00 N	24.18 E	957.8	0.6	10.1	-0.02	1004.0
45	29.69 N	24.16 E	958.4	-0.1	9.2	-0.01	1005.5
46	29.41 N	24.18 E	958.7	-0.8	8.3	-0.01	1006.0
47	29.15 N	24.23 E	959.0	-1.6	7.6	-0.01	1006.0
48	28.92 N	24.30 E	959.0	-2.3	6.9	0.00	1005.9
49	28.70 N	24.38 E	958.4	-2.0	6.4	0.03	1005.7
50	28.50 N	24.45 E	957.2	-1.6	6.0	0.04	1005.3
51	28.31 N	24.50 E	955.6	-1.2	5.6	0.05	1004.8
52	28.13 N	24.53 E	954.0	-0.8	5.3	0.04	1004.3
53	27.97 N	24.56 E	952.5	-0.4	5.1	0.04	1003.9
54	27.81 N	24.56 E	951.3	0.0	4.9	0.03	1003.5
55	27.65 N	24.57 E	950.2	-0.3	4.6	0.03	1002.8
56	27.51 N	24.59 E	949.1	-0.7	4.3	0.03	1002.1
57	27.38 N	24.62 E	948.0	-1.0	4.0	0.03	1001.1
58	27.25 N	24.66 E	946.7	-1.4	3.7	0.04	1000.1
59	27.13 N	24.72 E	945.2	-1.8	3.4	0.04	998.8
60	27.03 N	24.79 E	943.6	-2.2	3.2	0.05	997.4
61	26.93 N	24.87 E	941.8	-2.0	2.8	0.05	996.1
62	26.84 N	24.94 E	940.0	-1.9	2.5	0.05	994.9
63	26.77 N	25.01 E	938.2	-1.7	2.1	0.05	993.7
64	26.71 N	25.07 E	936.3	-1.6	1.8	0.05	992.7
65	26.66 N	25.12 E	934.6	-1.5	1.4	0.05	991.9

Table A2 (continued)

66	26.62 N	25.18 E	932.8	-1.4	1.1	0.05	991.1
67	26.58 N	25.22 E	931.1	-1.2	1.2	0.05	990.5
68	26.54 N	25.26 E	929.5	-1.1	1.3	0.05	989.6
69	26.50 N	25.30 E	927.9	-1.0	1.4	0.04	988.7
70	26.45 N	25.34 E	926.3	-1.0	1.5	0.04	987.7
71	26.40 N	25.37 E	924.6	-0.9	1.6	0.05	986.6
72	26.35 N	25.41 E	922.9	-0.9	1.7	0.05	985.4
73	26.30 N	25.44 E	921.2	-0.9	1.0	0.05	984.6
74	26.28 N	25.48 E	919.3	-1.0	0.4	0.05	984.2
75	26.28 N	25.51 E	917.2	-1.1	-0.2	0.06	984.4
76	26.30 N	25.55 E	915.1	-1.1	-0.9	0.06	984.9
77	26.34 N	25.59 E	912.7	-1.1	-1.5	0.07	985.8
78	26.39 N	25.63 E	910.1	-1.1	-2.0	0.08	987.3
79	26.46 N	25.67 E	907.3	-0.7	-1.8	0.08	988.3
80	26.51 N	25.69 E	904.5	-0.4	-1.8	0.08	989.1
81	26.57 N	25.69 E	901.8	0.0	-1.8	0.07	990.0
82	26.63 N	25.69 E	899.2	0.3	-1.8	0.07	990.9
83	26.69 N	25.67 E	896.9	0.6	-2.0	0.06	991.7
84	26.76 N	25.65 E	894.9	0.7	-2.1	0.05	992.2

TRAJECTORY NUMBER 3

START: LAT 41.8 DEG N PRESSURE LEVEL 700 HPA
LON 32.5 DEG E TIME 12 UTC ON 1. 1.97

END: TIME 0 UTC ON 29.12.96

ANALYSIS FIELDS FROM TIME 12 UTC ON 1. 1.97

HOURS	LAT	LON	LEVEL	U-WIND	V-WIND	W-WIND	PS
0	41.78 N	32.49 E	700.0	16.0	0.2	-0.12	970.5
1	41.77 N	31.79 E	706.0	15.6	1.0	-0.20	999.1
2	41.73 N	31.13 E	714.3	15.0	1.5	-0.26	1018.0
3	41.67 N	30.49 E	724.0	14.4	1.9	-0.28	1025.8
4	41.60 N	29.88 E	734.7	13.7	2.2	-0.31	1026.7
5	41.53 N	29.31 E	747.7	13.0	2.5	-0.41	1024.3
6	41.45 N	28.76 E	765.0	12.2	2.5	-0.56	1020.4
7	41.36 N	28.25 E	784.8	11.6	2.7	-0.54	1015.2
8	41.27 N	27.76 E	802.7	11.2	2.9	-0.46	1010.2
9	41.17 N	27.28 E	817.3	11.0	3.2	-0.35	1006.2
10	41.06 N	26.82 E	828.7	10.8	3.7	-0.28	1003.2
11	40.94 N	26.36 E	838.2	10.4	4.0	-0.25	1001.3
12	40.81 N	25.93 E	846.6	9.9	4.0	-0.22	1000.2
13	40.68 N	25.52 E	853.1	9.1	3.7	-0.15	1000.6
14	40.57 N	25.14 E	857.3	8.8	3.3	-0.08	1001.9
15	40.47 N	24.77 E	859.5	8.8	2.9	-0.04	1004.2
16	40.38 N	24.39 E	860.6	9.0	2.8	-0.03	1007.1
17	40.29 N	24.01 E	861.5	9.2	3.0	-0.02	1010.2
18	40.18 N	23.61 E	861.3	9.5	3.8	0.04	1010.9
19	40.04 N	23.20 E	857.1	9.8	4.3	0.20	1004.5
20	39.89 N	22.78 E	845.9	10.3	5.0	0.44	987.6
21	39.72 N	22.34 E	828.0	11.1	5.9	0.56	964.1
22	39.51 N	21.86 E	811.2	11.4	6.8	0.35	947.2
23	39.28 N	21.39 E	807.1	10.6	7.3	-0.15	951.8
24	39.04 N	20.97 E	818.8	8.8	7.5	-0.50	973.2
25	38.80 N	20.64 E	838.2	7.1	7.4	-0.57	994.8

Table A2 (continued)

26	38.56	N	20.38	E	856.6	5.8	7.4	-0.45	1008.4
27	38.33	N	20.15	E	870.5	5.3	7.2	-0.32	1014.2
28	38.10	N	19.94	E	880.9	5.1	6.9	-0.26	1015.4
29	37.88	N	19.73	E	890.0	5.1	6.5	-0.25	1014.1
30	37.68	N	19.52	E	898.9	5.1	6.1	-0.25	1011.9
31	37.48	N	19.30	E	907.4	6.0	6.4	-0.22	1010.3
32	37.26	N	19.04	E	913.8	6.8	6.8	-0.14	1009.3
33	37.04	N	18.75	E	917.6	7.3	7.3	-0.07	1009.3
34	36.79	N	18.46	E	919.5	7.3	7.7	-0.03	1009.8
35	36.54	N	18.17	E	920.1	7.0	7.9	0.00	1010.0
36	36.28	N	17.89	E	919.2	6.7	8.0	0.05	1010.1
37	36.04	N	17.63	E	916.9	6.4	7.2	0.08	1010.0
38	35.81	N	17.38	E	914.0	6.2	6.6	0.08	1009.8
39	35.60	N	17.13	E	911.4	6.1	6.2	0.06	1009.5
40	35.40	N	16.89	E	910.1	6.1	6.2	0.01	1009.0
41	35.20	N	16.65	E	910.7	6.0	6.4	-0.05	1008.4
42	34.98	N	16.41	E	913.6	5.9	6.8	-0.11	1008.1
43	34.77	N	16.17	E	917.9	6.6	6.5	-0.12	1008.0
44	34.56	N	15.90	E	922.3	7.2	6.1	-0.12	1008.0
45	34.37	N	15.60	E	926.1	7.8	5.7	-0.10	1008.0
46	34.19	N	15.29	E	929.0	8.2	5.3	-0.06	1008.0
47	34.03	N	14.97	E	930.7	8.4	4.9	-0.03	1008.2
48	33.88	N	14.64	E	931.5	8.4	4.5	-0.01	1008.5
49	33.74	N	14.31	E	931.9	8.6	4.0	-0.01	1009.1
50	33.62	N	13.97	E	932.6	9.0	3.6	-0.03	1009.5
51	33.51	N	13.61	E	933.9	9.3	3.3	-0.04	1009.8
52	33.40	N	13.24	E	935.8	9.6	3.1	-0.07	1010.0
53	33.30	N	12.87	E	938.5	9.9	3.1	-0.08	1010.7
54	33.20	N	12.48	E	941.0	10.1	3.5	-0.06	1011.4
55	33.07	N	12.08	E	941.5	10.8	4.3	0.03	1010.4
56	32.92	N	11.66	E	937.7	11.3	5.1	0.18	1004.7
57	32.74	N	11.22	E	929.0	11.5	5.8	0.30	993.4
58	32.55	N	10.79	E	918.7	10.9	6.2	0.27	980.9
59	32.34	N	10.38	E	911.6	10.0	6.3	0.13	973.2
60	32.14	N	10.02	E	909.1	9.0	6.1	0.01	972.4
61	31.96	N	9.69	E	909.7	8.5	5.5	-0.05	975.8
62	31.79	N	9.37	E	911.7	8.1	4.9	-0.07	980.8
63	31.64	N	9.07	E	914.1	7.9	4.4	-0.07	985.3
64	31.50	N	8.77	E	916.7	7.8	4.1	-0.07	988.0
65	31.37	N	8.48	E	919.0	7.7	3.8	-0.06	989.0
66	31.25	N	8.19	E	920.5	7.6	3.7	-0.03	988.6
67	31.13	N	7.91	E	920.9	7.3	3.5	0.01	987.5
68	31.02	N	7.63	E	920.1	7.2	3.2	0.04	986.1
69	30.92	N	7.37	E	918.5	7.0	2.9	0.05	984.9
70	30.84	N	7.10	E	916.6	6.9	2.4	0.05	984.1
71	30.77	N	6.84	E	914.8	6.9	1.9	0.05	983.8
72	30.72	N	6.59	E	913.3	6.8	1.4	0.04	983.5
73	30.68	N	6.32	E	911.9	7.2	0.7	0.04	983.7
74	30.67	N	6.04	E	910.3	7.7	0.0	0.05	984.1
75	30.69	N	5.75	E	908.6	8.1	-0.8	0.05	985.0
76	30.73	N	5.43	E	906.9	8.7	-1.6	0.05	985.8
77	30.79	N	5.09	E	904.8	9.4	-2.4	0.07	985.6
78	30.88	N	4.72	E	901.7	10.4	-3.4	0.11	983.0
79	30.98	N	4.33	E	897.3	10.1	-2.3	0.13	976.6
80	31.04	N	3.95	E	892.4	10.0	-1.3	0.14	967.4
81	31.06	N	3.58	E	887.7	9.8	-0.4	0.12	958.3
82	31.06	N	3.21	E	883.8	9.5	0.5	0.09	951.8
83	31.04	N	2.86	E	881.0	9.2	1.1	0.07	948.7

Table A2 (continued)

84	30.99 N	2.51 E	878.9	9.1	1.3	0.06	948.4

TRAJECTORY NUMBER 4

START: LAT 41.8 DEG N PRESSURE LEVEL 500 HPA
LON 32.5 DEG E TIME 12 UTC ON 1. 1.97

END: TIME 0 UTC ON 29.12.96

ANALYSIS FIELDS FROM TIME 12 UTC ON 1. 1.97

HOURS	LAT	LON	LEVEL	U-WIND	V-WIND	W-WIND	PS
0	41.78 N	32.49 E	500.0	16.1	-2.1	0.02	970.5
1	41.84 N	31.77 E	501.8	16.9	-1.5	-0.12	1005.4
2	41.91 N	31.02 E	507.5	17.4	-2.7	-0.19	1027.2
3	42.03 N	30.26 E	512.9	17.4	-4.5	-0.10	1031.0
4	42.18 N	29.52 E	514.1	16.6	-5.3	0.04	1026.8
5	42.34 N	28.82 E	511.3	15.5	-4.5	0.12	1021.5
6	42.46 N	28.15 E	507.8	14.9	-2.6	0.08	1012.5
7	42.50 N	27.47 E	505.5	16.3	-0.3	0.05	999.9
8	42.50 N	26.73 E	503.3	17.5	0.3	0.07	988.4
9	42.50 N	25.96 E	500.4	17.7	-0.6	0.09	974.2
10	42.55 N	25.19 E	497.9	17.2	-2.2	0.05	951.1
11	42.65 N	24.44 E	495.8	16.7	-3.6	0.06	928.9
12	42.76 N	23.70 E	491.5	16.7	-3.6	0.18	921.0
13	42.83 N	22.93 E	484.9	18.5	-0.8	0.18	923.9
14	42.83 N	22.08 E	480.8	19.9	0.7	0.04	928.9
15	42.81 N	21.18 E	481.1	21.0	0.7	-0.06	913.5
16	42.80 N	20.23 E	482.9	21.8	0.2	-0.04	881.6
17	42.81 N	19.26 E	482.8	22.5	-1.2	0.04	882.3
18	42.88 N	18.25 E	478.4	23.3	-2.9	0.20	925.8
19	42.92 N	17.23 E	471.7	22.5	0.5	0.17	977.6
20	42.85 N	16.25 E	468.0	22.0	3.8	0.03	1018.8
21	42.71 N	15.28 E	468.7	21.9	4.8	-0.07	1021.1
22	42.57 N	14.31 E	470.1	22.3	4.0	-0.01	971.4
23	42.46 N	13.31 E	468.3	23.6	2.4	0.11	935.9
24	42.42 N	12.23 E	463.6	25.7	0.2	0.14	965.1
25	42.38 N	11.09 E	460.0	26.3	2.0	0.07	1006.9
26	42.27 N	9.93 E	457.1	26.4	4.7	0.09	993.2
27	42.10 N	8.77 E	451.0	26.9	5.9	0.24	980.5
28	41.92 N	7.57 E	442.2	28.0	4.9	0.25	1006.0
29	41.79 N	6.32 E	434.5	29.6	3.4	0.17	1006.8
30	41.69 N	5.01 E	429.4	31.1	2.6	0.11	1004.6
31	41.58 N	3.68 E	424.7	30.3	4.4	0.15	1006.0
32	41.42 N	2.39 E	419.1	29.0	5.0	0.16	977.8
33	41.28 N	1.16 E	414.1	28.2	3.7	0.11	974.5
34	41.20 N	0.04 W	412.6	27.4	1.8	-0.02	950.6
35	41.17 N	1.20 W	413.0	26.8	-0.2	0.00	897.9
36	41.19 N	2.35 W	411.6	26.6	-1.0	0.08	879.1
37	41.17 N	3.44 W	410.2	24.0	2.2	0.00	885.6
38	41.06 N	4.43 W	411.4	22.1	4.2	-0.07	897.0
39	40.92 N	5.37 W	414.4	21.4	4.7	-0.10	906.4
40	40.76 N	6.28 W	417.7	21.3	4.8	-0.08	920.8
41	40.61 N	7.19 W	419.9	21.6	4.7	-0.04	937.2
42	40.47 N	8.12 W	420.9	22.0	4.2	-0.02	965.5
43	40.33 N	9.04 W	421.1	21.6	4.1	0.00	997.2
44	40.21 N	9.96 W	420.6	21.7	3.4	0.03	1007.9

Table A2 (continued)

45	40.11 N	10.87 W	419.0	21.5	3.2	0.06	1006.0
46	40.00 N	11.77 W	416.1	20.7	3.5	0.10	1005.7
47	39.88 N	12.61 W	412.8	19.4	3.6	0.09	1006.6
48	39.78 N	13.40 W	410.4	18.1	2.9	0.05	1007.1
49	39.72 N	14.14 W	409.0	16.9	0.8	0.03	1006.6
50	39.71 N	14.82 W	408.6	15.8	-0.4	-0.01	1006.2
51	39.73 N	15.46 W	410.0	14.5	-0.5	-0.07	1006.0
52	39.73 N	16.05 W	413.2	13.3	0.0	-0.11	1006.1
53	39.73 N	16.59 W	417.2	12.4	0.4	-0.12	1006.0
54	39.72 N	17.10 W	421.1	12.0	0.4	-0.10	1006.1
55	39.73 N	17.61 W	424.0	12.0	-1.6	-0.07	1006.5
56	39.80 N	18.12 W	426.0	12.3	-2.6	-0.05	1007.2
57	39.88 N	18.64 W	427.5	12.5	-2.1	-0.04	1008.0
58	39.92 N	19.17 W	428.8	12.5	-0.4	-0.03	1008.7
59	39.90 N	19.69 W	430.0	12.4	1.8	-0.03	1009.1
60	39.82 N	20.22 W	430.5	12.5	3.3	0.01	1009.4
61	39.75 N	20.78 W	428.1	14.1	0.7	0.13	1009.9
62	39.76 N	21.39 W	422.3	14.9	-1.3	0.19	1010.5
63	39.82 N	22.01 W	416.8	14.6	-2.1	0.12	1010.9
64	39.88 N	22.61 W	416.1	14.2	-1.7	-0.08	1011.1
65	39.91 N	23.21 W	422.9	14.1	-0.4	-0.29	1011.5
66	39.89 N	23.79 W	435.4	13.7	1.5	-0.40	1012.0
67	39.86 N	24.38 W	446.8	14.1	0.9	-0.23	1012.0
68	39.84 N	24.99 W	453.0	14.6	0.1	-0.12	1011.7
69	39.85 N	25.61 W	459.3	14.8	-0.8	-0.24	1011.7
70	39.89 N	26.22 W	472.9	14.3	-1.6	-0.52	1011.9
71	39.95 N	26.81 W	494.6	13.7	-1.9	-0.69	1011.9
72	40.02 N	27.39 W	518.9	14.0	-2.5	-0.64	1010.8
73	40.14 N	28.01 W	538.4	15.3	-5.2	-0.45	1010.6
74	40.33 N	28.68 W	554.7	16.4	-6.1	-0.45	1011.0
75	40.52 N	29.41 W	571.9	17.9	-5.4	-0.50	1012.2
76	40.67 N	30.21 W	585.9	19.2	-4.0	-0.24	1012.7
77	40.78 N	31.05 W	588.7	19.8	-2.4	0.08	1011.2
78	40.86 N	31.90 W	593.8	20.2	-2.2	-0.39	1008.2
79	40.97 N	32.79 W	606.5	20.9	-4.7	-0.28	1009.3
80	41.11 N	33.71 W	604.3	22.0	-5.0	0.44	1011.4
81	41.23 N	34.69 W	598.4	23.3	-1.7	-0.18	1012.4
82	41.27 N	35.69 W	627.4	22.2	-0.8	-1.46	1010.8
83	41.36 N	36.62 W	668.3	21.4	-4.4	-0.80	1009.4
84	41.52 N	37.54 W	678.9	21.3	-5.0	-0.29	1009.7

NOTES: IMS MODEL

1) LATITUDES AND LONGITUDES ARE IN DEGREES.

2) PRESSURE LEVELS ARE IN HECTOPASCALS (HPA).

3) THE FOLLOWING ABBREVIATIONS ARE USED:

U-WIND - U-COMPONENT OF WIND (METRES PER SECOND)
V-WIND - V-COMPONENT OF WIND (METRES PER SECOND)
W-WIND - VERTICAL WIND COMPONENT (PASCALS PER SECOND)
PS - SURFACE PRESSURE (HPA)

Table A3. The concentrations of measured species in this study (ng.m^{-3})

dd	mm	yy	Na	Mg	Al	Ca	Cl	K	Sc	V
22	4	95	216.2		247.1		152.7	235.6		2.9
23	4	95	692.6		92.4		311.2	73.9		1.5
24	4	95	140.9		90.5		124.6	97.2		1.1
25	4	95	181.6		270.1		236.2	195.2		1.2
26	4	95	545.6		1218.8		705.2	290.6		2.3
27	4	95	824.9		390.0		755.4	272.3		3.3
28	4	95	760.9		582.6		321.2	350.9		5.2
29	4	95	330.9		382.0		114.3	214.9		4.3
30	4	95	319.5		358.9		69.2	290.6		2.2
1	5	95	383.4		193.8		493.2	263.1		1.6
2	5	95	1238.1		357.5		108.3	67.1		1.6
3	5	95	1046.3		275.6		1115.0	338.2		1.7
4	5	95	525.1		215.7		662.7	217.6		2.0
5	5	95	445.5		209.3		279.7	311.2		2.6
6	5	95	137.2		243.0		212.5	179.6		1.6
7	5	95	298.2		352.5		89.7	159.0		2.1
8	5	95	257.5		133.1		209.3	124.7		3.1
9	5	95	315.3		215.8		201.2	212.0		3.1
10	5	95	478.6		411.0		204.3	287.6		5.4
11	5	95	373.2		776.9		146.2	321.5		2.7
12	5	95	348.7		1488.3		144.1	394.4		3.3
13	5	95	345.4		309.5		206.2	249.3		3.9
25	5	95	237.7		279.8		83.0	207.7		2.7
26	5	95	489.1		361.6		114.8	222.4		3.7
27	5	95	236.3		703.4		25.9	342.3		3.8
28	5	95	434.1		1199.5		754.1	553.3		6.0
29	5	95	298.6		783.2		87.9	394.6		3.5
30	5	95	274.0		532.6		183.5	319.9		2.8
31	5	95	201.5		263.2		244.4	133.6		1.2
1	6	95	170.9		303.7		68.0	168.2		1.8
2	6	95	267.4		504.7		125.1	288.1		4.1
3	6	95	334.7		603.2		195.9	268.2		4.2
4	6	95	293.5		658.7		189.7	310.7		3.4
5	6	95	234.6		380.4		272.5	192.4		1.4
6	6	95	309.8		439.6		242.9	192.0		1.5
7	6	95	315.5		493.7		253.7	252.7		1.7
8	6	95	505.0		342.6		385.6	225.4		2.2
9	6	95	591.6		356.0		808.2	158.8		1.4
10	6	95	486.3		647.5		494.7	286.1		1.6
11	6	95	338.0		632.4		238.1	277.7		1.9
12	6	95	306.7		850.3		122.7	340.2		1.1
15	6	95	407.8		813.3		280.8	292.2		1.6
16	6	95	272.2		303.8		53.2	304.1		2.3
17	6	95	186.7		661.7		55.0	295.8		1.8
18	6	95	178.1		386.1		42.8	180.4		1.7
19	6	95	365.6		159.0		284.1	105.8		0.9
20	6	95	490.5		97.3		489.7	120.8		1.5
21	6	95	290.6		242.5		138.6	164.2		2.4
22	6	95	114.4		336.3		49.3	130.1		2.6
23	6	95	193.0		134.3		219.3	61.8		1.7
25	6	95	250.8		374.0		62.7	174.8		3.3
26	6	95	726.1		208.6		496.8	154.3		3.3
27	6	95	122.0	72.1	27.6		262.6	74.2		0.9
21	9	95	373.5	227.7	470.1		42.1	363.3		3.3
22	9	95	265.7	149.0	359.3		16.6	226.6		8.1
23	9	95		46.4	43.2	82.3	316.6	209.5		0.6
24	9	95		38.1	5.2	71.7	269.5	67.8		0.3
25	9	95		59.9	25.7	190.5	217.5	276.1		0.4

Table A3 (continued)

26	9	95		76.2	125.5	220.4	77.5	277.0	1.3
27	9	95		39.6	94.3	175.5	78.4	693.7	1.2
28	9	95		39.6	83.3	221.6	60.0	199.9	1.1
29	9	95		135.6	246.8	567.2	560.8	2013.6	1.7
30	9	95		60.5	56.5	175.9	244.1	222.7	1.2
1	10	95		27.9	45.7	373.3	299.1	407.7	0.5
2	10	95		51.2	45.6	296.5	484.0	1508.8	0.6
3	10	95		37.6	71.1	201.0	299.8	121.8	1.6
4	10	95		37.2	56.8	157.2	432.6	154.7	1.9
5	10	95		14.2	59.3	199.7	300.7	225.3	2.0
6	10	95		22.8	68.2	405.2	254.8	1033.0	2.0
7	10	95	254.5	44.3	134.6	4.4	165.5	147.2	1.6
8	10	95	327.4	62.9	225.8	36.9	214.3	208.0	2.9
9	10	95	280.0	54.8	183.4	33.6	131.3	185.7	3.6
10	10	95	189.4	31.1	81.6	11.7	147.8	133.1	1.7
11	10	95	351.1	34.3	46.1	0.2	201.9	138.8	1.8
12	10	95	339.7	30.0	26.1	34.6	236.2	126.3	1.2
13	10	95	354.9	44.1	42.5	113.3	469.2	141.7	1.2
14	10	95	369.5	54.6	142.3	63.6	767.1	179.9	2.4
15	10	95	870.5	79.7	127.8	48.0	641.0	238.1	3.7
16	10	95	1599.6	170.7	77.4	189.6	2416.1	214.1	1.2
17	10	95	780.7	92.3	36.7	183.9	2863.5	193.0	0.9
18	10	95	519.0	85.6	79.8	232.6	773.3	190.5	0.9
19	10	95	383.0	49.5	32.6	74.3	412.8	205.0	0.9
20	10	95	325.2	70.0	166.5		553.4	265.4	3.1
21	10	95	52.4	149.4	226.7		1421.6	351.5	6.5
22	10	95	1167.3	176.7	107.2		1355.7	171.6	1.6
24	10	95	770.3	62.8	60.6		407.4	230.7	1.1
25	10	95	549.6	65.6	87.4		397.5	269.8	3.9
26	10	95	317.7	41.6	36.1		340.7	151.3	2.2
27	10	95	385.3	18.2	26.6		244.7	127.8	1.5
28	10	95	371.5	33.5	72.2		291.2	89.2	1.5
29	10	95	201.4	18.1	57.6		53.3	86.8	3.1
30	10	95	299.7	84.2	196.0		219.7	238.0	5.8
31	10	95	299.7	58.9	172.6		179.8	232.2	2.3
1	11	95	312.8	57.4	146.6		215.2	241.7	2.5
2	11	95	356.5	77.7	185.1		186.7	214.1	3.4
3	11	95	422.1	77.2	195.6		330.1	119.6	1.5
5	11	95	611.4	123.4	197.0		1032.5	86.0	0.7
6	11	95	390.2	25.8	28.9		293.6	108.8	0.6
7	11	95	512.1	14.1	73.9		86.4	22.7	1.2
8	11	95	232.5	32.8	101.3		99.2	248.2	2.9
9	11	95	110.4	21.3	37.7		123.2	50.3	2.2
10	11	95	148.1	49.6	119.3		65.2	158.2	3.1
13	11	95	141.0	35.3	75.6	153.6	222.8	148.5	3.9
14	11	95	249.7	75.9	279.7	133.0	90.1	126.3	1.2
15	11	95	384.8	125.3	520.6	241.1	277.3	151.8	1.7
17	11	95	179.6	103.9	158.2	252.2	283.6	98.5	1.4
19	11	95	333.0	79.6	190.7	109.0	356.7	60.4	0.8
20	11	95	853.6	31.8	108.0	295.9	276.2	93.1	1.5
21	11	95	37.0	10.0	92.4	107.6	119.0	32.4	0.6
22	11	95	258.4	57.8	129.6	19.5	76.2	46.4	1.2
23	11	95	153.8	21.8	153.7	37.5	80.0	56.6	2.6
25	11	95	127.3	34.8	131.2	199.2	41.9	93.0	4.9
26	11	95	52.7	20.2	119.4	91.4	65.6	88.5	1.9
27	11	95	42.8	20.1	84.8	97.8	247.0	95.6	0.8
28	11	95	45.4	29.3	145.6	45.1	47.8	66.5	1.6
29	11	95	75.7	85.7	266.9	402.1	134.9	148.6	1.5
30	11	95	115.6	90.7	170.0	243.4	153.9	197.9	6.5

Table A3 (continued)

1	12	95	417.1	76.1	80.3	148.3	241.6	25.6		2.1
2	12	95	435.8	73.5	110.8	116.1	51.0	87.8		3.1
3	12	95	79.6	36.8	234.4	22.7	105.5	12.0		2.9
4	12	95	86.1	31.0	91.5	74.0	216.8	80.0		1.3
5	12	95	215.0	76.6	137.8	306.8	636.7	218.1		1.3
6	12	95	259.9	60.1	122.5	85.5	385.5	61.6		1.4
23	5	96	338.7	127.1	297.8	388.9	489.8	80.7		1.6
24	5	96	544.2	98.5	246.1	155.7	439.1	17.0	0.0417	2.4
'25-27		96	534.3	164.8	174.4	233.9	427.3	110.6	0.0298	1.9
28	5	96	298.0	151.1	396.2	477.5	151.0	85.5	0.0705	3.2
29	5	96	554.7	163.5	244.9	353.2	261.7	76.8	0.0430	1.9
30	5	96	308.9	169.9	367.3	224.0	229.8	121.2	0.0729	2.1
31	5	96	1115.2	269.4	554.0	206.3	1043.2	317.7	0.0946	2.9
2	6	96	296.0	101.1	321.3	107.1	134.0	86.1	0.0645	2.4
3	6	96	386.0	81.6	152.0	468.4	314.2	31.8	0.0305	1.2
4	6	96	149.0	50.1	309.6	196.7	139.6	64.1	0.0419	3.0
5	6	96	364.2	147.9	796.0	259.9	225.3	166.6	0.1054	5.4
6	6	96	509.3	141.3	503.8	283.1	350.8	129.3	0.0771	1.3
7	6	96	230.9	137.2	853.7	83.4	178.6	109.1	0.1074	2.4
8	6	96	134.3	104.6	428.9	173.1	157.6	70.1	0.0785	2.3
9	6	96	170.7	142.3	395.2	267.9	157.7	44.5	0.0569	1.8
10	6	96	156.8	104.3	282.1	250.2	249.5	26.6	0.0565	1.0
11	6	96	178.1	115.9	320.1	191.3	349.4	53.9	0.0679	1.4
12	6	96	172.9	104.1	305.9	299.8	140.7	39.0	0.0557	2.1
13	6	96	107.2	96.8	304.1	278.4	118.1	62.4	0.0556	1.8
14	6	96	416.3	190.2	271.2	545.6	543.2	76.9	0.0485	1.7
15	6	96	312.1	83.9	49.1	164.1	351.6	29.5	0.0103	0.6
16	6	96	249.3	74.2	82.6	176.9	247.7	66.2	0.0149	0.9
18	6	96	308.0	79.6	161.7	309.5	294.4	38.7	0.0269	1.0
19	6	96	403.2	86.1	280.8	238.0	319.3	53.7	0.0542	1.9
20	6	96	358.7	115.5	248.4	276.1	245.3	70.2	0.0541	3.5
21	6	96	201.4	95.8	218.1	247.6	165.2	29.3	0.0382	2.1
22	6	96	115.5	115.8	281.5	374.4	183.2	20.8	0.0487	1.2
23	6	96	249.0	137.5	284.8	529.0	252.1	36.1	0.0585	0.4
24	6	96	76.8	83.3	210.1	223.3	61.6	26.1	0.0414	1.4
25	6	96	141.0	104.9	219.0	345.9	149.5	26.6	0.0379	1.5
26	6	96	97.7	165.6	292.4	561.7	98.8	35.6	0.0533	0.9
27	6	96	448.5	349.4	810.5	763.8	117.4	125.1	0.1668	4.7
28	6	96	574.0	128.4	270.8	249.0	594.5	28.1	0.0482	1.5
29	6	96	285.5	117.7	222.2	341.5	261.7	10.3	0.0426	1.7
30	6	96	331.4	202.6	219.2	480.9	397.5	42.7	0.0447	1.2
1	7	96	297.3	208.1	260.8	314.3	260.3	85.2	0.0518	1.4
3	7	96	392.3	329.6	426.2	828.7	209.4	55.7	0.0868	2.0
4	7	96	677.0	258.7	493.4	435.4	184.5	101.3	0.0990	3.6
5	7	96	408.8	231.0	380.9	456.4	401.0	60.3	0.0653	2.0
6	7	96	295.3	232.6	519.5	374.9	235.8	140.2	0.0961	2.4
7	7	96	227.3	220.5	919.2	283.2	178.9	195.5	0.1903	3.0
8	7	96	246.6	380.4	1268.8	555.0	138.5	313.3	0.2785	3.2
9	7	96	384.6	303.7	824.8	1284.1	211.1	235.4	0.1854	3.4
10	7	96	720.8	243.7	583.0	457.7	381.3	181.9	0.1318	2.4
11	7	96	600.1	157.3	383.4	293.4	826.0	153.1	0.0729	1.9
12	7	96	726.9	131.0	236.8	434.4	626.7	121.5	0.0426	1.2
13	7	96	1211.2	226.1	703.9	378.0	1054.8	230.5	0.1305	2.3
14	7	96	1265.9	274.8	1016.8	289.0	959.0	371.0	0.1694	2.9
16	7	96	731.1	238.8	898.6	276.9	445.0	278.6	0.1735	2.0
17	7	96	1600.9	196.1	489.4	257.6	1187.0	144.6	0.0388	2.4
18	7	96	435.4	103.0	146.3	281.5	331.4	45.1	0.0304	0.6
20	7	96	250.5	148.9	333.7	465.2	244.6	71.9	0.0670	1.7
21	7	96	333.0	106.9	257.1	206.5	279.2	108.5	0.0524	1.1

Table A3 (continued)

24	7	96	350.2	171.7	413.5	659.2	276.9	130.7	0.0909	1.5
26	7	96	474.9	159.2	370.0	365.9	376.2	87.2	0.0729	2.2
27	7	96	412.6	178.1	315.8	439.8	264.3	56.8	0.0473	3.4
28	7	96	237.3	213.6	263.3	891.3	202.6	85.2	0.0462	2.1
29	7	96	315.5	134.2	187.5	570.7	230.0	32.2	0.0359	1.3
30	7	96	245.9	138.6	391.6	453.5	148.6	115.3	0.0784	1.5
31	7	96	424.9	283.0	548.5	725.5	327.7	431.2	0.1018	2.3
1	8	96	365.5	345.8	638.0	956.3	308.8	422.8	0.1191	3.6
2	8	96	279.7	510.6	925.3	1612.5	245.0	444.0	0.1634	2.7
3	8	96	875.4	330.3	805.3	620.1	697.7	434.9	0.1552	3.5
4	8	96	376.8	146.5	492.7	333.9	248.4	373.6	0.1020	2.3
10	11	96	486.5	120.9	50.1	313.1	436,5	110.9	0.0035	2.1
11	11	96	203.4	122.1	125.3	945.9	233.5	184.0	0.0160	1.1
12	11	96	153.3	96.1	117.6	396.1	225.1	232.9	0.0222	3.2
13	11	96	287.9	99.7	179.7	331.0	558.2	371.4	0.0367	4.9
15	11	96	196.7	93.8	223.1	259.4	102.1	256.2	0.0460	6.5
16	11	96	157.7	79.5	171.3	282.8	158.7	207.7	0.0317	5.3
17	11	96	137.3	101.0	191.5	454.6	179.9	217.6	0.0404	1.7
18	11	96	433.1	237.0	434.1	970.2	255.4	258.4	0.0869	2.2
19	11	96	506.4	518.7	1150.1	1304.7	259.2	661.0	0.2424	3.0
20	11	96	621.1	339.5	621.1	538.7	564.8	245.3	0.1358	3.3
21	11	96	471.5	290.0	611.6	496.0	361.9	229.2	0.1136	2.7
22	11	96	785.4	129.3	60.6	208.4	604.2	124.2	0.0166	0.9
23	11	96	388.5	123.9	76.5	261.2	364.7	125.6	0.0120	0.9
24	11	96	347.4	131.9	144.6	545.9	237.8	147.1	0.0252	1.3
25	11	96	767.6	159.4	230.0	364.2	622.1	104.1	0.0348	2.0
26	11	96	751.0	184.4	108.6	498.0	722.5	219.1	0.0170	3.0
27	11	96	475.2	140.5	165.5	490.6	377.4	81.6	0.0230	1.4
28	11	96	168.2	68.0	51.7	224.2	132.6	84.9	0.0156	1.0
29	11	96	332.4	79.4	93.9	317.9	302.3	131.5	0.0090	0.9
1	12	96	89.2	77.3	82.0	469.8	78.5	55.9	0.0313	1.0
2	12	96	393.9	106.2	88.9	384.0	307.0	56.9	0.0216	0.6
3	12	96	227.9	122.7	225.7	486.3	207.7	105.5	0.0490	1.4
4	12	96	439.2	102.7	241.5	307.5	279.8	168.0	0.0546	4.0
5	12	96	399.8	70.4	158.7	109.3	315.1	156.7	0.0343	1.6
7	12	96	241.3	37.8	36.6	199.6	240.0	85.8	0.0040	0.5
8	12	96	131.6	45.8	247.1	70.5	100.2	111.9	0.0490	0.7
9	12	96	159.4	41.0	22.1	122.8	114.6	83.6	0.0029	0.7
10	12	96	304.5	43.2	26.5	179.8	243.9	111.9	0.0045	0.6
11	12	96	98.3	41.9	74.8	243.8	115.8	138.6	0.0192	1.4
12	12	96	124.1	3.3	151.3	11.5	98.3	139.5	0.0300	3.2
13	12	96	150.0	29.7	68.8	99.2	27.0	83.4	0.0113	2.5
14	12	96	131.1	93.9	205.4	163.1	97.0	102.1	0.0606	2.2
16	12	96	640.7	172.9	90.3	244.3	548.1	125.7	0.0201	2.2
17	12	96	364.3	137.0	252.9	181.2	357.4	150.5	0.0726	1.9
19	12	96	413.6	147.9	250.7	343.7	201.9	96.4	0.0692	1.9
20	12	96	414.1	93.9	142.5	237.2	341.5	154.8	0.0406	2.1
23	12	96	706.4	231.8	305.1	329.7	585.0	170.8	0.0793	3.0
24	12	96	999.0	183.3	187.3	226.5	872.9	143.7	0.0727	2.0
26	12	96	255.6	61.6	29.5	78.0	67.3	59.0	0.0088	1.2
30	12	96	402.1	190.4	604.6	402.7	308.7	234.2	0.1010	5.6
3	1	97	248.1	155.5	269.8	338.1	276.1	287.5	0.0562	7.2
5	1	97	571.1	185.0	288.5	285.6	275.7	160.4	0.0503	6.2
7	1	97	479.9	104.6	65.0	159.5	192.0	226.4	0.0105	2.7
10	1	97	345.1	120.5	71.5	218.1	360.8	186.0	0.0139	1.4
11	1	97	105.2	116.2	89.5	256.1	272.2	215.7	0.0248	0.9
12	1	97	1338.0	262.4	80.4	239.0	297.9	172.2	0.0230	2.4
13	1	97	846.0	148.0	39.2	165.5	144.3	111.2	0.0046	1.8
15	1	97	194.4	100.6	124.6	187.8	43.5	148.0	0.0244	3.5
16	1	97	536.6	159.0	178.2	387.1	34.2	174.4	0.0395	5.8

Table A3 (continued)

17	1	97	299.7	79.4	178.3	349.9	39.5	281.2	0.0367	15.1
18	1	97	213.9	51.2	112.6	153.5	160.1	201.2	0.0289	4.4
19	1	97	228.8	41.5	177.0	268.8	90.8	330.6	0.0336	16.1
20	1	97	296.6	96.5	317.1	303.0	68.2	288.8	0.0772	21.4
21	1	97	287.0	55.5	86.3	165.4	144.5	128.8	0.0195	9.7
22	1	97	329.8	48.7	41.9	146.1	346.0	205.1		3.3
23	1	97	178.4	32.6	69.0	104.5	125.7	133.9	0.0109	1.5
24	1	97	369.3	64.3	226.0	325.6	222.2	174.3	0.0532	3.9
25	1	97	448.5	72.1	30.3	78.5	408.1	49.9	0.0014	1.0
26	1	97	3009.8	493.4	236.5	560.3	2687.3	363.0	0.0451	13.6
27	1	97	577.8	95.8	44.9	193.1	377.9	75.4	0.0028	4.1
28	1	97	479.7	98.2	176.2	282.5	69.3	132.9	0.0409	8.3
29	1	97	1269.9	206.2	108.4	183.2	957.6	142.5	0.0196	6.0
30	1	97	997.8	149.0	42.4	163.6	1068.5	55.1	0.0052	0.6
8	3	97	248.4	84.0	257.1	300.9	219.3	124.0	0.0430	3.3
9	3	97	450.6	99.4	99.8	198.7	442.5	87.0	0.0227	1.7
10	3	97	284.4	72.3	144.0	168.6	348.4	129.1	0.0283	1.4
11	3	97	328.1	116.2	107.4	192.3	300.5	139.5	0.0176	1.5
14	3	97	298.3	156.5	253.4	394.3	189.2	161.5	0.0410	2.3
16	4	97	190.3	114.2	164.3	314.8	209.2	82.9	0.0379	1.9
17	4	97	362.3	69.2	64.6	53.2	344.2	63.7	0.0111	1.2
18	4	97	240.3	70.8	128.8	184.2	195.9	66.6	0.0249	1.8
19	4	97	333.3	221.6	328.0	642.1	197.7	98.3	0.0546	2.8
20	4	97	200.6	97.3	253.1	196.3	130.4	71.7	0.0429	1.6
21	4	97	968.1	416.2	766.3	1025.5	913.6	212.8	0.1424	2.3
22	4	97	492.0	658.0	2212.9	2421.5	397.3	390.9	0.5187	6.2
23	4	97	1360.1	1021.3	4576.4	4725.5	1459.2	1668.2	1.3762	12.6
24	4	97	346.4	129.1	130.3	219.1	316.1	92.0	0.0461	1.5
25	4	97	472.3	136.6	343.2	167.8	296.9	149.5	0.0648	3.8
26	4	97	154.5	105.6	277.0	167.3	115.1	136.3	0.0610	2.6
27	4	97	96.0	37.8	48.0	61.3	126.8	62.2	0.0050	1.1
28	4	97	138.3	96.3	215.8	220.6	124.6	144.9	0.0334	3.3
29	4	97	574.8	222.6	253.6	575.5	643.6	163.1	0.0522	1.4
30	4	97	1020.5	306.4	168.8	559.3	1484.4	136.0	0.0332	1.8
1	5	97	371.2	228.4	121.2	518.7	314.1	96.8	0.0298	1.9
2	5	97	215.6	313.1	409.5	777.0	144.2	194.2	0.0831	3.9
3	5	97	380.1	194.7	472.8	381.4	292.2	245.6	0.0958	5.5
4	5	97	95.4	101.7	354.1	229.8	122.7	135.7	0.0758	3.5
5	5	97	152.7	216.8	713.8	788.3	174.7	174.5	0.1335	4.7
6	5	97	198.2	407.3	796.9	1461.3	134.6	188.9	0.1430	3.8
8	5	97	293.4	570.0	1625.6	1428.2	303.9	342.1	0.2736	3.2
9	5	97	255.1	500.7	1303.9	1705.5	223.0	293.6	0.2478	4.1
10	5	97	618.9	419.2	861.1	1096.5	659.9	231.7	0.1572	3.8
11	5	97	698.4	414.6	744.1	610.5	576.1	225.9	0.1405	4.1
12	5	97	832.0	404.3	932.7	693.2	701.7	340.8	0.1778	4.6
13	5	97	260.3	259.1	637.7	507.5	252.0	213.6	0.1290	2.6
14	5	97	344.1	261.6	482.3	593.2	306.8	159.0	0.0867	2.0
15	5	97	163.4	126.6	195.8	223.4	169.2	80.9	0.0338	2.0
16	5	97	79.7	95.2	229.2	199.1	31.9	92.5	0.0392	3.6
17	5	97	63.0	69.9	148.4	110.6	11.0	70.4	0.0247	4.9
18	5	97	102.8	189.3	373.3	523.2	69.5	127.6	0.0643	4.2
19	5	97	54.0	85.8	165.4	322.9	55.6	70.6	0.0227	1.5
20	5	97	103.7	142.5	384.3	264.1	36.7	137.5	0.0749	5.1
21	5	97	207.0	462.7	1086.8	1753.2	75.6	286.1	0.1983	4.2
22	5	97	253.7	469.7	980.2	1566.1	179.6	239.8	0.1917	6.6
23	5	97	778.8	602.4	869.1	1508.0	700.7	174.9	0.1619	2.9
24	5	97	618.8	186.1	134.7	306.3	593.2	67.8	0.0248	1.4
25	5	97	200.6	173.9	218.9	329.0	203.1	87.1	0.0382	2.2
26	5	97	532.9	116.3	83.4	306.4	421.5	85.8	0.0112	0.9
27	5	97	173.6	43.9	61.0	60.1	148.1	100.9	0.0125	0.4

Table A3 (continued)

28	5	97	214.4	116.4	129.9	676.8	196.1	94.1	0.0222	0.9
29	5	97	303.8	225.1	377.6	448.1	285.2	147.9	0.0640	2.3
30	5	97	290.3	71.7	171.8	141.2	247.7	105.9	0.0359	2.3
31	5	97	100.9	82.0	217.7	384.5	102.1	115.3	0.0356	2.9
01	6	97	270.5	60.8	89.3	140.4	265.1	72.8	0.0143	2.6
2	6	97	108.0	169.7	158.4	1237.5	87.4	74.3	0.0232	0.9
3	6	97	213.8	222.7	611.6	1305.6	154.5	167.1	0.1017	6.7
4	6	97	475.5	174.1	143.7	661.2	357.0	98.4	0.0389	2.3
5	6	97	204.1	140.9	133.9	759.9	90.0	64.0	0.0189	1.8
6	6	97	283.2	242.6	386.2	1435.2	266.6	141.0	0.0749	1.8
7	6	97	771.2	249.9	458.9	937.4	481.1	196.3	0.0867	6.5
8	6	97	503.2	174.4	343.0	302.8	49.3	172.0	0.0721	4.9
9	6	97	396.6	130.8	290.9	390.3	304.7	194.0	0.0786	3.6
10	6	97	266.9	137.9	287.7	391.5	92.7	158.4	0.0511	2.6
11	6	97	127.7	67.8	184.3	99.3	67.3	113.7	0.0417	2.8
12	6	97	151.2	88.9	227.9	97.2	118.5	115.1	0.0397	2.4
13	6	97	95.9	83.9	288.1	175.2	63.4	131.1	0.0641	5.5
14	6	97	101.1	118.0	294.3	773.4	57.6	149.7	0.0637	16.5
15	6	97	113.1	148.2	424.0	921.9	122.4	149.6	0.0827	3.6
16	6	97	514.0	125.9	319.4	99.9	313.4	143.5	0.0586	3.0
17	6	97	79.6	81.5	163.4	454.8	87.1	100.0	0.0250	2.8
18	6	97	225.6	190.2	352.4	1165.2	179.5	137.9	0.0612	1.7
19	6	97	710.7	207.1	239.2	301.1	616.4	102.4	0.0479	2.6
20	6	97	690.4	372.2	1119.2	876.2	626.6	268.6	0.2183	4.1
21	6	97	597.8	220.2	459.8	391.8	391.1	147.7	0.0712	3.3
22	6	97	359.1	293.8	1299.9	35.8	372.3	255.5	0.2397	5.3
23	6	97	83.9	230.5	216.4	585.7	98.6	73.5	0.0377	1.1
24	6	97	319.3	233.4	304.0	615.0	294.3	79.4	0.0468	2.1
25	6	97	239.0	198.0	294.6	468.9	186.7	117.8	0.0466	1.9
26	6	97	228.7	205.7	262.3	433.4	207.8	108.9	0.0522	1.7
27	6	97	158.2	140.8	180.7	329.3	145.3	71.4	0.0291	1.5
28	6	97	185.0	228.5	201.0	479.3	178.1	80.8	0.0305	2.0
29	6	97	109.0	263.6	284.3	623.4	134.3	102.5	0.0479	2.4
02	7	97	213.2	298.8	581.0	697.6	183.2	204.7	0.1036	3.2
03	7	97	247.7	137.6	235.4	264.1	178.1	105.8	0.0440	1.4
04	7	97	181.8	196.1	280.8	660.4	143.3	166.9	0.0487	1.9
05	7	97	126.9	330.2	648.2	1400.0	133.9	246.8	0.1131	2.7
06	7	97	233.8	511.5	1209.7	1903.1	142.4	309.6	0.2153	3.5
07	7	97	1346.2	804.3	2025.3	1846.2	980.2	485.3	0.3914	6.5
08	7	97	597.4	237.1	571.5	492.7	383.1	139.7	0.0937	1.9
09	7	97	463.0	220.1	410.4	407.3	243.3	132.0	0.0730	3.5
10	7	97	189.9	146.4	364.3	347.0	79.0	89.6	0.0623	3.3
11	7	97	236.5	84.1	134.6	217.6	100.7	79.2	0.0219	1.3
12	7	97	247.7	174.3	217.9	605.3	188.9	73.7	0.0325	0.9
13	7	97	273.3	75.2	105.6	45.3	195.5	85.8	0.0168	0.8
14	7	97	375.5	83.5	58.7	74.8	250.1	65.7	0.0115	1.4
15	7	97	270.6	64.9	95.0	149.1	110.4	85.0	0.0234	1.6
16	7	97	219.9	56.2	68.0	90.1	139.0	72.8	0.0087	0.7
17	7	97	179.9	57.0	91.1	138.7	111.0	94.0	0.0181	1.7
18	7	97	74.5	62.9	87.2	206.7	64.0	66.5	0.0123	0.8
19	7	97	175.6	194.9	434.9	566.8	45.0	142.2	0.0800	2.5
20	7	97	723.4	182.6	144.5	297.7	550.0	112.1	0.0251	1.4
21	7	97	249.4	123.7	156.8	287.1	194.9	73.8	0.0291	1.1
22	7	97	150.0	65.6	115.1	224.1	80.0	64.6	0.0174	0.9
23	7	97	132.0	65.5	110.9	33.5	44.5	99.2	0.0161	1.7
24	7	97	259.2	57.0	122.9	79.7	127.7	86.3	0.0207	1.7
25	7	97	68.0	107.5	141.2	133.5	50.6	162.1	0.0258	2.0
26	7	97	138.2	143.8	438.8	157.8	115.0	166.6	0.0623	2.0

Table A3 (continued)

dd	mm	yy	Cr	Mn	Fe	Co	Zn	As	Se	Br
22	4	95	0.6		228.0		14.4			
23	4	95	0.3		107.8		7.6			
24	4	95	0.2		123.1		5.0			
25	4	95	0.4		240.6		6.7			
26	4	95	0.9		789.1		26.9			
27	4	95	0.8		327.9		38.4			
28	4	95	1.0		390.6		30.2			
29	4	95	0.6		277.1		34.4			
30	4	95	0.6		315.7		10.7			
1	5	95	0.5		264.6		9.6			
2	5	95	0.8		290.6		0.1			
3	5	95	0.7		277.7		14.3			
4	5	95	0.7		168.8		11.3			
5	5	95	0.7		250.8		7.2			
6	5	95	0.7		201.4		13.3			
7	5	95	1.0		292.4		25.9			
8	5	95	0.9		291.7		35.3			
9	5	95	1.0		222.3		34.7			
10	5	95	1.1		273.9		14.8			
11	5	95	1.7		513.7		8.7			
12	5	95	1.8		881.4		8.6			
13	5	95	0.8		214.3		26.0			
25	5	95	0.8		172.7		6.1			
26	5	95	0.8		260.1		10.8			
27	5	95	1.6		494.1		20.5			
28	5	95	2.0		1034.1		11.9			
29	5	95	1.4		545.3		9.9			
30	5	95	0.9		360.3		7.1			
31	5	95	0.6		188.1		9.0			
1	6	95	0.6		222.8		8.1			
2	6	95	1.3		445.3		29.7			
3	6	95	1.1		418.7		10.7			
4	6	95	1.2		399.4		5.5			
5	6	95	1.1		272.6		9.4			
6	6	95	0.8		301.3		7.5			
7	6	95	0.8		396.2		7.6			
8	6	95	0.7		265.2		7.2			
9	6	95	0.9		218.9		3.1			
10	6	95	1.2		416.9		6.0			
11	6	95	1.3		400.9		6.0			
12	6	95	1.4		500.6		8.1			
15	6	95	2.1		490.2		10.9			
16	6	95	0.6		181.2		3.5			
17	6	95	0.9		403.9		3.9			
18	6	95	0.7		297.7		11.5			
19	6	95	0.3		112.0		4.6			
20	6	95	0.5		65.6		9.2			
21	6	95	0.7		120.3		11.8			
22	6	95	0.7		236.9		20.8			
23	6	95	0.3		115.8		5.3			
25	6	95	0.7		248.5		14.6			
26	6	95	0.5		97.1		8.5			
27	6	95	0.6		17.8		71.6			
21	9	95	1.1		427.7		23.8			
22	9	95	0.8		256.3		44.9			
23	9	95	0.3		30.1		4.9			
24	9	95	0.0		24.3		11.8			
25	9	95	0.1		44.9		4.3			

Table A3 (continued)

26	9	95	0.2	106.8	2.8
27	9	95	0.5	83.4	35.6
28	9	95	0.6	93.2	24.9
29	9	95	0.9	176.9	65.8
30	9	95	0.8	47.7	18.8
1	10	95	0.1	47.9	47.4
2	10	95	0.6	15.1	54.6
3	10	95	0.5	47.0	31.6
4	10	95	1.3	61.6	23.9
5	10	95	0.3	42.0	8.2
6	10	95	0.2	97.0	34.4
7	10	95	3.3	158.2	7.9
8	10	95	1.5	174.7	13.3
9	10	95	2.2	174.3	7.8
10	10	95	0.5	161.0	10.3
11	10	95	1.3	115.5	5.2
12	10	95	0.5	76.5	10.4
13	10	95	1.1	99.2	14.8
14	10	95	1.5	141.2	7.1
15	10	95	0.7	237.7	16.7
16	10	95	0.3	91.8	8.2
17	10	95	0.8	47.8	7.8
18	10	95	1.2	81.9	9.9
19	10	95	0.1	61.1	6.6
20	10	95	1.7	260.9	18.9
21	10	95	1.5	141.7	50.6
22	10	95	0.5	90.6	9.0
24	10	95	0.5	66.6	15.6
25	10	95	0.9	196.2	36.9
26	10	95	0.8	137.7	21.6
27	10	95	1.5	66.6	15.0
28	10	95	0.4	57.4	14.5
29	10	95	0.4	86.3	17.7
30	10	95	0.5	299.0	48.7
31	10	95	1.0	248.6	35.6
1	11	95	0.7	293.2	34.4
2	11	95	1.3	415.8	39.4
3	11	95	0.2	156.8	11.4
5	11	95	0.3	133.5	4.2
6	11	95	0.2	37.7	23.1
7	11	95	1.1	123.5	14.1
8	11	95	0.8	44.1	47.8
9	11	95	0.2	10.3	17.4
10	11	95	1.2	146.1	34.5
13	11	95	0.1	42.5	19.1
14	11	95	0.8	216.2	6.7
15	11	95	2.7	443.5	8.0
17	11	95	0.5	9.6	12.2
19	11	95	0.4	105.3	6.7
20	11	95	0.2	76.4	0.0
21	11	95	0.1	52.4	0.2
22	11	95	0.1	53.0	1.2
23	11	95	0.4	26.5	16.4
25	11	95	0.4	106.9	42.0
26	11	95	0.4	29.4	12.4
27	11	95	0.3	112.5	6.8
28	11	95	0.1	82.9	11.3
29	11	95	0.4	166.2	8.7
30	11	95	0.8	318.2	55.1
1	12	95	0.2	46.0	2.3

Table A3 (continued)

2	12	95	0.1		8.9		7.3			
3	12	95	0.1		14.3		1.6			
4	12	95	0.0		65.7		4.7			
5	12	95	0.0		109.8		11.3			
6	12	95	0.0		64.9		6.2			
23	5	96	0.4		197.8		12.0			
24	5	96	0.3	9.9	154.5	0.450	9.5	0.97	0.16	10.0
`25-27		96	0.2	9.5	68.3	0.262	4.4	1.59	0.75	5.5
28	5	96	0.3	11.7	305.8	0.227	9.7	1.39	0.10	7.6
29	5	96	0.3	7.6	266.8	0.057	9.5	3.16	1.00	13.5
30	5	96	0.4	9.9	287.7	0.135	8.7	1.16	0.94	7.3
31	5	96	0.3	15.9	520.6	0.072	4.0	0.69	1.51	11.7
2	6	96	0.6	13.7	433.9		1.3	0.34	0.16	4.1
3	6	96	0.6	9.1	194.9	0.093	7.3	0.56	0.38	10.0
4	6	96	0.2	7.5	180.4	0.295	4.5	0.53	0.25	2.9
5	6	96	1.2	21.7	477.0	0.104	8.3	0.70	1.07	6.0
6	6	96	0.6	8.8	420.3		7.5	0.53	0.03	6.7
7	6	96	0.7	17.0	862.3	0.169	3.2	0.47		7.4
8	6	96	0.4	10.5	355.8	0.083	5.1	0.38	0.02	4.2
9	6	96	1.3	10.3	309.3	0.008	2.5	0.38	0.15	5.6
10	6	96	0.5	8.5	227.2	0.016	3.0	0.27		3.6
11	6	96	0.5	6.7	311.8	0.253	5.2	0.42		7.7
12	6	96	0.7	7.6	273.6	0.166	6.7	0.53	0.78	3.5
13	6	96	0.3	8.6	244.2	0.248	2.4	0.54	0.57	5.4
14	6	96	0.3	10.9	226.0	0.036	8.1	1.05		6.9
15	6	96	0.2	1.9	53.9		1.3	0.15	0.48	6.7
16	6	96	0.3	8.2	116.7	0.041	3.0	0.26	0.45	4.4
18	6	96	0.3	5.7	141.5	0.113	3.6	0.28	0.47	4.4
19	6	96	0.3	7.6	256.9	0.050	2.0	0.41	0.05	4.2
20	6	96	3.6	10.7	294.6	0.254	7.3	2.23	0.96	8.8
21	6	96	0.4	10.2	244.3	0.253	5.8	1.01	0.42	3.0
22	6	96	1.1	7.0	191.3		3.2	0.45	0.63	4.4
23	6	96	3.8	7.0	231.3	0.010	4.9	0.68	0.28	3.9
24	6	96	0.2	4.2	149.8	0.045	10.4	2.43	0.60	5.9
25	6	96	0.3	4.0	148.5	0.302	3.8	0.63	0.37	2.6
26	6	96	0.2	6.0	190.5		3.6	0.44	0.10	3.4
27	6	96	1.0	17.7	664.0	0.492	13.8	1.42	0.45	6.8
28	6	96	0.3	9.6	263.8	0.054	3.8	0.98	0.26	7.2
29	6	96	0.4	11.7	231.3	0.670	2.8	0.51		3.8
30	6	96	0.5	7.5	202.9	0.149	6.1	0.45	0.66	4.7
1	7	96	0.3	6.9	178.4	0.265	2.0	0.62	0.55	4.2
3	7	96	0.6	8.1	297.1	0.373	2.3	0.85	0.58	5.7
4	7	96	0.3	14.3	403.2	0.053	9.9	1.35	1.62	5.8
5	7	96	0.5	9.2	247.2	0.935	2.7	0.94	0.97	5.2
6	7	96	0.7	13.8	578.0	0.745	2.4	1.23	0.64	6.4
7	7	96	0.5	21.9	793.4	0.082	11.0	1.45	1.60	5.6
8	7	96	0.6	22.8	910.8	0.927	13.1	1.03	4.02	9.5
9	7	96	1.0	16.4	603.7	1.272	13.4	1.15	1.38	8.2
10	7	96	0.7	17.7	425.9	1.240	8.2	1.00	2.29	6.2
11	7	96	1.4	27.6	284.2		13.0	0.83	1.95	5.6
12	7	96	0.3	7.1	202.9	0.146	4.5	0.79	2.12	5.5
13	7	96	0.7	11.4	714.5	0.201	10.5	0.96		9.0
14	7	96	1.7	35.5	810.5	0.168	3.1	1.23	1.27	10.0
16	7	96	1.4	24.0	673.8	0.030	2.5	1.30	0.33	7.0
17	7	96	0.6	10.6	170.2	0.658	3.1	0.54		8.9
18	7	96	0.2	2.8	147.7	0.233	2.9	0.16		4.0
20	7	96	0.5	15.8	321.3	0.016	2.8	1.81		4.9
21	7	96	0.5	6.6	227.1	0.078	1.8	0.52	0.55	4.4
24	7	96	0.7	12.7	327.3	0.164	6.0	0.51	0.28	6.2
26	7	96	0.4	9.6	421.3	0.043	2.2	0.59	0.39	7.9

Table A3 (continued)

27	7	96	0.6	11.9	286.5		12.6	1.15	0.14	6.3
28	7	96	0.2	6.2	263.6	0.082	7.6	0.50	0.22	6.2
29	7	96	0.2	3.9	154.4	0.092	7.1	0.45	0.25	6.4
30	7	96	0.2	12.0	359.8	0.018	8.0	0.66	0.26	9.6
31	7	96	1.8	16.1	537.1		18.7	1.23	0.38	11.2
1	8	96	0.8	15.9	679.8	0.370	31.2	1.21	1.01	11.6
2	8	96	1.2	18.2	589.0	0.327	7.5	0.96	0.55	7.2
3	8	96	1.7	16.6	522.6	0.479	1.9	1.11	1.14	13.1
4	8	96	1.0	11.6	378.6	0.141	2.3	0.99	0.32	4.6
10	11	96	0.5	1.6	46.8		3.1	0.80	0.33	6.9
11	11	96	0.4	4.0	185.1	0.081	1.8	1.96		2.8
12	11	96	1.1	9.1	467.4		9.0	3.17	0.33	3.1
13	11	96	2.1	13.1	403.4	0.263		4.60	0.64	6.7
15	11	96	1.8	19.0	562.9	0.187	20.1	5.83	0.33	6.8
16	11	96	0.8	12.4	292.3	0.373	16.2	5.78	0.40	6.2
17	11	96	0.5	9.4	426.3	0.100	17.7	4.62	0.12	6.5
18	11	96	1.4	8.6	386.8		10.1	3.30	0.04	8.2
19	11	96	2.3	17.7	808.3	0.224	12.2	2.62	0.22	9.4
20	11	96	4.9	12.1	552.1	0.095	15.5	2.00	0.04	11.7
21	11	96	3.1	12.8	599.3	0.185	4.2	1.41	0.57	8.6
22	11	96	1.6	2.0	95.7		3.7	0.78		7.1
23	11	96	1.7	2.9	52.1		3.2	0.97	0.13	7.3
24	11	96	1.3	3.9	181.1	0.105	5.9	1.59	0.17	9.3
25	11	96	2.5	4.5	282.4	0.524	10.8	1.41	0.74	10.6
26	11	96	1.0	6.4	120.1	0.028	9.2	1.75	0.29	9.2
27	11	96	0.9	5.4	208.6	0.227	1.4	1.16	0.21	8.7
28	11	96	1.5	2.0	40.5		2.7	0.53		4.8
29	11	96	1.3	3.0	115.4	0.256	5.0	1.38	0.53	7.5
1	12	96	1.6	9.7	559.7	0.138	4.7	1.87		3.8
2	12	96	0.8	2.7	176.5	0.490	3.2	0.69	0.04	5.3
3	12	96	2.1	3.4	255.9	0.096	6.9	1.04	0.12	5.6
4	12	96	2.8	15.2	568.9	0.029	17.6	2.95	0.23	8.2
5	12	96	0.6	5.0	191.5	0.072	7.0	1.57	0.09	4.3
7	12	96	0.7	1.9	68.1	0.068	3.0	0.70		3.2
8	12	96	1.0	2.8	162.3	0.185	6.4	0.96		3.5
9	12	96	1.0	1.8	70.3	0.027	2.4	0.57		2.2
10	12	96	0.5	2.3	99.2		2.2	0.61	0.37	3.3
11	12	96	0.6	5.8	335.1	0.022	14.1	2.37	0.08	4.3
12	12	96	3.0	10.3	538.4	0.169	8.4	2.77	0.28	5.5
13	12	96	1.0	4.6	192.2	0.075	5.7	1.62	0.10	6.0
14	12	96	1.7	7.8	304.0	0.289	12.1	3.88	0.07	8.5
16	12	96	1.1	3.8	106.9	0.788	23.3	5.22	0.18	11.3
17	12	96	1.5	6.6	251.9	0.266	28.2	3.41	0.19	10.4
19	12	96	2.1	9.9	421.1	0.514	24.3	3.48	0.00	9.4
20	12	96	0.9	3.8	218.4	0.270	17.2	2.36	0.32	7.3
23	12	96	2.9	5.9	350.2	0.586	62.4	2.32	0.05	13.2
24	12	96	1.4	4.9	280.8	0.326	36.2	1.14	0.14	11.0
26	12	96	0.6	1.1	94.8	0.190	8.7	0.91		4.7
30	12	96	0.8	11.3	481.5	0.370	12.3	2.42	0.14	8.7
3	1	97	1.0	6.2	207.6	0.173	12.2	2.72	0.53	10.6
5	1	97	1.7	5.3	293.8	0.091	8.6	3.10	0.18	6.2
7	1	97	0.8	3.7	80.6	0.121	3.1	1.85	0.31	5.2
10	1	97	1.4	10.6	338.1	0.080	5.0	2.09	0.15	5.9
11	1	97	1.5	5.4	279.0	0.109	8.6	2.94	0.20	9.7
12	1	97	2.3	7.6	99.7	0.228	8.8	4.07	1.23	9.7
13	1	97	1.0	3.3	55.9	0.122	7.5	2.31		6.4
15	1	97	1.8	21.0	107.1	0.131	5.6	1.65	0.15	6.5
16	1	97	1.8	14.3	244.3	0.115	12.1	3.30	0.78	13.3
17	1	97	1.9	15.2	307.0	0.032	61.3	8.56	1.31	12.4
18	1	97	2.8	6.2	235.8	0.296	12.7	4.41	0.17	7.8

Table A3 (continued)

19	1	97	2.1	19.9	719.0	0.331	19.5	5.61	0.49	8.1
20	1	97	3.3	22.4	646.7	0.971	69.4	10.70	1.55	16.4
21	1	97	3.3	12.7	183.2	0.057	31.3	4.12	0.61	5.7
22	1	97	4.3	1.4	42.5	0.042	14.6	1.70		6.2
23	1	97	1.3	3.1	80.2	0.003	11.1	1.65	0.27	4.9
24	1	97	2.1	8.9	404.6	0.503	21.7	4.59	0.52	10.5
25	1	97	1.2	1.0	55.7	0.101	6.6	0.32	0.12	3.6
26	1	97	4.5	15.1	398.7	0.049	26.8	9.54		24.1
27	1	97	1.0	16.3	124.8		4.4	0.81	0.06	8.8
28	1	97	2.9	8.3	455.2	0.062	23.4	3.10	0.43	14.7
29	1	97	1.6	7.9	154.5	0.561	16.0	3.22	0.74	12.6
30	1	97	0.3	0.8	74.0	0.071	2.3	0.22		7.7
8	3	97	1.2	10.6	207.4	0.113	11.8	1.72	0.19	7.9
9	3	97	1.4	6.2	164.8	0.089	5.3	1.20	0.16	9.3
10	3	97	1.1	7.1	153.6	0.549	3.7	1.25	0.43	4.9
11	3	97	0.4	3.8	112.1	0.353	3.4	1.99	0.16	5.9
14	3	97	0.9	9.1	183.3	0.022	6.1	3.02	0.32	7.3
16	4	97	1.2	5.0	189.1	0.152	15.8	2.06	0.01	10.9
17	4	97	1.2	2.0	42.8	0.278	4.1	0.92	0.01	4.9
18	4	97	1.2	3.4	99.2	0.074	4.7	1.85		8.2
19	4	97	1.2	7.7	237.5	0.045	6.1	1.48	0.09	9.4
20	4	97	2.2	4.4	171.8	0.011	3.3	0.60		13.7
21	4	97	2.4	11.6	547.1	0.273	6.8	0.98		16.7
22	4	97	6.1	26.0	1817.7	0.892	21.4	2.12	0.32	21.4
23	4	97	7.4	69.4	4151.7	1.680	30.9	2.16		17.3
24	4	97	4.4	17.1	278.9	0.138	63.5	0.60	0.28	6.0
25	4	97	2.8	22.4	272.1	0.038	122.5	0.91	1.18	4.4
26	4	97	2.1	11.6	287.3	0.171	7.4	1.34	0.12	7.0
27	4	97	1.2	4.1	74.0		8.8	0.57		1.9
28	4	97	2.1	11.0	223.8	0.302	22.8	1.38	0.26	6.2
29	4	97	2.4	8.9	249.0	0.044	13.2	1.29		6.1
30	4	97	2.0	4.1	103.3	0.421	4.3	8.96	1.00	12.3
1	5	97	2.0	6.9	127.3	0.267	27.7	7.12	0.27	3.4
2	5	97	3.2	23.3	386.1	0.147	114.7	1.46	0.33	9.2
3	5	97	1.5	32.7	439.7	0.038	49.0	1.52	1.45	9.7
4	5	97	3.1	10.5	287.2	0.012	27.6	2.87	0.30	6.4
5	5	97	1.9	18.2	533.1	0.427	62.9	2.47	0.61	12.7
6	5	97	1.5	15.8	512.2	0.268	39.9	1.15	0.09	10.8
8	5	97	2.3	19.7	886.7	0.430	15.6	0.63		8.0
9	5	97	1.6	15.9	832.4	0.414	27.6	1.24	0.33	9.1
10	5	97	1.3	16.0	562.5	0.339	31.5	2.91	0.37	10.4
11	5	97	1.7	22.1	620.6	0.323	52.3	2.24	0.72	10.2
12	5	97	3.7	33.1	907.8	0.249	18.5	1.41	0.62	10.8
13	5	97	2.1	17.2	615.9	0.144	11.8	1.08	0.58	7.3
14	5	97	1.3	10.9	357.7	0.065	7.2	0.99	0.44	7.2
15	5	97	1.2	9.1	242.6	0.145	27.5	0.61	0.39	4.8
16	5	97	2.4	13.1	324.9		35.0	1.02	0.31	5.3
17	5	97	0.9	8.7	124.0		13.7	1.06	0.20	4.5
18	5	97	1.8	15.8	395.9		24.4	1.09	0.29	7.3
19	5	97	0.8	12.5	239.4		16.0	1.04	0.13	4.8
20	5	97	2.5	24.2	430.6	0.102	19.9	3.10	0.38	6.4
21	5	97	1.8	24.0	723.4	0.271	19.7	1.32	0.21	8.0
22	5	97	1.9	23.4	749.2	0.340	65.1	2.51	0.56	9.9
23	5	97	3.3	14.1	677.1	0.060	13.8	1.29	0.01	11.9
24	5	97	1.1	2.4	123.8		4.2	0.60	0.18	5.9
25	5	97	0.9	9.2	246.2	0.022	33.1	0.67	0.39	6.0
26	5	97	2.0	8.6	94.4	0.048	5.4	0.36	0.25	6.2
27	5	97	1.8	2.6	77.2		14.1	0.30	0.02	6.3
28	5	97	0.4	4.1	93.3		8.8	0.27		5.3
29	5	97	2.6	9.8	246.9	0.308	13.1	1.04		8.0

Table A3 (continued)

30	5	97	3.0	18.3	203.8	0.009	29.0	0.81	0.29	6.7
31	5	97	2.1	14.9	273.0	0.003	15.0	0.82	0.36	8.4
01	6	97	1.6	5.9	68.1	0.076	27.5	0.87	0.33	2.8
2	6	97	1.3	3.1	91.3		8.6	0.64	0.23	1.5
3	6	97	2.6	16.9	407.4	0.059	58.0	1.52	0.33	5.8
4	6	97	0.5	4.2	96.6	0.133	34.9	0.78		2.7
5	6	97	0.3	3.2	106.4	0.008	8.8	0.63		1.9
6	6	97	0.9	8.0	297.0		5.7	1.08	0.18	3.8
7	6	97	2.3	20.5	393.1	0.052	38.3	2.13	0.42	5.9
8	6	97	1.5	16.7	335.8	0.052	37.0	2.14	0.81	4.0
9	6	97	1.7	20.9	315.0	0.400	22.2	0.98	0.62	2.7
10	6	97	1.6	17.5	336.5	0.007	23.2	0.77	0.70	3.7
11	6	97	1.4	8.9	268.1		13.8	0.68	0.14	4.7
12	6	97	1.4	17.7	222.8		62.9	1.22	0.11	3.9
13	6	97	1.4	11.2	272.4	0.092	73.9	1.77	0.29	6.5
14	6	97	1.4	14.7	202.3	1.128	106.2	2.41	1.40	8.5
15	6	97	1.9	12.3	342.4	0.042	94.3	1.70	0.70	7.8
16	6	97	3.2	20.2	239.2	0.129	27.4	1.87	0.41	10.7
17	6	97	0.8	7.7	113.2	0.037	12.9	0.94	0.45	7.1
18	6	97	1.0	8.8	164.6	0.037	22.6	1.05	0.08	3.4
19	6	97	1.6	14.2	138.4	0.241	8.9	1.86	0.44	12.3
20	6	97	2.5	16.2	711.9	0.242	24.3	1.31	0.33	10.3
21	6	97	1.4	9.6	312.2	0.098	14.9	1.89	0.41	5.3
22	6	97	6.7	19.4	664.0	0.146	19.0	8.72		13.3
23	6	97	0.6	8.1	138.8		22.9	1.17	0.18	5.5
24	6	97	0.4	8.2	239.5	0.095	13.5	2.02	0.33	4.0
25	6	97	1.3	8.2	226.3	0.106	7.5	1.42	0.23	6.3
26	6	97	0.3	5.7	251.9	0.034	9.0	0.71	0.50	7.5
27	6	97	0.7	11.3	193.5		7.0	0.61	0.50	3.7
28	6	97	2.0	15.9	191.3		5.9	0.58	0.32	7.0
29	6	97	2.6	12.8	252.8	0.095	28.4	0.65	0.80	6.7
02	7	97	1.7	14.8	338.6	0.167	13.6	1.08	0.58	4.9
03	7	97	1.0	5.6	220.1		14.9	0.62	0.07	8.8
04	7	97	0.8	9.9	168.1	0.070	19.8	0.67	0.55	7.0
05	7	97	1.4	12.7	363.3	0.199	14.4	1.14	0.13	5.0
06	7	97	3.8	22.4	749.6	0.354	11.8	1.95	0.18	10.4
07	7	97	6.1	27.2	1432.3	0.249	41.8	1.59		17.7
08	7	97	1.7	9.5	292.5	0.668	16.5	1.09	0.24	10.9
09	7	97	4.6	9.2	305.1	0.776	54.9	1.55		12.8
10	7	97	2.0	9.3	282.0	0.126	50.8	1.35	0.71	8.3
11	7	97	0.8	4.5	137.1	0.107	4.8	0.61	0.27	7.9
12	7	97	0.8	5.6	179.3		12.7	0.47		6.7
13	7	97	1.5	4.8	97.8	0.721	8.0	0.60	0.40	6.5
14	7	97	0.8	5.0	79.4	0.284	6.8	0.43	0.43	7.6
15	7	97	2.2	6.7	101.1	0.092	8.6	0.29	1.87	5.6
16	7	97	0.6	6.7	84.7	0.024	9.3	0.25	0.20	4.3
17	7	97	1.6	6.8	95.3		5.4	0.42	0.11	6.0
18	7	97	2.7	8.8	100.6	0.003	4.5	0.34	0.13	4.2
19	7	97	2.9	15.3	287.9	0.098	11.9	1.02		7.7
20	7	97	1.6	4.1	78.9	0.246	5.3	0.41	0.23	3.9
21	7	97	1.2	3.0	135.9	0.174	10.2	0.80	0.09	2.6
22	7	97	1.0	4.0	84.4		23.8	0.46	0.33	2.5
23	7	97	1.4	4.3	91.4	0.046	14.5	0.62	0.09	1.9
24	7	97	2.3	14.2	148.4	0.424	21.8	0.54	0.29	3.3
25	7	97	2.1	7.0	136.2	0.118	14.6	0.51	0.30	2.6
26	7	97	3.0	16.1	420.5	0.313	40.4	0.55	0.20	2.6

Table A3 (continued)

dd	mm	yy	Mo	Cd	Sb	La	Ce	Sm	Au	Hg
22	4	95		0.24						
23	4	95		0.13						
24	4	95		0.10						
25	4	95		0.14						
26	4	95		0.27						
27	4	95		0.26						
28	4	95		0.31						
29	4	95		0.29						
30	4	95		0.16						
1	5	95		0.15						
2	5	95		0.22						
3	5	95		0.18						
4	5	95		0.17						
5	5	95		0.19						
6	5	95		0.33						
7	5	95		0.42						
8	5	95		0.51						
9	5	95		0.38						
10	5	95		0.38						
11	5	95		0.24						
12	5	95		0.09						
13	5	95		0.25						
25	5	95		0.18						
26	5	95		0.23						
27	5	95		0.35						
28	5	95		0.34						
29	5	95		0.28						
30	5	95		0.21						
31	5	95		0.57						
1	6	95		0.25						
2	6	95		0.32						
3	6	95		0.32						
4	6	95		0.36						
5	6	95		0.22						
6	6	95		0.24						
7	6	95		0.24						
8	6	95		0.27						
9	6	95		0.08						
10	6	95		0.14						
11	6	95		0.09						
12	6	95		0.11						
15	6	95		0.32						
16	6	95		0.17						
17	6	95		0.14						
18	6	95		0.51						
19	6	95		0.19						
20	6	95		0.18						
21	6	95		0.20						
22	6	95		0.34						
23	6	95		0.15						
25	6	95		0.28						
26	6	95		0.19						
27	6	95		0.14						
21	9	95		0.20						
22	9	95		0.34						
23	9	95		0.05						
24	9	95		0.09						
25	9	95		0.08						
26	9	95		0.09						

Table A3 (continued)

27	9	95	0.11
28	9	95	0.08
29	9	95	0.10
30	9	95	0.11
1	10	95	0.13
2	10	95	1.16
3	10	95	0.15
4	10	95	0.15
5	10	95	0.08
6	10	95	0.05
7	10	95	0.14
8	10	95	0.19
9	10	95	0.17
10	10	95	0.17
11	10	95	0.08
12	10	95	0.11
13	10	95	0.13
14	10	95	0.16
15	10	95	0.26
16	10	95	0.05
17	10	95	0.06
18	10	95	0.06
19	10	95	0.13
20	10	95	0.23
21	10	95	0.59
22	10	95	0.14
24	10	95	0.10
25	10	95	0.53
26	10	95	0.39
27	10	95	0.18
28	10	95	0.10
29	10	95	0.23
30	10	95	0.72
31	10	95	2.51
1	11	95	2.91
2	11	95	2.65
3	11	95	0.13
5	11	95	0.07
6	11	95	0.12
7	11	95	0.24
8	11	95	0.23
9	11	95	0.20
10	11	95	0.23
13	11	95	0.29
14	11	95	0.15
15	11	95	0.11
17	11	95	0.10
19	11	95	0.05
20	11	95	0.19
21	11	95	0.20
22	11	95	0.15
23	11	95	0.39
25	11	95	0.60
26	11	95	0.28
27	11	95	0.25
28	11	95	0.20
29	11	95	0.16
30	11	95	0.54
1	12	95	0.19
2	12	95	0.21

Table A3 (continued)

3	12	95		0.10					
4	12	95		0.40					
5	12	95		0.45					
6	12	95		0.12					
23	5	96		0.14					
24	5	96		0.14	0.3193	0.1333		0.017	0.003052
25-27		96		0.15	0.2424	0.0899	0.0578	0.012	0.000548
28	5	96		0.38	0.5358	0.2527	0.2743	0.030	0.002220
29	5	96		0.33	0.5502	0.1447	0.0575	0.020	0.000770
30	5	96		0.10	0.2828	0.2097	0.2488	0.028	0.001212
31	5	96		0.16	0.2290	0.3268	0.1996	0.044	0.000846
2	6	96		0.21	0.1222	0.2241	0.1496	0.035	0.000049
3	6	96		0.10	0.1811	0.1010	0.1138	0.016	0.000199
4	6	96		0.15	0.1154	0.1361	0.0904	0.017	0.000380
5	6	96		0.09	0.2537	0.3704	0.2159	0.049	0.000310
6	6	96		0.15	0.2064	0.2725	0.4524	0.037	
7	6	96		0.03	0.1492	0.4579	0.6616	0.063	0.000188
8	6	96		0.01	0.1393	0.3012	0.3381	0.040	0.000213
9	6	96		0.04	0.1099	0.2255	0.1600	0.030	0.000081
10	6	96		0.09	0.0737	0.1908	0.1265	0.026	0.000076
11	6	96		0.12	0.1234	0.1986	0.2936	0.031	
12	6	96		0.09	0.1628	0.1824	0.1214	0.024	0.000489
13	6	96		0.13	0.1934	0.1864	0.1628	0.026	0.000656
14	6	96		0.08	0.2753	0.1617	0.3110	0.029	0.000033
15	6	96		0.09	0.1164	0.0408	0.0464	0.006	0.000141
16	6	96		0.04	0.1109	0.0560	0.0481	0.008	0.000560
18	6	96		0.25	0.1931	0.1250		0.014	0.001530
19	6	96		0.32	0.2228	0.1583	0.3127	0.024	0.000090
20	6	96		0.20	0.3624	0.1607	0.1259	0.021	0.000158
21	6	96		0.12	0.1992	0.1029	0.0179	0.016	0.000013
22	6	96		0.16	0.1630	0.1447	0.0881	0.020	0.000033
23	6	96		0.22	0.2477	0.1547	0.2505	0.023	0.000038
24	6	96	1.14	0.29	0.2226	0.1214	0.1682	0.016	0.000223
25	6	96	0.52	0.23	0.1350	0.1193	0.0391	0.017	0.000430
26	6	96	0.60	0.14	0.0895	0.1508	0.0238	0.020	0.000291
27	6	96	0.41	0.22	0.5133	0.6148	0.7997	0.069	0.000215
28	6	96	0.55	0.13	0.2743	0.1585	0.1137	0.023	0.000110
29	6	96	0.27	0.06	0.1502	0.1363	0.2845	0.020	0.000302
30	6	96	0.21	0.20	0.1231	0.1236	0.0949	0.019	0.000140
1	7	96	0.28	0.12	0.1903	0.1465	0.2082	0.021	0.000124
3	7	96	0.20	0.15	0.2473	0.2451	0.1370	0.034	0.000123
4	7	96	0.07	0.17	0.2552	0.2832	0.2927	0.040	0.000051
5	7	96	0.30	0.25	0.2201	0.2214	0.1899	0.033	0.000185
6	7	96	0.15	0.31	0.2909	0.2953	0.2562	0.044	0.000213
7	7	96	0.16	0.18	0.3839	0.5672	0.8300	0.085	0.000235
8	7	96	0.09	0.49	0.2529	0.7058	1.0267	0.109	0.000229
9	7	96	0.19	0.15	0.3215	0.4773	0.4840	0.073	0.000170
10	7	96	0.14	0.19	0.3146	0.2991	0.6241	0.046	0.000141
11	7	96	0.21	0.21	0.1978	0.2508	0.3263	0.036	0.000122
12	7	96	0.38	0.15	0.1747	0.1543	0.1776	0.021	0.000060
13	7	96	0.31	0.19	0.2307	0.4413	1.0067	0.066	0.000391
14	7	96	0.12	0.21	0.2569	0.5453	0.6260	0.110	0.000003
16	7	96	0.23	0.23	0.3123	0.5360	0.7326	0.082	
17	7	96	0.48	0.12	0.1832	0.2352	0.3642	0.030	
18	7	96	0.17	0.06	0.0584	0.0827	0.0947	0.013	
20	7	96	0.26	0.14	0.2669	0.2147	0.2646	0.031	
21	7	96	0.32	0.09	0.1180	0.1511	0.2111	0.022	
24	7	96	0.33	0.07	0.1194	0.2869	0.3093	0.041	
26	7	96	0.44	0.11	0.1802	0.2309	0.3660	0.031	0.000545
27	7	96	0.49	0.22	0.4732	0.1910	0.2502	0.024	0.003169

Table A3 (continued)

28	7	96	0.30	0.19	0.3477	0.1740		0.022	0.001776	
29	7	96	0.28	0.08	0.1472	0.1063	0.1380	0.013	0.003111	
30	7	96	0.66	0.19	0.2474	0.2354	0.3933	0.033	0.002106	
31	7	96	0.69	0.17	0.3293	0.3102	0.5179	0.042	0.003673	
1	8	96	0.40	0.36	0.3848	0.3448	0.4265	0.048	0.005592	0.0575
2	8	96	0.83	0.27	0.2842	0.4510	0.6793	0.066	0.001854	0.0594
3	8	96	0.23	0.24	0.3248	0.4074	0.2130	0.058	0.002264	
4	8	96	0.67	0.10	0.2886	0.2919	0.4607	0.044	0.000194	0.0084
10	11	96	0.53	0.15	0.2437	0.0329	0.0817	0.004	0.000665	0.0481
11	11	96	0.25	0.28	0.3118	0.1326		0.021	0.000479	0.0208
12	11	96	0.34	0.28	0.3175	0.0741		0.009	0.000940	0.0115
13	11	96	0.75	0.32	0.5280	0.1055	0.1204	0.014		0.0247
15	11	96	0.70	0.54	0.7194	0.1316	0.1393	0.017		0.0301
16	11	96	0.83	0.41	0.7105	0.1043		0.013		0.0170
17	11	96	0.47	0.33	0.7636	0.1131	0.0799	0.016		0.0332
18	11	96	0.83	0.31	0.3653	0.2321	0.2679	0.034		0.0190
19	11	96	0.50	0.55	0.3498	0.5515	0.8364	0.088		0.0278
20	11	96	0.70	0.19	0.3064	0.3582	0.5095	0.052	0.000295	0.0562
21	11	96	0.42	0.44	0.2475	0.3538	0.4379	0.048	0.000646	0.0310
22	11	96	0.50	0.24	0.2201	0.0407	0.0222	0.005	0.000709	0.0621
23	11	96	0.77	0.15	0.1517	0.0696	0.1671	0.006	0.000780	0.0509
24	11	96	0.40	0.13	0.2164	0.0972	0.0778	0.009	0.000491	0.0530
25	11	96	0.47	0.32	0.1850	0.1347	0.2709	0.016	0.003112	0.0432
26	11	96	0.52	0.22	0.3037	0.0650		0.008	0.001832	0.0497
27	11	96	0.43	0.17	0.2393	0.0915	0.1694	0.012	0.000680	0.0445
28	11	96	1.05	0.18	0.0795	0.0443		0.005	0.002365	0.0361
29	11	96	0.67	0.23	0.1735	0.0600		0.006	0.000298	0.0273
1	12	96	0.29	0.15	0.2921	0.0946	0.0487	0.014	0.000533	0.0344
2	12	96	0.53	0.20	0.2360	0.0772	0.0147	0.011	0.000393	0.0398
3	12	96	0.40	0.20	0.3574	0.1600	0.1906	0.022	0.000210	0.0394
4	12	96	0.57	0.35	0.4960	0.1576	0.0779	0.021	0.000451	0.1164
5	12	96	0.61	0.23	0.3306	0.0920	0.0928	0.013	0.000350	0.0620
7	12	96	0.50	0.15	0.1632	0.0339		0.004	0.000451	0.0488
8	12	96	0.79	0.22	0.2242	0.1294	0.0057	0.019	0.001412	0.0641
9	12	96	0.24	0.14	0.1641	0.0255		0.002	0.000528	0.0311
10	12	96	1.03	0.14	0.1589	0.0298		0.003	0.000413	0.0690
11	12	96	0.51	0.22	0.3766	0.0536		0.008	0.000347	0.0851
12	12	96	0.74	0.45	0.4032	0.0920	0.0454	0.013	0.000714	0.0860
13	12	96	0.24	0.24	0.3566	0.0469		0.004	0.001037	0.0266
14	12	96	0.40	0.17	0.4240	0.1694	0.1617	0.021	0.000806	0.0208
16	12	96	0.48	0.46	0.4436	0.0744	0.0950	0.009	0.001587	0.0358
17	12	96	0.40	0.24	0.3880	0.2042	0.1806	0.027	0.001112	0.0364
19	12	96	0.33	0.18	0.4176	0.1976	0.3239	0.028	0.000465	0.0346
20	12	96	0.34	0.13	0.3475	0.1190	0.2078	0.016	0.000200	0.0191
23	12	96	0.31	0.24	0.3587	0.2702	0.2916	0.033	0.000768	0.0449
24	12	96	0.30	0.11	0.2046	0.2459	0.2742	0.034	0.000465	0.0296
26	12	96	0.41	0.13	0.6521	0.0264	0.0441	0.003	0.000664	0.0117
30	12	96	0.24	0.17	0.3425	0.4037	0.5673	0.058	0.000252	0.0132
3	1	97	0.51	0.25	0.4663	0.2005	0.1999	0.027	0.000465	0.0329
5	1	97	0.34	0.23	0.3686	0.1937	0.1844	0.024	0.001451	0.0121
7	1	97	0.34	0.17	0.2545	0.0433		0.006	0.000087	0.0132
10	1	97	0.49	0.09	0.3271	0.0595	0.0717	0.008	0.000313	0.0368
11	1	97	0.31	0.61	0.5682	0.0759		0.009	0.001086	0.0466
12	1	97	0.38	0.15	0.4793	0.0484		0.006		0.0082
13	1	97	0.48	0.05	0.2668	0.0256		0.002	0.000128	
15	1	97	0.65	0.10	0.3199	0.0716	0.0841	0.011	0.000088	0.0378
16	1	97	0.32	0.56	0.6142	0.1331		0.015	0.000465	0.0135
17	1	97	0.32	2.11	1.1950	0.1769	0.1181	0.015	0.000880	0.0416
18	1	97	0.36	0.48	1.4299	0.1019	0.0826	0.011	0.001408	0.0137
19	1	97	0.72	0.54	0.6774	0.1144	0.1052	0.016	0.000328	0.0735

Table A3 (continued)

20	1	97	0.62	0.74	1.4419	0.2764	0.3130	0.029	0.000825	0.0304
21	1	97	0.69	0.44	0.6198	0.0722		0.006	0.000765	0.0243
22	1	97	1.43	0.54	0.5395	0.0304		0.003	0.001998	0.0257
23	1	97	0.36	0.36	1.3994	0.0349	0.0155	0.005	0.000023	0.0282
24	1	97	0.27	0.27	0.6957	0.1781	0.0175	0.020	0.000117	0.0529
25	1	97	0.18	0.12	0.0744	0.0191	0.1607	0.002		0.0100
26	1	97	0.83	1.08	1.2223	0.2365	0.1292	0.021	0.001959	0.0337
27	1	97	1.34	0.32	0.2145	0.0242		0.005		0.0508
28	1	97	0.30	0.24	0.6147	0.1604	0.0866	0.017	0.000404	0.0377
29	1	97	0.09	0.57	0.8125	0.0748		0.008	0.000907	0.0483
30	1	97	0.25	0.08	0.1813	0.0296		0.003	0.001311	0.0151
8	3	97	0.50	0.19	0.3016	0.1405	0.1694	0.020	0.000473	0.0449
9	3	97	0.30	0.13	0.2754	0.0626	0.1392	0.010	0.000040	0.0123
10	3	97	0.82	0.08	0.8394	0.0894	0.0081	0.011	0.000099	0.0556
11	3	97	0.14	0.10	0.2322	0.0784		0.006	0.000050	0.0098
14	3	97	0.35	0.18	0.3243	0.1192	0.1292	0.019	0.000138	0.0413
16	4	97	0.65	0.42	0.4449	0.1297	0.1004	0.016	0.000353	0.0571
17	4	97	0.22	0.38	0.2484	0.0426		0.005	0.000397	0.0483
18	4	97	0.11	0.58	0.5656	0.0954		0.011	0.001125	0.0229
19	4	97	0.27	0.49	0.4268	0.1635	0.1846	0.023	0.000121	0.0675
20	4	97	0.20	0.21	0.2163	0.1779	0.1619	0.024	0.000481	0.0870
21	4	97	0.57	0.33	0.3892	0.5220	0.6374	0.068	0.001374	0.1395
22	4	97	0.81	0.35	0.6025	1.8066	3.1773	0.269	0.001503	0.0595
23	4	97		0.46	0.7494	4.7471	7.2459	0.719	0.002045	0.0338
24	4	97	0.08	0.32	0.1946	0.0847		0.013	0.000659	0.0285
25	4	97	0.08	0.37	0.2332	0.1831	0.1020	0.024	0.000564	0.0290
26	4	97	0.27	0.46	0.5391	0.1774	0.1523	0.021	0.000758	0.0738
27	4	97	0.18	0.35	0.1981	0.0274		0.004	0.000082	0.0725
28	4	97	0.08	0.46	0.4558	0.1313	0.1239	0.018	0.001872	0.1009
29	4	97	0.19	0.45	0.3131	0.1482	0.0738	0.021	0.000755	0.1188
30	4	97		0.36	0.5688	0.0947	0.2155	0.012	0.000707	0.0472
1	5	97	0.06	0.76	0.2998	0.0675		0.011	0.000637	0.0785
2	5	97	0.12	0.68	0.4516	0.2749	0.2908	0.037	0.000707	0.0971
3	5	97	0.09	0.46	0.4716	0.3459	0.1844	0.046	0.000393	0.0160
4	5	97	0.11	0.66	0.7444	0.2384	0.1209	0.035	0.000340	0.0229
5	5	97	0.06	0.71	0.7632	0.3772	0.4185	0.056	0.003105	0.0197
6	5	97	0.78	0.41	0.4690	0.4383	0.4913	0.068	0.000081	0.0295
8	5	97	0.62	0.30	0.2229	0.8807	0.9913	0.127	0.000453	0.0176
9	5	97	0.59	0.30	0.3593	0.8162	1.0442	0.114	0.000163	0.0259
10	5	97	0.59	0.38	0.3977	0.5101	0.6624	0.071	0.000072	0.0554
11	5	97	0.47	0.77	0.4386	0.4830	0.5923	0.068	0.000401	0.0417
12	5	97		0.63	0.5346	0.6589	0.4531	0.086	0.000441	0.0711
13	5	97	0.54	0.31	0.5468	0.4281	0.4233	0.060	0.000587	0.0379
14	5	97	0.02	0.25	0.3318	0.2728	0.1694	0.037	0.000299	0.0267
15	5	97	0.06	0.23	0.3244	0.0965	0.0449	0.034	0.000192	0.0111
16	5	97		0.55	0.2841	0.1463	0.0687	0.016	0.000571	0.0270
17	5	97	0.30	0.43	2.4288	0.0752	0.0498	0.011	0.000348	0.0190
18	5	97	0.25	0.38	0.3423	0.2284	0.3227	0.031	0.000355	0.0395
19	5	97	0.22	0.21	0.2357	0.0889	0.0762	0.012	0.000218	0.0200
20	5	97	0.18	0.57	0.5383	0.2169	0.4208	0.031	0.000361	0.0129
21	5	97	0.35	0.47	0.4590	0.5957	1.0035	0.084	0.000263	0.0340
22	5	97	0.42	0.44	0.6862	0.5866	1.0039	0.085	0.000079	0.0337
23	5	97	0.31	0.27	0.4008	0.4983	0.6019	0.078	0.000259	0.0873
24	5	97	0.15	0.10	0.1219	0.0841	0.0713	0.012	0.000057	0.0422
25	5	97	0.47	0.28	0.3148	0.1345	0.0301	0.019	0.000413	0.1226
26	5	97	0.25	0.06	0.1429	0.0477		0.007	0.000143	0.0591
27	5	97	0.14	0.08	2.5805	0.0424		0.005	0.000040	0.0758
28	5	97	0.13	0.04	0.0959	0.0689	0.0529	0.009	0.000174	0.0360
29	5	97		0.19	0.2690	0.2176		0.027	0.000305	
30	5	97	0.14	0.28	0.3262	0.1012		0.013	0.000125	0.0199

Table A3 (continued)

31	5	97	0.12	0.36	0.7371	0.1669	0.2940	0.021	0.000117	0.0820
01	6	97	0.14	0.23	0.2490	0.0594		0.006	0.000184	0.0229
2	6	97	0.13	0.13	0.2316	0.0780	0.0314	0.010	0.001058	0.0047
3	6	97	0.15	0.35	0.7456	0.2930	0.5601	0.040	0.000571	0.0083
4	6	97		0.16	0.2664	0.0626		0.006		0.0163
5	6	97	0.11	0.28	0.1268	0.0667		0.009	0.000249	0.0254
6	6	97	0.27	0.29	0.2455	0.2525	0.2956	0.030	0.000488	0.0708
7	6	97	0.41	0.42	0.3560	0.2346	0.3354	0.033	0.000171	0.1353
8	6	97		0.44	0.3176	0.1739		0.024	0.000199	0.0077
9	6	97		0.45	0.2405	0.1599		0.019		0.0469
10	6	97		0.36	0.3883	0.1728		0.021		0.0321
11	6	97	0.19	0.26	0.2310	0.1210	0.0778	0.017	0.000047	0.0828
12	6	97	0.16	0.33	0.1977	0.1164	0.1152	0.016		0.0830
13	6	97	0.16	0.41	0.6026	0.1953		0.028	0.000166	0.0342
14	6	97	0.50	0.56	0.6724	0.1889		0.025	0.000153	0.0494
15	6	97	0.36	0.35	0.4695	0.2534		0.043	0.000065	0.0664
16	6	97	0.32	0.26	0.3435	0.1850	0.0323	0.026	0.000291	0.1302
17	6	97	0.49	0.18	0.1946	0.1013	0.1801	0.014	0.000277	0.1739
18	6	97	0.29	0.28	0.3208	0.1820	0.1534	0.024	0.000318	0.0270
19	6	97	0.23	0.26	0.3853	0.1621	0.0349	0.021	0.000702	0.0575
20	6	97	0.13	0.28	0.3410	0.7498	1.2964	0.108	0.000130	0.0430
21	6	97	0.30	0.25	0.3508	0.2718	0.3485	0.038	0.000138	0.0544
22	6	97	0.78	0.84	0.5733	0.6683	0.2267	0.092	0.001242	0.0950
23	6	97	1.17	0.26	0.4149	0.1221	0.1614	0.018	0.000269	0.0473
24	6	97	1.11	0.28	0.3269	0.1511	0.1254	0.023	0.000544	0.0850
25	6	97	0.55	0.24	0.2883	0.1466	0.0461	0.024	0.000235	0.0266
26	6	97	1.24	0.12	0.2324	0.1666	0.2186	0.025	0.000669	0.0749
27	6	97	0.73	0.07	0.2231	0.1117	0.1154	0.015	0.008401	0.0610
28	6	97	0.86	0.16	0.2365	0.1427	0.1135	0.017	0.007823	0.0602
29	6	97	0.90	0.22	0.2373	0.1784	0.1200	0.024	0.004373	0.0998
02	7	97	0.48	0.23	0.3761	0.3312	0.3265	0.047	0.013386	0.0483
03	7	97	0.50	0.16	0.1596	0.1630	0.0116	0.021	0.007042	0.0653
04	7	97	0.49	0.21	0.2956	0.1541	0.1937	0.024	0.000906	0.0334
05	7	97	0.44	0.42	0.5884	0.3232	0.3833	0.049	0.004317	0.0017
06	7	97	0.70	0.52	0.7024	0.7009	1.0631	0.101	0.003356	0.0087
07	7	97	1.00	0.44	0.4328	1.2729	2.4160	0.191	0.016277	0.0470
08	7	97	0.10	0.12	0.1356	0.3256	0.2097	0.050	0.004908	0.0916
09	7	97	0.23	0.30	0.3946	0.2545	0.0500	0.034	0.020834	0.0053
10	7	97	0.37	0.27	0.2985	0.2065	0.0375	0.031	0.016013	
11	7	97	0.34	0.08	0.1827	0.0862		0.014	0.009609	0.0299
12	7	97	0.38	0.05	0.2960	0.1171	0.0420	0.018	0.003611	0.0449
13	7	97	0.45	0.11	0.2090	0.0487	0.0222	0.010		
14	7	97	0.62	0.06	0.1732	0.0568		0.005	0.001116	0.0523
15	7	97	0.55	0.07	0.0810	0.0573		0.007	0.002375	0.0419
16	7	97	0.63	0.06	0.4674	0.0394		0.006	0.014763	0.0297
17	7	97	1.24	0.12	0.1677	0.0578		0.009		0.0410
18	7	97	0.56	0.17	0.2280	0.0611		0.008		0.0242
19	7	97	0.56	0.35	0.4534	0.2790	0.2608	0.040		0.0146
20	7	97	0.55	0.16	0.1574	0.0776		0.010		0.0618
21	7	97	0.83	0.21	0.2206	0.1068	0.0777	0.014	0.000030	0.0331
22	7	97	0.78	0.19	0.1385	0.0725		0.013	0.000387	0.1292
23	7	97	0.75	0.23	0.2218	0.0611	0.0611	0.009	0.000084	0.0806
24	7	97	0.71	0.23	0.4402	0.0794	0.0126	0.017	0.000208	0.0791
25	7	97	0.73	0.21	0.8973	0.0990	0.0678	0.014	0.000295	0.0623
26	7	97	0.87	0.28	0.4984	0.2608	0.2122	0.037	0.000026	0.0894

Table A3 (continued)

dd	mm	yy	Cu	Ni	Pb	NO3	SO4	NH4	SPM
22	4	95	1573.7	2.0	9.0	2248.2	8192.5	1804.1	
23	4	95	1153.3	1.0	5.4	885.5	6232.0	1250.5	
24	4	95	1044.7	0.7	4.2	1049.9	5541.7	1046.7	
25	4	95	1348.8	1.0	5.1	625.1	4542.5	826.7	
26	4	95	1588.8	2.1	4.1	1432.6	3453.7	435.9	
27	4	95	933.1	2.2	10.1	2234.9	4132.1	803.3	
28	4	95	891.0	3.0	8.6	2577.2	4464.9	776.9	
29	4	95	936.5	2.4	11.8	1969.4	4369.4	1561.8	
30	4	95	1188.2	1.4	5.6	2238.7	6345.1	1844.6	
1	5	95	924.8	1.0	3.8	1804.8	5042.6	1342.6	
2	5	95	1555.6	1.2	5.8	710.9	2193.9	643.2	
3	5	95	490.9	0.9	3.9	1259.8	2362.1	581.4	
4	5	95	333.7	1.1	3.5	1026.8	2769.1	655.5	
5	5	95	394.0	1.5	4.2	1091.1	6738.7	882.1	
6	5	95	397.7	0.9	6.7	637.5	4630.6	908.6	
7	5	95	371.0	1.5	12.5	877.9	5827.5	976.1	
8	5	95	578.6	1.7	18.9	982.2	6102.8	1042.8	
9	5	95	355.6	2.1	28.3	1522.8	5918.6	1098.9	
10	5	95	390.6	2.4	8.6	828.9	7797.3	1472.0	
11	5	95	493.1	2.2	8.3	869.2	5886.3	1002.0	
12	5	95	456.8	1.8	5.8	789.7	2695.8	481.6	
13	5	95	534.5	1.8	8.5	1357.7	5304.1	839.1	
25	5	95	789.7	1.1	6.1	586.9	8374.3	1345.5	
26	5	95	986.5	2.0	5.9	1117.6	8462.0	1233.7	
27	5	95	1011.9	2.2	11.5	1050.0	7955.4	1244.2	
28	5	95	1071.7	2.9	8.7	2048.2	9390.9	1330.8	
29	5	95	825.0	2.2	7.8	930.3	8567.9	1132.5	
30	5	95	899.7	1.5	5.5	962.3	5353.1	625.2	
31	5	95	1031.3	1.0	8.2	458.4	7502.4	907.4	
1	6	95	901.4	1.0	6.2	439.4	5005.4	766.8	
2	6	95	989.0	2.3	10.0	1217.6	5381.9	816.4	
3	6	95	979.6	2.4	8.2	1384.0	8554.0	1102.8	
4	6	95	840.5	1.9	8.9	952.3	4382.2	605.7	
5	6	95	893.0	1.1	7.6	857.4	5161.4	718.9	
6	6	95	917.6	1.4	7.1	962.2	5581.8	760.1	
7	6	95	955.1	1.1	5.7	672.6	4575.8	584.0	
8	6	95	880.8	1.2	4.8	1020.3	4474.2	461.5	
9	6	95	818.9	0.8	2.2	1090.3	2843.2	235.5	
10	6	95	931.9	2.5	3.8	1363.9	2812.0	279.5	
11	6	95	839.3	1.2	2.8	551.3	3138.2	197.6	
12	6	95	1143.0	1.6	4.0	698.6	2267.4	158.4	
15	6	95	589.1	2.7	3.8	759.3	3132.4	280.7	
16	6	95	878.3	0.7	3.2	560.8	2843.5	300.5	
17	6	95	915.1	1.2	4.3	617.8	2450.9	191.8	
18	6	95	1282.9	1.2	8.0	1154.6	7049.2	960.3	
19	6	95	1159.5	0.6	4.8	577.8	3158.9	405.4	
20	6	95	1730.1	0.4	3.5	939.3	2972.9	431.6	
21	6	95	1847.9	0.7	5.9	961.5	3807.2	689.9	
22	6	95	1579.0	0.8	10.1	564.4	7263.8	942.8	
23	6	95	836.0	0.6	1.8	567.7	1954.5	204.6	
25	6	95	886.3	1.0	5.9	833.5	4708.9	1312.1	
26	6	95	1000.2	0.9	5.8	1236.6	5617.6	1856.4	
27	6	95	380.8	1.6	3.4	533.9	1893.2	793.3	
21	9	95	680.9	2.6	9.4	853.6	2251.0	786.0	
22	9	95	41.1	2.5	13.6	1058.1	5432.7	1909.7	
23	9	95	52.4	1.6	2.5	359.2	2211.1	853.3	
24	9	95	43.4	0.6	1.8	402.9	1283.2	1445.7	
25	9	95	29.3	0.6	1.2	291.6	1077.9	493.8	
26	9	95	20.8	1.4	3.0	631.9	2090.5	864.3	

Table A3 (continued)

27	9	95	44.4	0.7	2.9	591.1	2651.3	2156.5
28	9	95	32.5	0.7	5.7	365.7	2952.7	1122.0
29	9	95	15.7	0.9	5.4	486.1	2184.5	747.5
30	9	95	23.4	1.3	7.9	754.5	3188.7	1233.2
1	10	95	20.4	1.0	7.6	492.9	2445.4	724.3
2	10	95	17.8	0.4	4.1	578.4	2296.6	709.5
3	10	95	13.4	0.6	8.5	805.9	2792.2	882.5
4	10	95	33.1	0.8	14.6	777.9	4920.5	1628.2
5	10	95	48.8	0.6	5.8	701.3	3732.6	1205.8
6	10	95	50.1	1.5	9.4	817.7	1934.3	502.0
7	10	95	22.5	1.8	7.6	607.8	2528.6	744.2
8	10	95	34.7	1.6	18.6	796.1	3908.5	912.0
9	10	95	32.5	1.6	13.6	660.0	3726.7	1239.1
10	10	95	31.9	1.2	13.4	789.6	3367.5	1178.9
11	10	95	28.3	1.0	27.2	658.8	3262.3	1026.0
12	10	95	17.8	1.1	8.7	475.0	2429.7	585.8
13	10	95	24.0	1.0	8.9	756.1	2946.7	714.7
14	10	95	20.5	0.8	13.5	1067.7	7532.7	1373.7
15	10	95	31.4	1.6	25.7	1316.3	13037.2	2749.1
16	10	95	35.3	0.7	5.2	1721.4	2836.9	616.3
17	10	95	21.5	0.3	6.5	1665.0	2417.5	492.4
18	10	95	25.7	0.8	5.6	1333.6	2174.1	577.4
19	10	95	13.2	1.1	5.5	1011.2	1522.6	973.7
20	10	95	22.4	1.7	24.6	868.7	4247.9	945.3
21	10	95	31.0	5.0	53.6	2180.5	6285.9	1505.7
22	10	95	18.3	0.7	2.1	1284.3	3398.5	344.3
24	10	95	20.8	0.6	3.4	1105.6	9130.5	1726.4
25	10	95	20.9	2.4	22.5	2408.1	12839.3	2923.4
26	10	95	24.7	0.8	11.4	1498.9	10031.7	2620.8
27	10	95	28.2	1.7	5.5	903.3	4558.6	1403.6
28	10	95	16.8	0.8	1.4	630.8	6320.8	1678.4
29	10	95	17.4	3.5	10.8	459.2	11752.3	2115.7
30	10	95	47.8	2.8	57.3	2297.0	21120.6	6989.7
31	10	95	53.1	4.0	75.6	1010.7	12974.2	3371.5
1	11	95	30.5	3.5	67.7	1261.7	14289.1	3819.5
2	11	95	14.5	4.3	26.7	1355.3	11773.5	3130.7
3	11	95	10.5	1.1	11.0	568.8	4052.2	1104.4
5	11	95	11.2	0.5	14.9	786.5	2947.0	966.3
6	11	95	11.2	0.8	20.4	463.4	2565.3	926.5
7	11	95	6.6	0.7	4.3	194.2	4683.5	946.8
8	11	95	21.6	1.5	25.3	388.9	5092.1	1079.2
9	11	95	10.5	0.9	7.6	233.1	5751.6	1178.5
10	11	95	6.8	2.3	18.1	702.1	7833.5	1892.0
13	11	95	15.9	1.6	9.7	1390.7	10412.8	2923.2
14	11	95	12.5	0.9	2.7	477.1	4603.5	1189.6
15	11	95	191.1	3.4	14.1	837.3	3310.0	1066.2
17	11	95	58.2	1.6	12.7	1231.8	3493.4	1511.6
19	11	95	30.8	0.6	0.9	485.3	2775.5	844.6
20	11	95	28.1	0.8	0.7	864.7	3182.6	1441.9
21	11	95	45.0	0.5	0.1	167.3	1296.6	598.6
22	11	95	27.9	0.3	0.2	233.7	3711.5	939.8
23	11	95	30.8	1.4	35.0	299.8	6355.2	3098.5
25	11	95	58.8	2.3	22.5	110.5	10852.6	2304.8
26	11	95	77.9	0.9	11.7	422.8	5258.8	1544.0
27	11	95	64.4	0.8	4.2	773.7	3029.5	1965.3
28	11	95	68.5	1.0	4.3	249.8	6338.8	2454.7
29	11	95	90.5	1.1	20.0	584.0	5653.6	2951.8
30	11	95	102.0	4.1	63.2	2046.6	7415.3	1856.4
1	12	95	85.6	0.9	9.3	638.5	6383.1	1927.6
2	12	95	80.7	1.8	12.8	214.2	7610.5	1863.9

Table A3 (continued)

3	12	95	84.1	0.9	17.0	396.0	7135.2	2157.2	
4	12	95	82.8	0.4	29.3	542.7	5506.6	2128.6	
5	12	95	118.5	0.6	32.6	1487.0	4561.9	2282.2	
6	12	95	67.4	0.7	7.6	861.4	3459.7	1340.4	
23	5	96	61.7	0.9	15.6	1332.7	3095.7	1292.1	
24	5	96	116.0	0.2	13.8	1994.4	7187.9	2947.0	
25-27		96	90.9	0.7	9.7	1166.0	6226.7	867.8	2223.3
28	5	96	70.4	1.3	47.2	1499.1	8319.6	2897.0	
29	5	96	45.1	0.6	20.9	1360.7	8896.4	3369.0	
30	5	96	35.8	0.7	9.9	1146.3	6094.5	2260.1	
31	5	96	81.1	0.6	10.2	1566.3	4504.4	1589.4	137.7
2	6	96	59.5	1.6	14.6	541.9	2259.7	757.1	
3	6	96	70.6	0.4	7.4	739.2	3342.3	1289.3	
4	6	96	46.3	0.8	8.7	655.7	3105.9	1130.1	
5	6	96	61.5	1.7	19.2	1461.4	4586.8	1869.8	
6	6	96	77.9	0.8	10.9	1074.9	5419.6	1579.7	
7	6	96	49.8	0.4	6.0	1323.9	3540.9	1095.0	
8	6	96	90.5	0.6	17.0	688.0	3018.4	919.9	
9	6	96	44.9	0.7	6.2	609.6	2985.1	858.1	
10	6	96	61.1	0.5	12.8	460.8	2872.0	782.9	
11	6	96	62.8	0.6	22.3	797.7	3753.7	1210.2	
12	6	96	42.6	0.6	8.1	688.7	10644.3	1658.0	
13	6	96	57.6	1.5	16.4	571.7	9383.5	1252.7	
14	6	96	57.2	0.5	42.9	1141.2	13574.9	1213.9	
15	6	96	24.4	0.1	3.6	831.3	4295.8	461.2	
16	6	96	70.9	0.3	7.3	990.0	6496.2	751.0	
18	6	96	57.0	0.4	8.7	1061.9	6251.5	787.8	
19	6	96	37.3	0.3	8.7	893.3	8632.0	1013.7	
20	6	96	26.8	1.1	14.5	1257.4	17784.0	1828.3	
21	6	96	44.8	0.7	11.8	787.1	14667.7	1479.4	
22	6	96	34.0	1.2	0.8	668.4	8557.6	1014.9	
23	6	96	25.1	1.3	15.5	399.2	2394.9	825.6	
24	6	96	31.9	0.1	10.6	382.1	7959.8	1841.7	
25	6	96	22.9	0.3	6.3	442.9	3423.4	1002.5	
26	6	96	16.8	0.0	0.7	443.2	2293.9	833.0	
27	6	96	13.5	1.6	37.7	1212.5	9302.3	2117.2	3870.7
28	6	96	12.1	0.0	4.8	665.0	2480.6	753.7	
29	6	96	7.9	0.2	6.8	627.1	2633.6	844.8	
30	6	96	10.6	0.3	8.9	572.6	2508.7	780.0	
1	7	96	8.3	0.5	8.0	612.7	2953.9	837.8	181.8
3	7	96	12.7	0.2	19.8	607.9	4509.9	1301.9	
4	7	96	8.6	0.4	16.3	824.8	10067.5	1399.8	
5	7	96	19.5	0.3	8.9	843.2	6300.1	2174.2	
6	7	96	16.4	0.1	15.5	982.7	8015.9	1917.3	
7	7	96	16.3	2.1	10.3	833.2	9221.9	2196.6	
8	7	96	14.0	2.6	6.6	1015.4	5612.8	2405.7	
9	7	96	15.7	1.5	7.5	757.0	5163.9	1404.0	
10	7	96	11.5	1.6	6.5	1319.0	7737.5	1216.9	
11	7	96	18.8	0.7	5.2	782.6	4582.8	1574.4	
12	7	96	26.9	0.3	4.7	830.8	3703.5	1427.5	
13	7	96	15.7	1.1	4.4	1424.9	4933.4	1184.7	
14	7	96	11.9	1.3	12.4	1458.7	6389.0	700.3	18443.9
16	7	96	16.5	1.5	8.1	1462.6	8027.5	2561.7	2987.9
17	7	96	14.0	0.6	4.6	1510.0	5522.7	2185.2	
18	7	96	10.3	0.1	1.4	545.0	1231.0	708.4	
20	7	96	18.1	0.7	8.1	673.6	5635.9	655.2	
21	7	96	23.8	0.4	5.0	539.7	3957.2	497.8	3656.6
24	7	96	10.7	0.4	3.8	673.4	3831.3	1528.5	26588.0
26	7	96	14.8	0.5	4.2	785.8	3606.4	2069.7	39232.6
27	7	96	34.3	1.1	9.1	803.2	4786.1	1006.1	36543.3

Table A3 (continued)

28	7	96	10.7	0.6	5.9	755.0	3690.0	1211.8	36396.1
29	7	96	9.1	0.2	4.0	558.5	3659.3	1259.7	34890.4
30	7	96	6.8	0.5	5.4	742.5	4842.8	1191.9	38777.2
31	7	96	35.1	1.5	3.4	1304.0	7817.5	1465.5	46369.9
1	8	96	10.2	2.6	0.9	1333.5	8208.9	2024.1	48334.4
2	8	96	8.9	2.0	13.6	1240.5	5573.7	2377.1	46935.9
3	8	96	10.6	2.7	30.5	1503.8	5744.2	1260.7	44558.1
4	8	96	22.1	1.6	9.4	950.7	5116.9	349.4	23639.2
10	11	96	18.8	1.0	18.6	978.3	1856.6	3152.8	27350.8
11	11	96	14.5	0.8	22.6	642.5	2023.0	800.8	37513.8
12	11	96	27.9	3.1	34.0	819.7	3797.2	927.0	40406.5
13	11	96	20.7	2.9	20.9	1164.2	5212.1	764.8	39380.4
15	11	96	21.9	4.3	34.7	891.0	9616.3	2381.3	46041.1
16	11	96	27.7	5.8	19.1	811.8	7226.1	2027.9	42434.8
17	11	96	18.4	1.4	16.3	902.4	4368.1	1599.6	41311.3
18	11	96	21.5	2.3	14.6	730.6	4312.1	1503.8	43268.1
19	11	96	22.4	5.3	16.9	1281.2	4081.6	1293.2	55035.5
20	11	96	27.6	3.0	39.9	1285.3	3861.1	1321.1	32761.4
21	11	96	14.5	3.0	33.6	979.5	2754.0	810.3	33920.2
22	11	96	23.9	2.5	31.4	770.3	1425.6	552.0	26629.0
23	11	96	21.0	1.5	26.7	803.1	1587.7	596.2	27245.0
24	11	96	29.2	7.2	12.6	1111.2	2065.3	803.0	30722.6
25	11	96	14.9	5.9	10.8	1098.6	2250.8	621.1	33096.1
26	11	96	21.5	4.9	23.3	1336.8	3916.7	1198.3	35672.8
27	11	96	16.3	9.0	12.7	814.6	1780.6	568.5	30756.0
28	11	96	20.9	1.9	6.3	393.9	864.9	460.6	25662.8
29	11	96	14.5	1.2	9.6	850.4	1742.8	787.1	26863.5
1	12	96	20.2	3.2	14.9	391.4	1864.3	555.2	24084.4
2	12	96	9.3	2.1	10.4	750.6	1669.6	566.2	26145.9
3	12	96	24.1	1.8	18.5	927.7	1672.1	614.7	26087.0
4	12	96	26.7	3.6	22.7	1552.0	3293.8	1245.0	38824.2
5	12	96	29.2	1.0	15.4	949.9	2531.8	922.2	23463.5
7	12	96	19.1	0.8	6.8	711.0	1810.2	737.0	25423.7
8	12	96	17.5	1.1	12.7	736.1	2430.2	943.0	28351.9
9	12	96	23.4	1.0	10.9	744.1	4800.4	1427.1	27972.0
10	12	96	21.7	0.9	9.5	568.6	2992.8	1025.7	25623.1
11	12	96	14.7	1.8	17.9	740.6	2502.3	1041.4	45844.0
12	12	96	16.9	2.1	25.5	1311.7	3601.3	1418.4	43667.9
13	12	96	23.8	1.8	26.1	454.7	6190.9	1497.5	33106.7
14	12	96	8.3	2.6	23.5	577.3	2996.7	886.7	22779.7
16	12	96	21.2	1.9	56.8	1928.0	3194.8	1177.6	36108.0
17	12	96	11.2	1.9	27.2	984.9	2843.0	923.0	25942.2
19	12	96	8.8	2.4	54.8	869.9	2439.6	848.1	28345.9
20	12	96	9.2	1.3	23.1	769.2	3642.4	883.1	19441.3
23	12	96	6.6	2.7	55.6	1285.7	3909.4	1078.2	32867.0
24	12	96	17.7	0.8	23.9	740.0	1802.7	423.5	20882.8
26	12	96	9.9	0.5	16.5	170.9	2181.8	426.0	12908.5
30	12	96	12.8	2.4	16.7	1097.9	4884.0	694.0	26568.5
3	1	97	17.5	2.6	40.0	1076.2	6395.6	1646.5	36427.7
5	1	97	20.2	2.7	46.0	1051.7	5774.1	1345.1	30091.3
7	1	97	13.4	1.3	21.1	607.1	5625.5	1212.6	29283.4
10	1	97	20.2	1.7	44.7	746.4	4254.4	1470.4	39340.4
11	1	97	13.0	2.0	60.3	725.4	3242.9	1320.3	47460.1
12	1	97	16.0	1.3	56.0	620.8	7822.1	1375.4	34384.5
13	1	97	26.6	0.8	22.3	353.8	6484.9	1170.7	23282.3
15	1	97	27.5	1.8	49.2	432.9	8412.7	1819.5	36764.3
16	1	97	6.1	2.3	59.6	593.4	9046.9	1683.7	41883.8
17	1	97	34.8	4.3	60.6	1615.9	15872.4	3274.4	60322.4
18	1	97	23.5	2.8	29.0	943.1	7587.2	1995.3	42760.9
19	1	97	29.2	5.8	37.5	1233.9	5556.9	1980.8	51705.8

Table A3 (continued)

20	1	97	23.4	11.3	54.3	742.0	17812.0	3320.9	62269.1
21	1	97	43.0	4.1	33.9	615.9	8338.3	2051.9	34808.9
22	1	97	141.7	6.8	21.9	1485.5	8016.9	2758.9	71128.4
23	1	97	20.2	2.7	16.1	716.7	4904.2	1503.9	30815.6
24	1	97	28.9	2.5	25.6	1183.3	2914.5	1279.1	43729.4
25	1	97	29.6	0.6	3.9	372.4	1514.4	354.7	86808.6
26	1	97	122.4	5.0	58.2	3883.0	9504.1	3409.0	
27	1	97	34.3	1.0	16.0	778.6	3703.9	734.4	43743.1
28	1	97	17.2	3.4	26.2	929.6	6114.8	1603.5	10487.9
29	1	97	8.2	1.7	29.0	1782.7	6167.7	1616.1	43878.7
30	1	97	10.4	0.1	5.2	535.3	1061.7	294.3	83787.6
8	3	97	15.2	1.5	17.0	1248.0	2342.9	1117.1	62832.3
9	3	97	24.9	0.8	11.2	1179.1	3826.5	1328.9	68427.4
10	3	97	21.7	0.8	11.9	856.6	4589.2	1620.5	75205.6
11	3	97	23.2	0.5	7.4	760.2	7576.5	1342.4	38249.5
14	3	97	25.7	0.8	12.9	721.5	8695.1	1817.7	54402.6
16	4	97	21.7	1.4	26.8	644.2	5184.3	1766.6	81965.6
17	4	97	19.6	0.8	8.3	751.8	2662.8	988.3	59507.2
18	4	97	7.1	1.1	40.5	756.0	5158.8	1453.8	76180.7
19	4	97	18.5	1.4	43.4	1184.9	4702.2	1561.5	72916.2
20	4	97	14.6	0.7	11.6	657.0	2457.5	929.9	59550.3
21	4	97	28.8	2.6	18.7	2975.3	6430.1	2081.8	107648.1
22	4	97	22.4	4.0	18.5	1915.3	3406.7	1200.0	103875.5
23	4	97	10.7	12.1	22.5	3598.0	5396.9	309.7	178262.7
24	4	97	15.0	1.1	12.0	728.1	2246.9	1165.7	63185.6
25	4	97	14.8	1.6	19.1	1007.8	3947.7	1418.0	64333.0
26	4	97	14.0	1.2	14.5	937.9	3062.3	1381.6	73308.5
27	4	97	13.6	0.6	7.5	404.6	1954.7	1123.3	50213.7
28	4	97	13.2	1.2	15.0	830.6	4097.0	1766.8	63813.9
29	4	97	10.0	1.1	14.6	851.5	4671.0	2125.4	67917.4
30	4	97	9.1	0.9	17.1	783.8	4294.3	1592.4	68292.9
1	5	97	16.0	1.1	23.4	987.4	5765.5	1957.3	59833.3
2	5	97	14.0	3.1	21.4	1554.5	3976.1	1649.9	64547.2
3	5	97	6.9	3.6	19.1	2296.6	5221.0	1907.5	66632.8
4	5	97	11.6	1.8	33.8	1257.1	5606.0	2209.4	77184.6
5	5	97	24.4	3.8	41.7	1516.7	6538.2	2214.8	73408.5
6	5	97	16.2	2.8	20.9	1157.2	3631.8	1572.1	64149.8
8	5	97	17.7	3.4	10.8	1476.6	2528.6	1371.7	76051.6
9	5	97	13.4	2.6	19.2	1358.2	3305.2	1463.0	73898.2
10	5	97	17.5	3.1	23.3	1390.0	3416.2	1103.7	79658.1
11	5	97	16.2	2.6	31.6	2100.5	3445.9	1260.1	84537.9
12	5	97	15.9	2.4	24.3	2141.0	4417.9	1469.3	104700.4
13	5	97	10.7	1.4	15.5	1399.5	3791.4	1343.9	66357.3
14	5	97	9.9	1.2	12.7	1097.4	3686.4	1320.6	68088.6
15	5	97	14.3	1.0	19.2	681.8	2776.3	1075.5	52990.7
16	5	97	17.3	1.9	33.1	1138.9	5554.6	1997.2	89462.3
17	5	97	21.8	2.0	26.2	422.9	6547.4	1682.7	61433.3
18	5	97	22.5	3.1	23.2	775.3	6818.5	1901.4	71690.6
19	5	97	22.4	1.2	15.3	850.1	3003.5	1340.4	55674.7
20	5	97	19.0	3.0	30.4	587.5	7678.1	1983.6	69529.2
21	5	97	13.4	3.4	20.2	1018.7	6160.1	1986.0	76191.4
22	5	97	24.9	3.3	42.6	1535.9	8974.2	2231.8	81702.6
23	5	97	12.2	1.2	28.7	1038.5	3751.4	1498.0	139117.4
24	5	97	10.6	0.6	8.5	1205.0	2347.4	1131.8	66013.3
25	5	97	27.0	0.6	19.5	1221.2	2199.1	1345.0	85457.0
26	5	97	16.9	0.4	7.6	737.6	1942.5	815.0	55503.3
27	5	97	20.2	0.6	14.7	443.3	1976.6	796.5	65782.1
28	5	97	15.9	0.4	7.8	428.0	1917.4	738.0	51469.2
29	5	97	8.7	1.6	17.0	1030.2	2982.7	1175.2	58400.5
30	5	97	13.4	1.1	33.4	421.9	3254.3	1262.0	54074.3

Table A3 (continued)

31	5	97	18.8	1.0	15.7	1040.1	4141.6	1678.0	62098.7
01	6	97	16.4	0.8	25.0	577.4	3348.3	1353.5	51443.1
2	6	97	10.5	0.6	10.9	330.0	2600.5	1195.9	54107.1
3	6	97	8.1	2.3	58.7	1521.7	6824.3	2001.3	72901.3
4	6	97	14.0	1.0	24.7	935.9	4038.0	1510.4	58578.7
5	6	97	13.0	1.0	11.7	513.1	2707.9	1172.4	54777.2
6	6	97	9.6	0.9	14.9	1096.2	5555.8	1757.2	73260.3
7	6	97	16.6	2.2	34.6	1633.7	7184.5	1845.2	67849.5
8	6	97	9.8	1.9	39.3	751.4	8927.7	1965.6	66562.4
9	6	97	12.0	1.6	26.9	1346.1	7380.1	1989.1	68618.9
10	6	97	7.4	1.1	39.8	1437.5	5697.1	1855.2	62616.0
11	6	97	14.8	1.0	15.6	426.2	4495.8	1559.6	56309.1
12	6	97	20.5	0.7	22.7	518.1	3758.2	1735.5	64364.7
13	6	97	12.6	1.5	36.9	965.8	7186.6	1858.2	62639.1
14	6	97	28.0	4.0	54.9	1138.1	10828.3	2034.5	74406.3
15	6	97	24.4	1.0	32.0	684.2	5505.7	1881.4	67283.3
16	6	97	34.5	0.7	20.7	896.4	4553.1	1803.0	64959.4
17	6	97	39.0	0.8	13.2	494.2	3395.6	1478.7	64709.6
18	6	97	38.2	0.8	16.9	518.8	4116.9	1548.4	266421.2
19	6	97	30.6	0.6	16.8	826.9	4065.8	1568.5	45931.1
20	6	97	23.6	1.7	19.9	946.3	3250.8	1328.9	72171.4
21	6	97	28.7	1.4	21.7	1249.3	3976.4	1540.6	66498.0
22	6	97	29.4	2.7	61.3	1479.5	5231.6	1945.2	229316.4
23	6	97	60.8	0.3	20.3	263.0	3806.6	1564.7	63548.6
24	6	97	30.2	0.9	18.3	587.2	3067.7	1259.6	76710.3
25	6	97	37.6	0.7	16.7	520.7	4658.6	1481.9	67781.9
26	6	97	35.1	0.4	8.0	670.3	3472.9	1268.4	70907.8
27	6	97	43.9	0.5	9.7	827.3	3791.7	1440.7	74818.3
28	6	97	47.1	0.7	22.3	534.3	3256.8	1279.9	93359.1
29	6	97	80.6	0.7	19.8	595.5	3828.7	1608.5	
02	7	97	37.4	1.4	23.1	693.5	5470.9	2034.0	27486.2
03	7	97	65.9	0.8	15.8	530.9	2741.7	1367.2	14211.5
04	7	97	56.6	1.1	15.4	590.8	3774.3	1556.0	15771.8
05	7	97	48.7	1.4	30.7	520.1	7433.8	2199.3	26199.3
06	7	97	38.3	1.2	36.7	473.2	4623.9	1501.3	29893.2
07	7	97	36.9	3.3	39.1	941.5	3236.6	1176.1	45532.1
08	7	97	38.1	0.3	18.8	547.8	2801.4	1120.0	19105.3
09	7	97	47.2	1.5	35.4	707.4	2911.1	3603.1	13341.6
10	7	97	44.7	0.8	38.1	509.4	5769.4	1228.0	21882.3
11	7	97	30.4	0.5	10.8	356.5	1173.3	817.0	13858.8
12	7	97	38.9	0.1	11.4	262.9	2190.8	897.1	11246.6
13	7	97	23.1	0.1	15.0	217.4	2608.6	1266.9	13074.9
14	7	97	49.9	0.1	9.6	245.6	1571.9	697.6	15801.0
15	7	97	52.7	0.6	8.5	308.6	2017.3	1694.3	17433.4
16	7	97	42.0	0.2	8.8	208.1	1262.6	783.8	13889.0
17	7	97	67.3	0.6	14.7	275.7	1168.5	895.0	9165.3
18	7	97	62.7	0.3	10.3	145.8	1009.9	886.4	2093.4
19	7	97	62.1	1.2	18.1	268.1	2121.4	1378.3	12005.9
20	7	97	31.5	0.5	10.6	396.8	1378.7	947.4	11554.8
21	7	97	47.9	0.6	15.5	332.0	1527.1	1159.4	16097.7
22	7	97	42.7	0.5	10.9	222.8	1281.9	853.0	16682.7
23	7	97	44.8	0.8	17.5	221.1	1984.5	1309.7	13520.4
24	7	97	60.1	0.8	12.4	317.5	4691.4	1370.0	16474.9
25	7	97	59.6	0.9	13.2	251.0	4422.3	1349.8	20091.3
26	7	97	70.4	1.1	23.9	289.9	3894.4	1278.2	18666.6

Table A4. The program used to count the end point numbers in each subregion

```
C
****************************************************************** *
C     *
*
C     *                       COMPUTER PROGRAM
*
C     *       TO FIND NUMBER OF DATA INSIDE THE SPECIFIED REGIONS
*
C     *
*
C
********************************************************************
      character*12 filein,fileout
      character *80 InLin, YrMon*4
      DIMENSION X(2000),Y(2000)
!,A(2000),BET(2000),ES(2000),AYS(2000)
      REAL TS(40,31), TN(31)

C     INPUT
DATA**********************************************************
      DATA T1A,T1B,T2A,T2B,T2C,T3A,T3B,T3C,T3D,T4/10*0./
      DATA T5A,T5B,T5C,T6,T7A,T7B,T7C,T7D,T8A,T8B,T9A,T9B/12*0./
      DATA T9C,T10,T11,T12,T13A,T13B,T14,T15A,T15B,T15C/10*0./
      DATA
T16A,T16B,T16C,T17A,T17B,T17C,T17D,T18A,T18B,T19A,T19B/11*0./
      DATA T19C,T19D,T19E,T19F,T20A,T20B,T21,T22A,T22B/9*0./
      DATA T23A,T23B,T23C,T24A,T24B,T25,T26A,T26B,T26C,T26D/10*0./
      DATA T27A,T27B,T27C,T27D,T27E,T27F,T27,T19AB,T19DE/9*0./
      DATA T28A,T28B,T28C,T28D,T28E,T28F,T29/7*0./
      DATA T30A,T30B,T30C,T30D,T30E,T31A,T31B/7*0./
      DATA T32A,T32B,T32C/3*0./

      Nfiles=0
      NDAYS=0
      IEND=1
      OPEN (1, File='FILES.LST', STATUS='OLD')
      READ (1,'(A)',END=100) FileIn
      IF (LEN_TRIM(FileIn).LE.1) GOTO 100
  7   FileOut(1:1)='T'
      FileOut(2:)=FileIn(2:5)//'.OUT'
      YrMon=FileIn(2:5)
      CLOSE (16)
      OPEN (UNIT=16,FILE=FileOut)
      DO I=1, 40
      DO J=1, 31
        TS(I,J)=0.
      ENDDO
      ENDDO
      NDays=1
  8   CLOSE (15)
      OPEN (UNIT=15,FILE=filein,status='old')
      Nfiles=Nfiles+1
      WRITE(6,'(I6,A)') Nfiles, '. '//Filein

C
********************************************************************
      CALL ZERO(T1A,T1B,T2A,T2B,T2C,T3A,T3B,T3C,T3D,T4,
     &      T5A,T5B,T5C,T6,T7A,T7B,T7C,T7D,T8A,T8B,T9A,T9B,
     &      T9C,T10,T11,T12,T13A,T13B,T14,T15A,T15B,T15C,
```

```
     &      T16A,T16B,T16C,T17A,T17B,T17C,T17D,T18A,T18B,T19A,T19B,
     &      T19C,T19D,T19E,T19F,T20A,T20B,T21,T22A,T22B,
     &      T23A,T23B,T23C,T24A,T24B,T25,T26A,T26B,T26C,T26D,
     &      T27A,T27B,T27C,T27D,T27E,T27F,T27,T19AB,T19DE,
     &      T28A,T28B,T28C,T28D,T28E,T28F,T29,
     &      T30A,T30B,T30C,T30D,T30E,T31A,T31B,
     &      T32A,T32B,T32C)

C     READ INPUT DATA AND COUNT NUMBER OF DATA INSIDE OF EACH
REGION******
      DO II=1, 7
        READ(15,'(A)') InLin
      ENDDO
      N=0
   1  READ (15,'(A)',END=2) InLin
      N=N+1
      READ (15,'(56X,2F8.3)',END=2) X(N), Y(N)
      READ (15,'(A)',END=2) InLin
      GOTO 1
   2  CONTINUE
      DO 50 J=1,N
!        XOK=X(J)
!        YOK=Y(J)
        FAC1=TAN((Y(J)+32.)/57.295)
        FAC2=TAN((90.-X(J))/114.6)
        Y(J)=37.-79.2123*FAC2/(((FAC1)**2.+1)**0.5)
        X(J)=(37.-Y(J))*FAC1+3.
!        WRITE(16,'(4F10.2)') XOK, YOK, X(J), Y(J)
        IF((X(J).LE.19.0).AND.(X(J).GE.16.0)) THEN
          IF((Y(J).LE.2.0).AND.(Y(J).GE.0.0)) THEN
            T1A=T1A+1
          ENDIF
        ENDIF
        IF((X(J).LE.18.0).AND.(X(J).GE.16.0)) THEN
          IF((Y(J).LE.4.0).AND.(Y(J).GE.2.0)) THEN
            T1B=T1B+1
          ENDIF
        ENDIF
        IF((X(J).LE.18.0).AND.(X(J).GE.16.0)) THEN
          IF((Y(J).LE.6.0).AND.(Y(J).GE.4.0)) THEN
            T2A=T2A+1
          ENDIF
        ENDIF
        IF((X(J).LE.23.0).AND.(X(J).GE.18.0)) THEN
          IF((Y(J).LE.7.0).AND.(Y(J).GE.2.0)) THEN
            T2B=T2B+1
          ENDIF
        ENDIF
        IF((X(J).LE.22.0).AND.(X(J).GE.19.0)) THEN
          IF((Y(J).LE.2.0).AND.(Y(J).GE.1.0)) THEN
            T2C=T2C+1
          ENDIF
        ENDIF
        IF((X(J).LE.22.0).AND.(X(J).GE.18.0)) THEN
          IF((Y(J).LE.13.0).AND.(Y(J).GE.9.0)) THEN
            T3A=T3A+1
          ENDIF
        ENDIF
        IF((X(J).LE.18.0).AND.(X(J).GE.16.0)) THEN
          IF((Y(J).LE.11.0).AND.(Y(J).GE.9.0)) THEN
            T3B=T3B+1
```

```
  ENDIF
ENDIF
IF((X(J).LE.23.0).AND.(X(J).GE.19.0)) THEN
  IF((Y(J).LE.9.0).AND.(Y(J).GE.7.0)) THEN
    T3C=T3C+1
  ENDIF
ENDIF
IF((X(J).LE.24.0).AND.(X(J).GE.22.0)) THEN
  IF((Y(J).LE.11.0).AND.(Y(J).GE.9.0)) THEN
    T3D=T3D+1
  ENDIF
ENDIF
IF((X(J).LE.23.0).AND.(X(J).GE.22.0)) THEN
  IF((Y(J).LE.13.0).AND.(Y(J).GE.11.0)) THEN
    T4=T4+1
  ENDIF
ENDIF
IF((X(J).LE.30.0).AND.(X(J).GE.23.0)) THEN
  IF((Y(J).LE.13.0).AND.(Y(J).GE.11.0)) THEN
    T5A=T5A+1
  ENDIF
ENDIF
IF((X(J).LE.26.0).AND.(X(J).GE.24.0)) THEN
  IF((Y(J).LE.14.0).AND.(Y(J).GE.13.0)) THEN
    T5B=T5B+1
  ENDIF
ENDIF
IF((X(J).LE.32.0).AND.(X(J).GE.30.0)) THEN
  IF((Y(J).LE.13.0).AND.(Y(J).GE.9.0)) THEN
    T5C=T5C+1
  ENDIF
ENDIF
IF((X(J).LE.32.0).AND.(X(J).GE.30.0)) THEN
  IF((Y(J).LE.15.0).AND.(Y(J).GE.13.0)) THEN
    T6=T6+1
  ENDIF
ENDIF
IF((X(J).LE.31.0).AND.(X(J).GE.28.0)) THEN
  IF((Y(J).LE.17.0).AND.(Y(J).GE.15.0)) THEN
    T7A=T7A+1
  ENDIF
ENDIF
IF((X(J).LE.28.0).AND.(X(J).GE.26.0)) THEN
  IF((Y(J).LE.16.0).AND.(Y(J).GE.14.0)) THEN
    T7B=T7B+1
  ENDIF
ENDIF
IF((X(J).LE.30.0).AND.(X(J).GE.28.0)) THEN
  IF((Y(J).LE.15.0).AND.(Y(J).GE.14.0)) THEN
    T7C=T7C+1
  ENDIF
ENDIF
IF((X(J).LE.32.0).AND.(X(J).GE.31.0)) THEN
  IF((Y(J).LE.16.0).AND.(Y(J).GE.15.0)) THEN
    T7D=T7D+1
  ENDIF
ENDIF
IF((X(J).LE.35.0).AND.(X(J).GE.32.0)) THEN
  IF((Y(J).LE.15.0).AND.(Y(J).GE.13.0)) THEN
    T8A=T8A+1
  ENDIF
```

```
ENDIF
IF((X(J).LE.33.0).AND.(X(J).GE.32.0)) THEN
  IF((Y(J).LE.17.0).AND.(Y(J).GE.15.0)) THEN
    T8B=T8B+1
  ENDIF
ENDIF
IF((X(J).LE.24.0).AND.(X(J).GE.20.0)) THEN
  IF((Y(J).LE.16.0).AND.(Y(J).GE.13.0)) THEN
    T9A=T9A+1
  ENDIF
ENDIF
IF((X(J).LE.20.0).AND.(X(J).GE.19.0)) THEN
  IF((Y(J).LE.17.0).AND.(Y(J).GE.15.0)) THEN
    T9B=T9B+1
  ENDIF
ENDIF
IF((X(J).LE.23.0).AND.(X(J).GE.20.0)) THEN
  IF((Y(J).LE.18.0).AND.(Y(J).GE.16.0)) THEN
    T9C=T9C+1
  ENDIF
ENDIF
IF((X(J).LE.26.0).AND.(X(J).GE.24.0)) THEN
  IF((Y(J).LE.17.0).AND.(Y(J).GE.14.0)) THEN
    T10=T10+1
  ENDIF
ENDIF
IF((X(J).LE.28.0).AND.(X(J).GE.26.0)) THEN
  IF((Y(J).LE.19.0).AND.(Y(J).GE.16.0)) THEN
    T11=T11+1
  ENDIF
ENDIF
IF((X(J).LE.31.0).AND.(X(J).GE.28.0)) THEN
  IF((Y(J).LE.21.0).AND.(Y(J).GE.17.0)) THEN
    T12=T12+1
  ENDIF
ENDIF
IF((X(J).LE.26.0).AND.(X(J).GE.24.0)) THEN
  IF((Y(J).LE.18.0).AND.(Y(J).GE.17.0)) THEN
    T13A=T13A+1
  ENDIF
ENDIF
IF((X(J).LE.24.0).AND.(X(J).GE.23.0)) THEN
  IF((Y(J).LE.18.0).AND.(Y(J).GE.16.0)) THEN
    T13B=T13B+1
  ENDIF
ENDIF
IF((X(J).LE.31.0).AND.(X(J).GE.28.0)) THEN
  IF((Y(J).LE.22.0).AND.(Y(J).GE.21.0)) THEN
    T14=T14+1
  ENDIF
ENDIF
IF((X(J).LE.26.0).AND.(X(J).GE.22.0)) THEN
  IF((Y(J).LE.21.0).AND.(Y(J).GE.18.0)) THEN
    T15A=T15A+1
  ENDIF
ENDIF
IF((X(J).LE.22.0).AND.(X(J).GE.21.0)) THEN
  IF((Y(J).LE.20.0).AND.(Y(J).GE.18.0)) THEN
    T15B=T15B+1
  ENDIF
ENDIF
```

```
IF((X(J).LE.25.0).AND.(X(J).GE.23.0)) THEN
  IF((Y(J).LE.22.0).AND.(Y(J).GE.21.0)) THEN
    T15C=T15C+1
  ENDIF
ENDIF
IF((X(J).LE.26.0).AND.(X(J).GE.23.0)) THEN
  IF((Y(J).LE.25.0).AND.(Y(J).GE.22.0)) THEN
    T16A=T16A+1
  ENDIF
ENDIF
IF((X(J).LE.27.0).AND.(X(J).GE.26.0)) THEN
  IF((Y(J).LE.25.0).AND.(Y(J).GE.23.0)) THEN
    T16B=T16B+1
  ENDIF
ENDIF
IF((X(J).LE.26.0).AND.(X(J).GE.25.0)) THEN
  IF((Y(J).LE.22.0).AND.(Y(J).GE.21.0)) THEN
    T16C=T16C+1
  ENDIF
ENDIF
IF((X(J).LE.32.0).AND.(X(J).GE.27.0)) THEN
  IF((Y(J).LE.26.0).AND.(Y(J).GE.23.0)) THEN
    T17A=T17A+1
  ENDIF
ENDIF
IF((X(J).LE.28.0).AND.(X(J).GE.26.0)) THEN
  IF((Y(J).LE.23.0).AND.(Y(J).GE.19.0)) THEN
    T17B=T17B+1
  ENDIF
ENDIF
IF((X(J).LE.31.0).AND.(X(J).GE.28.0)) THEN
  IF((Y(J).LE.23.0).AND.(Y(J).GE.22.0)) THEN
    T17C=T17C+1
  ENDIF
ENDIF
IF((X(J).LE.32.0).AND.(X(J).GE.29.0)) THEN
  IF((Y(J).LE.27.0).AND.(Y(J).GE.26.0)) THEN
    T17D=T17D+1
  ENDIF
ENDIF
IF((X(J).LE.32.0).AND.(X(J).GE.31.0)) THEN
  IF((Y(J).LE.20.0).AND.(Y(J).GE.16.0)) THEN
    T18A=T18A+1
  ENDIF
ENDIF
IF((X(J).LE.33.0).AND.(X(J).GE.32.0)) THEN
  IF((Y(J).LE.19.0).AND.(Y(J).GE.17.0)) THEN
    T18B=T18B+1
  ENDIF
ENDIF
IF((X(J).LE.37.0).AND.(X(J).GE.34.0)) THEN
  IF((Y(J).LE.17.0).AND.(Y(J).GE.16.0)) THEN
    T19A=T19A+1
  ENDIF
ENDIF
IF((X(J).LE.38.0).AND.(X(J).GE.33.0)) THEN
  IF((Y(J).LE.19.0).AND.(Y(J).GE.17.0)) THEN
    T19B=T19B+1
  ENDIF
ENDIF
IF((X(J).LE.40.0).AND.(X(J).GE.34.0)) THEN
```

```
  IF((Y(J).LE.22.0).AND.(Y(J).GE.19.0)) THEN
   T19C=T19C+1
  ENDIF
 ENDIF
 IF((X(J).LE.36.0).AND.(X(J).GE.35.0)) THEN
  IF((Y(J).LE.23.0).AND.(Y(J).GE.22.0)) THEN
   T19D=T19D+1
  ENDIF
 ENDIF
 IF((X(J).LE.40.0).AND.(X(J).GE.36.0)) THEN
  IF((Y(J).LE.25.0).AND.(Y(J).GE.22.0)) THEN
   T19E=T19E+1
  ENDIF
 ENDIF
 IF((X(J).LE.41.0).AND.(X(J).GE.37.0)) THEN
  IF((Y(J).LE.28.0).AND.(Y(J).GE.25.0)) THEN
   T19F=T19F+1
  ENDIF
 ENDIF
 IF((X(J).LE.18.0).AND.(X(J).GE.15.0)) THEN
  IF((Y(J).LE.15.0).AND.(Y(J).GE.11.0)) THEN
   T20A=T20A+1
  ENDIF
 ENDIF
 IF((X(J).LE.15.0).AND.(X(J).GE.12.0)) THEN
  IF((Y(J).LE.17.0).AND.(Y(J).GE.14.0)) THEN
   T20B=T20B+1
  ENDIF
 ENDIF
 IF((X(J).LE.14.0).AND.(X(J).GE.12.0)) THEN
  IF((Y(J).LE.14.0).AND.(Y(J).GE.11.0)) THEN
   T21=T21+1
  ENDIF
 ENDIF
 IF((X(J).LE.20.0).AND.(X(J).GE.18.0)) THEN
  IF((Y(J).LE.15.0).AND.(Y(J).GE.13.0)) THEN
   T22A=T22A+1
  ENDIF
 ENDIF
 IF((X(J).LE.19.0).AND.(X(J).GE.18.0)) THEN
  IF((Y(J).LE.16.0).AND.(Y(J).GE.15.0)) THEN
   T22B=T22B+1
  ENDIF
 ENDIF
 IF((X(J).LE.47.0).AND.(X(J).GE.42.0)) THEN
  IF((Y(J).LE.21.0).AND.(Y(J).GE.16.0)) THEN
   T23A=T23A+1
  ENDIF
 ENDIF
 IF((X(J).LE.47.0).AND.(X(J).GE.40.0)) THEN
  IF((Y(J).LE.25.0).AND.(Y(J).GE.21.0)) THEN
   T23B=T23B+1
  ENDIF
 ENDIF
 IF((X(J).LE.47.0).AND.(X(J).GE.41.0)) THEN
  IF((Y(J).LE.28.0).AND.(Y(J).GE.25.0)) THEN
   T23C=T23C+1
  ENDIF
 ENDIF
 IF((X(J).LE.41.0).AND.(X(J).GE.37.0)) THEN
  IF((Y(J).LE.13.0).AND.(Y(J).GE.7.0)) THEN
```

```
          T24A=T24A+1
        ENDIF
      ENDIF
      IF((X(J).LE.47.0).AND.(X(J).GE.41.0)) THEN
        IF((Y(J).LE.16.0).AND.(Y(J).GE.7.0)) THEN
          T24B=T24B+1
        ENDIF
      ENDIF
      IF((X(J).LE.44.0).AND.(X(J).GE.28.0)) THEN
        IF((Y(J).LE.7.0).AND.(Y(J).GE.0.0)) THEN
          T25=T25+1
        ENDIF
      ENDIF
      IF((X(J).LE.28.0).AND.(X(J).GE.19.0)) THEN
        IF((Y(J).LE.1.0).AND.(Y(J).GE.(-3.0))) THEN
          T26A=T26A+1
        ENDIF
      ENDIF
      IF((X(J).LE.24.0).AND.(X(J).GE.23.0)) THEN
        IF((Y(J).LE.2.0).AND.(Y(J).GE.1.0)) THEN
          T26B=T26B+1
        ENDIF
      ENDIF
      IF((X(J).LE.28.0).AND.(X(J).GE.24.0)) THEN
        IF((Y(J).LE.5.0).AND.(Y(J).GE.1.0)) THEN
          T26C=T26C+1
        ENDIF
      ENDIF
      IF((X(J).LE.28.0).AND.(X(J).GE.26.0)) THEN
        IF((Y(J).LE.6.0).AND.(Y(J).GE.5.0)) THEN
          T26D=T26D+1
        ENDIF
      ENDIF
     IF((X(J).LE.27.0).AND.(X(J).GE.23.0)) THEN
        IF((Y(J).LE.32.0).AND.(Y(J).GE.25.0)) THEN
         T27A=T27A+1
        ENDIF
     ENDIF
     IF((X(J).LE.29.0).AND.(X(J).GE.27.0)) THEN
        IF((Y(J).LE.32.0).AND.(Y(J).GE.26.0)) THEN
         T27B=T27B+1
        ENDIF
     ENDIF
     IF((X(J).LE.32.0).AND.(X(J).GE.29.0)) THEN
        IF((Y(J).LE.32.0).AND.(Y(J).GE.27.0)) THEN
         T27C=T27C+1
        ENDIF
     ENDIF
     IF((X(J).LE.34.0).AND.(X(J).GE.32.0)) THEN
        IF((Y(J).LE.32.0).AND.(Y(J).GE.25.0)) THEN
         T27D=T27D+1
        ENDIF
     ENDIF
     IF((X(J).LE.37.0).AND.(X(J).GE.34.0)) THEN
        IF((Y(J).LE.31.0).AND.(Y(J).GE.26.0)) THEN
         T27E=T27E+1
        ENDIF
     ENDIF
     IF((X(J).LE.47.0).AND.(X(J).GE.37.0)) THEN
        IF((Y(J).LE.31.0).AND.(Y(J).GE.28.0)) THEN
         T27F=T27F+1
```

```
         ENDIF
      ENDIF

      IF((X(J).LE.34.0).AND.(X(J).GE.33.0)) THEN
         IF((Y(J).LE.17.0).AND.(Y(J).GE.15.0)) THEN
          T28A=T28A+1
         ENDIF
      ENDIF
      IF((X(J).LE.35.0).AND.(X(J).GE.34.0)) THEN
         IF((Y(J).LE.16.0).AND.(Y(J).GE.15.0)) THEN
          T28B=T28B+1
         ENDIF
      ENDIF
      IF((X(J).LE.41.0).AND.(X(J).GE.35.0)) THEN
         IF((Y(J).LE.16.0).AND.(Y(J).GE.13.0)) THEN
          T28C=T28C+1
         ENDIF
      ENDIF
      IF((X(J).LE.42.0).AND.(X(J).GE.37.0)) THEN
         IF((Y(J).LE.17.0).AND.(Y(J).GE.16.0)) THEN
          T28D=T28D+1
         ENDIF
      ENDIF
      IF((X(J).LE.42.0).AND.(X(J).GE.38.0)) THEN
         IF((Y(J).LE.19.0).AND.(Y(J).GE.17.0)) THEN
          T28E=T28E+1
         ENDIF
      ENDIF
      IF((X(J).LE.42.0).AND.(X(J).GE.40.0)) THEN
         IF((Y(J).LE.21.0).AND.(Y(J).GE.19.0)) THEN
          T28F=T28F+1
         ENDIF
      ENDIF
      IF((X(J).LE.37.0).AND.(X(J).GE.32.0)) THEN
         IF((Y(J).LE.13.0).AND.(Y(J).GE.7.0)) THEN
          T29=T29+1
         ENDIF
      ENDIF
      IF((X(J).LE.24.0).AND.(X(J).GE.23.0)) THEN
         IF((Y(J).LE.9.0).AND.(Y(J).GE.2.0)) THEN
          T30A=T30A+1
         ENDIF
      ENDIF
      IF((X(J).LE.26.0).AND.(X(J).GE.24.0)) THEN
         IF((Y(J).LE.11.0).AND.(Y(J).GE.5.0)) THEN
          T30B=T30B+1
         ENDIF
      ENDIF
      IF((X(J).LE.28.0).AND.(X(J).GE.26.0)) THEN
         IF((Y(J).LE.11.0).AND.(Y(J).GE.6.0)) THEN
          T30C=T30C+1
         ENDIF
      ENDIF
      IF((X(J).LE.30.0).AND.(X(J).GE.28.0)) THEN
         IF((Y(J).LE.11.0).AND.(Y(J).GE.7.0)) THEN
          T30D=T30D+1
         ENDIF
      ENDIF
      IF((X(J).LE.32.0).AND.(X(J).GE.30.0)) THEN
         IF((Y(J).LE.9.0).AND.(Y(J).GE.7.0)) THEN
          T30E=T30E+1
```

```
        ENDIF
     ENDIF


     IF((X(J).LE.34.0).AND.(X(J).GE.32.0)) THEN
        IF((Y(J).LE.20.0).AND.(Y(J).GE.19.0)) THEN
         T31A=T31A+1
        ENDIF
     ENDIF
     IF((X(J).LE.34.0).AND.(X(J).GE.31.0)) THEN
        IF((Y(J).LE.23.0).AND.(Y(J).GE.20.0)) THEN
         T31B=T31B+1
        ENDIF
     ENDIF

     IF((X(J).LE.35.0).AND.(X(J).GE.34.0)) THEN
        IF((Y(J).LE.23.0).AND.(Y(J).GE.22.0)) THEN
         T32A=T32A+1
        ENDIF
     ENDIF
     IF((X(J).LE.36.0).AND.(X(J).GE.32.0)) THEN
        IF((Y(J).LE.25.0).AND.(Y(J).GE.23.0)) THEN
         T32B=T32B+1
        ENDIF
     ENDIF
     IF((X(J).LE.37.0).AND.(X(J).GE.34.0)) THEN
        IF((Y(J).LE.26.0).AND.(Y(J).GE.25.0)) THEN
         T32C=T32C+1
        ENDIF
     ENDIF
50  CONTINUE

    TS(1,NDays)  = T1A+T1B
    TS(2,NDays)  = T2A+T2B+T2C
    TS(3,NDays)  = T3A+T3B+T3C+T3D
    TS(4,NDays)  = T4
    TS(5,NDays)  = T5A+T5B+T5C
    TS(6,NDays)  = T6
    TS(7,NDays)  = T7A+T7B+T7C+T7D
    TS(8,NDays)  = T8A+T8B
    TS(9,NDays)  = T9A+T9B+T9C
    TS(10,NDays)  = T10
    TS(11,NDays)  = T11
    TS(12,NDays)  = T12
    TS(13,NDays)  = T13A+T13B
    TS(14,NDays)  = T14
    TS(15,NDays)  = T15A+T15B+T15C
    TS(16,NDays)  = T16A+T16B+T16C
    TS(17,NDays)  = T17A+T17B+T17C+T17D
    TS(18,NDays)  = T18A+T18B
    TS(19,NDays)  = T19A+T19B+T19C+T19D+T19E+T19F
    TS(20,NDays)  = T20A+T20B
    TS(21,NDays)  = T21
    TS(22,NDays)  = T22A+T22B
    TS(23,NDays)  = T23A+T23B+T23C
    TS(24,NDays)  = T24A+T24B
    TS(25,NDays)  = T25
    TS(26,NDays)  = T26A+T26B+T26C+T26D
    TS(27,NDays)  = T27A+T27B+T27C+T27D+T27E+T27F
    TS(28,NDays)  = T28A+T28B+T28C+T28D+T28E+T28F
    TS(29,NDays)  = T29
```

```
      TS(30,NDays) = T30A+T30B+T30C+T30D+T30E
      TS(31,NDays) = T31A+T31B
      TS(32,NDays) = T32A+T32B+T32C
      IEND=1
      READ (1,'(A)',END=90) FileIn
      IF (LEN_TRIM(FileIn).LE.1) GOTO 90
      IEND=0
      IF (NDays.GE.31.OR.YrMon.NE.FileIn(2:5)) GOTO 90
      NDays=NDays+1
      GOTO 8

  90  CONTINUE
C
********************************************************************

C     WRITE THE
RESULTS***************************************************

      WRITE(16,12)  (TS(1,IDy), IDy=1, NDays)
  12  format(8HPORTUGAL,10X,31F5.0)
      WRITE(16,13)  (TS(2,IDy), IDy=1, NDays)
  13  FORMAT(5HSPAIN,13X,31F5.0)
      WRITE(16,14)  (TS(3,IDy), IDy=1, NDays)
  14  format(6HFRANCE,12X,31F5.0)
      WRITE(16,15)  (TS(4,IDy), IDy=1, NDays)
  15  format(11HSWITZERLAND,7X,31F5.0)
      WRITE(16,16)  (TS(5,IDy), IDy=1, NDays)
  16  format(5HITALY,13X,31F5.0)
      WRITE(16,17)   (TS(6,IDy), IDy=1, NDays)
  17  format(7HALBANIA,11X,31F5.0)
      WRITE(16,18)  (TS(7,IDy), IDy=1, NDays)
  18  format(13HEX-YUGOSLAVIA,5X,31F5.0)
      WRITE(16,19)  (TS(8,IDy), IDy=1, NDays)
  19  format(6HGREECE,12X,31F5.0)
      WRITE(16,20)  (TS(9,IDy), IDy=1, NDays)
  20  format(7HGERMANY,11X,31F5.0)
      WRITE(16,21)  (TS(10,IDy), IDy=1, NDays)
  21  format(7HAUSTRIA,11X,31F5.0)
      WRITE(16,22)  (TS(11,IDy), IDy=1, NDays)
  22  format(7HHUNGARY ,11X,31F5.0)
      WRITE(16,23)  (TS(12,IDy), IDy=1, NDays)
  23  format(7HROMANIA,11X,31F5.0)
      WRITE(16,24)  (TS(13,IDy), IDy=1, NDays)
  24  format(14HCZECHOSLOVAKIA,4X,31F5.0)
      WRITE(16,25)  (TS(14,IDy), IDy=1, NDays)
  25  format(8HMOLDAVIA,10X,31F5.0)
      WRITE(16,26)  (TS(15,IDy), IDy=1, NDays)
  26  format(7HPOLLAND,11X,31F5.0)
      WRITE(16,27)  (TS(16,IDy), IDy=1, NDays)
  27  format(12HWHITE RUSSIA,6X,31F5.0)
      WRITE(16,28)  (TS(17,IDy), IDy=1, NDays)
  28  format(7HUKRANIA,11X,31F5.0)
      WRITE(16,29)  (TS(18,IDy), IDy=1, NDays)
  29  format(8HBULGARIA,10X,31F5.0)
      WRITE(16,34)  (TS(19,IDy), IDy=1, NDays)
  34  format(6HTURKEY,12X,31F5.0)
      WRITE(16,35)  (TS(20,IDy), IDy=1, NDays)
  35  format(7HENGLAND,11X,31F5.0)
      WRITE(16,36)  (TS(21,IDy), IDy=1, NDays)
  36  format(7HIRELAND,11X,31F5.0)
      WRITE(16,37)  (TS(22,IDy), IDy=1, NDays)
```

```
   37   format(15HHOLLAND-BELGIUM,3X,31F5.0)
        WRITE(16,38)   (TS(23,IDy), IDy=1, NDays)
   38   format(11HMIDDLE EAST,7X,31F5.0)
        WRITE(16,39)   (TS(24,IDy), IDy=1, NDays)
   39   format(11HEAST AFRICA,7X,31F5.0)
        WRITE(16,40)   (TS(25,IDy), IDy=1, NDays)
   40   format(13HMIDDLE AFRICA,5X,31F5.0)
        WRITE(16,41)   (TS(26,IDy), IDy=1, NDays)
   41   format(11HWEST AFRICA,7X,31F5.0)
        WRITE(16,42)   (TS(27,IDy), IDy=1, NDays)
   42   format(10HEX-U.S.S.R,8X,31F5.0)
        WRITE(16,43)   (TS(28,IDy), IDy=1, NDays)
   43   format(12HEASTERN MED.,6X,31F5.0)
        WRITE(16,44)   (TS(29,IDy), IDy=1, NDays)
   44   format(12HCENTRAL MED.,6X,31F5.0)
        WRITE(16,45)   (TS(30,IDy), IDy=1, NDays)
   45   format(12HWESTERN MED.,6X,31F5.0)
        WRITE(16,46)   (TS(31,IDy), IDy=1, NDays)
   46   format(14HWEST BLACK SEA,4X,31F5.0)
        WRITE(16,47)   (TS(32,IDy), IDy=1, NDays)
   47   format(14HEAST BLACK SEA,4X,31F5.0)

        DO IDy=1, NDays
         TN(IDy)=0
         DO J=1, 32
           TN(IDy)=TN(IDy)+TS(J,IDy)
         ENDDO
        ENDDO
        WRITE(16,53)   (TN(IDy), IDy=1, NDays)
   53   format(5HTOTAL,13X,31F5.0)
        CLOSE (16)
        IF (IEND.EQ.0)   GOTO 7
        STOP

  100   IF (NDays.EQ.0)
       &  WRITE(*,'(A/A/A)') ' *** ERROR ***',
       &     '         File:  FILES.LST  does not exist!',
       &     '         Use the command:  DIR  B9*.TXT  /-P /B >
FILES.LST'
        STOP
        END

        SUBROUTINE  ZERO(T1A,T1B,T2A,T2B,T2C,T3A,T3B,T3C,T3D,T4,
       &       T5A,T5B,T5C,T6,T7A,T7B,T7C,T7D,T8A,T8B,T9A,T9B,
       &       T9C,T10,T11,T12,T13A,T13B,T14,T15A,T15B,T15C,
       &       T16A,T16B,T16C,T17A,T17B,T17C,T17D,T18A,T18B,T19A,T19B,
       &       T19C,T19D,T19E,T19F,T20A,T20B,T21,T22A,T22B,
       &       T23A,T23B,T23C,T24A,T24B,T25,T26A,T26B,T26C,T26D,
       &       T27A,T27B,T27C,T27D,T27E,T27F,T27,T19AB,T19DE,
       &       T28A,T28B,T28C,T28D,T28E,T28F,T29,
       &       T30A,T30B,T30C,T30D,T30E,T31A,T31B,
       &       T32A,T32B,T32C)

          T1A=0.
          T1B=0.
          T2A=0.
          T2B=0.
          T2C=0.
          T3A=0.
          T3B=0.
          T3C=0.
```

```
T3D=0.
T4=0.
T5A=0.
T5B=0.
T5C=0.
T6=0.
T7A=0.
T7B=0.
T7C=0.
T7D=0.
T8A=0.
T8B=0.
T9A=0.
T9B=0.
T9C=0.
T10=0.
T11=0.
T12=0.
T13A=0.
T13B=0.
T14=0.
T15A=0.
T15B=0.
T15C=0.
T16A=0.
T16B=0.
T16C=0.
T17A=0.
T17B=0.
T17C=0.
T17D=0.
T18A=0.
T18B=0.
T19A=0.
T19B=0.
T19C=0.
T19D=0.
T19E=0.
T19F=0.
T20A=0.
T20B=0.
T21=0.
T22A=0.
T22B=0.
T23A=0.
T23B=0.
T23C=0.
T24A=0.
T24B=0.
T25=0.
T26A=0.
T26B=0.
T26C=0.
T26D=0.
T27A=0.
T27B=0.
T27C=0.
T27D=0.
T27E=0.
T27F=0.
T27=0.
```

```
  T19AB=0.
  T19DE=0.
  T28A=0.
  T28B=0.
  T28C=0.
  T28D=0.
  T28E=0.
  T28F=0.
  T29=0.
  T30A=0.
  T30B=0.
  T30C=0.
  T30D=0.
  T30E=0.
  T31A=0.
  T31B=0.
  T32A=0.
  T32B=0.
  T32C=0.
 END_
```

Table A5. An example of an output file obtained from the program given in Table A4.

	17.04.97	18.04.97	19.04.97	20.04.97	21.04.97	22.04.97
PORTUGAL	0	0	0	0	0	0
SPAIN	0	0	0	0	0	0
FRANCE	0	0	0	0	0	0
SWITZERLAND	0	0	0	0	0	0
ITALY	15	0	0	0	0	4
ALBANIA	0	0	0	0	0	0
EX-YUGOSLAVIA	0	23	0	0	0	0
GREECE	0	11	0	0	0	0
GERMANY	0	0	0	0	0	0
AUSTRIA	0	0	0	0	0	0
HUNGARY	0	7	4	0	0	0
ROMANIA	0	0	7	0	0	0
CZECHOSLOVAKIA	0	6	0	0	0	0
MOLDAVIA	0	0	0	0	0	0
POLLAND	0	8	3	0	0	0
WHITE RUSSIA	0	0	13	0	0	0
UKRANIA	0	0	3	0	0	0
BULGARIA	0	2	7	0	0	0
TURKEY	21	21	19	24	21	14
ENGLAND	0	0	0	0	0	0
IRELAND	0	0	0	0	0	0
HOLLAND-BELGIUM	0	0	0	0	0	0
MIDDLE EAST	0	0	0	0	4	0
EAST AFRICA	0	0	0	0	0	0
MIDDLE AFRICA	0	0	0	0	0	9
WEST AFRICA	0	0	0	0	0	19
EX-U.S.S.R	0	0	27	0	0	0
EASTERN MED.	8	0	0	22	49	23
CENTRAL MED.	40	0	0	38	10	9
WESTERN MED.	0	0	0	0	0	6
WEST BLACK SEA	0	1	1	0	0	0
EAST BLACK SEA	0	0	0	0	0	0
TOTAL	84	79	84	84	84	84

	24.04.97	25.04.97	26.04.97	27.04.97	28.04.97	29.04.97
PORTUGAL	0	0	0	0	0	0
SPAIN	0	0	0	0	0	0
FRANCE	0	0	0	0	0	0
SWITZERLAND	0	0	0	0	0	0
ITALY	0	0	0	0	0	0
ALBANIA	0	0	0	0	0	0
EX-YUGOSLAVIA	0	0	0	0	0	0
GREECE	37	0	0	0	0	0
GERMANY	0	0	0	0	0	0
AUSTRIA	0	0	0	0	0	0
HUNGARY	0	0	0	0	11	0
ROMANIA	0	29	17	0	0	0
CZECHOSLOVAKIA	0	0	0	0	0	0
MOLDAVIA	0	4	0	0	0	0
POLLAND	0	0	0	0	0	0
WHITE RUSSIA	0	0	0	0	0	0
UKRANIA	0	0	0	2	50	0
BULGARIA	0	10	0	0	0	0
TURKEY	11	9	38	5	2	40
ENGLAND	0	0	0	0	0	0
IRELAND	0	0	0	0	0	0
HOLLAND-BELGIUM	0	0	0	0	0	0
MIDDLE EAST	0	0	0	0	0	0
EAST AFRICA	0	0	0	0	0	0
MIDDLE AFRICA	0	0	0	0	0	0
WEST AFRICA	0	0	0	0	0	0
EX-U.S.S.R	0	0	0	13	3	4
EASTERN MED.	10	0	0	0	0	0
CENTRAL MED.	0	0	0	0	0	0
WESTERN MED.	0	0	0	0	0	0
WEST BLACK SEA	15	8	15	8	1	0
EAST BLACK SEA	11	24	14	56	17	40
TOTAL	84	84	84	84	84	84

VITA

Duran Karakaş was born in Çekerek, Yozgat on February 01, 1965. He received his B.S. degree in Chemistry Education from Middle East Technical University in June 1990. He received his M.Sc. in June 1993 in Chemistry Department of METU. He worked as a graduate assistant in chemistry department of METU from 1990 to 1999. From October 01, 1997 to June 01, 1998 he worked as a visiting scientist at Massachusetts Institute of Technology, Nuclear Reactor Laboratory, Cambridge MA, U.S.A. His main areas of interest are atmospheric pollution (both aerosols and wet-dry depositions of atmospheric pollutants), pollution marker elements, long-range transport of pollutants and water pollution.