INVESTIGATION OF THE CHEMICAL COMPOSITION OF THE LOWER TROPOSPHERIC AEROSOLS IN THE EASTERN MEDITERRANEAN REGION: IMPLICATIONS REGARDING SOURCES AND LONG-RANGE TRANSPORT

BY

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IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE DEGREE
OF

MASTER OF SCIENCE

IN

MARINE SCIENCES

MARCH 2001

Approval of the Graduate School of Marine Sciences

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ABSTRACT

INVESTIGATION OF CHEMICAL COMPOSITION OF THE LOWER TROPOSPHERIC AEROSOLS IN THE EASTERN MEDITERRANEAN REGION: IMPLICATIONS REGARDING SOURCES AND LONG-RANGE TRANSPORT

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From January 1996 to December 1998 samples of 409 aerosols arriving at a rural site on the Turkish coast of the eastern Mediterranean (Erdemli) were collected by a hi-vol pump. The collected aerosol filter samples were analyzed by flame atomic absorption spectrophotometer and ion chromatography for trace elements (Al, Fe, Ca, Mg, Mn and Zn) and for water-soluble ions (Cl^-, Br^-, NO_3^-, $SO_4^=$, $C_2O_4^=$, $CH_3SO_3^-$, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}), respectively. The combined data set provided concentration values for 17 elements and ions. In addition, three dimensional (3D), three days backward trajectories of air masses arriving daily at the Erdemli site at 900, 850, 700 and 500 hPa barometric pressure levels have been calculated to determine potential source regions. Analysis of lower layer and higher layer air mass trajectories indicated distinctly different potential source regions. The lower layer trajectories indicated that the dominating group of air masses originates from the west, north and east and accounting for 74% at 900 hPa and accounting for 72% at 850 hPa, respectively. The upper layer trajectories indicated a rapid transport from the south-southeasterly sector (the North African continent) have frequencies of 36% at 700 hPa and 61% at 500 hPa over the 10 year period.

The results depicted that the seasonal variability of the atmospheric concentrations of the trace elements and ions determined at the Erdemli site was related to occurrence of precipitation. Atmospheric concentration of measured species (except marine elements) decreased to their minimum values during winter season due to precipitation scavenging, whereas, during dry summer months the lack of precipitation resulted in the accumulation of aerosols in the atmosphere. During the transitional seasons, although there was still precipitation, the elements associated with mineral particles exhibited sporadic but intense concentration peaks. Air mass backward trajectories associated with geochemical tracer (Al) indicated that, throughout these seasons, incursion of Sahara dust governed the fluctuation in the atmospheric concentrations of the elements.

The results obtained from factor analysis and enrichment factors suggested presence of three sources contributing to the determined concentrations. These were: crustal material, marine and anthropogenic sources. Furthermore, the results of factor analysis suggested that atmospheric aerosols over Cilisian Basin dominated by emissions of natural sources. Annually, 4%, 10%, 35% and 79% sea salt contribution were assessed on observed concentrations of Ca^{2+}, $SO_4^{=}$, K^{+} and Mg^{2+}, respectively.

The results obtained from biogeochemical tracers and air mass back trajectories showed the origin of the crustal elements and the detected high sulfate levels. During the period of sampling –25 African dust events were identified by an abrupt increase in the Al, Fe, Ca and also Mn and Zn concentration in the atmosphere. The average concentrations of the elements for the identified dates were calculated as 1569, 1146, 5532, 17.9 and 27.9 ng m^{-3} for Al, Fe, Ca , Mn and Zn, respectively. The average concentrations of the same elements for the remaining samples (where there was no recorded mineral dust transport) were much lower (262, 255, 2212, 6.8 and 17.5 ng m^{-3} for Al, Fe, Ca, Mn and Zn, repectively). In addition, 3-day back trajectory analysis indicate that air masses originating from Black Sea Region and Mediterranean Sea have MSA and nss-$SO_4^{=}$ values two times as much as than those calculated for air masses of samples originating from European and former Soviet Union. And elevated biogenic contributions to nss-$SO_4^{=}$ in summer period (reaches up to 50%) suggest that there is major source of oceanic emissions of DMS in the eastern Mediterranean or surrounding seas (e.g. Black Sea).

Keywords: aerosol, eastern Mediterranean, trace metals, water-soluble ions, enrichment factors/diagrams, factor analysis, air mass back trajectories, long range transport, Sahara, geobiochemical tracers.

ÖZ

DOĞU AKDENİZ BÖLGESİ AŞAĞI TROPOSFERİK PARÇACIKLARIN KİMYASAL YAPISININ İNCELENMESİ: KAYNAKLARA GÖRE YORUMLAR VE UZUN MENZİLLİ TAŞINIM

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Ocak 1996 ve Aralık1998 tarihleri arasında Doğu Akdeniz'in Türkiye kıyısındaki Erdemli bölgesine ulaşan hava kütlelerinden 409 adet aerosol örnekleri yüksek debili hava pompası kullanılarak toplanmıştır. Toplanan örneklerde atomik soğurma spektrofotometre ve iyon kromatografi cihazları kullanılarak sırası ile iz metaller (Al, Fe, Ca, Mn, Mg, Zn) ve sulu ortamda çözünebilen iyonlar (Cl^-, Br^-, NO_3^-, $SO_4^=$, $C_2O_4^=$, $CH_3SO_3^-$, Na^+, NH_4^+, K^+, Mg^{2+},Ca^{2+}) ölçülmüştür. Buna ek olarak, örnekleme bölgesine (Erdemli) 900, 850, 700 ve 500 hPa barometrik basınç seviyelerinde ulaşan hava kütlelerinin üç günlük geriye dönük üç boyutlu yörüngeleri hesaplanmıştır. Elde edilen sonuçlar, Erdemli istasyonunda toplanan aerosol filtrelerinde ölçülen iz metal ve suda çözünebilen iyonların derişimlerindeki mevsimsel değişimlerin yerel yağışlarla yakından ilgili olduğunu göstermiştir. Geçiş mevsimlerinde (ilkbahar ve sonbahar) yağışlar devam etmesine rağmen alüminyum-silikat yapısında zenginleşmiş elementlerin derişimlerinde ani yükselmeler görülmüştür. Faktör analizden ve zenginleşme katsayılarının hesaplanmasından elde edilen sonuçlar toprak, deniz ve antropojenik kaynaklı aerosollerin etkisinde olduğunu göstermiştir. Hava kütlelerinin üç günlük geri yörüngeleri ve biojeokimyasal izleyicilerin birlikte kullanılması toprak kaynaklı elementlerin ve gözlenen yüksek sülfat derişimlerinin kaynaklarını açıklamıştır. Örnekleme süresi boyunca 25 adet Afrika kaynaklı toz olayı tespit edilmiştir ve bu günlere ait örneklerdeki Al, Fe, Ca, Mn ve Zn derişimlerinde ani yükselmeler gözlenmiştir. Hesaplanan biyojenik sülfatın (%50'lere ulaşmakta) toplam sülfata katkısı, yaz aylarında birincil sülfat kaynağının çevre denizlerdeki (Akdeniz ve Karadeniz) biyolojik üretimden (DMS) kaynaklanabileceği fikrini ortaya çıkarmaktadır.

Anahtar kelimeler: aerosol, doğu Akdeniz, iz metaller, suda çözünebilir iyonlar, zenginleşme faktörü/diyagramı, faktör analizi, kaynaklar, geriye dönük hava kütleleri, uzun mesafeli taşınım

ACKNOWLEDGEMENTS

I am deeply grateful to my supervisor Assoc.Pro. Nilgün.N. Kubilay for her guidance, endless encouragement, supervision, suggestions in the every phase of this work.

I also would like to thank to Assoc.Prof. Nikos Mihalopoulos in the Environmental Chemistry Processes Laboratory, for his supervision and friendly criticism during four months laboratory work at University of Crete. I would like also to thank Constantina Economou for her friendship and helpfulness.

I extend my sincere thank to Sıdıka Ergin for helping Atomic Absorption Spectrometry, Mehmet Durmaz for helping collection of filters.

I wish express my appreciation to Serkan Sancak for supplying old but useful computer.

Thanks are also due to the Start Fellowship program for four months stay in Crete to work in the laboratory of ECPL at University of Crete.

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CHAPTER I

INTRODUCTION

1.1. Aim of the Study

Aerosols play a primary role in many geophysical and geochemical global processes. They can modify the earth's radiation budget. In the absence of clouds, the scattering and absorption of radiation is mainly controlled by aerosol particles. In cloudy areas, the radiation regime is dominated by cloud effects; however, cloud properties are dependent on aerosol particles which serve as nuclei for condensation and ice formation. Thus, aerosols can affect cloud formation and, in turn cloud albedo, cloud lifetimes and precipitation processes. Aerosols also serve as reaction surfaces in the atmosphere and are the sinks for many gas-phase species. Furthermore, aerosols can affect the PH and chemical composition of rain, once deposited these can have an impact on oceanic and continental biogeochemical systems. Due to these events, last two decades atmospheric compartment has received special interest.

Atmospheric transport supplies both natural and man-made materials from continents to both coastal and open seas. These substances include mineral dust, plant residues, heavy metals, nitrogen species from combustion processes and fertilisers, pesticides, a wide range of synthetic organic compounds from industrial and domestic sources. Recent reviews in the field (Duce et al., 1991; Jickells, 1995, 1999) make it evident that the atmosphere is not only the significant, but in some cases, the dominant pathway by which metals and nutrients reach the ocean. Atmospheric processes appear to play a primary role in supplying trace metals (Martin et al., 1989; Guieu et al., 1997; Guerzoni et al., 1999; Ridame et al., 1999), as well as nitrogen and phosphorus (Herut et al., 1999) to the Mediterranean Sea. Trace metal inputs are quantitatively significant, and some cases exceed riverine inputs (e.g. Pb, Cu, Cd in the western Mediterranean; Guieu et al., 1991). Therefore, atmospheric inputs may exert many different effects on the marine environment, and it is necessary to understand the magnitude and geographical distribution of the atmospheric fluxes of these materials to both coastal and open seas.

This study aims to identify the chemical composition of aerosols, determine short (daily) and long-term (seasonal) variation of the aerosol concentration with respect to meteorological conditions and long range transport and assess the contribution of the natural and anthropogenic (man-made) sources atmosphere over the eastern Mediterranean.

1.2. Overview of the Atmospheric Aerosol

The atmosphere is not simply a mixture of gases. Every cubic centimeter of air contains up to thousands of suspended particles; most of these are only a fraction of a micrometer in diameter. Particulate matter in the atmosphere is commonly refered to as "aerosol", although the term properly applies to the multiphase mixture of solid or liquid particles dispersed in a gas.

Prospero *et al.* (1983) defined a number of aerosol types on the basis of their composition and sources, and a summary of their classification is given in Table 1.1. The components that make up the world aerosol originate from two different kinds of processes: (a) the direct formation of particles (e.g. during crustal weathering, sea-salt generation, volcanic emissions), and (b) the indirect formation of particles in the atmosphere itself by chemical reactions and by the condensation of gases and vapours.

Table 1.1. The classification of aerosols on the basis of their composition or sources[a]

1.NATURAL AEROSOLS
  - **1.1.** Sea spray residues
  - **1.2.** Windblown mineral dust
  - **1.3.** Volcanic effluvia
  - **1.4.** Biogenic materials
  - **1.5.** Smoke from the burning of land biota
  - **1.6.** Natural gas-to-particle conversion products

2.ANTHROPOGENIC AEROSOLS
  - **2.1.** Direct anthropogenic particle emissions
  - **2.2.** Products from the conversion of anthropogenic gases

[a] Based on Prospero *et al.* (1983)

The shapes of atmospheric particles are rarely uniform and the expressions generally used to describe the size of aerosols are geometric size. It has been suggested that atmospheric particles have in general a multi-modal distribution. A generalized relationship between the processes responsible for the generation of aerosol particles and their size spectra is illustrated in Figure 1.1. This figure shows the modal peaks, together with the particle formation and removal mechanism. The particles are divided into two broad groups, fine particles ($d<2$ μm) and coarse particles ($d>2$ μm) and there are three size maxima, two in the fine class and one in the coarse class.

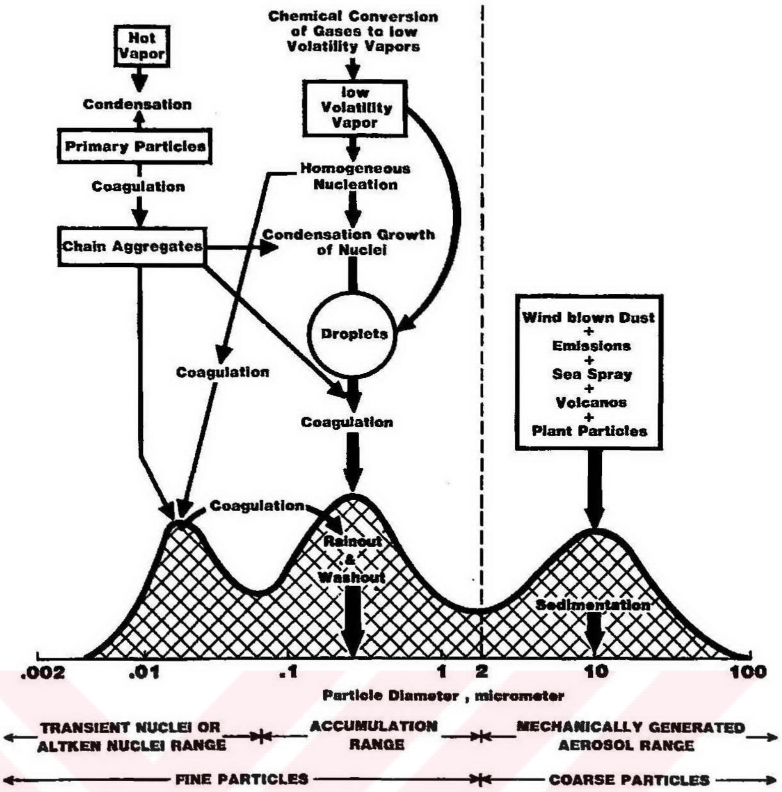


Figure 1.1. Schematic representation of the three modes and of the processes involved in generation and removal of atmospheric particles (taken from Salomons and Förstner, 1984).

The maxima in the fine mode relate to two particle populations; those in the Aitken nuclei range (<0.1 μm) and (b) those in the accumulation range (0.1-2 μm). Aitken nuclei originate predominantly from combustion sources, which are chiefly anthropogenic, but also include volcanic emissions and forest fires. Particles in the accumulation mode are thought to result primarily from the coagulation of Aitken nuclei into larger aggregates, or by condensation of reaction products, or water, onto primary particles. In contrast, particles in the coarse mode (> 2 μm) can be formed in a number of ways, which include the following: (1) as a result of mechanical processes, e.g. erosion and sea spray, (2) as the result of the incomplete combustion of other particles. These particles have a limited residence time in the atmosphere (typically only few days), as a result of their high settling velocities. During unstable weather, such as high wind speeds the lifetime of coarse particles in the atmosphere can be prolonged, resulting in them being transported over greater than normal distances (Salomons and Förstner, 1984; .Jaenicke, 1998).

Troposheric aerosol within the planetery boundary layer (which is defined as the region of the atmosphere where surface effects are important and its depth is order of 1 km, but varies significantly with the time of day and with meteorological conditions) can be broadly classified as marine and continental. The continental aerosol has components derived from soils, minerals, biogenic sources, combustion and gas-to-particle conversion. The continental aerosol may be classified into rural (remote), urban and desert dust storm aerosol. Table 1.2. shows a recent estimate of the various contributions to the aerosol source.

Table 1.2. Global sources of atmospheric aerosols (X 10^6 tonnes per year). (taken from Turco, 1999).

Aerosol Sources	Total Emissions $D < 25$ μm	Emissions $D < 1$ μm
Manmade		
Primary:		
Industrial dust	40-130	20-65
Soot	10-30	10-30
Biomass burning	50-190	50-190
Windblown dust	820	140
Gas-Particle Conversion of:		
SO_2 : Smelters / power plants	120-180	120-180
NO_X: Autos / power plants	20-50	5-10
Anthropogenic VOCs	5-25	5-25
Total Manmade Sources	1065-1425	350-640
Natural		
Primary:		
Windblown dust	1000-3000	265
Forest fires	3-150	2-75
Sea salt	1000-10000	20-100
Volcanoes	4-10000	0.4-100
Organics	26-50	-
Gas-Particle Conversion of:		
DMS, H_2S	60-110	60-110
Volcanic SO_2	10-30	10-30
Biogenic NO_X	10-40	10-40
Biogenic VOCs	40-2000	40-2000
NH_3 to NH_4^+ salts	80-270	80-270
Total Natural Sources	2233-25650	487-2990

Fitzgerald (1991) has compiled a review of the characteristics of particles within the marine boundary layer (MBL) that are of marine origin. This aerosol is considered to define the "background"; that is, it is representative of air masses that have resided over the ocean for a sufficient time period (on the order of 10 days) to minimise influences from anthropogenic aerosol. Near the East Coast of the United States, measurements indicate that total particle number concentrations are typically near 6000

cm^{-3}, reflecting continental influences. The background concentrations range from less than 100 cm^{-3} to a mean of about 200 cm^{-3} over the Pacific Ocean. Sea salt is the most important component of larger particles ($d > 1$ μm) with a variable fraction of continental mineral dust. About 90-95 % of the number concentration is accounted for by particles with diameters less than 0.6 μm, although they represents only about 5 % of the total aerosol mass. These small particles consist primarily of non-sea-salt sulfate, presumably generated from oxidation of reduced sulfur compounds; principally dimethylsulfide (DMS) emitted from the ocean.

A fundamental distinction between the fine and coarse particle fractions lies in the source mechanisms that produce them. Mechanical processes (anthropogenic and natural) produce the relatively large particles in the coarse mode; examples are sea spray, windblown dust, fly-ash and volcanic ash. The chemical composition of the coarse fraction reflects these sources: crustal elements (Fe, Ca, Si, Al, etc.) and seawater species (Na, Cl, etc.) are commonly detected. The mechanically produced particles are examples of primary emissions, that is, particles that have been emitted directly to the atmosphere. Aerosol that has formed in the atmosphere by physical or chemical transformations is termed secondary aerosol. An example is sulfate, which forms downwind of an industrial source, as emitted gases are chemically converted to condensable species, which are then incorporated into particles. This process is known as gas-to particle conversion and is the mechanism by which aerosol particles serve as sinks in the chemical cycles of several important tropospheric trace gases.

Ionic species are important components of the fine-particle fraction, and commonly include sulfate ($SO_4^{=}$), nitrate (NO_3^-), and ammonium (NH_4^+). Sulfate and nitrate, derived from sulfuric acid (H_2SO_4) and nitric acid (HNO_3), are fully oxidized end products of the atmospheric cycles of sulfur and nitrogen compounds and they partition to the particulate phase because of their low volatilities and /or their high solubility in water. Ammonia dissolves in wetted particles and serves as a neutralizing species, so that, in the lower troposphere, sulfate and nitrate anions are usually found as fully or partially neutralized species such as ammonium sulfate [$(NH_4)_2SO_4$] or ammonium bisulfate ($NH_4H\ SO_4$), or as salts such as sodium nitrate ($NaNO_3$) if cations such as sodium or calcium are present.

Nitrogen (N_2)is the most abundant element in the Earth's atmosphere, comprising approximately 80% of the total. The N_2 molecule is extremely stable and plays almost no chemical role. Minor constitutents such as nitrous oxide (N_2O), nitric oxide (NO), nitrogen dioxide (NO_2), nitric acid (HNO_3) and ammonia (NH_3) are chemically reactive and play roles in the formation of acid deposition, photochemical smog and tropospheric aerosols, and the destruction of stratospheric ozone. The nitrogen oxides, NO and NO_2, are rapidly interconvertible, and exist in dynamic equilibrium. For convenience, the sum of two species referred to as NO_x (NO_x= NO+ NO_2). Large amount of NO_x are released by combustion processes, particularly as a result of industrial activity and the intensive use of automobiles. Biomass burning and microbial production in soils are other important sources of NO_x. In relatively clean environments the emission of some nitrogen compounds (*e.g.* N_2O, NO, NH_3) results primarily from a wise range of complex biological processes in soils. The use of nitrogen fertilizers, required for intensive agriculture, is believed to enhance the flux of N_2O to the atmosphere. The consumption of nitrogenous fertilizers alters the nitrogen cycle through enhanced emissions of ammona, nitrous oxide and nitric oxide to the atmosphere.

Fossil fuel combustion dominates the NO_x budget in industrialized areas, while the contribution of soil – biogenic emissions is important in rural areas and may dominate in tropical regions or near heavily fertilized soils.

Sulfur is a chemical element essential to life on earth. Living organisms, including plants, assimilate sulfur, while at the same time sulfur in various forms is released by living organisms as an end product metabolism. The major sulfur gases include dimethyl sulfide (CH_3 S CH_3 or DMS), carbonyl sulfide (OCS), hydrogen sulfide (H_2S), dimethyl disulfide (DMDS), carbon disulfide (CS_2) and sulfur dioxide (SO_2). Over the past centuries, the sulfur cycle has been increasingly perturbed by human activities. Today, globally, anthropogenic emissions constitute almost 75% of the total sulfur emission budget with 90% occurring in the Northern Hemisphere. Excluding biomass burning, natural emission sources (marine+terrestrial+volcanic) constitute 24 of the total emission budget with 13 % in the Northern Hemisphere and 11 % in the Southern Hemisphere. Once in the atmosphere, DMS, H_2S, OCS and CS_2 are oxidised by reactions primarily with OH to form SO_2 and eventually H_2SO_4 or CH_3SO_3H (methane sulphonic acid or MSA).

Dimethyl sulfide is the dominant biogenic sulfur compound (Bates et al., 1992). Under natural conditions, this gas is the primary contributor to the atmospheric burden of non-sea-salt (nss) sulfate which is the concentration of sulfate found in marine aerosols in excess of that found in seawater.

A major natural component of the aerosol is formed by desert dust. While most of the dust is of natural origin, changes in land use must have increased the amounts of dust injected into the atmosphere (see Table 1.2).

The factors that influence the particulate concentration in the atmosphere include particle sources and emission rates, chemical reaction, the time and location and also the efficiency of particle removal processes.

Removal processes are important in determining the behaviour of aerosols in the atmosphere. Generally the removal can take place by two main processes, dry and wet deposition. Dry deposition term covers all the processes by which aerosols deposit onto the surface (land or sea) from the atmosphere without precipitation. Wet deposition is achieved by two paths: (1) Rainout processes which take place within cloud, via nucleation of material into pre-existing cloud elements, (2) Washout or Rainout processes which take place below the cloud through the impaction or and interception of aerosols by the falling precipitation.

Atmospheric aerosols are important for several reasons. First, they serve to transport of nonvolatile material from one place to another. An important example of this is the transport of crustal minerals, such as iron, to the world's ocean, where they may serve as sources of nutrients to marine organisms

Aerosols are chemically and physically much more complex than gaseous pollutants, and the overall process governing aerosol loadings, properties and distributions is much more complex than for primary pollutants such as SO_2. Aerosols are very heterogeneous in composition and sources, ranging from seasalt, dust to sulfates, nitrate, organics and soots, as well as mixtures of these materials. The relative influence of a certain aerosol species on the regional atmospheric characteristics depends on the source strength and on the actual atmospheric conditions. Aerosols can also be studied as tracers of atmospheric activity in terms of their production, transport and deposition. Andreae and Crutzen (1997) have reviewed the role of aerosols in atmospheric chemistry, and discussed their importance as climatic (through scattering and absorption of light) and chemical and physical agents (providing surfaces for heterogeneous reactions for trace gases). Because different species behave differently in the atmosphere, it is important to distiguish the aerosols in terms of their chemical – and physical (and optical) properties and to assess their relative abundance in the atmosphere. Ultimately, this kind of investigation provides guidelines for environmental policy makers. Prospero (1999) has commented on this issue with respect to the implications of synoptic scale transport of Saharan mineral dust to the United States, regarding regional air quality standards. The changing concentrations of aerosol particles also an effect on air quality, impairing visibility and affecting human health. Several aircraft crashes have been attributed to reduced visibility due to pollution haze layers (Prospero *et al.*, 1999) and to severe sand and dust storms (Ganor, 1994). When inhaled, aerosol particles affect the lung and respiratory track (WHO, 1997).

The human perturbation of global climate by the introduction into the atmosphere of large amounts of infrared-absorbing gases is now well studied, and this "greenhouse effect" is presently under discussion for global political mitigative action. However, recent studies show that atmospheric aerosols, and especially submicrometer-sized particles, also have a potent influence on global climate. The climatic effect of aerosols stems from the fact that they physically affect the heat balance of the Earth, both directly by reflecting and absorbing solar radiation and by absorbing and emitting some terrestrial infrared radiation and indirectly by influencing the properties and processes of clouds, and, possibly, by changing the heterogeneous chemistry of reactive greenhouse gases (e.g. O_3) (Charlson and Heintzenberg, 1995; Schwartz, 1996). Changes in the heat balance due to anthropogenic or externally imposed changes are referred to as forcings. The climatic effect of aerosols is in the direction of cooling (under most circumstances) and is of magnitude comparable to that of the greenhouse warming.

1.3. The Atmospheric Transport of Aerosols to the Ocean

Most of the continentally-derived material (both natural and anthropogenic) that is contributed to the world aerosol is initially injected into the planetery boundary layer (PBL) of the atmosphere. The top of the PBL is often marked by a layer of high static stability (when the temperature increases with height, this called an inversion) which inhibits the transfer of material to the upper atmosphere (Prospero, 1981). The primary transport path for material from the continents to the sea surface may be via the boundary layer. The major transport path over longer distances is probably via the free atmosphere above the boundary layer. The rate of exchange between the troposphere and the boundary layer will affect the distance an aerosol component can be transported in the atmosphere.

A review of the global atmospheric flow patterns and storm tracks showed the potential importance of long-range transport of natural and man – made aerosols into the oceans, especially eastward from North America, westward from Africa, eastward from southern south America, eastward from Asia and into the Polar regions (Figure 1.2).

Figure 1.2. Major source regions and atmospheric transport directions (taken from WMO, 1991).

Regions where mineral aerosol (mineral dust) originates coincide with major deserts of the world (Figure 1.2). Large dust storms that carry particles thousands of kilometers originate in such areas as the Sahara, the southern coast of the Mediterranean, the Arabian Peninsula and the lower Volga in the former Soviet Union. Other major areas are north and western China with its great deserts, central Australia, southwest United States and the southwest Africa.

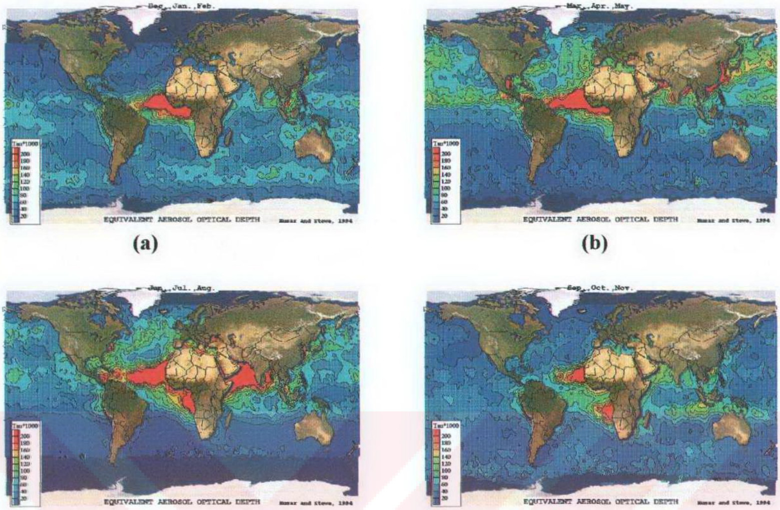
Most anthropogenic emissions are located in the Northern Hemisphere and they are concentrated in the midlatitudes, especially eastern North America, Europe and eastern Asia (Figure 1.2).

Aerosols play substantial roles in the earth's radiation balance and climate and atmospheric chemistry and are involved in important biological and chemical processes in the oceans (Andrea and Crutzen, 1997; Duce *et al.*, 1991). The deposition of dust from the continents is thought to enhance biological productivity in the oceans, the production of non-seasalt sulfate from ocean sources influences the formation clouds, and the injection of seasalt aerosols can affect the removal of ozone in the troposphere. Hence, sampling of aerosols near the ocean/atmosphere boundary is important with respect to understanding short and long term changes in climate, atmospheric chemistry and ocean productivity.

Certain marine phytoplankton release gaseous dimethylsulfide (DMS) which is transported across the ocean/atmosphere boundary to the marine boundary layer where atmospheric chemical reactions convert DMS to non-sea-salt (NSS) particles. This combination of biology, biogeochemistry, physical transport and atmospheric chemistry leads to the oceans being the major source of NSS aerosols which affect climate as they are important in the formation of clouds. The quantitative relationship between phytoplankton productivity and DMS emissions to the marine boundary layer remains elusive (Andrea and Crutzen ,1997). Seasalt aerosols are involved in complex heterogeneous reactions, which are thought to deplete the ozone concentrations in the marine boundary layer of the Polar Regions. Dust and combustion products can be important sources of trace metals and anthropogenic organic compounds to lakes, estuaries and oceans. The Iron Hypothesis is built around the argument that phytoplankton production in large regions of world's oceans is limited by iron which is supplied, in the main, by continental dust (Duce and Tindale, 1991; Martin *et al*., 1991). Dust is transported long distances from Asia and Africa across large expanses of the North Pacific and Atlantic Ocean (Arimato *et al*., 1992; Prospero *et al*., 1989) and deposited on the oceans in short episodic events and in strong seasonal pulses. The episodic nature of aerosol transport to and from the oceans is a real challenge to sample in a comprehensive manner from ships or aircraft. Shipboard studies of upper ocean biology and chemistry have rarely coincided with a dust deposition event. Hence, the enhancement of biological production by dissolved iron released from a dust event remains a hypothesis. Confirmation of the Iron Hypothesis requires long-term measurements of dust input along with simultaneous measurements of the physical, chemical and biological variability of the upper oceans. Sampling systems 3-10 m above the sea surface on buoys are well positioned to study processes associated with aerosol deposition and production near the ocean/atmosphere boundary. In contrast to ships, buoys can stay on station for 3-12 months, thus providing a less expensive and alternative platform for long-term time-series research and monitoring programs and for short-term field experiments. Buoys can be moved to strategic research regions. Aerosol data from islands cannot be accurately related to the deposition of dust and the production of seasalt, DMS and NSS aerosols taking place hundreds of miles away on the oceans. Having buoy-mounted aerosol samplers remotely controlled from shore would open up new research possibilities. Sampling could be based on satellite pictures of dust clouds, volcanic eruptions, biomass burning or increased biological productivity.

As a result of the dearth of in situ measurements, much of the large-scale features of aerosol transport over the oceans are derived from satellite imagery. Routine monitoring of global aerosol optical thickness (AOT) fields over the ocean derived from the sensors like Advenced Very – High Resolution Radiometer (AVHRR) and Coastal Zone Color Scanner (CZCS) give amount of solar radiation backscattered over the oceans by aerosols, thereby providing a synoptic estimate of aerosol source regions and distribution patterns. Some of the most striking features visible in these global maps are large-scale dust plumes especially those found in the tropical Atlantic, the Arabian Sea, the Mediterranean and the northwest Pacific (Husar *et al.*, 1997; Stegmann and Tindale, 1999; Moulin *et al.*, 1997; 1998).

Figure 1.3 shows a colour composite of the mean AVHRR AOT for four seasons (taken from Husar *et al.*, 1997). The AOT distributions in the Figure clearly show that areas of increased AOT are associated with continental sources. The continents are often fringed by regions of high AOT and in some regions the continents appear to emit long "plumes" of enhanced AOT. The plume in the low-latitude North Atlantic Ocean (NOA) is associated with mineral dust that is transported out of North Africa. Figure 1.3 shows a large seasonal change in the location and density of the AOT plumes over the (NOA). These patterns are due to seasonal changes in the distribution of dust storm activity (which is related in part to seasonal rainfall patterns) and also to the seasonal shift of large-scale circulation. Pollution plumes are also evident over the mid-latitude NAO. During the spring and summer, a large AOT plume emerges from the East Coast of the USA and extends to the central NAO. There is also a substantial transport of pollutants out of Europe to the west. In the North Pacific, a large plume emerges from the East Coast of Asia in the spring. This plume is associated with the transport of mineral dust and pollution aerosols from sources in Asia. Although there is considerable evidence of a substantial continental influence in the coastal regions of Asia in other seasons, there is no indication of a major plume comparable to that in the spring.



(a) **(b)** **(c)** **(d)**

Figure 1.3. AVHRR aerosol optical thickness, four seasons. The Figure incorporates data for the period July 1989 to June 1991 (after Husar *et al.*, 1997).

A second type of AOT distribution consists of isolated patches that do not appear to be linked continental sources. These distributions show much weaker spatial gradients, which would be consistent with more diffuse large-scale sources (oceanic emissions). An example is the belt of of slightly increased AOT values that extends over much of the southern oceans at 30° - 60° S in Figure a. Oceanic sources of atmospheric aerosols are also of interest. In the absence of pollutant aerosols the dominant submicron aerosol component over the oceans are believed to be non-sea-salt $SO_4^=$ results from the oxidation of biologically produced dimethylsulfide (DMS) emitted from the oceans (Charlson *et al.*, 1987).

Figure 1.3 shows that on a global scale the highest AOT values occur in the summer and the lowest during the winter.

The Mediterranean is impacted by pollutants from Europe and mineral dust from North Africa; these combine to produce relatively high AOT values, which are visible in global satellite imagery (Figure 1.3). The Figure shows a pronounced seasonal aerosol cycle with a maximum in summer and minimum in winter. The spring-summer distributions show a distinct gradient with the highest values near the northern coast of Africa.

In the following section the AOT distributions will be discussed in terms of current knowledge of aerosols over the oceans. Although satellite estimates of AOT integrate over the thickness of the atmospheric column, the aerosol measurements, at best, approximate concentrations in the boundary layer.

Table 1.3 summarises the mean concentrations of mineral dust at selected island stations in the Atlantic, Pacific and coastal seas namely the Mediterranean and the Arabian Seas (geographical locations of the islands are indicated in Figure 1.4).

Table 1.3. Aerosol concentrations from different oceanic regions.
Reproduced after Prospero (1996).

Station	Al ng m^{-3}	Dust* µg m^{-3}	NO_3^- µg m^{-3}	nss-$SO_4^=$ µg m^{-3}	NH_4^+ µg m^{-3}
NORTH PACIFIC					
Western Pacific					
Cheju, Korea	1650.7	20.63	5.07	9.32	3.76
Okinawa	1119.1	13.99	1.86	4.16	1.08
Hong Kong	967.0	12.09	2.61	6.69	2.74
Taiwan	317.0	3.96	2.06	5.40	1.45
Central Pacific					
Shemya	107.3	1.34	0.22	0.37	0.13
Midway	62.6	0.78	0.27	0.53	0.006
Oahu	54.6	0.68	0.35	0.50	0.04
SOUTH PACIFIC					
American Somoa	1.5	0.02	0.11	0.37	-
NORTH ATLANTIC					
Mace Head, Ireland	37.8	0.47	1.49	2.03	0.91
Bermuda	447.4	5.59	1.06	2.19	0.31
Izana, Tenerife	1782.6	22.28	0.77	0.92	0.33
Barbados	1163.8	14.55	0.53	0.78	0.11
INDIAN OCEAN					
Arabian Sea	1227.0(1)	15.34	1.23(2)	2.08(2)	0.29(2)
Tropical southern Indian Ocean	13(1)	0.16	0.46(2)	0.80(2)	0.046(2)
Mediterranean Sea	936(3)	11.70	1.45(4)	3.74(4)	1.22(4)

*Dust concentration computed from Al based on crustal abundance of 8 %.
(1)Chester *et al.* (1991); (2) Johansen *et al.* (1999); (3) Chester *et al.* (1993); (4)Medinets, (1996).

There are many dust sources in Asia, most notably the large deserts in China (Gobi and Takla Makan) and especially in the spring when there is wide-spread dust they can be transported great distances. In Japan and Korea during the spring, they often experience extensive dust hazes that are caused by yellow dust (Kosa) that can be traced sources in Asia. Recently, the discharge of NO_x and SO_2 gases in the atmosphere has dramatically increased with the development of industry in the east Asian area. The Kosa aerosol, containing a high percentage of alkaline elements such as Ca, would be expected to react with acidic gaseous substances, including NO_x and SO_2, during transport through the atmosphere. It has been demonstrated that significant amounts of NO_3^- and $SO_4^=$ in the Kosa aerosol are introduced during transport by reaction with NO_x and SO_2 at a remote island off Japan (Prospero, 1996 and references cited therein; Nishikawa *et al.*, 1991).

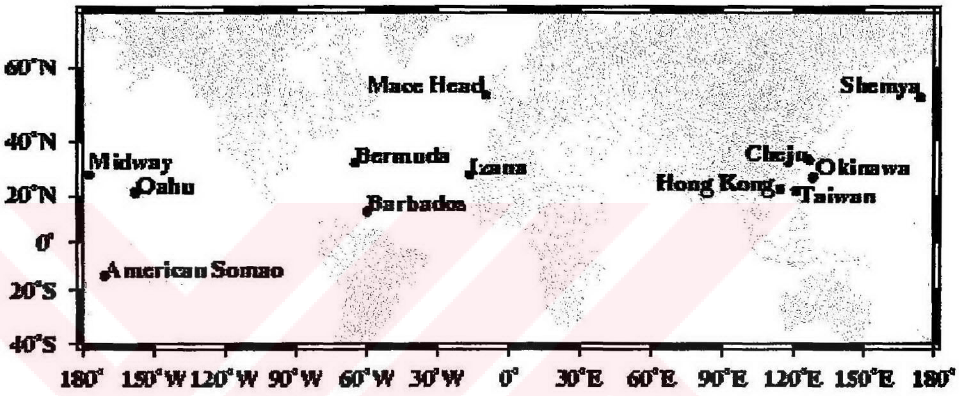


Figure 1.4. Locations of the islands mentioned in Table 1.4.

Accordingly the high mineral dust and aerosol water soluble species (NO_3^-, $SO_4^=$ and NH_4^+) concentrations measured at the island stations close to the coast of Asia in the western Pacific atmosphere are attributed to the transport of pollutants along with the desert dust.

The effects of continental transport are much greater over the north Pacific than the south Pacific. Dust concentrations are highest in the mid-latitude of the north Pacific and lowest in the equatorial Pacific and the south Pacific. Substantially lower values of mineral dust and aerosol water-soluble species (NO_3^-, $SO_4^=$ and NH_4^+) concentrations measured at the American Somoa (South Pacific) indicate that the effect of continental sources is minimal. The data from several years of continous sampling in a Pacific island network reveal that nitrate and sulfate concentrations in the north Pacific were much greater than in the south Pacific and were co-seasonal with Asian dust transport (Prospero *et al.*, 1985; Prospero and Savoie, 1989; Savoie *et al.*, 1989a; Savoie and Prospero, 1989). The sources of low nitrate and non-sea-salt sulfate measured at the relativel pristine site of American Somoa were attributed to natural sources (lightning and the stratosphere as sources for NO_x and atmospheric oxidation of reduced sulphur gases, primarily DMS, emitted from ocean for nss-sulfate).

The North Atlantic Ocean (NAO) is a relatively small ocean basin closely bordered by large continental landmasses and many highly industrialised nations. Large quantities of mineral dust are transported from sources in North Africa across large areas of the tropical Atlantic during the much of the year. Table 1.4. presents the mean concentrations of the major aerosol species measured at various sites in the NAO. Mineral dust is the major non-sea-salt aerosol component at all sites except Mace Head. The African dust transport affects a very large area of the NAO, producing similar seasonal pattern of aerosol Al concentrations at Barbados, Bermuda, and Tenerife, a summer maximum and a winter minimum. The long-term aerosol data record from Barbados reveals that the concentrations of both nitrate and nss-sulfate were significantly correlated with those of Saharan dust indicating that substantial fractions of both are transported across the tropical North Atlantic in association with the dust (Prospero, 1996; Savoie *et al.*, 1989b).

The seasonal mean AOT for the Arabian Sea peaks sharply in JJA period (see Figure 1.3.c). The aerosol data from the Arabian Sea clearly show that dust concentrations are very large and values are comparable to those along the West Coast of Africa. The highest mean concentrations of nitrate, nss-sulfate and mineral aerosol were observed during dust outbreaks transported from desert regions of the Middle East (Prospero, 1996; Savoie *et al.*, 1987). Relatively lower concentrations in the southern Indian Ocean than the Arabian Sea aerosols were explained by the prevailing southwester monsoons, which transport oceanic air northward.

The aerosol concentrations of the Mediterranean atmosphere (Table 1.4) resemble to the other oceanic places where the long range dust transport results in high concentrations of dust and water-soluble ionic species.

Anthropogenic aerosols were investigated in the eastern Mediterranean area where particularly during summer high pollution loads are encountered. Annual mean sulfate concentrations in this region are on the order of 10 $\mu g\ m^{-3}$ and largely attributed to the import of pollution from nearby source regions (Mihalopoulos *et al.*, 1987; Luria *et al.*, 1996; Ganor *et al.*, 2000).

Moulin *et al.* (1998) used the results of an 11.5-year (June 1983 to December 1994) daily monitoring of dust optical depth to present and explain the general pattern of dust transport over the Mediterranean basin. The long-term analysis evidences well-defined spatio-temporal structures of the African dust transport over the Mediterranean as shown by monthly climatological maps of the dust optical depth in Figure 1.5 (taken from Moulin *et al.*, 1998). Despite a large daily variability, climatological results show a clear seasonal cycle with maximum during the dry season: dust transport begins over the eastern basin in spring and spreads over the western basin in summer. These patterns are shown to be related to both cyclogenesis over North Africa and rainfall over the Mediterranean Sea.

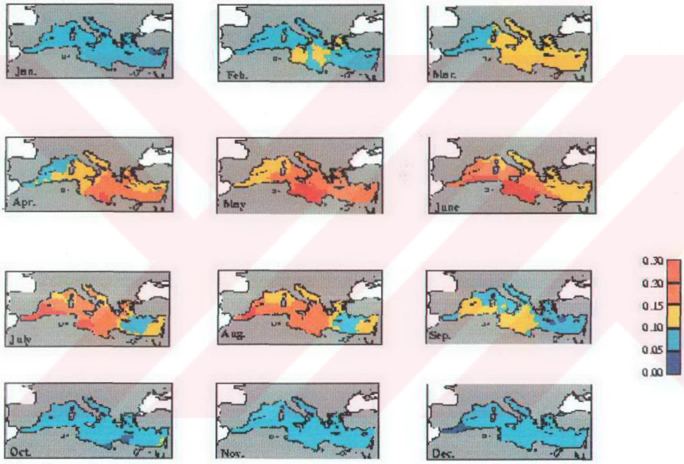


Figure 1.5. Monthly 11-year average of dust optical depths (taken from Moulin *et al.*, 1998).

The discussion of mineral dust effect on the Mediterranean biogeochemical processes and climate is complicated by the fact that African dust is not necesseraily a "pure" soil product. Measurements over the eastern and western Atlantic (Savoie *et al.*, 1989; Prospero, 1996; Prospero *et al.*, 1999) show that dust is associated with chemical species that suggest pollution source. For example, the concentrations of NO_3^-, non-sea-salt-$SO_4^=$ and NH_4^+ in dust-laden African air masses is substantially greater than that expected for "background" ocean air. Pollutans derived from sources in Europe and

North Africa become mixed with dust over Africa where the high concentration of dust provide a large area on which the reaction of pollutant species can take place (Dentener *et al.*, 1996). One consequences of this process is that the size distribution of some species such as sulfate, which is usually found predominantly on the submicrometer fraction, can be shifted to larger size particles (Li-Jones and Prospero, 1998). The concentration of many elements that are typically associated with pollutant sources are often greatly increased in dust. In particular Zn, Mo, Cd, As, Sb and Se are enriched by factors ranging 10 to 500 (Güllü *et al.*, 1996). It is not clear to what extent these enriched elements are due to pollution inputs and how much is naturally a part of the dust matrix. The origin of the elements is important because it is well established that the anthropogenic component is much more soluble than the soil component (Chester *et al.*, 1996).

It is also necessary to consider possible interactions between local emissions and advected African dust.

CHAPTER II

MATERIALS AND METHODS

2.1. Sampling Site Description

The proper site for dealing with atmospheric composition studies should (UNEP/WMO, 1998).

(a) Provide a true representation of the receptor defined in the study objectives.
(b) Have no major obstruction such as tall buildings.
(c) Be as far away as possible from localised sources of contamination (e.g. motor traffic, industries, stacks).
(d) Provide meteorological data if possible.
(e) Be accessible and secure from tempering.

The choice of atmospheric sampling station was located at Erdemli (36° 33′ 54″ N and 34° 15′ 18″ E, Figure 2.1) situated at a rural area on the southeastern coast of Turkey gave the opportunity to meet the above requirement. The sampling tower was positioned at the harbour jetty of the institute in 1990. The immediate vicinity around the sample tower consists of lemon trees, cultivated land and greenhouses. The nearest city centres are located 7 and 45 km to the east of the sampling station, Erdemli and Mersin respectively. Pulp and paper industry exist 45 km to the west of the sampling station and petroleum refinery, soda, chromium, fertilizer industries and a thermic power plant are located 45 km east of the sampling station.

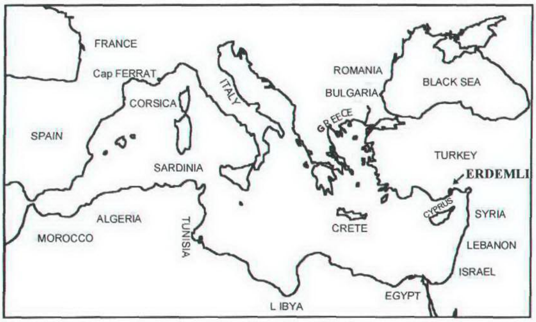


Figure 2.1. Location of the sampling station at Erdemli

The site should therefore represent a good monitoring station for the air at the Turkish Mediterranean coast and for estimating atmospheric input to the eastern part of the Mediterranean Sea.

2.2 Atmospheric Aerosol Sampling

2.2.1. Aerosol Collection

Aerosol filter samples were collected from January-December1996, from January-May 1997and from February-December 1998. During this period 409 aerosol samples were collected. Aerosol samples were sampled using a commercially manufactured high volume collection system. The principle of the sampling is to draw the air through a filter by means of a high flow vacuum pump that allows suspended particles to be collected on the filter surface. Collected filters were stored at 4°C in a refrigerator in protective polyethylene bags, awaiting chemical analyses.

The type of filter media chosen for the sampling of aerosols depends upon several factors such as, price, availability, efficiency of filtration and the ability to maintain its characteristic and integrity in the sampling condition. The most commonly used filter media with the high volume samples are the glass fiber and cellulose fiber (the best known is Whatman 41) filters. The glass filters have high efficiency, are non-hygroscopic and low flow resistance. However this filter has also many drawbacks (UNEP/WMO, 1998) such as

(a) High trace element background
(b) Since the filter is alkaline, the surface causes more formation of artifact particulate mattter by oxidation and adsorption of acidic gases such as sulphur dioxide and nitric acid present in sampled air.
(c) They are fragile, hence need more careful handling.

In the present study Whatman 41 (20.3×25.4 cm, Whatman International Ltd, Maidstone, England) cellulose filters were chosen as the filter media for the following reasons:

(a) Low background of trace elements.
(b) Cheap and available.
(c) Easy to handle.
(d) Relatively easy to digest for subsequent chemical analysis.

However Whatman 41 also has some drawbacks such as, the formation of artifact particles of nitrate (Savoie *et al.*, 1987).

The sampling program was corrected by using'field blanks'. These were filters processed in the same way as the samples collected on the tower with the exception that no air was passed through the filters. Field blank filters were removed from their storage boxes and mounted on the filter holder, then dismounted and stored in protective polyethylene bags for later analyses. Extreme care, to minimise contamination of the aerosol samples, was taken during the collection and handling of atmospheric samples.

Filters are not the only source of high blank values in the sampling of atmospheric particles. Sample handling, reagents and water used in laboratory procedures, glassware and plastic ware used all adds to the blank values of the parameters that were being measured. In order to have reliable results, concentrations measured in untreated filters, water used for washing glass and plastic ware in the laboratory and dilution, acids used in digesting samples were carefully checked.

Handling of filters was done by paying extreme attention to avoid contamination. Filters were never touched by hand. They were touched only with teflon forceps and polyethylene gloves were always worn. Handling of filters after they returned to the laboratory was performed within a Laminar Flow Clean Hood to avoid sample contamination from laboratory air.

To assess the blank (40 blank filters) contributions from the filter papers, the blank to sample ratio for each element, cation and anion are presented in Figure 2.2, Figure2.3.a and Figure2.3.b, respectively.

It can be seen that the contribution from Whatman-41 filter papers was significant only for Zn (≅13%). For other elements the subtracted blank values are less than 8% of the mean concentrations of the elements. For all cations and anions the contribution from Whatman-41 filter papers was found to be less than 2% and 6%, respectively, throughout the sample collection period at Erdemli.

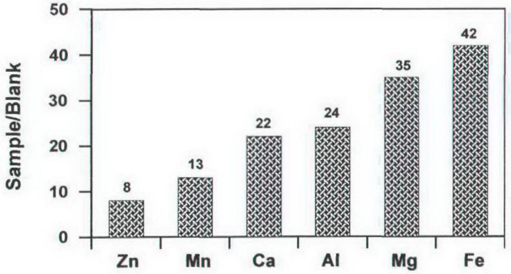


Figure 2.2. Sample to blank ratios of elemental concentrations in Whatman-41 filter papers.

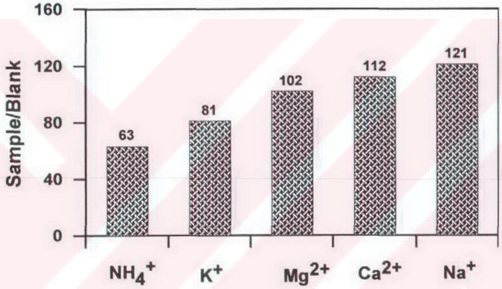


Figure 2.3.a. Sample to blank ratios of the cation concentrations in Whatman-41 filter papers.

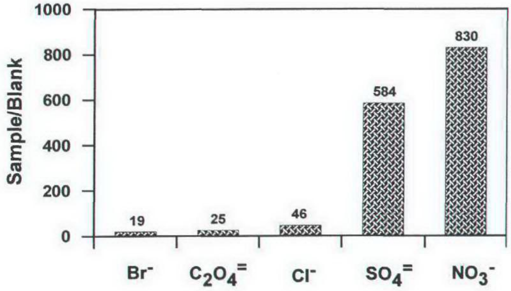


Figure2.3.b. Sample to blank ratios of the anion concentrations in Whatman-41 filter papers.

2.2.2. Sample Manipulation

Both at the sampling site and in the laboratory extreme care was taken to minimize contamination of the filters. Nevertheless, regular field blank assessments were carried out to ensure close monitoring of potential contamination effects.

All filters were carried to the sampling tower within their storage boxes. Polyethylene gloves were worn during sample manipulations. Filters were unloaded from their storage box and mounted on the filter holder using Teflon covered tweezers. To change the filter, once a sample had been collected, the sampler pump was switched off and the filter paper was folded in half, such that their exposed side faced inwards. The folded filter was then placed into a polyethylene bag on which the period of sampling was noted.

2.3. Aerosol Chemical Analysis

2.3.1. Analytical Techniques

There has been a continual development in the number and sophistication of techniques for elemental analysis. Atmospheric scientists who are performing research into atmospheric trace elements and ions have to select the most appropriate technique among a wide variety of available analytical techniques and methods. A major criterion in the choice of technique is based on the techniques' detection limit. The detection limits of the chosen analytical techniques should be low enough to determine the chosen analyte at the expected sample concentration. Other criteria applied include sensitivity, precision, accuracy, time and cost per analysis. Based on the above criteria atomic absorption spectrometry (AAS) was used for determination of trace elements and ion chromatography (IC) was used for the measurements of ions. A summary of the analytical techniques used for trace elements and ions detections are presented in Table 2.1.

Table 2.1. Analytical techniques used for trace elements and ions

Analytical Techniques	Measured Species	N
FAAS (Flame Atomic Absorption Spectrophotometer)	Al, Fe, Ca, Mg, Mn, Zn	407
IC (Ion Chromatography)	Na^+,NH_4^+,K^+,Mg^{2+},Ca^{2+} Cl^-,Br^-,NO_3^-,SO_4^{2-},$C_2O_4^{2-}$,MSA^-	409

N: Number of samples determined

2.3.2. Atomic Absorption Spectrophotometer (AAS)

Atomic absorption spectrometry (AAS) is a widely used and accepted technique capable of determining trace levels of elements or metals in a wide variety of samples, including biological, clinical, environmental, food, and geological samples, having both good accuracy and precision. AAS is a simple and rapid procedure that can be used to determine trace elements in aerosol samples. Throughout this study particulate airborne samples were analyzed for those elements of interest by the flame mode of a computer controlled GBC-906 model (GBC Scientific Equipment Pty Ltd. Australia) atomic absorption spectrophotometer equipped at the factory with a deuterium (D_2) lamp for background correction.

A total of 407 collected aerosol samples were analyzed using flame atomic absorption spectrometry (FAAS) with an attachment of an FS3000 autosampler, providing automatic sample change. The autosampler carousel held 10 standards and 60 samples, with separate position for 'rinse', 'blank' and 'rescale standard'. The aerosol samples were analyzed for Al, Fe, Ca, Mg, Mn and Zn. In the flame mode the sample was introduced in the flame as homogenous liquid enabling atomisation to occur. The atoms are then exited by a light source emitting radiation with a characteristic wavelength. The decrease in energy (owing to atomic absorption) was then measured. With the exception of Al, all elements were determined using an air-acetylene flame. Al was determined in a nitrous oxide-acetylene flame since this element may form thermally more stable refractory oxides and its atomization, therefore, occurs at higher temperatures.

The instrument was calibrated against a series of standard solutions. Stock standard solutions were prepared from pure compounds. Compounds used to prepared stock solutions, were dried and after equilibration at room temperature, weighed and dissolved in 0.1 N nitric acid so that their final concentration was 1000 ppm. Standard solutions were subsequently prepared by dilution of the stock standard solutions.

In the context of the current work the analytical detection limit is defined as being 'twice the standard deviation of the blank values'. Using the procedural blank concentrations and the average sampled volume of 1939 m^3, the calculated detection limits in the aerosol samples (in ng/m^3) were: Al (19), Fe (11), Ca (32), Mg (24), Zn

(2.7) and Mn (2.1). Mean blank values and corresponding standard deviations were given in Table2.

Table2.2. Average blank concentrations for trace elements and corresponding standard deviations.

Element	Art. Mean Blank Values (±σ)
Al	0.25(0.09)
Fe	0.15(0.05)
Ca	1.50(0.16)
Mg	0.50(0.12)
Mn	0.010(0.010)
Zn	0.034(0.013)

σ standard deviation

2.3.2.1. Preparation of the Samples for AAS

In order to determine elemental concentrations in aerosols by atomic absorption spectrometry, it is necessary to dissolve the material into solution. This is achieved by acid digestion. The analysis of aerosol samples collected throughout this study utilized Kubilay's (1996) procedure for acid dissolution.

PTFE (polytetrafluoroethylene) beakers were cleaned by refluxing with 65% HNO_3 Merck Suprapure for 6 hours and subsequently rinsed with Milli Q water before use. A quarter of the aerosol filter was transferred into a 50 mL polytetrafluoroethylene (PTFE) beakers in a Laminar Air Flow bench (Clean LAF HF906). This would provide a clean atmosphere, minimizing sample contamination. 25 mL of HNO_3 were then added. The beaker was then covered with a PTFE lid and placed on a hot plate at temperature of 120-130°C to facilitate the dissolution of the filter and aerosol material. The HNO_3 was refluxed for 72-96 hrs to dissolve filter material. The digest solution was then evaporated, until about 10mL was left. 5 mL of 40% HF Merck Suprapure was then added to destroy the silicate matrix. Silicon is a good indicator of the presence of mineral dust, however, it evaporates as $SiF_4(g)$

then removed from the hotplate and allowed to cool. The residue was dissolved using Milli Q water and was poured into a 50mL graduated flux and made up to volume with Milli Q water. The solution was transferred to a labeled polyethylene sample bottles. A reagent and filter blank determination was carried out using the same procedure. The solutions were kept refrigerator at 4°C until analysis.

Since metals are adsorbed on the walls of the container and are not removed by simply rinsing with distilled water, sample bottles and all other glassware used in the analysis were left in 10% HNO_3 solution for 24 hrs to desorb metals from the walls of the containers before use. They were then rinsed 3 times with distilled water and 3 times with Milli Q water and left to dry in a clean hood.

2.3.3. Ion Chromatography (IC)

Ion chromatography is the coupling of a chromatographic technique and ab ionic detection system. The method has been a widely used for the simultaneous and rapid analysis of inorganic and organic ions contained in different matrixes such as natural waters, rain samples and water extracted aerosol samples. During this study ion chromatography was used to determine both anion and cation concentrations in aerosol samples.

Daily collected (n=409) aerosol samples were analyzed using ion chromatography at ECPL (Environmental Chemistry Processes Laboratories) at the University of Crete. Equipment and conditions of the ion chromatography instrument are presented in Table 2.2.

The ion chromatographic system was calibrated using standard solutions. Standard solutions were prepared from stock solutions with the appropriate dilutions. Stock standard solutions were prepared from the pure salts of NaCl, NaBr, $NaNO_3$, K_2SO_4, $H_2C_2O_4.2H_2O$ and NaCl, NH_4Cl, KCl, $MgSO_4$,$CaCl_2.2H_2O$. In addition, CH_3SO_3Na was utilized to prepare standard solutions of MSA (methanesulfonate).

Table 2.3. Apparatus and conditions of the ion chromatography instrument

Apparatus Solution Condition	Anions	Organic anion	Cations
Eluent	$NaHCO_3$(1.7mM) $NaCO_3$(1.8mM)	$B_4Na_2O_7.10H_2O$ (2.5mM)	MSA 20mM
Pump	Alltech Mod 325	Alltech Mod 325	Marathon
Entrance of the sample	Autosampler Marathon	Autosampler Marathon	Autosampler Marathon
Loop	20µL	200µL	20µL
Pre-column	AG4A-SC	AG4A-SC	CG12
Column	AS4A-SC	AS4A-SC	CS12
Membrane suppressor	ASRS I	ASRS I	CSRS I
Detector	Measures conductivity 320 Alltech	Measures conductivity 320 Alltech	Measures conductivity CDM2 Dionex
Flux	2mL/min	2mL/min	1mL/min

Extracted aerosol samples were determined using the defined optimized analytical conditions. Before injection of the sample to the separation column, samples were filtered through a 0.45 µm and 0.2µm filters in order to remove any particulates. This procedure was necessary because any particles in the sample solution may cause irreversible damage to the separation column. For the analysis of the organic anion MSA (methanesulphonate) two more filters were used in order to remove Cl^- from the sample solution as an exorbitant amount of it 'compresses' the organic anion and can possibly act as an obstacle in the smooth analysis of organic anions. These two filters are made from Ag resin and acidic resin, respectively. The first filter removes Cl^- as AgCl (Ag^++Cl^-) ,the second one 'holds back' the Ag^+ so as to protect the separation column from its deterioration.

For the analysis of atmospheric aerosol samples, the commonly used definition of the detection limit is 'twice the standard deviation of the blank values'. Using the total procedural blank concentrations and the average sampled volume of 1939 m^3, the calculated detection limits in aerosol samples (in ng/m^3) were: Cl^- (15), Br^- (1), NO_3^- (4), SO_4^{2-} (7), $C_2O_4^{2-}$ (3), Na^+ (28), NH_4^+ (20), K^+ (4), Mg^{2+} (10), Ca^{2+}(51). Average blank concentrations and corresponding standard deviations were given inTable2.

Table2.4. Average blank concentrations for ions and corresponding standard deviations

Ion	Art. Mean Blank Value (±σ)
Cl^-	1.220(0.091)
Br^-	0.012(0.006)
NO_3^-	0.049(0.024)
$SO_4^=$	0.156(0.042)
$C_2O_4^=$	0.084(0.018)
Na^+	0.287(0.169)
NH_4^+	0.426(0.121)
K^+	0.045(0.024)
Mg^{2+}	0.052(0.061)
Ca^{2+}	0.288(0.309)

σ standard deviation

2.3.3.1. Preparation of the Samples for IC

In order to determine ion concentrations in aerosol samples by ion chromatography, it is necessary to bring the material into aqueous solution phase (apparatus, conditions and solutions were listed in Table 2.2).

One eight of the aerosol filters were placed into a 25 mL polyethylene beaker and 20 mL of nanopure water (18Ω) was added. Lids were screwed into place and beakers were placed into a supersonic shaker and agitated for a total of 45 minutes. Afterwards, filters were removed using clean pleat and a 100μL of chloroform ($CHCl_3$) was added in order to prevent any kind of microbiological degradation. All manipulations of the aerosol samples were carried out in a laminar air flow bench which provided a clean working atmosphere. Extracted aerosol samples were stored at 4°C until analysis.

2.4. Quality Assurance

The accuracy of the AAS analysis throughout this work was continuously verified using standard reference materials. Two different standard reference materials from the Community Bureau of Reference (CRM-142, light sandy soil) and National Research Council (BCSS-1) were digested and analyzed at the same time under the same conditions as the aerosol samples. The standard reference materials were analyzed prior to the first digested sample run. The results from the analyses of the two standard reference materials and associated standard deviations are presented in Table 2.3 with their certified values. In general, very good agreement of the determined values with the certified values were obtained for the elements of interest.

Table 2.5. Concentrations of elements observed in standard reference materials CRM-142 and BCSS-1.

	CRM-142		BCSS-1	
Element	Measured	Expected	Measured	Expected
Al_2O_3	90.4± 5.12	(94.8)	11.6± 0.51	11.83± 0.41
Fe_2O_3	28.03± 1.3	(28)	4.72± 0.11	4.70± 0.14
CaO	48.9± 2.3	(49.4)	0.770± 0.04	0.760± 0.074
MgO	11.6± 1.4	(10.9)	2.50± 0.11	2.44± 0.23
Mn	569± 17	(569)	228± 10	229± 15
Zn	95.9± 3.5	92.4±4.4	117± 6	119± 12

Values in brackets are not certified values. For CRM-142 and BCSS-1 Al_2O_3, Fe_2O_3, CaO and MgO concentrations were given as mg/g and %, respectively. Mn and Zn concentrations were given in µg/g.

Analysing simulated acid rain samples prepared by the World Meteorological Organisation (WMO) Precipitation Reference Laboratory (PRL) for intercomparision allowed an assessment of the accuracy of the generated analytical results. Results of measured and expected values are listed in Table 2.4. High X and low X refer to the highest and the lowest values reported by the participated laboratories, respectively. Sulfate and nitrogen species (nitrate and ammonium) were reported as S and N, respectively.

Table 2.6. Concentrations of ions observed in inter- comparison simulated rain water. All concentrations were given in mL/L.

	SO_4^{2-} (S)	NH_4^+ (N)	NO_3^- (N)	Cl^-	Ca^{2+}	K^+	Mg^{2+}	Na^+
Expected 1	4.010	0.844	2.160	2.843	0.401	0.782	0.122	1.847
2	3.800	0.790	1.390	0.938	0.005	0.097	0.086	0.493
3	2.280	0.342	0.860	1.130	0.150	0.534	0.097	1.345
Std. Dev 1	0.219	0.066	0.052	0.111	0.042	0.046	0.016	0.087
2	0.203	0.052	0.048	0.074	0.025	0.012	0.010	0.045
3	0.105	0.031	0.032	0.072	0.029	0.046	0.010	0.066
Low X 1	3.507	0.680	2.050	2.580	0.300	0.680	0.078	1.592
2	3.292	0.650	1.283	0.755	0.001	0.068	0.050	0.347
3	1.996	0.255	0.765	0.913	0.070	0.386	0.065	1.160
High X 1	4.684	1.030	2.300	3.130	0.520	0.880	0.163	2.072
2	4.420	0.911	1.536	1.115	0.100	0.123	0.104	0.600
3	2.515	0.407	0.940	1.310	0.224	0.646	0.116	1.490
Measured 1	4.533	0.906	2.303	2.850	0.300	0.800	0.080	1.800
2	4.133	0.824	1.468	1.000	-	0.080	0.050	0.600
3	2.367	0.329	0.903	1.200	0.080	0.500	0.070	1.300

2.5. Air-mass Back Trajectories

Kinematic air mass back trajectories were calculated daily at 1200 UT for 1989 through 1998. Trajectories were calculated 3 days back, a sufficient duration to diagnose long-range transport. Using a 10 year trajectory database, we examined the climatological airflow patterns and the differences in transport patterns for four arrival elevations and we will subsequently discuss the role of the vertical component of the transport.

The European Centre for Medium Range Weather Forecast (ECMWF, Reading, UK) global wind analyses are used for the computation of backward trajectories based on integration of the archived three-dimensional wind field at every 6-hr intervals interpolated with a small (one hour) time increment (Mc Grath, 1989). The accuracy of the trajectories used in this work has been assessed by Kubilay *et al.* (2000) using mineral dust as a geochemical tracer.

We selected four arrival elevations: 900, 850, 700 and 500hPa. These levels represent flow below, near and above the planetary boundary layer (PBL) depth in the eastern Mediterranean basin (Dayan *et al.*, 1996). To establish climatology of trajectories, cluster analysis, a multivariate statistical technique, is used to group trajectories according to wind speed and direction. This procedure uses a mathematical criterion to ensure similarity among the trajectories in each group or cluster. Each transport cluster can then be described by a mean trajectory or "cluster mean" that best represents all the trajectories in that cluster. In this way, many trajectories can be efficiently summarised (Harris and Kahl, 1990).

CHAPTER III

RESULTS AND DISCUSSION

3.1. Climatology of the Meteorological Parameters of the Erdemli Station for the Assessment of Atmospheric Transport and Deposition of Aerosols

The Mediterranean Sea is a semi-enclosed Sea, surrounded by the three continents of Europe, Africa and Asia with a narrow connection to the Atlantic Ocean through the Strait of Gibralter. It contains one of the most extreme oligotrophic waters in the world with an increasing oligotrophy nature to the east. The Mediterranean is sensitive to hazardous pollutants and / or nutrient type elements through either inputs from rivers or deposition from the atmosphere. Initially it was assumed that the main source of material to inland seas such as the Mediterranean was, through the discharge of waste into coastal waters. However it is now accepted that the atmospheric path may be quantitatively equal or more important for certain type of species. The main question is what meteorological factors control atmospheric transport and deposition. To answer this question the following section of the thesis summarizes the climatology of the meteorological parameters influencing the Erdemli station, which is located on the eastern Mediterranean coast.

The aerosol chemical constituent concentration would increase rapidly if there was no removal mechanism. Removal of atmospheric aerosol particles and their associated elements and species by precipitation is one of the most important natural processes in the transformation of aerosols. Thus, the most important meteorological constraints on the observed concentrations patterns of aerosol chemical compositions at a ground station are the influence of the wind speed and direction and mixing as well as the precipitations both locally and during their transport from distant sources.

Climatically, the Mediterranean region is generally characterised by warm winters (November - February) dominated by rainfall and dry summers (June-September). The transitional seasons, spring and autumn are of very different lengths. The relatively long spring season (March through May) is noted for periods of unsettled winter-type weather, associated with an increased occurrence of North African cyclones; the rest of this period is very similar to that in the summer. Autumn usually lasts only one month (October) and is characterised by an abrupt change from the summer to the unsettled weather of winter (Brody and Nestor, 1980).

Moulin *et al.* (1998) explained the temporal variability of African dust transport climatology using the principles of atmospheric synoptic circulation. This controls the frequency of mobilization, transport and of the washout by precipitation which influences the residence time of particles in the atmosphere for the Mediterranean region. The seasonal climatology of the precipitation (Figure 3.1) which they referred to in their study indicates that the Mediterranean is heavily affected by precipitations in winter and autumn whereas during spring the precipitations are low. During summer, the whole Mediterranean becomes dry, and the atmospheric transport of aerosols from distant origins can then develop efficiently.

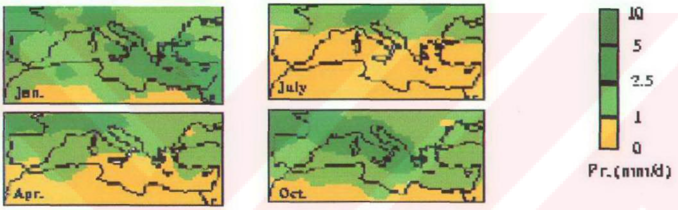


Figure 3.1. Climatological maps of monthly precipitations between 1979 and 1988 (after Moulin *et al.*, 1988).

Monthly average atmospheric temperatures (°C) and amount of rain (mm) for 28 years period (1971-1998) at the Erdemli station are shown in Figure3.2. The seasonality of the local precipitation amount at the Erdemli station display similar seasonal variations to that of the whole Mediterranean region (Figure 3.1). It is clearly demonstrated that the sampling site is mostly wet in the winter and dry in the summer months.

The local ambient temperature (which is affected by solar radiation) starts to increase in April and reaches its maximum in July – August and then decreases to its minimum winter value. In the summer months, the removal of aerosol particles by wet deposition is minimum and the possibility of photochemical formation of aerosol particles from their gaseous precursors is maximum at the sampling site. Accordingly the maximum concentration of the measured aerosol components are expected to be relatively higher in the summer months compared to those in winter moths.

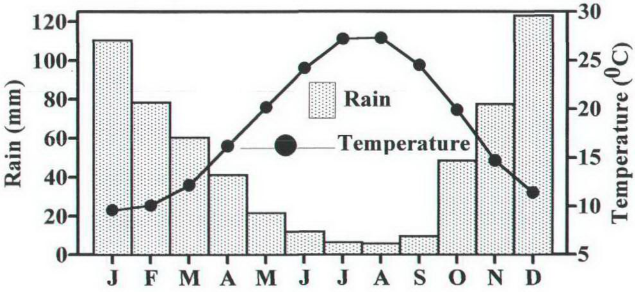
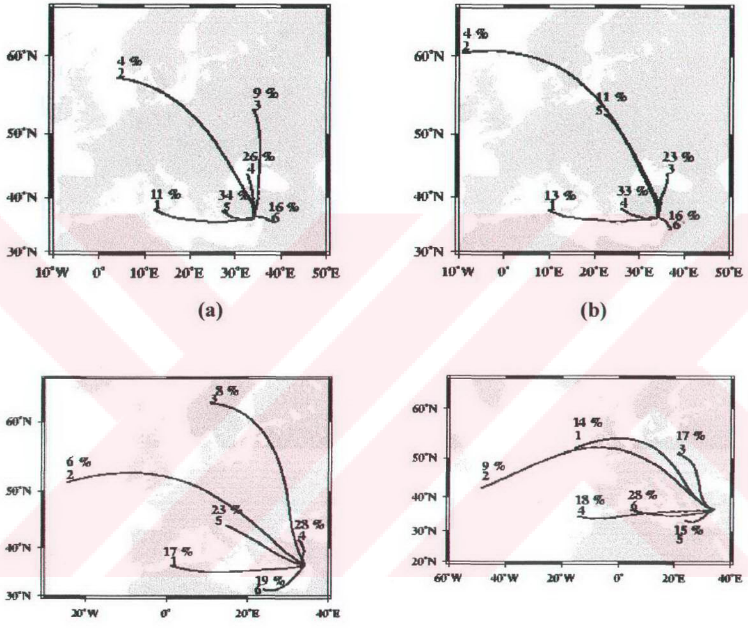


Figure 3.2. Monthly average amount of precipitation and temperature (28 years) at the Erdemli station.

The 10-year database of daily 3-day back trajectories allows a quantification the frequency with which specific source regions (of aerosols) contribute to the material transported across the eastern Mediterranean. Figure 3.3. shows the cluster-mean trajectories at the four different atmospheric levels for the period of ten years (1989-1998). The cluster-mean plots contain the following information: (1) the mean trajectory for each cluster and paired numbers, (2) showing the percent of all complete 3-day back trajectories in each cluster (top); and (3) the assigned cluster numbers (bottom).

The lower layer trajectories (Fig.3.3.a,b) indicate a dominating group of clusters (4,5,6) originating from the west, north and east and accounting for 74 % at 900 hPa and (3,4,6) accounting for 72 % of the trajectories at 850 hPa, respectively. Cluster 1 from the west occurs 11 and 13 % of the time, representing long fetch maritime air masses from the western Mediterranean Sea at both pressure levels. The remaining clusters presenting north-north east continental flow pattern (2 and 3 at 900 hPa) and (2 and 5 at 850 hPa), respectively occurs 13 % and 15 % of the time.

Clusters indicating rapid transport from the south-southwesterly sector (the North African continent) have frequencies of 36 % (1+6) at 700 hPa and 61 % (4+5+6) at 500 hPa over the 10 year period (Fig.3.3.c,d). Slower northerly flow originating from the Black Sea accounts for 28 % of the time (cluster 4, Fig.c) at 700 hPa. It appears from Fig. that the transport from Europe mostly occurs above the boundary layer as well as the transport originating from North African continent. The easterly component in winds arriving at Erdemli diminishes at 700 and 500 hPa levels (Kubilay *et al.*, manuscript in preparation).



(a) (b)

(b) (d)

Figure 3.3. Atmospheric flow patterns for the period 1989-1998, depicted by cluster-mean trajectories arriving at Erdemli; (a) 900, (b) 850, (c) 700 and (d) 500 hPa. The numbers show the percent of complete trajectories occuring in that cluster (top) and cluster number (1-6) (bottom).

3.2. Chemical Characterisation of Aerosol Samples Collected from Erdemli

3.2.1. General Characteristics of Data

The atmospheric concentrations of aerosol associated elements (Al, Fe, Ca, Mg, Mn and Zn), water soluble anions (Cl^-, Br^-, NO_3^-, $SO_4^=$, $C_2O_4^=$, $CH_3SO_3^-$ (MSA$^-$)) and cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) were measured by Atomic Absorption

Spectrometry (AAS) and Ion Chromotography (IC) respectively on a series of aerosol samples collected at the Erdemli station over the period from January 1996 to December 1998. Table.3.1. presents the arithmetic and geometric mean concentrations with their associated standard deviations, median and range of the concentration values for the 17 analysed elements and ions together with the calculated non-seasalt fractions of some ions for the whole sampling period (N=408 samples). Among the species studied at least $SO_4^=$, K^+, Mg^{2+} and Ca^{2+} have a mixed origin (sea salt, marine biotic, anthropogenic and soil). Since the seasalt contribution to the total aerosol concentrations of the species will behave like Na^+ (indicator of sea spray), the only fraction of the species of interest here is the non-seasalt (or excess) portion of the total concentrations. Assuming that all the measured Na^+ has a marine origin, the sea salt contribution to the observed concentrations of the above mentioned species can be calculated using the following expression:

$$\text{nss-}X = X_T - X_{SS}$$

where X_{SS} is the sea salt fraction of the element of interest; X_T is the total concentration of the element measured in the aerosol samples. X_{SS} is defined by;

$$X_{SS} = (X_{BK} / Na_{BK})\, Na_{sample}$$

where X_{BK} / Na_{BK} = the concentration ratio of element X to Na in bulk seawater given by Riley and Chester (1975).

If sodium ion is chosen as a tracer, then the sea salt contribution amount to, on average 4, 10, 35 and 79 % for the considered ions, Ca^{2+}, $SO_4^=$, K^+ and Mg^{2+}, respectively.

For Ca and Mg, the AAS concentrations were higher than those determined by IC (up to a factor of 5 for Mg and 1.6 for Ca on the average). A large part of the discrepancy is likely due to the fact that IC only measures the water-soluble fraction.

The concentration ranges of each element and ion species are very wide resulting in high standard deviations from the mean concentrations. Such high standard deviations are not unusual for the data sets belonging to aerosol and precipitation samples data (Mamane, 1987; Bergametti *et al.*, 1989a; Kubilay and Saydam, 1995; Güllü *et al.*, 1998; Özsoy and Saydam, 2000; Özsoy *et al.*, 2000) and do not imply poor sampling and analytical protocol. The observed variations are due to the large variability of the atmospheric concentrations of measured species. Such a large variation is a result of contributing environmental factors influencing the aerosol concentrations. These factors include meteorological processes, variations in chemical transformations in the atmosphere and the variations in the source types and emission strengths.

Table 3.1. The aerosol element and water soluble ion concentrations (ng m^{-3}) for the Erdemli station.

	Arith.Mean (±σ)	Geo.Mean (±σ)	Median	Min-Max
Al	908(2406)	550(2.7)	626	7- 47305
Fe	754(1515)	437(2.5)	580	47- 29013
Ca	4184(7437)	3090(2.1)	3229	372-139054
Mg	2074(2291)	1698(1.8)	1750	341-39307
Mn	15.1(19.3)	9.8(3.0)	11.9	0.1-323
Zn	25.5(20.1)	19.5(2.1)	20.7	1-174
Cl^-	4633(7310)	2692(2.7)	2486	6-69442
Br^-	19.3(24)	13.5(2.1)	13.2	0.3-242
NO_3^-	3336(2463)	2630(2.3)	3097	3-34265
$SO_4^=$	7498(5288)	6026(2.2)	5782	8-45386
nss-$SO_4^=$	6777(5170)	5129(2.4)	5098	1-35466
$C_2O_4^=$	175(141)	91(5.4)	162	1-1186
Na^+	2872(4053)	1778(2.6)	1859	16-39406
NH_4^+	2219(1398)	1738(2.5)	1892	1-9556
K^+	302(236)	246(2.0)	249	2-2783
nss-K^+	195(160)	151(2.2)	152	1-1323
Mg^{2+}	437(483)	316(2.2)	325	2-4836
nss-Mg^{2+}	94(116)	76(2.6)	86	1-1468
Ca^{2+}	2664(2156)	2178(2.1)	2416	5-34464
nss-Ca^{2+}	2554(2108)	2042(2.2)	2335	4-32957
MSA^-	42(52)	20(3.6)	16	1-383

σ standard deviation

To determine the typical ambient concentration of any element in the atmosphere at any site, the median is more useful than the arithmetic mean since the latter will be strongly influenced by a few very high values. The median will more adequately represents the typical concentration during normal distributed data. However, in terms of total deposition (flux) the arithmetic mean is more useful because in this case the occasional extreme values may contribute significantly. For example, it has been shown that 30 % of the annual mineral dust deposition on the Eastern Mediterranean occurred in two sporadic dust intrusion events from the North African continent (Kubilay *et al.*, 2000).

The arithmetic and geometric means of the measured parameters are the most frequently 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 difference 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 to have a log-normal distribution. The concentrations of atmospheric trace substances are generally log normally distributed and log-normal distributed data set can be better described by the geometric mean and the corresponding standard deviations (Ott, 1990; Savoie and Prospero, 1977).

As can be seen from Table 3.1, the geometric mean and the median values are almost identical which implies that the concentrations of the elements and ions have approximately log-normal frequency distribution.

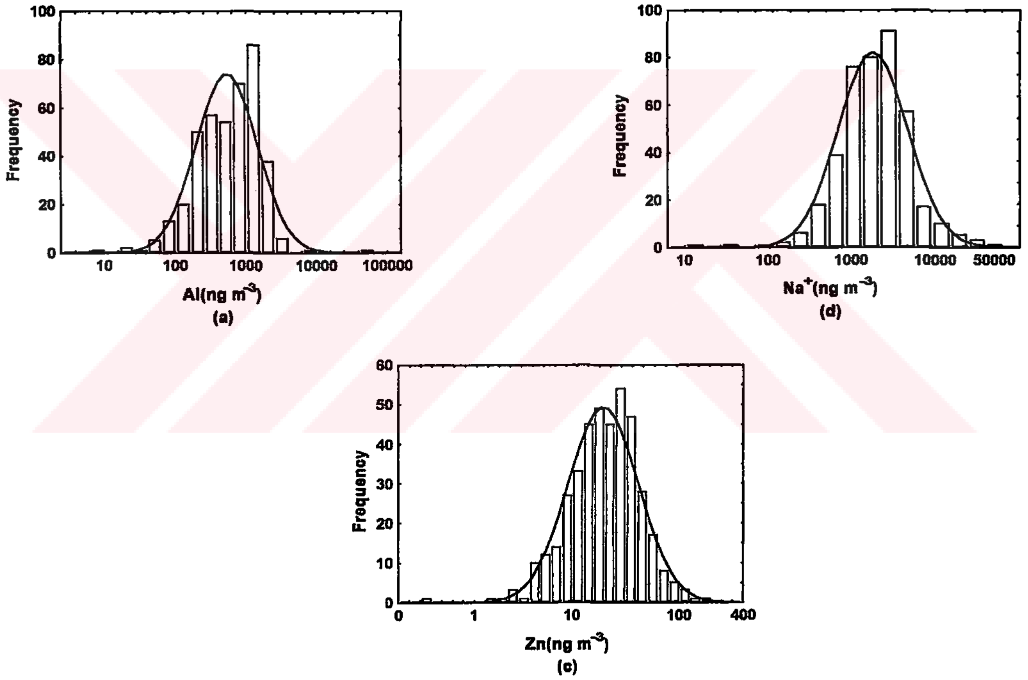


Figure 3.4. The frequency histograms of the log-transformed aerosol concentrations of the elements (Al, Zn) and water soluble Na together with their expected normal distribution curves.

The log-normal distribution of the atmospheric concentrations of the trace species were verified by a goodness of fit using the Kolmogorov- Smirnov test within the 'Statistica' statistical software. The population distribution for the aerosol elements and ionic species were found to be of a log-normal type within the 95 % confidence level.

Examples of the frequency histograms of the log-transformed data and the associated expected normal distribution curves, for Al, Zn and Na^+ are given in Figure 3.4.

3.2.2. Comparison of the Current Chemical Constituent Aerosol Concentrations with Data from the Literature

Before attempting to describe and explain the temporal variability of the elemental and ionic aerosol concentrations for the present study, a comparison is made of with the current dataset with those from other land-based atmospheric sampling programs carried out at European coastal sites. This comparison is presented on Table 3.2. The comparative studies were conducted at different time periods with different sampling and analytical methodologies, it must therefore be stressed that the data in Table 3.2. should be regarded as no more than an indication of elemental concentrations expected in the lower atmosphere.

To be able to investigate any differences and/or similarities in the concentrations of the elements in the atmosphere over the eastern and western parts of the Mediterranean, data from EROS 2000 project's sites are used as comparisons. The EROS 2000 project on biogeochemical processes in the western Mediterranean was launched in 1988 within the framework of the European Communities' Environmental Research and Development Programme and lasted during 6 years. One of the principal aims of the EROS 2000 project was to gain an understanding of the marine cycles of trace metals in the western Mediterranean Sea. To achieve this it was necessary to evaluate the relative importance of both fluvial and atmospheric inputs of the trace metals to the sea surface and water column. In order to collect atmospheric samples a network of stations was established on several islands and coastal zones (Blanes, Tour Du Valat, Cap Ferrat, Corsica, Sardinia) of the north western Mediterranean (Figure 3.4). Selected studies for the north-western Mediterranean were located at Blanes (Chester *et al.*, 1991); Tour du Valat (Guieu, 1991); Cap Ferrat (Chester *et al.*, 1990); Corsica (Bergametti *et al.*, 1989a) and Sardinia (Guerzoni *et al.*, 1999). And from other coastal locations which are Amasra (Black Sea) (Karakaş, 1999); Antalya (north-eastern Mediterranean) (Güllü *et al.*, 1998); Liverpool (Irish Sea) (Chester *et al.*, 2000) and Tel Shikmona (south-eastern

Mediterranean) (Herut *et al.*, 2001). Detailed descriptions of the sampling sites are given below. The sampling site;

Corsica, north-western Mediterranean (Bergametti *et al.*, 1989a)

A continous aerosol sampling program has been undertaken at a coastal location in northwestern Corsica. Three hundred and seventy four aerosol samples were collected from April 1985 to April 1986. Samples were analysed by X-ray fluoresecence and by flameless atomic absorption techniques.

Sardinia, western Mediterranean (Guerzoni *et al.*, 1999)

Aerosol sampling covered two periods at Capo Carbonara, a remote coastal station in sutheast Sardinia; 1 October 1990-30 April 1991 and 1 May-30 September 1992. Major elements were analysed by flame atomic absorption spectrophotometer and trace elements were analysed using the graphite furnace mode.

Blanes, north-western Mediterranean (Chester *et al.*, 1991)

Forty nine aerosol samples were collected at the Blanes site at various times over the period February, 1989 to June 1989. The trace metals were determined by either flame or flameless atomic absorption techniques.

Tour du Valat, north-western Mediterranean (Guieu, 1991)

One hundred and five aerosol samples were collected during November 1988 to May 1989 and analyses were performed by either flame or flameless atomic absorption techniques.

Cap Ferrat, north-western Mediterranean (Chester *et al.*, 1990)

The Cap Ferrat station was occupied for October 1988 and from February 1989, to July 1989. During the site occupation 70 aerosol samples were collected.

Liverpool, An urban site located on the coastal rim of Irish Sea (Chester *et al*, 2000)

The sample collections were carried out over two periods; 19 July 1994 to 20 December 1994 (30 samples) and 22 March 1995 to 5 March 1996 (30 samples). The metals were determined either flame or flameless atomic absorption peocedures.

Antalya, north-eastern Mediterranean (Güllü *et al.*, 1998).

A total of 600 aerosol samples were collected daily between March 1992 and December 1993. Measurement of ions was performed using ion chromotography and UV/VIS spectrometry. Samples were analysed for trace metals by INAA and by flameless atomic absorption techniques.

Amasra, Turkish western Black Sea coast (Karakaş, 1999)

Three hundred and fifty five aerosol samples were collected during May 1996 through July 1997. Measurement of ions was performed using ion chromotography and UV/VIS spectrometry. Samples were analysed for trace metals by INAA and by flameless atomic absorption techniques.

Erdemli, north-eastern Mediterranean (present study; Kubilay and Saydam, 1995)

Sample collections were carried out over two periods; August 1991-December 1992 (339 samples) (Kubilay and Saydam, 1995) and January 1996 to December 1998 (400 samples). Samples were analyzed for elements by AAS and for water soluble ions by IC.

Tel Shikmona, south-eastern Mediterranean (Herut *et al.*, 2001)

Samples were collected at Tel Shikmona from October 1994 to December 1997 (96 samples). Analyses of elements were performed by utilizing flame and flameless modes of AAS. The relative locations of all the sampling sites are presented in Figure 3.5.

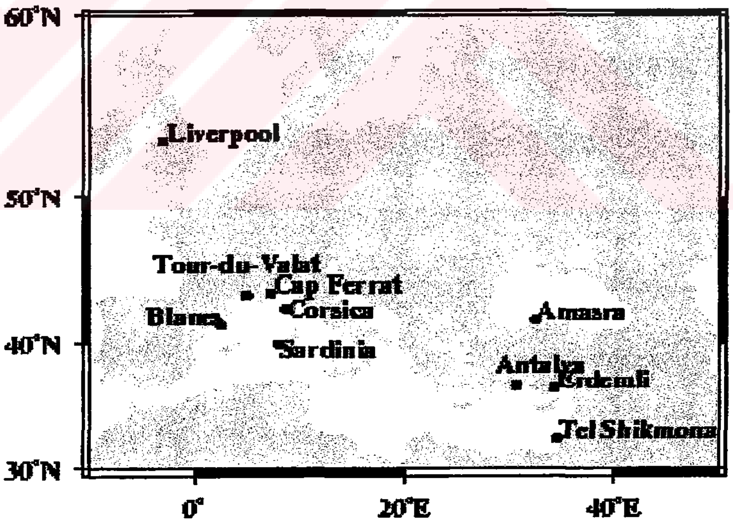


Figure 3.5. Location of the land-based collection sites for aerosol samples.

Bulk samples were collected by means of hi-vol aerosol samplers without pre-impactor (except at the Amasra and Antalya sites) at all the above mentioned sites. Pre-impactors with a cut size of 10 μm (PM_{10}) were attached to the hi-vol samplers utilized at the Antalya and Amasra sites. The pre-impactor removes particles with diameters larger than 10 μm from the air stream before they reach the filter; and hence may underestimate aerosol trace elemental concentrations.

The comparison of the concentrations measured at Erdemli with those reported elsewhere in the Mediterranean could serve to demonstrate the differences between the patterns of transport in the eastern and western parts of the Mediterranean. The mean concentration of each element in aerosols exhibits substantial spatial variations. Aerosol trace metal concentrations are presented as geometric means as they are more representative whereas the arithmetic mean is usually biased by the presence of a small number of large peaks in the data.

Considering the comparison of aerosol trace metal concentrations presented in Table 3.2 a number of features may be identified.

(i) Aerosols from the two eastern Mediterranean coastal sites, Erdemli and Tel Shikmona, have generally similar concentrations of trace metals except for Zn. The source of Zn enrichment at Israeli site is most likely due to urban 'hot spot' source(s) in close vicinity to the sampling site. Lower concentrations of soil related elements (Al, Fe) at Antalya and Amasra relative to the other two eastern Mediterranean sites (Erdemli and Tel Shikmona) probably result from the differences in the sampling techniques. A pre-impactor with 10 μm cut point is used in the sampling procedure of the Antalya and Amasra sites (Güllü *et al.*, 1998; Karakaş, 1999). Simultaneous sampling of atmospheric particles with and without such preimpactor in the Antalya site have demonstrated that approximately 30 % of the crustal mass is removed from the sampling stream by the preimpactor (Kuloğlu, 1997). It has been shown that during wet and dry deposition of Saharan dust at Sardinia the dust particle diameters show a bimodal structure, with maxima at < 10 μm and > 10 μm particle diameters (Guerzoni *et al.*, 1997). Accordingly the lower concentrations found at Antalya and Amasra may be a result of the size selective sampling method used at the sites partially missing the aerosols originating from crustal sources.

At Amasra there are no distinct winter-summer differences in rainfall intensity and event frequency and temperature differences as the north-eastern Mediterranean stations (Antalya and Erdemli). The difference between the concentrations measured at Amasra and at the northeastern Mediterranean sites can be explained partly by the more extensive aridity in the Mediterranean region where resuspension of soil is easier than in the vegetation covered Black Sea coast. The elemental concentrations are similar in two remote coastal sites (Corsica and Sardinia). Aerosols from European coastal sites (Liverpool, Blanes, Tour du Valat and Cap Ferrat) have generally similar characteristics with respect to their trace metal concentration levels.

The major difference in the aerosol concentrations observed in this study and Tel Shikmona and those located in the western basin is higher observed concentrations of crustal derived elements, specifically, Al and Fe. This is not surprising owing to the greater dominance and proximity of surrounding arid regions to the Eastern Basin. Although the aerosol concentrations of crustal elements, Al and Fe in the atmosphere at the Erdemli site are about twice as high as those detected at the western stations, the concentration of Mn is comparable for both basins. This element has a mixed origin; its concentration being affected by both crustal and anthropogenic sources. It has been shown that the main contribution to aerosol Mn concentration at Erdemli is from the crust whereas it has a greater contribution from anthropogenic emissions to the north western Mediterranean marine aerosol (Kubilay, 1996).

Since the water soluble aerosol ion composition ($SO_4^{=}$, NO_3^- and NH_4^+) has not been reported for the northwestern Mediteranean sites (see Fig.3.5) the data from EMEP's (Co-operative programme for monitoring and evaluation of the long range transmission of air pollutants in Europe) stations were adopted in the comparative study.

Previously it has been demonstrated that a strong interrelationship between sulphur emissions in continental Europe and the acidification of Scandinavian lakes exists. From these studies it was agreed to instigate active international cooperation to combat acidification of freshwater systems (The 1972 United Nations conference on the Human Environment in Stockhom). In 1979 the Convention on Long-range Transboundary Air Pollution was signed by 34 Governments and the European Community (EC). Subsequently the Convention has been extended by eight protocols, one of them being the EMEP.

Table 3.2. Geometric average trace metal concentrations for particulate aerosols from a number of sites (refer to Fig.3.5).

Element	Liverpool[1]	Blanes[2]	Tour du Valat[3]	Cap Ferrat[4]	Corsica[5]	Sardinia[6]	Amasra[7]	Antalya[8]	Erdemli	Tel Shikmona[9]
Al	317	390	380	370	168	480	210	300	550①	720
Fe	340	316	275	320	144	278	200	230	437①	798
Mn	8.4	10	13	11	5.3	7.4	8.7	6.11	9.8①	14.5
Zn	36	50	60	41	19	21	10	11.3	19.5①	85
Pb	43	50	56	58	16	14	12	13	30②	33.6
Cd	-	0.60	0.51	0.36	-	0.3	0.21	-	0.19②	0.19

① This study.
② Kubilay and Saydam (1995).

[1] Chester *et al.* (2000); [2] Chester *et al.* (1991); [3] Guieu (1991b); [4] Chester *et al.* (1990); [5] Bergametti *et al.* (1989a); [6] Guerzoni *et al.* (1999); [7] Karakaş (1999); [8] Güllü *et al.* (1998); [9] Herut *et al.* (2001)
Concentrations are given in ng m^{-3} of air, (-) indicates no data reported.

Initially, the EMEP programme focused on assessing the effect of transboundary transported pollutants and their influence on acidification and eutrophication of aquatic systems. Acidic and eutrophic pollutants originate primarily from anthropogenic emissions of sulphur dioxide (SO_2), nitrogen oxides (NO_x) and ammonia (NH_3). Most of SO_2 and NO_x is emitted to the atmosphere via the combustion of fossil fuel in electricity generating power stations, industrial plants, residential heating, commercial and service sectors. Road transport, shipping and aircraft are significant sources of NO_x emissions. NH_3 emissions are related to agricultural activities such as storage of manure, soil fertilising, animal husbandry, etc.

When emitted to the atmosphere, acidic and eutrophic pollutants may remain in the atmosphere for several days and therefore, be dispersed and carried over long distances by air mass movement. They can be transported across national boundaries and cause deleterious environmental effects far from the source of emission. Acidic pollutants are removed from the atmosphere by wet ("acid rain") or dry (direct uptake by vegetation and surfaces) deposition.

The EMEP programme includes samples/data collection at 82 stations in 26 participating countries (Hjellbrekke et al., 1997). Turkey is one contributor to the program. Atmospheric samples (precipitation, aerosols) have been collecting in Ankara (Çubuk) as a part of the program. The locations of the sampling stations within the EMEP project are denoted with a number 1 in Figure 3.6. Within the program research activities, special attention has been made to the study of the aerosol and rain composition of sulphur and nitrogen compounds. However, few marine sampling sites have been included in the observation network. Therefore data on atmospheric pollutants over the European seas are urgently needed and are of great importance for the understanding of pollutant distributions and transformations and subsequent deposition over European seas.

In 1987-1991 the research vessels of the UkrSCES carried out 127 research cruises during which studies of pollution of the atmosphere over the Mediterranean Sea by sulphur and nitrogen compositions were conducted (Medinets, 1996). The main regions of the Mediterranean Sea where continous observations were conducted are indicated on Figure 3.6 as I, II, III, IV, V and VI. The sampling stations are indicated as G, A, E, BS and J and were occupied during the following studies respectively; Mihalopoulos *et al.* (1997) at Crete; Güllü *et al.* (1998) at Antalya, present study at Erdemli, Karakaş (1999) at a coastal site of the Black Sea (Amasra) and Luria *et al.* (1989, 1996) at Jerusalem (Fig.3.6), respectively.

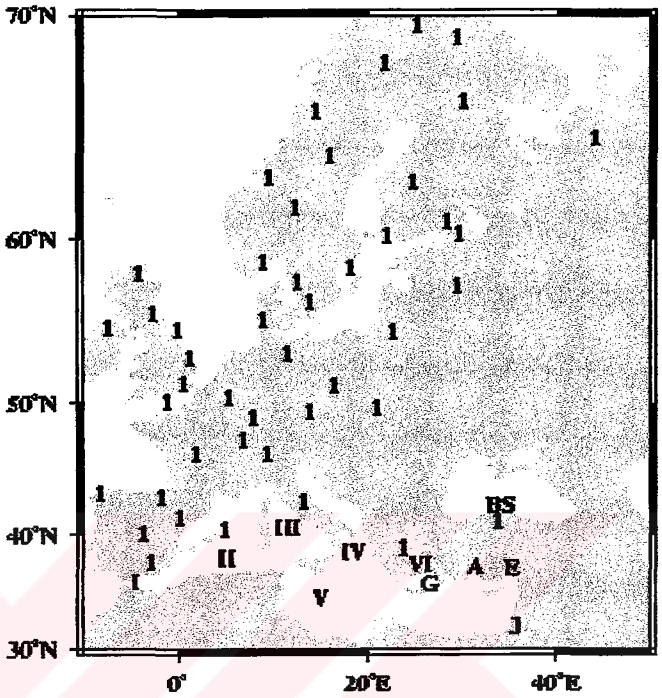


Figure 3.6. Locations of the sampling stations where aerosol water soluble aerosol data exist.

Sulfate concentrations over the Mediterranean are comparably higher than those over continential Europe (Figure 3.7). The maximum annual average sulfate concentration of 9.89 µg m^{-3} has been observed by Luria *et al.* (1996) in Jerusalem (1987-1988, 409 samples) along the Israeli coast. In the earlier study of Luria *et al.* (1989) it has been declared that the measured concentrations of sulfate ions ranged from as low as 2 µg m^{-3} observed during the winter season to a maximum of > 50 µg m^{-3} obtained during the summer. Several indicators (lack of correlation between particulate sulfate and primary pollutants and origin of air mass back trajectories) suggested that the origin of the sulfate in the region is not from local sources but the result of long range transport.

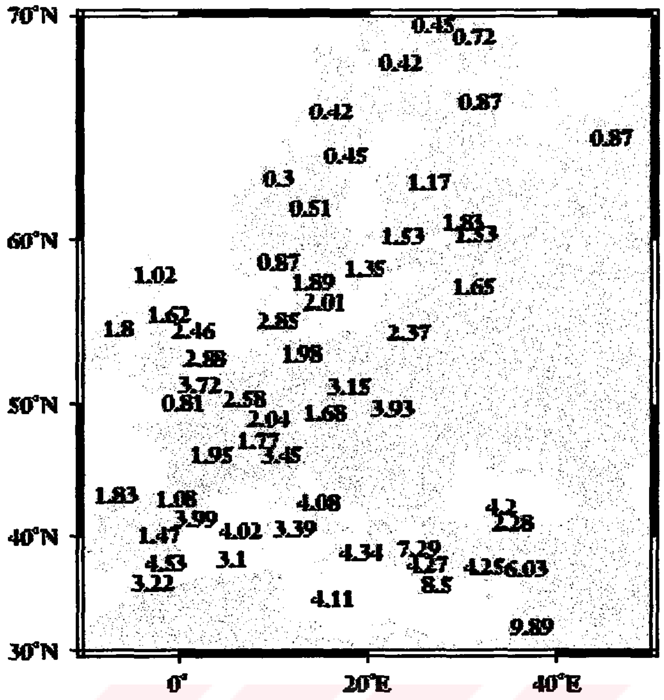
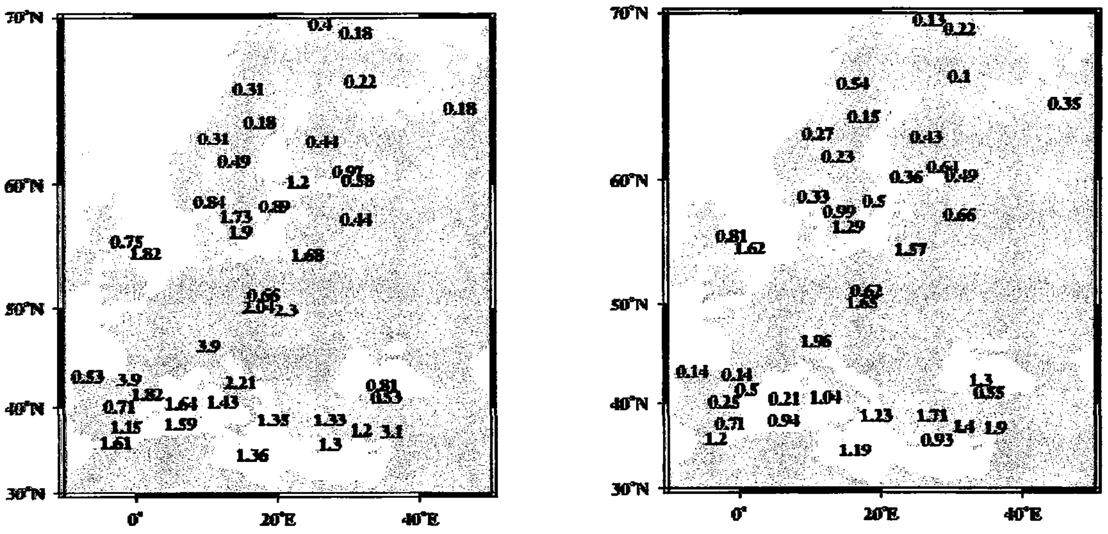


Figure 3.7. Geographical variation of the average aerosol $SO_4^=$ concentrations ($\mu g\ m^{-3}$).

Concentration of aerosol water soluble nitrate at the Erdemli station (3.1 $\mu g\ m^{-3}$) is higher than those values reported for the Mediterranean and Black Sea coast (Figure 3.8.a). Aerosols are not only a physical mixture of fractions from air masses of continental and oceanic origin but also the product of chemical and photochemical reactions that occur in the atmosphere during transport from emission source to the sampling site. Characterization of individual particles at a coastal site in Israel, during the summer months provided direct evidence on the formation of nitrate (by the reaction of gaseous NO_2 and HNO_3 with sea salt or/and mineral dust particles). (Mamane and Mehler, 1987a; Mamane and Gottlieb, 1992). The higher level of nitrate at the Erdemli site might be the result of heterogenous reactions of gaseous nitrogen compounds with sea-salt and/or mineral dust particles. Ammonium concentration at the Erdemli site (1.9 $\mu g\ m^{-3}$) is consistent with those from previous measurements (see Figure 3.8.b).



(a) (b)

Figure 3.8. Geographical variations of the aerosol water soluble ions.
(a) NO_3^-; (b) NH_4^+

As a result, in contrast to the anthropogenic trace metals (Pb and Cd) the ionic concentrations of the Erdemli aerosols (presumably anthropogenic originated, $SO_4^=$, NO_3^-) are higher than those previous measured in the western Mediterranean marine aerosol. This interesting conclusion might arise from local emissions and/or long range transport and photochemical oxidation of gaseous compounds to particulate forms.

3.2.2.1. Comparison of Observations Carried Out at a Coastal/Rural (Erdemli) and a Inland Semiarid Site (Sde Boker) in the Eastern Mediterranean Basin

As shown in the previous sections the elemental and water soluble ionic composition and the mean concentration level of the aerosols collected at the Erdemli site are more representative to those results reported from the Israeli sites. In this regard the aerosol data set under a program labeled “Aerosol Radiation and Chemistry Experiment” (ARACHNE) offer the most appropriate comparison for the data collected during the present study. This program was initiated in 1995 in order to improve the knowledge on the radiative properties of atmospheric aerosols, their origin and spatio-temporal distributions and within this aim a set of long – term measurements were made in Sde Boker, Israel, located in the Negev desert

(Formenti, 2000; Formenti *et al.*, 2000; Andreae *et al.*, 2000). Sde Boker is about 100 km inland from the eastern Mediterranean Sea being located in the northern part of the Negev Desert (Figure 3.9). The annual rainfall at Sde Boker occurs exclusively in the winter, and is about 100 mm whereas at Erdemli the annual rainfall is about 600 mm.

The aerosol sampling at Sde Boker were performed with a two stage PM_{10} filter unit with the coarse (2-10 μm) and fine (< 2 μm) size fractions.

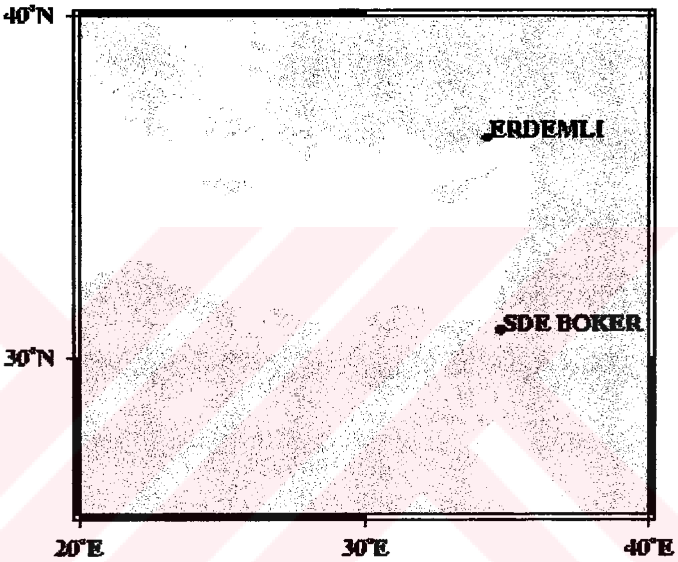


Figure 3.9. The Location of Sde Boker.

The chemical composition and temporal variation of aerosols over the Israeli and Turkish coast of the eastern Mediterranean resemble each other. Long term measurements performed at both coastal sites have shown that in the summer period the concentration of sulfate particles reach their maximal values (Luria *et al.*, 1996; Özsoy *et al.*, 2000). Outbreaks of Saharan dust being observed to be very frequent in the winter-spring period and minimal during the summer period (Ganor, 1994; Kubilay *et al.*, 2000).

ARACHNE comprises of a long term component with intensive field campaigns. The sampling period of the study coinceded with the sampling period of the present study conducted at the Erdemli site.

In Table 3.3. the arithmetic means of elemental and ionic concentrations (ng m^{-3}) for the present study are compared with results from ARACHNE investigation at Sde Boker in Israel. Although the data do not refer to the same size fraction (in

Erdemli the total suspended matter with a hi-vol pump was collected rather than the PM_{10} aerosol work at Sde Boker) results are similar with respect to concentration levels and chemical composition characteristics.

To illustrate in more detail the physical and chemical properties of the aerosol at Sde Boker, Andreae *et al.* (2000) selected days in February 1996 (Case I) and in May 1997 (Case II) that represent "dust" and "pollution" events, respectively. Five day back trajectory analysis (Figure 3.10a) shows that air masses reaching Sde Boker at -960 and –900 hPa on 10 Feb., i.e. during the "dust" events, originated from northern Libya and Egypt. This is consistent with the findings of Dayan (1986), that elevated concentrations of suspended particulates are observed in Israel during the winter and spring period when synoptic conditions bring air from North Africa. The trajectories also indicate the passage of the airmasses over the Mediterranean or Red Sea which could explain the presence of the sea-salt aerosol component.

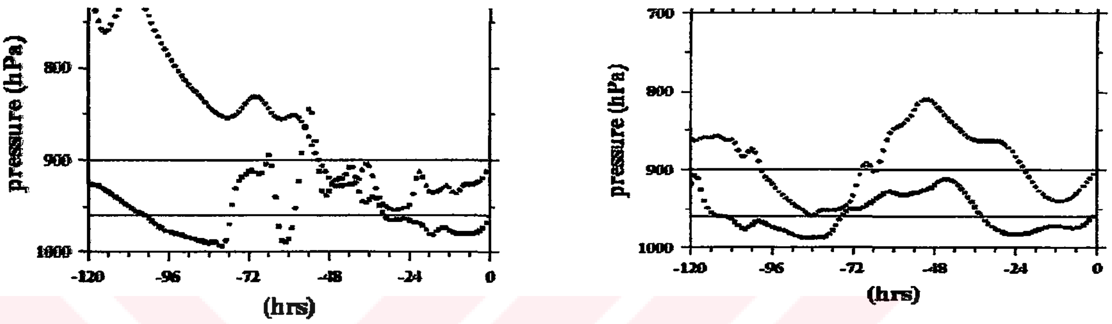
Table 3.3. Comparision of mass concentrations (ng m^{-3}) of chemical species for the aerosols collected at Erdemli and Sde Boker over different time periods.

	Long Term		**June – July 1996**		**Case Study(I)**		**Case Study(II)**	
Chemical	***Erdemli***	***Sde Boker***[1]	***Erdemli***	***Sde Boker***[2]	***Erdemli***	***Sde Boker***[1]	***Erdemli***	***Sde Boker***[1]
Species	**1996-1998**	**1995-1998**			**12-14 Feb.1996**	**8-11 Feb.1996**	**6-8 May 1997**	
Al	908	1867(88%)	897	1880	2213	47932(98%)	574	870(87%)
Fe	754	1245(87%)	695	1320	1661	30030(98%)	504	710(81%)
Ca	4184	6538(88%)	2933	7080	5779	59863(97%)	3237	3687(88%)
Mg	2074	919(85%)	1875	980	5743	14404(99%)	1440	553(81%)
Na	2872	1187(83%)	2208	1330	-	5061(99%)	2010	873(77%)
K	302	589(75%)	302	600	-	9175(98%)	241	316(67)
Cl	4633	1077(99%)	2508	1130	-	5751(99%)	2108	427(74%)
Br	19.3	28.5(42%)	-	-	-	BDL	11.4	21(47%)
Mn	15.1	24.2(83%)	17	30	34.4	447(98%)	13.7	18.2(63%)
Zn	25.5	32.5(47%)	27	30	22.8	101.7(96%)	27.6	157(25%)
P	-	339(73%)	-	-	-	487(96%)	-	56.9(100%)
Si	-	3786(85%)	-	-	-	68332(97%)	-	1739(85%)
S	-	2667(25%)	-	3530	-	3597(95%)	-	4918(13%)
$SO_4^=$	7498	8000*	8952	9990	-	10791*	19636	14754*
NO_3^-	3336	-	3937	3300	-	-	8809	-
NH_4^+	2219	-	2245	3220	-	-	5756	-

[1] Andreae *et al.* (2000); [2] Formenti (2000)

The percentage of total concentration measured in coarse size fraction is given in the paranthesis.

* $SO_4^=$ concentration estimated from reported S.



(a) (b)

Figure 3.10. Five day air mass back trajectories at 960 and 900 hPa arriving at Sde Boker (left hand side) and Erdemli (right hand side). The lower panels show the altitute (pressure level) of the air mass along the trajectories.
(a) 10 Feb. 1996; **(b)** 12 Feb. 1996

Due to technical problems with the sampler at Erdemli, samples could not be collected during the period betweeen 8-11 Feb. 1996. Air mass back trajectories arriving at Erdemli between 8 Feb.- 14 Feb all originated from North Africa. As can be seen from the lower panel of Figure 3.10.b, the vertical movement of the trajectories presented ascending types of motion. This is consistent with the findings made by Kubilay *et al.* (2000), that ascending trajectories originated over north Africa represents cyclonic motion which have the potential to transport mineral dust to the eastern Mediterranean region.

Back trajectory analysis (Figure 3.11) indicates that during the period 6-8 May near surface air masses (>900 hPa) originate from central Anatolia, Bulgaria, Romania, Ukraine and Poland.

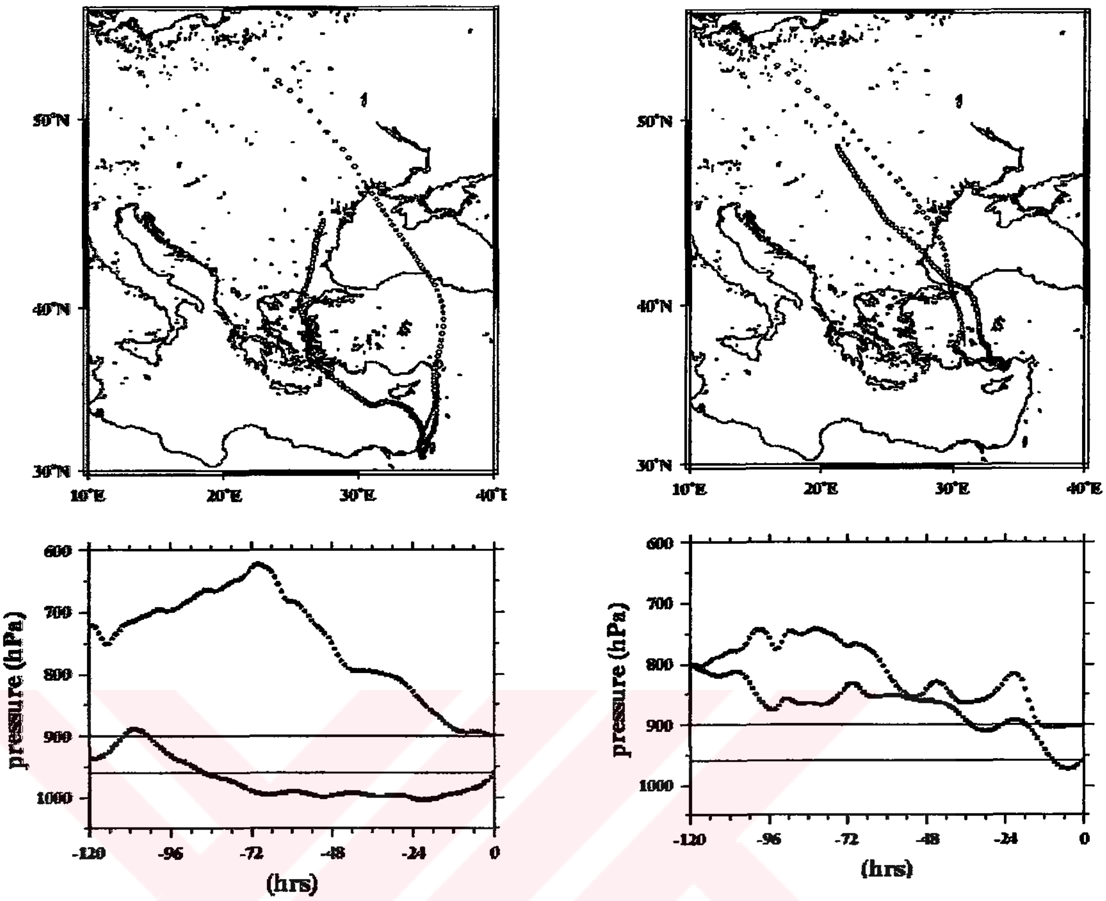


Figure 3.11. Five day air mass back trajectoreis arriving at -960 and –900 hPa levels to Sde Boker and Erdemli on 7 May 1997.

Measurements made in Sde Boker (Andreae *et al.,* 2000) showed that air masses originating in these countries, as well as Germany, Balkans, and Greece are generally associated with high levels of pollutants.

It is apparent from Table 3.3 that the long term average concentration of crustal elements (Al, Fe, Ca, and Mn) are much higher in Sde Boker than those detected at Erdemli. The majority of their total concentrations (more than 80 %) occurred in the coarse size fraction. The coarse size fraction mode at Sde Boker is dominated by silicate and calcium carbonate dust. The average concentrations of sea spray originated elements (Na, Cl and Mg) are lower than the levels observed at Erdemli. This observation is reasonable as Sde Boker is an inland station whereas Erdemli station is located on the coast.

About 50 % of the mean concentrations of Zn and Br at Sde Boker were detected on the coarse mode which indicates that the abundance of these two elements on aerosols are effected by both natural (soil, sea salt) and anthropogenic emissions (combustion, biomass burning).

Data on water soluble ions (sulfate, nitrate and ammonium) at Sde Boker were reported only for the intensive campaign of June-July 1996 period. However the elemental S concentrations were reported for all the sampling period (Table 3.3). Formenti (2000) compared water soluble $SO_4^=$ measured by IC and elemental S (by PIXE) for the samples collected during the June-July 1996 sampling campaign. She found a strong correlation between these two species. Linear regression yielded mass ratios $SO_4^= / S$ of 2.5 for the fine and 3.3 for the coarse fraction, this being very close to the mass ratio of 3 if all the S is present as $SO_4^=$. Accordingly it is feasible to estimate water soluble aerosol $SO_4^=$ from the reported elemental S concentrations. On a long term basis only 25 % of S at Sde boker was found associated with the coarse fraction whereas remaining 75 % occurred on the fine fraction indicating that most of the time aerosol S was originated from combustion sources. In contrast to this result, the samples collected during a Saharan outbreak of mineral dust (reported as Case I in Table 3.3) at Sde Boker, 95 % of the total S was found on the coarse fraction. From the discussion in Section 3.2.1 it follows that only 15% (on average) of the coarse S is attributable to sea salt. A proportion of the sulfate in the atmosphere may in principle present in the form of mineral sulfate, mainly as $CaSO_4$ (gypsum). Previous investigations are controversial: Gypsum is not regarded as a component of the mineral aerosol over Israel (Ganor and Mamane, 1982), although traces have been found in air filter samples (Foner and Ganor, 1992). The results of a mineralogical analysis of Saharan mineral dust transported to Israel by Falkovich *et al.* (2000) have shown that non-clay minerals in the samples are composed of 29 % calcite (Ca), 29 % quartz (Si), 26 % dolomite (just Mg with Ca) and only 5 % gypsum ($CaSO_4$). The analysis of the individual mineral dust particles in the sample indicated that the particles contained Si, Al, Mg, K, Ca, S, Fe and only negligible amounts of Na and Cl were observed. Luria *et al.* (1996) considered the contribution from any mineral source to the high sulfate concentrations observed over Israel to be insignificant. It is quite likely that $CaSO_4$ was formed in the atmosphere by reactions between SO_2 or H_2SO_4 and $CaCO_3$ and does not originate from gypsum mineral dust. In conclusion, the coarse fraction of S in Sde Boker were assumed to be in the form of $CaSO_4$.

Uptake of SO_2 or H_2SO_4 and NO_x or HNO_3 and subsequent conversion to $SO_4^=$ and NO_3^- on the particle surface occurs due to the alkalinity of soil dust (as it is in Sde Boker and Erdemli) which explains the presence of sulfate and nitrate associated with dust particles (Zhang *et al.*, 1994; Dentener *et al.*, 1996; Levin *et al.*, 1996; Ganor *et al.*, 1998).

The percentage of coarse fraction of S on the sum of the coarse and fine fractions were only 13 % during the Case II (see Table 3.3) when air masses carried pollutant to Sde Boker (see Fig.3.11). It has been concluded during ARACHNE, $SO_4^=$ and S concentrations at Sde Boker are very good indicators of anthropogenic pollution particularly in fine fraction, in which contributions from mineral and sea-salt components were negligible (Formenti, 2000). On the other hand, Wakshal and Nielsen (1982) suggested presence of a fine sulfate aerosol formed over the Mediterranean Sea from volatile biogenic sulfur compounds and deposited inland of Israel. Since size segragated samples were not collected at Erdemli site it is not possible to differentiate between the contribution of fine and coarse fractions to the total measured sulfate concentrations.

Although they were not measured at the Erdemli station the aerosol Si and P concentrations reported for the Sde Boker site were included in Table 3.3. These two elements occurred on the coarse fraction indicating a soil origin. As can be seen from the Table the Si and P concentration during Case I were 40 and 8 times higher than the concentrations detected in Case II, respectively. These two elements serve as macronutrients to the surface ocean. The S and P enrichments in Saharan outbreak of dust in the eastern Mediterranean highlights the importance of Saharan dust as an important route for nutrient inputs.

3.3. Temporal Variations of the Aerosol Composition at Erdemli

Short and long-term temporal variations in the concentrations of chemical constituents may provide information on the mechanisms of aerosol transport from source regions to receptor sites, aerosol formation and factors affecting these processes. Temporal variations of aerosol composition are generally studied within two time scales. Short term variations highlight the episodic changes in the concentrations, whereas long-term variations define the average changes at seasonal time scales. Concentrations o f aerosol elements and ions in this study and elsewhere show large variations from one day to another. These variations are accounted by (i) changes in emission strengths, (ii) local meteorology and (iii) transport patterns. One to two orders of magnitude difference in the concentrations of elements and ions in both aerosol and rainwater samples have been reported for the eastern and western Mediterranean atmosphere (Bergametti *et al.*, 1989; Kubilay and Saydam, 1995; Güllü *et al.*, 1998; Al-Momani *et al.*, 1998; Özsoy and Saydam, 2000; Özsoy *et al.*, 2000; Kubilay *et al.*, 2000).

Episodic changes tend to be more pronounced for soil and sea salt derived elements and ions. Investigation of short-term variations can provide useful information on the source regions and transport patterns affecting the concentrations of elements and ions content of aerosols in the study area and specific meteorological patterns that give rise to elevated levels of natural crustal particles.

Long-term variations in the concentrations of elements and ions can, provide information on factor affecting aerosol population at the receptor site. Such variations could be due to factors such as, seasonal variation in the emissions (this being particularly the case 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. The seasonal (monthly) and short-term variations in the concentrations of chemical constituents are discussed in sections 3.3.1 and 3.3.2, respectively.

3.3.1. Seasonal Variations in the Concentrations of the Elements and Ions at the Erdemli Site

The mean monthly average aerosol concentration of each element and water soluble ions are presented in Figure 3.12. On the basis of the highlighted temporal variations in their concentrations, elements and ions can be divided into the following groups.

Group (1) : The ions Cl$^-$, Br$^-$, Na$^+$ and Mg^{+2} show a pronounced winter maximum and summer minimum. Seasonal concentration values of these sea spray originated elements were affected by meteorological factors. Storms are more frequent and more active during the winter period, therefore these weather conditions enhanced the concentration of sea salts throughout the winter months. Whereas, during the summer period sea salt generation is at its minimum owing to weak winds and calm sea surface. Therefore, sea-salt particles are generated locally as a function of local wind speed and concentration of these particles show winter maximum. In general these findings are in agreement with those observations made at other stations which are located in the Mediterranean region (Bergametti *et al.*, 1989; Mihalopoulos *et al.*, 1997; Güllü *et al.*, 1998).

Group (2) : Nitrate, ammonium, non-seasalt sulfate and methane sulfonate concentrations indicated a winter minimum and summer maximum. Seasonal cycle of nitrate may be affected by meteorological conditions. Atmospheric particulate nitrate is due mainly to the transfer of HNO_3(g), and possibly of NO_2(g), NO_3(g) and N_2O_5(g), onto particle surfaces and their subsequent reaction with various particle compounds (Pakkanen *et al.*, 1996). Photochemical formation, which becomes active under summer condition with sufficient solar radiation and temperature, enhances the concentrations of nitrate.

Mamane and Gottlieb (1992) performed laboratory experiments to study the heterogeneous reactions of nitric acid and nitrogen dioxide with sea salt and with different kinds of soil particles. Their study indicated that both gases reacted with seasalt and various soil particles in the dark. Under ultraviolet radiation the formation of nitrate on sea-salt particles was increased, but remained relatively unchanged on the soil particles.

Therefore it is likely that photochemical formation of particulate nitrate increases during summer time (also the driest period). During the summer period, homogeneous conversion of SO_2 to particulate sulfate can be assumed to be the main oxidation mechanism under conditions prevailing over the eastern Mediterranean region (Luria *et al.*, 1996). These authors have recently reported a clear seasonal variation in sulfate concentration with highest values (occasionally exceeding 50 $\mu g \, m^{-3}$ in Jerusalem) occuring in the summer. Using air masses trajectories they showed that air masses originating from highly polluted and polluted areas were enhanced in sulfate concentration. Additionally Ganor *et al.* (2000) have emphasised that high sulfate concentrations over the eastern Mediterranean during summer may be ascribed to sulfate originating from biogenic productivity in the marine environment. The observed high non-sea salt sulfate concentrations during summer time at Erdemli station can be attributed to both anthropogenic and biogenic sulfate emissions. Seasonal variations of the MSA aerosol concentration were also observed at different marine locations by Saltzman *et al.* (1986), Mukai *et al.* (1995), Prospero *et al.* (1995) and Mihalopoulos *et al.* (1997). They found an annual cycle with mean values enhanced in the summer relative to in the winter similar to those observed at the Erdemli sampling station. Ammonium showed a maximum during summer, whereas, this ion species indicated a maximum peak in winter at Antalya, which is another sampling station located on the Mediterranean coast of Turkey (Güllü *et al.*, 1998). During the summer the ambient air temperature is high and the soil is dry, therefore, these conditions are favorable for the enhancement of the ammonia flux into the atmosphere. These conditions may cause profound summer peak of ammonium. In addition, Mn and Zn show summer peak. These peak concentrations occur during the dry season when the dry deposition is at its maximum.

Group (3) : This group consists of Al, Fe and Ca, which includes crustal elements, however, Fe and Ca may have contributing anthropogenic sources. These elements indicate two peaks during spring and summer seasons. Although wet deposition is still effective during spring the dust loadings are increased by transport with cyclones originating from North Africa, which are known to be the main agents in the eastern Mediterranean (Alpert *et al.*, 1990). Kubilay *et al.*, (2000) have recently shown that higher dust concentrations and total deposition are during transitional seasons (spring and autumn) compared to those encountered during the summer and winter seasons. However, those concentrations observed during the transition seasons are comparable with the values detected during the summer season for the present study.

Group (4) : Calcium did not show any clear seasonality in its aerosol concentrations. However potassium had two peaks, one during the winter and the other being observed during the summer season. The winter peak might be related to enhanced sea salt generation, whereas , combustion of land biota may lead to the enhanced summer concentrations of potassium. Oxalate shows two peaks during the summer and autumn. Increased traffic owing to greater tourism and the burning of vegetation and forest around the vicinity may be sources of oxalate, leading to its enhanced observed concentrations. The existance of oxalate $(COO)_2^{=}$ in tropospheric aerosols and precipitation has been demonstrated and a significant correlation of airborne oxalate with airborne nitrate has been noted, suggesting a pollution source (Norton *et al.*, 1983). It has been further postulated that the mechanism of oxalate production is via gas or aerosol-phase photooxidation of tetrachloro-ethylene or aromatic hydrocarbons.

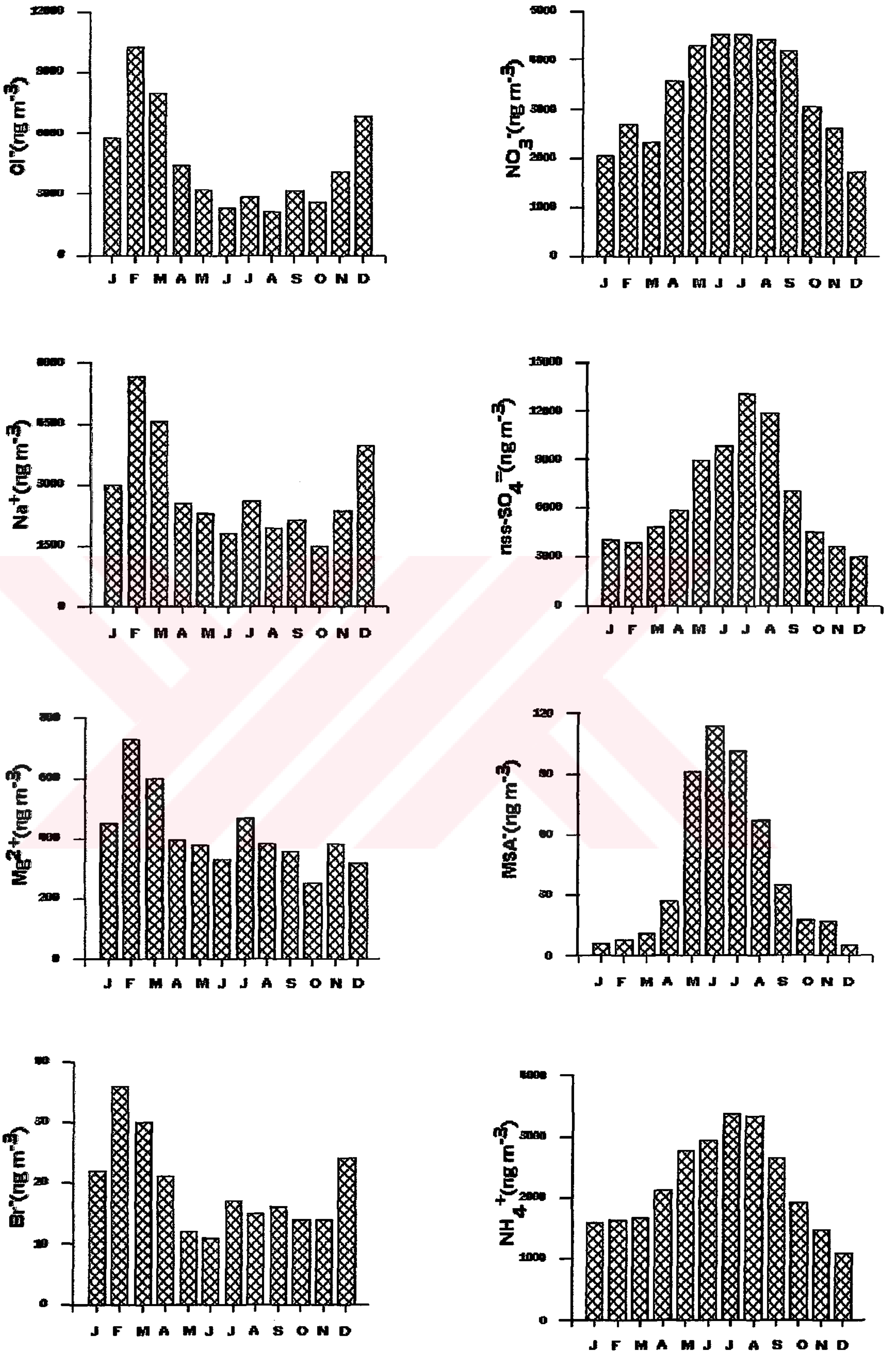


Figure 3.12. Mean seasonal variation of aerosol element and water soluble ionic species concentrations at Erdemli from January 1996 to December 1998.

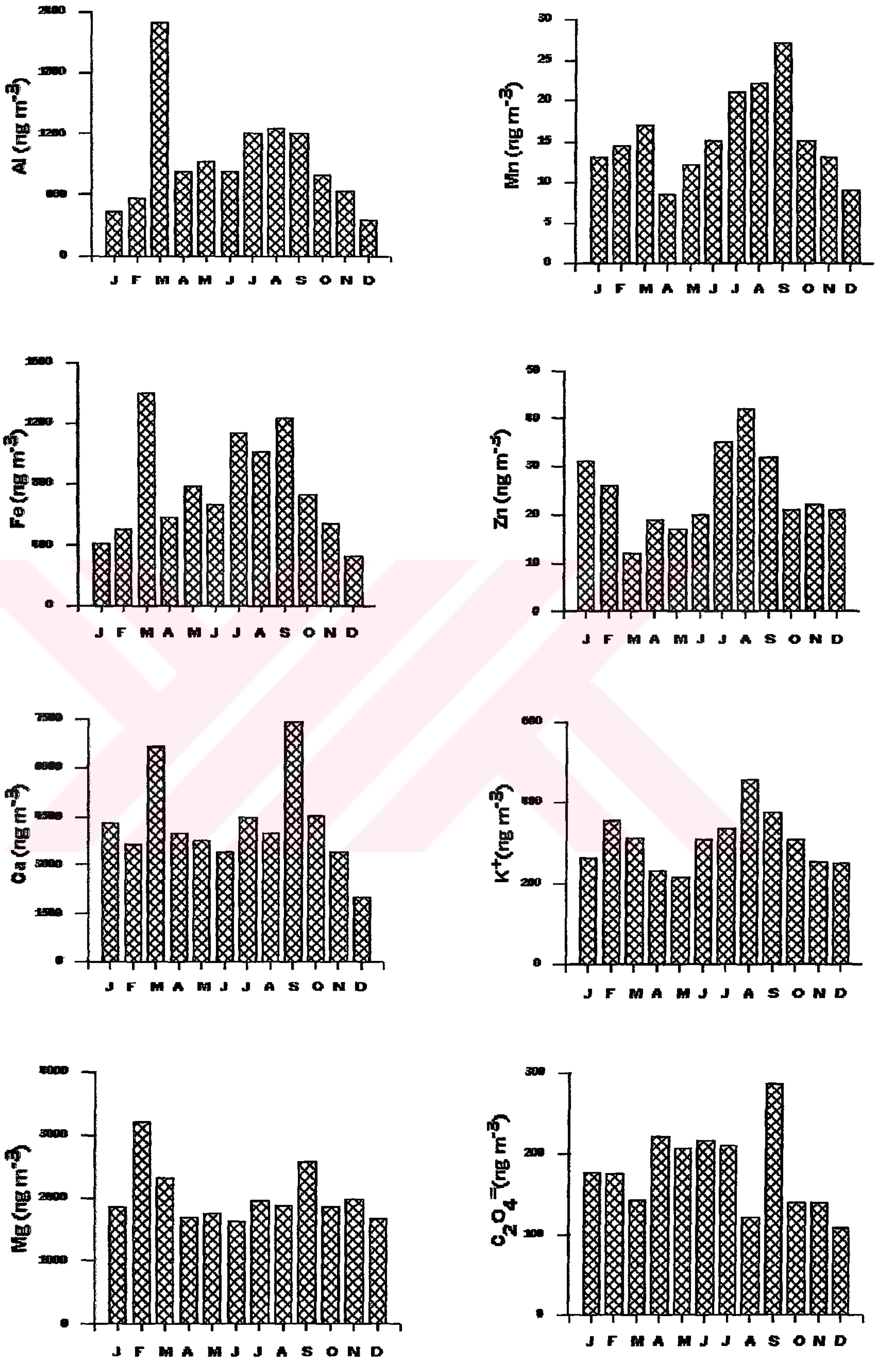


Figure 3.12. (*continued*).

3.3.2. Short-Term (Daily) Variations of Chemical Composition of Aerosols

The temporal variations in the concentrations of trace elements (Al, Fe, Ca, Mg, Mn, Zn) and ions (nss-$SO_4^{=}$, MSA^-, NO_3^-, NH_4^+, Na^+, Cl^-, Br^-, Mg^{2+}) with daily local rainfall between January 1996 and December 1998 are given in Figure 3.13. It is apparent from Figures, that concentrations of all trace species are highly variable on a daily time scale. During rainy days aerosol constituent concentrations demonstrated drastic decrease, since wet deposition removes the particles from the atmosphere very efficiently. Concentrations may change an order of magnitude from day to day. Such high daily variation in the concentrations of trace species has been reported over the Mediterranean atmosphere (Bergametti *et al.*, 1989; Kubilay and Saydam 1995; Güllü *et al.*, 1998; Guerzoni *et al.*, 1999). Özsoy and Saydam (2000) have recently stated the particulate Al concentrations in rain water collected at the Erdemli station. These authors indicated that in some cases (i.e. during dust events) particulate Al concentrations were very high in rain water, for example, 8-9 February 1996 and 13 March 1997 Al concentrations were found to be 49725 and 20690 $\mu g\ l^{-1}$,respectively. In the present study, Al aerosol concentrations during the corresponding days were 317 and 285 ng m^{-3}, respectively.

Sea salt components Na, Cl, Mg and Br demonstrate higher concentrations and stronger variations during the winter season. Daily variability of these components is due to the local meteorological factors. Sea spray is produced primarily by bursting bubbles (Blanchard and Cipriano, 1983). Storms are more frequent and more active during the winter period, therefore these weather conditions enhanced the concentration of sea salts throughout the winter time. Whereas, during the summer period sea salt generation is at minimum owing to relatively weaker winds and calmer sea surface.

The short term changes in the concentrations of the crustal elements such as Al, Fe, Mn, Ca were noted. Generally particulate Al concentrations in the atmosphere are associated almost exclusively with aluminosilicate components and for this reason Al is often employed as an indicator of the dust episodes (Chester *et al.*, 1984; Guerzoni *et al.*, 1989; Kubilay and Saydam, 1995; Güllü *et al.*, 1998; Guerzoni *et al.*, 1999). Low concentrations of elements associated with crustal material are frequently observed during the winter when the soil on both the local and surrounding masses is damp due to precipitation. Whereas, during this season high concentrations of crustal elements are observed when the air mass trajectories originate from north Africa and occasionally from the Middle East. During the transitional seasons (spring and autumn) elements are associated with crustal material indicative of intense episodic peaks. Between these events the concentrations diminish to comparable magnitudes to observed in winter. It was noted that during the summer period concentrations of these elements varied less markedly. Since the soil is dry in summer, this period is a favorable for the resuspensions of local soil particles.

Concentrations of pollution derived trace species like nss-$SO_4^{=}$, NO_3^{-}, Zn also demonstrate a daily variation. During the winter period these elements exhibit lower concentrations compared to those detected during the summer season. This difference may be attributed to the accumulation of the particles in the atmosphere during the summer owing to the lower rate of removal via wet deposition.

The only known source of MSA (methanesulfonate) is the oxidation of DMS, substantial amounts of which are emitted to the atmosphere from marine biological activity. Once DMS (dimthylsulfide) has entered the atmosphere, it is exposed to oxidation primarily with OH and NO_3 radicals, producing MSA and SO_2 (subsequently converted into nss-$SO_4^{=}$). It has shown that the concentration of DMS in surface waters is controlled by biological activity and it is major volatile sulfur species in the ocean (Barbard *et al.*, 1982; Andrea *et al.*, 1983; Andrea and Barnard, 1984). MSA concentrations were very low during the winter time. In contrast, concentrations of MSA show an increasing trend during the spring and exhibits a pronounced peak during the summer period. Mihalopoulos *et al.* (1997) has also, reported the same seasonal pattern at Finokalia (an other Eastern Mediterranean station located on Crete).

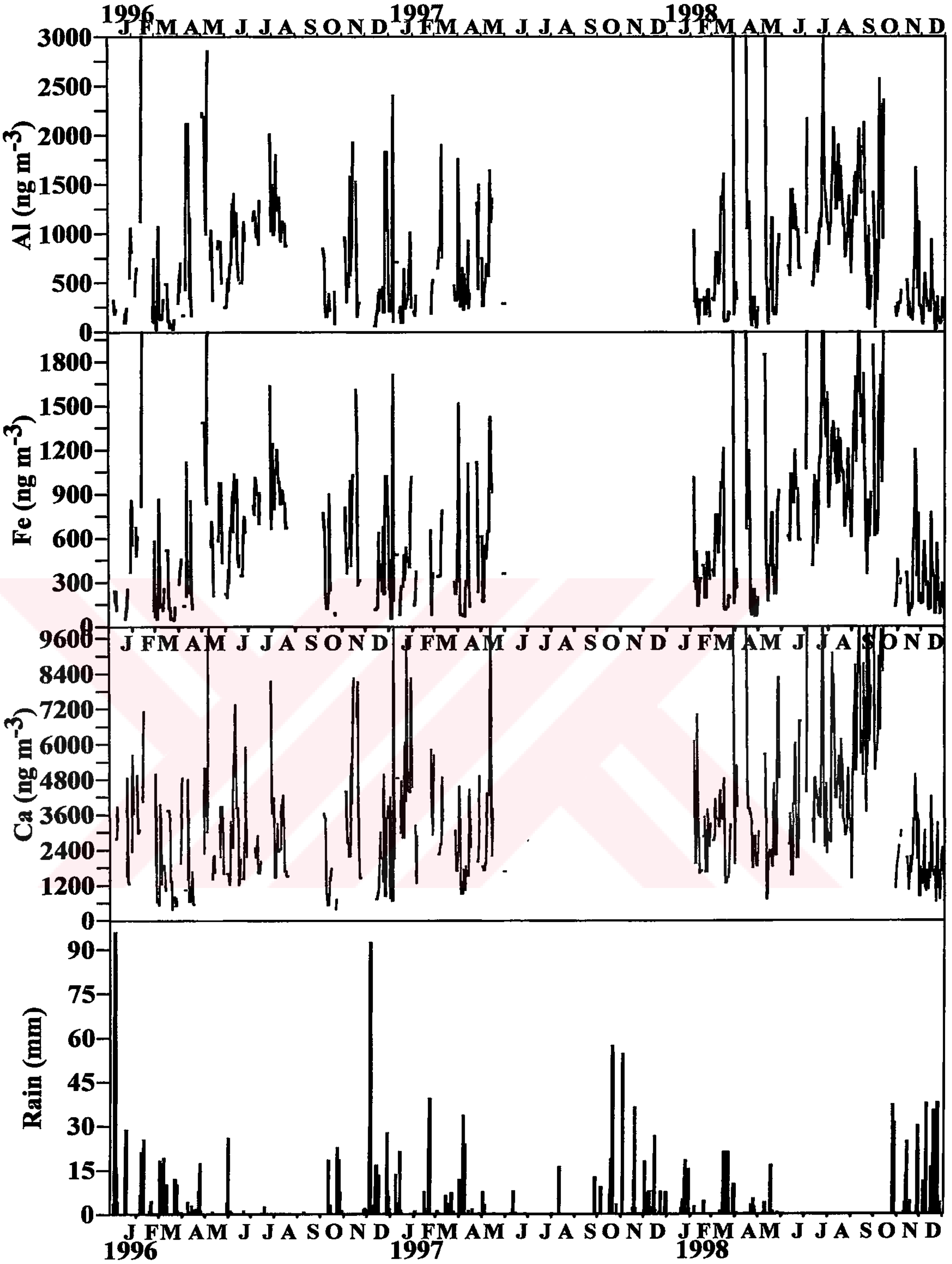


Figure 3.13. Time series of daily averages of aerosol elemental and water soluble ionic composition from January 1996 to December 1998.

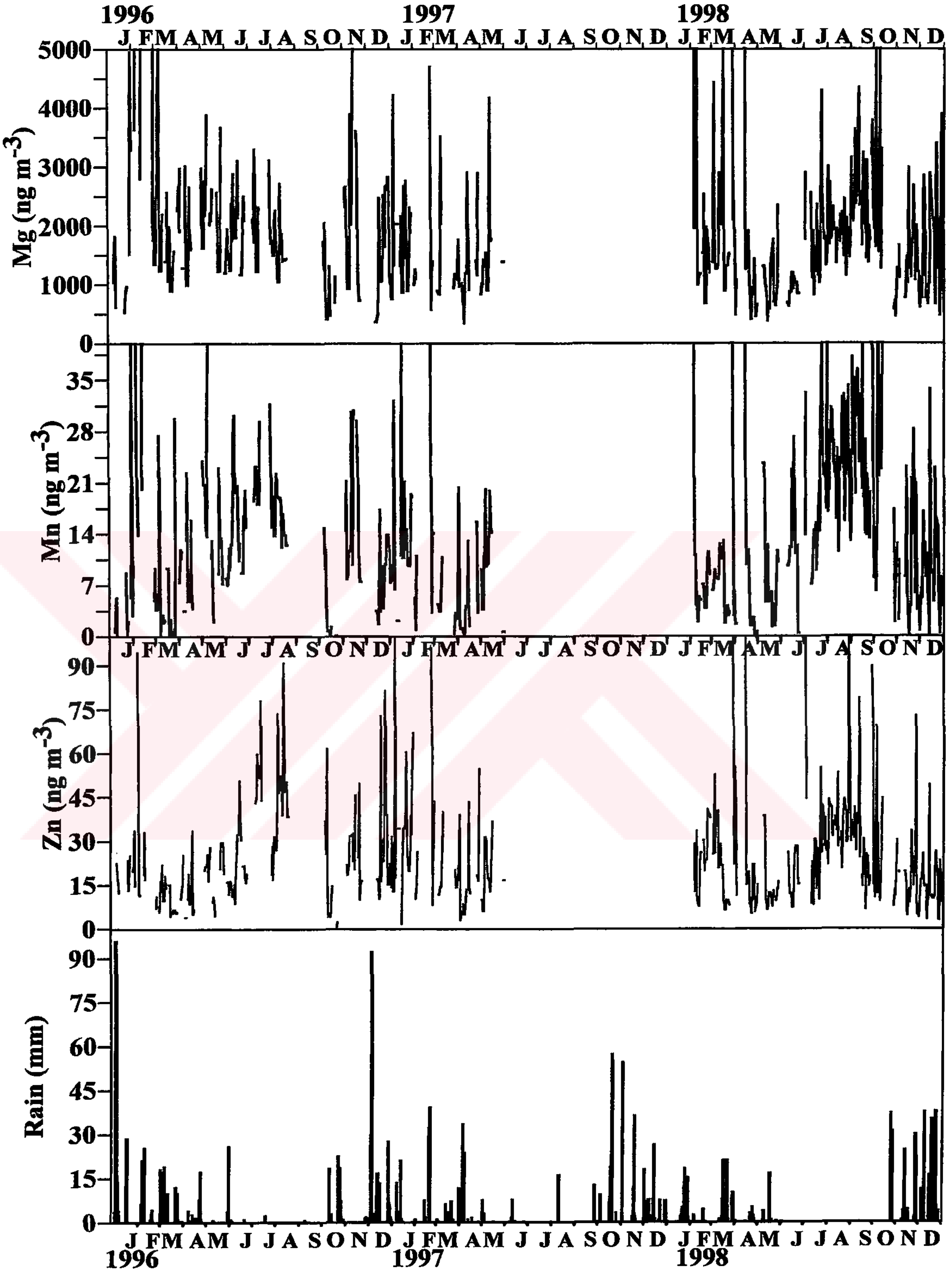


Figure 3.13. (*continued*)

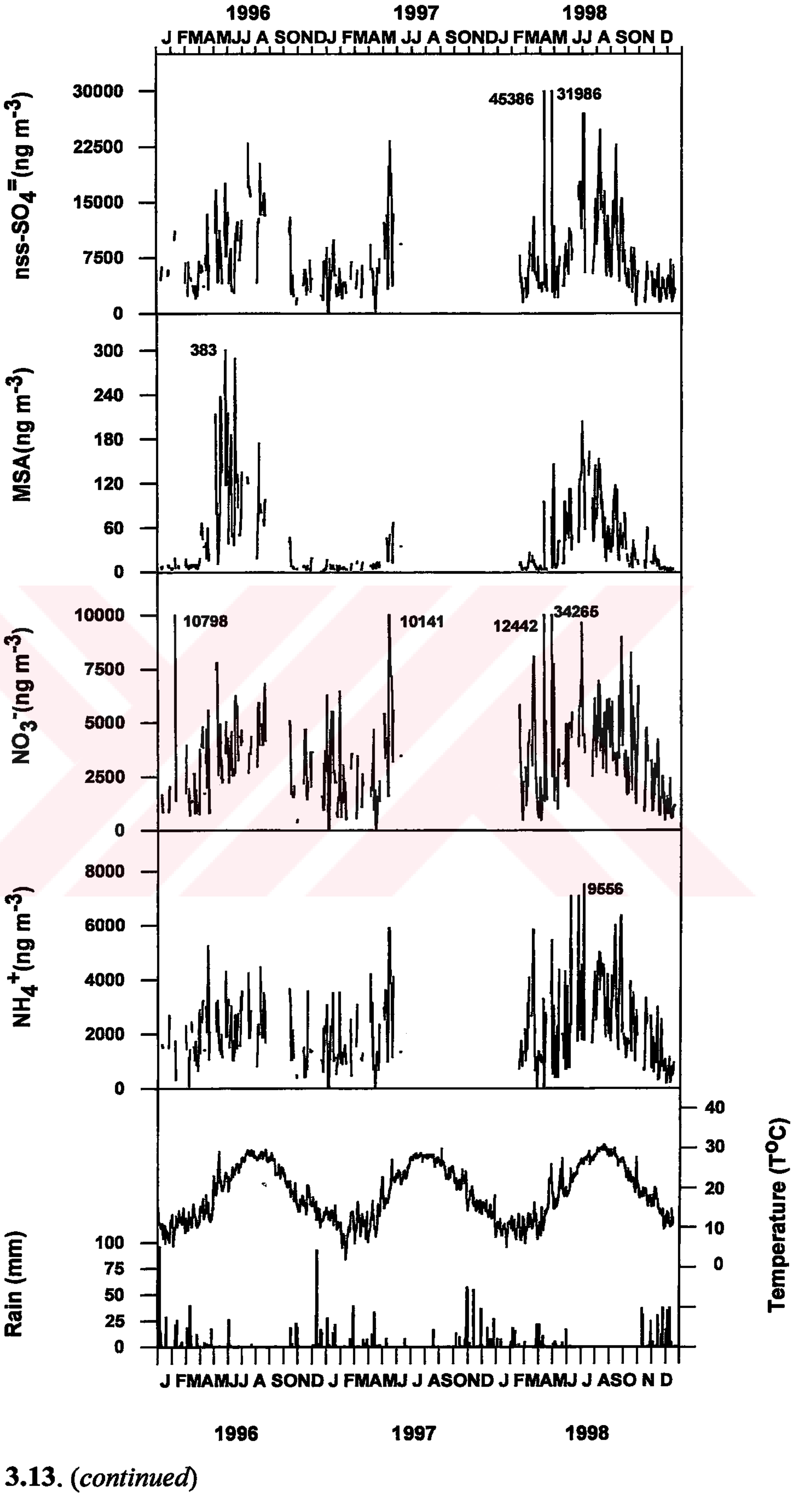
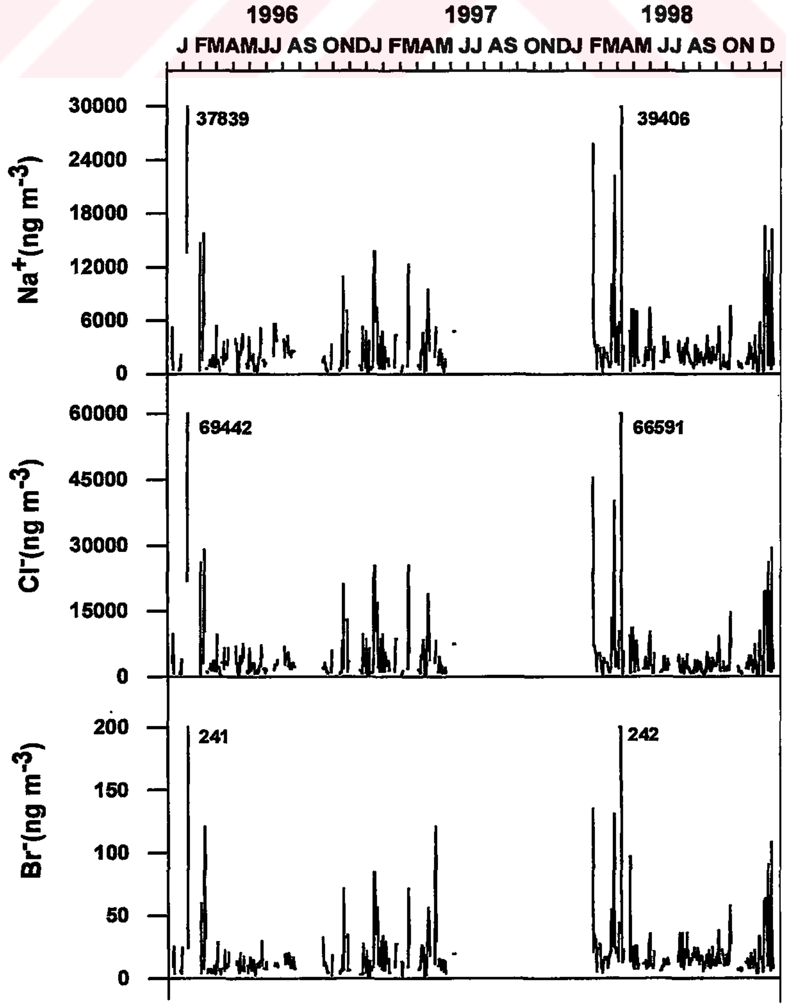


Figure 3.13. (*continued*)


1996
1997
1998
J FMAMJJ AS ONDJ FMAM JJ AS ONDJ FMAM JJ AS ON D
Na+(ng m-3)
30000
24000
18000
12000
6000
0
37839
39406
Cl-(ng m-3)
60000
45000
30000
15000
0
69442
66591
Br-(ng m-3)
200
150
100
50
0
241
242

3.3.1 Influence of Local Rain Events on Aerosol Chemical Constitutent Concentrations

The effect of rain events on observed concentrations of elements have been discussed previously for the Eastern Mediterranean basin atmosphere (Kubilay and Saydam,1995; Güllü *et al.*, 1998; Kubilay *et al.*, 2000; Özsoy *et al.*, 2000). In the Section 3.3 it was shown that long-term and short-term variations in the species concentrations were affected by local rain events.

Average elemental cocentration for wet and dry periods and the ratios of the elemental concentrations in wet to dry periods are presented in Table 3.4. It is apparent from Table that all species, except marine elements (Cl,Br, Na, Mg) and K, have higher average concentration in dry period. The corresponding ratios varied between 1.2 and 2.89. The differences in the ratios may be explained by differences in scavenging efficiencies of different sized particles and elemental solubility in rainwater (Buat-Menard and Duce. 1986; Eder and Dennis, 1990; Galloway *et al.*, 1993). Galloway *et al.*,(1993) have shown that the scavenging ratios vary significantly from one species to another and with elements assocaited with the largest sized aerosol fraction being scavenged most efficiently.

The decrease in the concentrations of crustal and anthropogenic elements due to rain depends on how efficiently particles are removed from the atmospheric compartment by the rain. Kubilay and Saydam (1995) stated that crustal derived elements (Al and Fe) are dominated by coarse particles having diameters larger than 10μm. Whereas, anthropogenic derived elements are associated mainly with fine particles (Stephen *et al.*, 1988). As expected, crustal elements are scavenged from the atmosphere more efficiently by local rain events compared to anthropogenic derived elements.

In contrast the concentration of marine derived elements (Cl$^-$, Br$^-$, Na$^+$, Mg^{2+}), are higher (low ratio) during wet days, as rain events in the eastern Mediterranean are generally associated with frontal storms which enhances sea salt generation. The differences between observed ratios of $SO_4^{=}$, Ca^{2+}, K$^+$ and their non sea salt fraction can be attributed to sea salt contribution on total concentrations of these ions. It is worthwhile to note that the difference between K$^+$ and its non sea salt fraction is more dramatic due to the relatively higher sea salt contribution on the total aerosol K$^+$ concentration compared to those observed concentrations of sulfate and calcium.

Saltzman *et al.* (1983) emphasis that there is a significant difference between the size distribution of aerosol MSA and nss-SO$_4^=$. As stated before rain events are much more intense in the winter season, since MSA is produced by biological activity it shows winter minimum and pronounced summer peak. Therefore, this difference might be attributed to the coupling of these two events.

Table 3.4. The ratio of elemental concentrations in dry days to average concentrations in wet days.

	Dry days	Wet days	ratio Dry/Wet
Al	1028±2672(326)	399±458(79)	2.58
Fe	865±1671(326)	299±318(80)	2.89
Mn	17±21(326)	7±6(80)	2.44
Ca	4740±8209(326)	1895±1395(80)	2.50
Mg	2150±2466(326)	1780±1394(80)	1.21
Zn	29±21(326)	12±8(80)	2.42
Cl$^-$	3662±(326)	8470±12832(83)	0.43
Br$^-$	16±14(326)	32±46(83)	0.50
NO$_3^-$	3720±2502(326)	1829±1583(83)	2.03
SO$_4^=$	8150±5163(326)	4907±4994(83)	1.66
C$_2$O$_4^=$	188±144(285)	132±120(81)	1.42
Na$^+$	2383±2567(325)	4792±7135(83)	0.49
NH$_4^+$	2464±1385(326)	1250±964(83)	1.97
K$^+$	303±183(325)	302±381(82)	1.00
Mg^{2+}	390±318(326)	626±846(83)	0.62
Ca^{2+}	2987±2269(326)	1355±751(83)	2.20
MSA$^-$	48±54(310)	20±35(81)	2.40
nss-SO$_4^=$	7551±5153(326)	3701±3943(83)	2.04
nss-K$^+$	214±157(325)	120±151(82)	1.78
nss-Ca^{2+}	2892±2202	1188±707(83)	2.43

3.4. Chemical Constituent Source Attribution

As the measurement of the elemental and ionic composition of aerosol provides limited direct information on their sources, several methods were used in the current to assign their sources to the aerosol population.

3.4.1. The Enrichment Factor

Enrichment Factors (EF) have been successfully used in the literature to indicate the dominant source of aerosol associated elements (Rahn, 1976; Chester et al., 1993).

Enrichment factors aim to identify elements present in aerosols at concentrations above those predicted if they were derived from any one particular precursor source. The crustal / marine enrichment factor is usually employed which assess the importance of crustal / sea salts as the source for aerosol associated elements. The element of interest in the aerosol population is normalised with respect to an indicator element considered to wholly originate from the precursor material. The general formula applied is

$$EF = \frac{(X / \mathrm{Re}\, f)aerosol}{(X / \mathrm{Re}\, f \,/\, source}$$

where X is the element aerosol concentration and Ref is the concentration of the reference element choosen for the EF calculation. The most common reference element for the marine enrichment factor is Na, the indicator elements used for the crustal enrichment factor calculations have been Si, Al or Ti (Rahn, 1976). Reference elements are selected such that they have high concentration in the ~~source~~ to which they refer to (e.g. Al in soil, Na in sea water).

Elements with crustal / marine EF close to unity are likely to have the crust / sea salts as their main source. These are called non enriched elements whereas elements with EF from both sources greater than unity (usually > 10) are called enriched elements and usually have another source (Rahn, 1976). In the present studies EFs crust (EF_c) were calculated relative to Al as the reference element using the elemental composition of upper crust reported by Wedepohl (1995) whereas EFs seawater (EF_s) were calculated relative to Na as the reference element using the bulk sea water composition reported by (Riley and Chester, 1975). The precise ratio of one element to the reference element will vary from source area to source area and an artifact also may arise from using wrong reference material (Rahn, 1976).

Usually, an arbitrary EF value of < 10 is accepted to indicate that an element in the aerosol has a dominant crustal or marine source and these elements are classed as the “non-enriched elements” (NEEs). In contrast, an EF value of >10 is considered to indicate that a significant proportion of an element has a non-crustal or non-marine source and would be termed as "anomalously enriched elements" (AEEs).

The seasonal mean of EF_c based on all the samples collected are listed in Table 3.5.

Table 3.5. Seasonal mean of the Crustal Enrichment Factor (EF_c).

	Annual	Winter	Summer	Spring-fall
Al	1.0	1.0	1.0	1.0
Fe	2.0	2.5	2.2	1.8
Mn	2.6	3.6	2.7	2.0
Ca	14.7	21.4	10.2	14.5
Mg	17.7	29.4	10.2	18.5
Zn	52.8	85.7	40.1	43.8

From the table it is clear that the elements Fe and Mn have mean $EF_c < 10$ and they are therefore considered to be non-enriched elements indicating a predominantly crustal source. In contrast the elements Ca, Mg and Zn have mean $EF_c > 10$ which indicating a mixture of sources. Ca and Mg are enriched elements in the local crust so that they showed enrichment relative to average crustal composition. Enrichment factors are a useful method of rationalising the data, but they must be interpreted cautiously. One should not rely only on data from mean crustal or sea water composition when estimating crustal or sea water fractions for aerosol elements because the mean values do not take into account regional mineralogical variabilities in precursor material. For example small enrichment of Ca and Mg at this site for the current study is a result of soil derived from predominantly a carbonate geological area around the sampling site or long-range transported mineral dust which is also enriched in $CaCO_3$. Therefore it can be stated that the EF_c values of Ca and Mg which are >10 are not necessarily enrichments , but artifacts of applying the incorrect reference material. The majority of EF values presented in the literature adopt average elemental composition rather than local crust. These were also chosen in calculating EF_c in the current study for the following reasons: (1) most aerosol analyses are not accompanied by corresponding analyses of local soil; (2) inter-worker standardization of enrichment factor calculation are easier when only a handful of global reference materials are used; and (3) use of a constant reference material by each worker makes all of enrichment factors comparable with the existing data in the literature. EF do, however, allow an internal comparative study to be made of the relative contributions of contrasting sources to elements in an aerosol population.

Moderate or high enrichment factors in polluted areas are attributable almost exclusively to anthropogenic sources. Moderate enrichments in rural area (as Erdemli site) may be from (a) natural soils which are enriched in certain elements relative to average crust (e.g. Ca and Mg in Erdemli site), or (b) the action of unrecognized natural sources such as forest fires, or vegetation. One of the biggest limitations on the use of aerosol-crust enrichment factors is due to the fact that the true crustal precursors to the aerosol, i.e., the true crustal reference material composition, is not yet known.

Rahn (1976) suggested a logarithmic relationship where the enrichment factor of an element is plotted against the concentration of the reference crustal element. The use of the logarithmic scale is useful since the data are not uniformly distributed and the concentration range is too great to be accomodated on a linear scale. From such diagrams (see Figure 3.14) one can see how the EF of a given element varies with the concentration of crustal material.

EF plots are useful tools to distinguish the natural and anthropogenic sources of slightly enriched elements. The EF values of elements only associated with crustal material do not change with changes in the aerosol Al concentrations and indicates a horizontal line around 1 in the EF diagram. Whereas, non-crustal elements are independent of the Al concentration. Therefore, EF values of non-crustal elements decrease with increasing Al concentration. An example of the EF_c diagrams are presented in Figure 3.14.

For the non-enriched element, Rahn (1976) suggested that in the EF diagram their points will fall along a line parellel to the x-axis (see EF diagrams of Fe and Mn in Figure 3.14). For elements in some samples the $EF_c < 1$, this is possibly due to the uncertainty in Mn and Al measurements or the use of the incorrect reference material.

It can be seen from EF_c diagram of Mg that the EF increases as the concentration of Al decreases and vice versa. It is apparent from the diagram that at the Erdemli site, Mg acts as an enriched element with respect to the crust due to large marine source. The Mg concentrations at low Al concentrations are mainly derived from sea salt production whilst at high Al concentration the source is crustal represented by the lower right hand area of the figure.

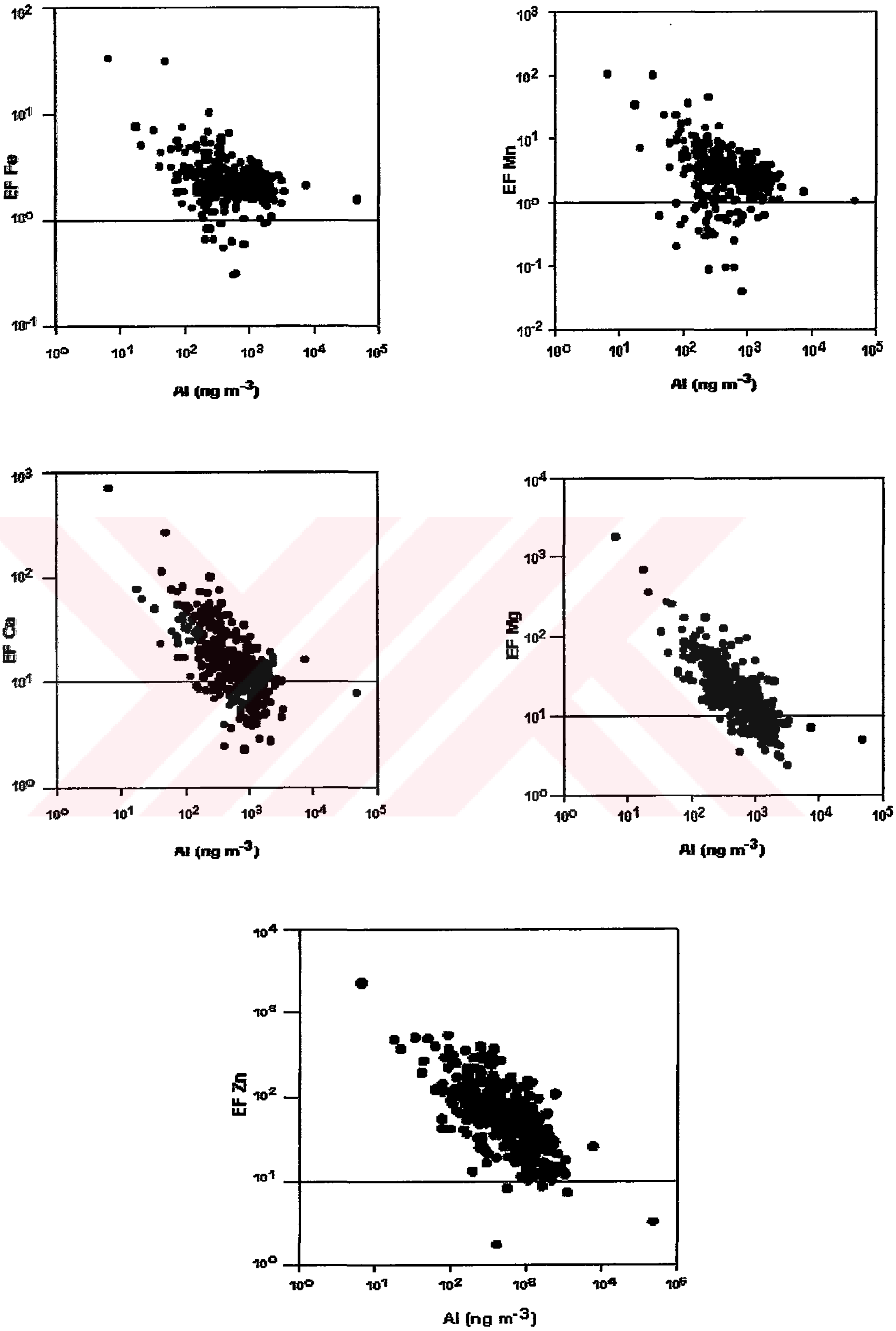
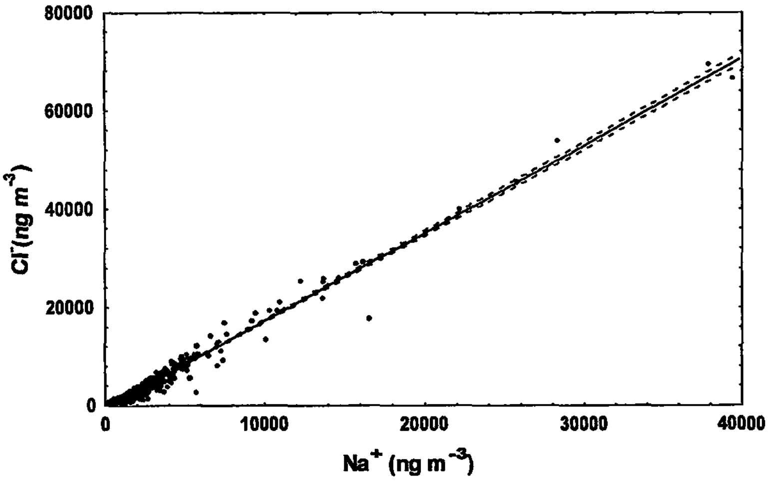


Figure 3.14. EF$_c$ – Al diagrams of elements.

Marine enrichment factors (EF_m) are frequently used at sites where sea salt contributes to the major fraction of the total particle mass. Marine enrichment factors are useful tool to assess the sea salt contribution to observed concentrations of elements. The sea water composition given by Riley and Chester(1975) and Na^+ as the reference element were used in the calculations.

Na and Cl are the major elements in sea salt. Na is also a significant element in soils while Cl is emitted during vegetation fires (Andreae *et al.*, 1998). Kubilay (1996) has indicated that crustal influence on observed sodium concentration can be significant in the Eastern Mediterranean. The contribution of crustal material on a measured sodium concentration was assessed to be approximately 22% of the total concentration. Cl and Br however are generally poor reference elements of sea water. Br has an anthropogenic source which originates from motor vehicles. Cl is a non-conservative element since it reacts with acid species (both inorganic and organic acids) in the atmosphere [$Cl^- + H^+ \rightarrow HCl\ (g)$], due to this reaction it evaporates as HCl acid and Cl is depleted from the particulate form. Mihalopoulos *et al.* (1997) have observed Cl evaporation in the aerosol composition at Finokalia (coastal station located at Eastern Mediterranean). The extent of chloride depletion in the coarse mode decreases with increasing particle size (Zuang *et al.*, 1999). Therefore, further investigations are needed to clarify this phenomenon at Erdemli.

In order to identify any relationship between Na and Cl a linear regression was performed within the 95% confidence limits (Figure 3.15). It may be concluded from Fig. that chloride is strongly associated with sodium. In addition, the slope of the regression line is identical to that of the [Cl^-] / [Na^+] ratio for bulk sea water (1.8), indicating the common origin, sea salts.



$[Cl^-] = 1.78\ [Na^+] - 471; r = 0.99$

Figure 3.15. Relationship between Cl^- and Na^+ derived from two and half years of aerosol samples.

The Cl/Na ratio in the daily collected samples is illustrated in Figure 3.16. Although, the slope of the regression between Na and Cl is 1.78 in all aerosol samples, it is apparent, especially during summer time, that this ratio decreases below the sea water ratio [Cl] / [Na] = 1.8. As mentioned before, this can be attributed to the evaporation of Cl or excess Na which originates from crustal material. In some cases the Cl^-/Na^+ ratio is above that of the bulk sea water ratio.

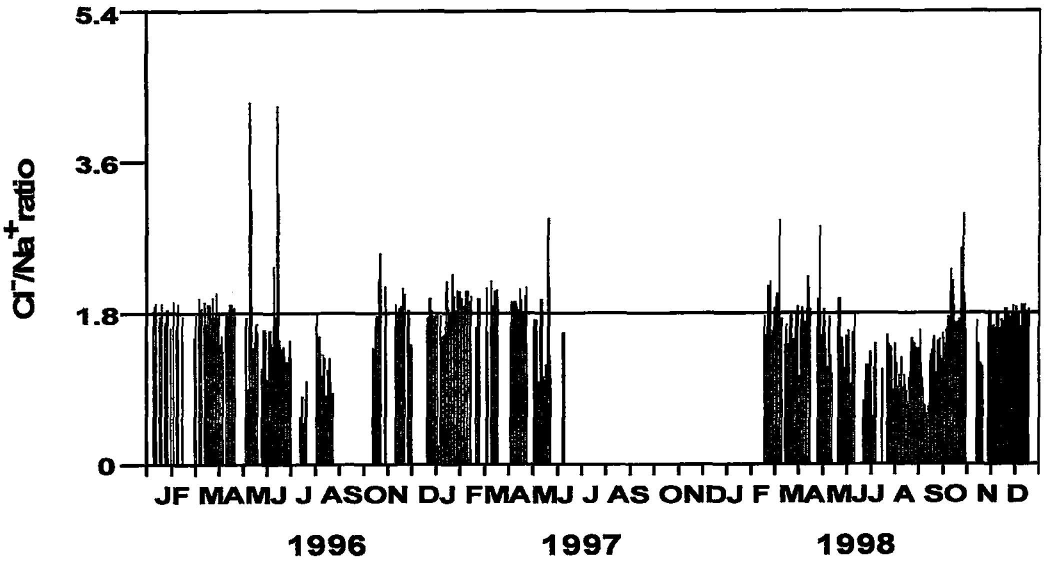


Figure 3.16. Cl^-/Na^+ ratio derived from 2 and half years of daily collected aerosol filter samples.

Observed higher ratios might be affected by anthropogenic Cl, which originates from activities such as vegetation burning.

Approximately 28% of the rain samples (87) were found to be acidic at Erdemli station (Özsoy and Saydam, 2000). Similarly, Singer *et al.* (1993) found 40% of the rain events (samples collected on Mt Carmel,Israel, Eastern Mediterranean) to be strongly acidic. Same authors, indicated that $SO_4^{=}$ is responsible for the acidity of the rainwater. It is clearly seen from Fig. that the Cl/Na ratio decrease with increasing nss-$SO_4^{=}$ concentration. This negative relationship between nss-$SO_4^{=}$ and Cl/Na ratio suggests that similar evaporation of Cl from sea salts is the reason for the observed small Cl/Na ratios especially during the summer. Additionally, linear regressions were performed between the Cl/Na ratio and acid species (both inorganic and organic acid) namely nss-$SO_4^{=}$, NO_3^-,and MSA^-. Negative correlation coefficients were found -0.66,-0.39,and -0.49, respectively.

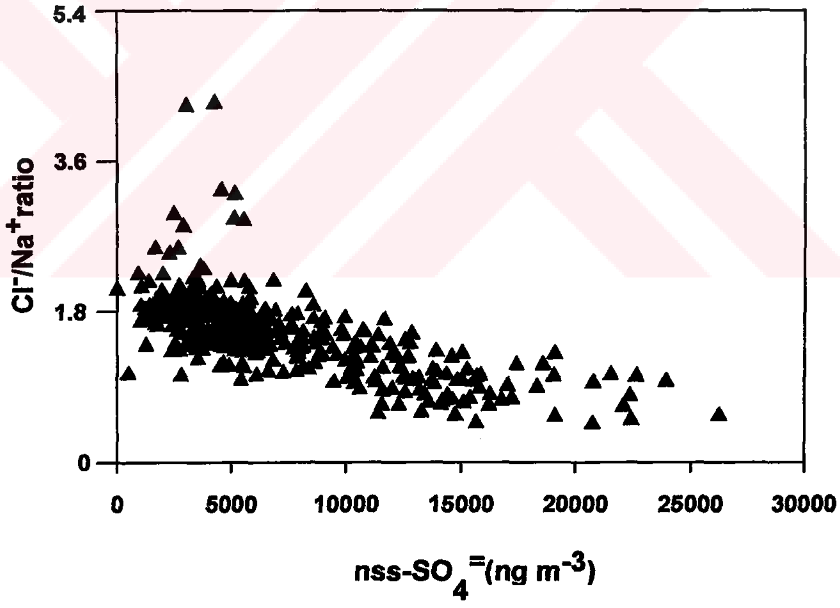


Figure 3.17. Relationship between Cl^-/Na^+ ratio and nss-$SO_4^{=}$.

As alluded to previously, EF diagrams are useful tools to distinguish between the importance of natural and anthropogenic sources, for the slightly enriched elements. The relationship between Na (reference element) and element of interest in an aerosol can be expressed in the form of an EF diagram, in which the enrichment factors are plotted against the concentration of Na in the aerosol population on a log-log scale (Figure 3.18). The EF_m of purely marine elements do not change with changes in the Na concentrations (since concentrations of both the marine element and Na change similarly with increasing and decreasing loading of sea salt particles in the atmosphere, EF_m will remain the same) resulting in a horizontal line on the EF diagram. In contrast, however the concentrations of non-sea-salt derived elements are independent of the Na concentrations in the aerosol population. Hence, EF_m values of these elements decrease linearly with increasing Na concentration.

Marine enrichment factors of ion species at Erdemli station are given in Table 3.6. Marine enrichment values for Cl, Br, Mg and K are about unity indicating that sea water is the major source for these elements (NEEs). As seen from Table Mg and Br ions indicate no distinct enrichment values in all seasons. However, enrichment factors for Cl decreases to 0.7 and EF_m value of K increases upto 5.1 in the summer period. Based on EF diagram, Cl exhibits a depletion at Na concentration around 1000 ng m^{-3}, as stated before, probably due to evaporation of Cl reacting with acidic species. The EF diagram of K indicates non-sea-salt contributions becoming important with decreasing Na concentrations which might be due to the contribution of both crustal source and of the burning of land biota. Higher summer EF of K can be attributed to the burning of land biota, which forest fires are typical during dry and hot summer period in the Mediterranean region. The EF diagram of Mg depicts no distinct enrichment from sea salts, except on occasions. These occasions may be attributed to contribution made by crustal material.

Table 3.6. Marine Enrichment Factors, [annual,(winter, summer and transitional seasons)]

	Annual	Winter	Summer	Spring-fall
Na^+	1.0	1.0	1.0	1.0
Cl^-	0.9	1.0	0.7	0.9
Br^-	1.2	1.2	1.2	1.3
$SO_4^=$	13.5	8.5	21.2	12.9
K^+	3.7	3.1	5.1	3.3
Mg^{2+}	1.5	1.4	1.6	1.5
Ca^{2+}	32.2	23.5	44.6	31.6

According to the EF values of sulfate and calcium, these constituents are referred to as anomalously enriched elements (AAEs). Annual EF values of sulfate and calcium are 13.5 and 32.2, respectively. EF values of these elements show distinct seasonality. Enrichment factors of these elements indicated lowest values in the winter, and reach their highest values in the summer period. During the

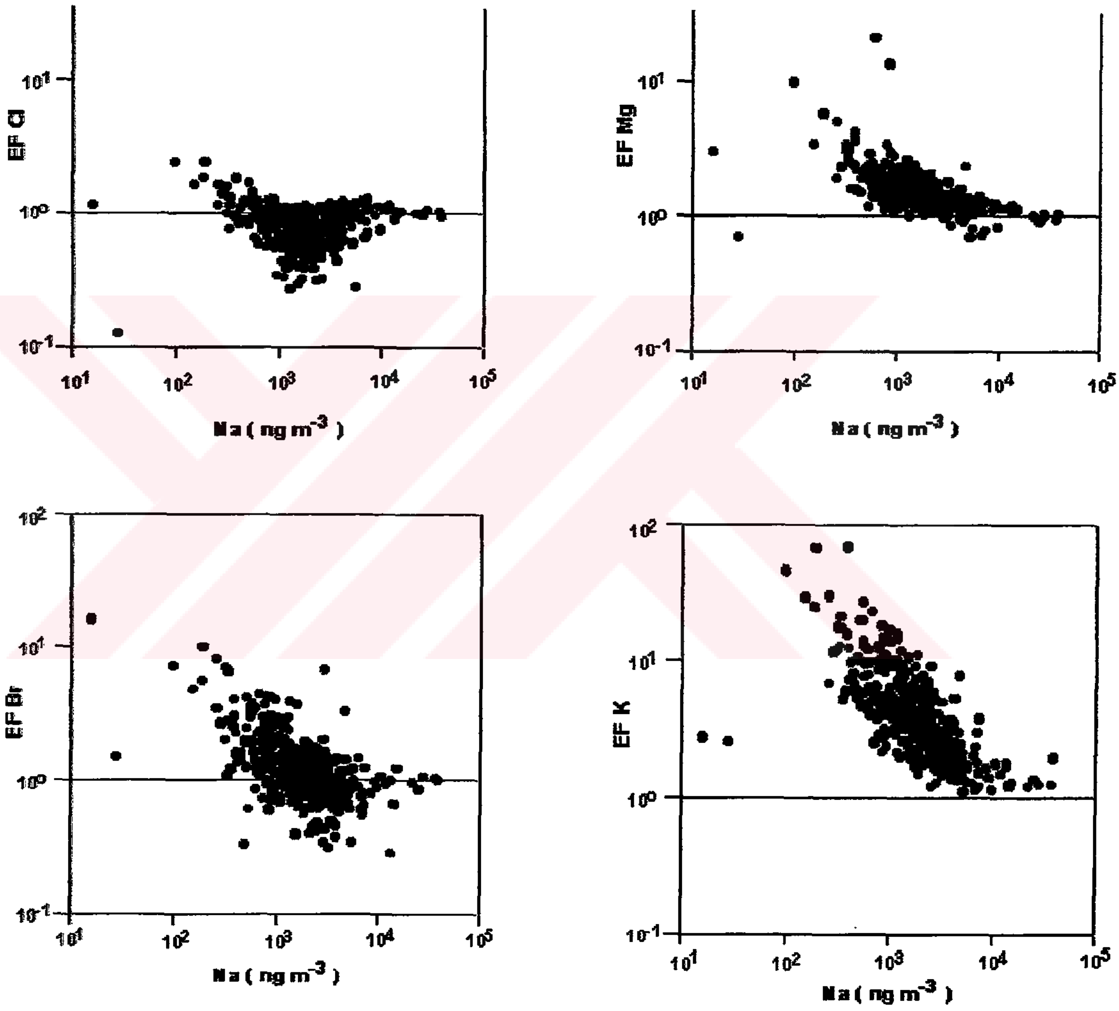


Figure 3.18. EF_m – Na diagrams of the aerosol water soluble species.

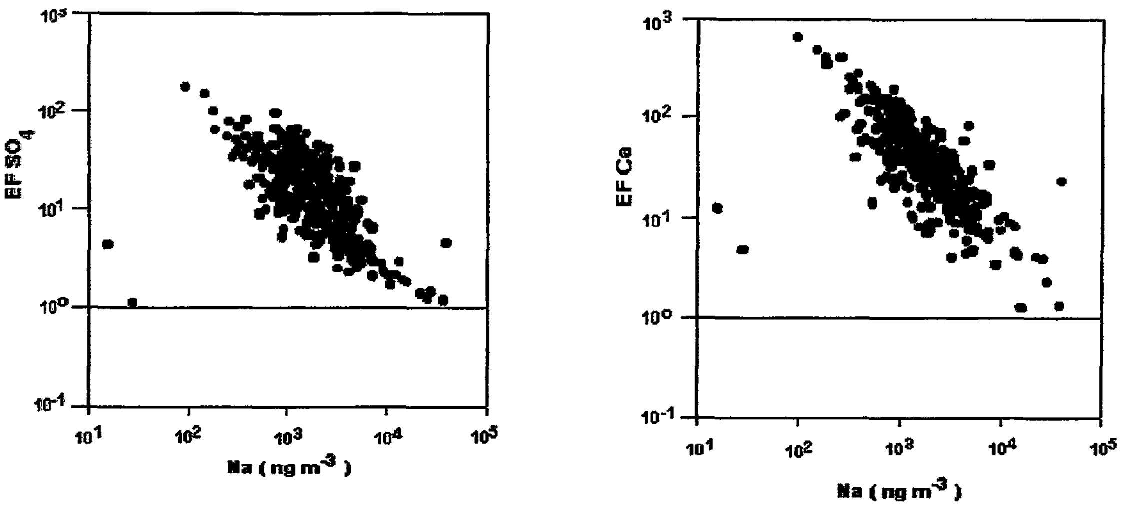


Figure 3.18. Continued.

3.4.2. Correlations Between Aerosol Chemical Constituent Concentrations

Correlations between variables indicate the degree to which they vary together. In aerosol data sets, a high correlation coefficient between any two species indicates one or more of the following (i) similar sources for the two species, (ii) similar generation mechanism or (iii) similar transport patterns.

The significance of the correlation coefficient depends on the number in the population. Since, for the current dataset, the number of the sample is very high, even a small correlation coefficient would be statistically significant. Generally, no correlation(0), weak(0-0.5), strong correlation (0.8-1), perfect correlation (1) terms are used during the interpretation of correlation coefficients for the current dataset.

The correlation coefficients (r) between the measured elements are depicted in Table 3.7. The crustal indicator, Al exhibits a strong correlation ($p<0.0001$) with Fe and is moderately correlated with Mn, Mg, Ca, K^+(also nss-K^+) and Ca^{2+}. Correlation coefficients (0.50) of Al with Zn ,which is an athropogenic element, is not surprising. As will be shown later, aerosol Zn behaves like crustal element during outbreaks of Saharan dust. Additionally the significant correlation between a NEE and an AEE may be due to the greater influence on the variability of aerosol concentrations of removal processes rather than elemental source. Removal processes are common to all aerosol associated constitutents irrespective of their source.

As expected, marine elements (Cl^-, Br^-, Na^+ and Mg^{2+}, $p<0.0001$) have strong correlation coefficient between each other, which indicates they are mainly derived from sea salt.

The anthropogenically derived ion nss-$SO_4^=$ is strongly correlated with NO_3^- and moderately correlated with MSA. Therefore it can be suggested that the observed concentration of the nss-$SO_4^=$ is associated with anthropogenic and bio-sulfur emissions. In addition, nitrate and non sea salt sulfate are moderately correlated with crustal elements, probably due to heterogeneous reactions occuring on aerosol surfaces or some fraction of these ions being derived from crustal dust. NH_4^+ is moderately correlated with nss-$SO_4^=$ and NO_3^-. Cl^- has a negative correlation coefficient with MSA and nss-$SO_4^=$ may reflect its displacement during sea salt reactions with these acidic species as stated before. Similar to crustal and marine elements K^+ is also modaretely correlated with anthropogenic species, indication of additional natural derived emissions possibly originated from the burning of biomass.

It is worthwhile to note that interpretation of correlation coefficients in rural data sets are substantially different from the interpretation of correlation coefficients derived from urban data sets. In urban aerosol studies, particles emitted from sources are immediatelycollected at the sampling site. Thus any correlations between species are inevitably due to similarities of their sources. However in rural sites aerosols are imported from long distance, during long range transport different air masses might be mixed and cause relative dilution or enrichment of elements and chemical reactions such as heterogeneous reactions between mineral particles and acidic species may occur. Consequently, in rural studies, strong correlation coefficients between measured variables do not necessarily indicate similar sources. Factor analysis offers a more versatile statistical toll to distinguish between possible sources.

Table 3.7. Relationships between the species in the atmospheric aerosol composition

	Al	Fe	Zn	Mn	Mg	Ca	Cl^-	Br^-	NO_3^-	$SO_4^=$	$C_2O_4^=$	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	MSA^-	$nssK^+$	$nssCa^{2+}$	NSSS
Al	1.00																			
Fe	0.88	1.00																		
Zn	0.50	0.62	1.00																	
Mn	0.63	0.74	0.52	1.00																
Mg	0.49	0.56	0.40	0.49	1.00															
Ca	0.64	0.74	0.53	0.55	0.50	1.00														
Cl^-	0.04	0.08	-0.01	0.04	0.45	0.05	1.00													
Br^-	0.21	0.28	0.17	0.20	0.51	0.27	0.82	1.00												
NO_3^-	0.54	0.64	0.51	0.49	0.24	0.47	0.00	0.10	1.00											
$SO_4^=$	0.46	0.55	0.47	0.42	0.26	0.28	0.14	0.25	0.79	1.00										
$C_2O_4^=$	0.06	0.12	0.08	0.14	0.12	0.18	0.11	0.05	0.18	0.06	1.00									
Na^+	0.10	0.16	0.07	0.11	0.42	0.05	0.95	0.80	0.13	0.34	0.06	1.00								
NH_4^+	0.38	0.44	0.40	0.35	0.06	0.31	-0.23	-0.12	0.69	0.69	0.04	-0.10	1.00							
K^+	0.53	0.65	0.46	0.54	0.58	0.51	0.52	0.66	0.57	0.62	0.11	0.59	0.30	1.00						
Mg^{2+}	0.28	0.34	0.17	0.27	0.52	0.18	0.87	0.78	0.26	0.47	0.08	0.92	0.01	0.70	1.00					
Ca^{2+}	0.68	0.78	0.56	0.57	0.43	0.67	0.12	0.26	0.82	0.72	0.19	0.20	0.64	0.70	0.36	1.00				
MSA^-	0.49	0.47	0.21	0.33	0.12	0.18	-0.16	-0.10	0.61	0.64	0.01	0.03	0.55	0.24	0.12	0.45	1.00			
$nssK^+$	0.61	0.72	0.58	0.62	0.39	0.60	0.01	0.25	0.66	0.59	0.07	0.09	0.50	0.81	0.25	0.76	0.32	1.00		
$nssCa^{2+}$	0.66	0.75	0.56	0.54	0.35	0.65	0.01	0.13	0.81	0.68	0.17	0.09	0.68	0.60	0.24	0.98	0.46	0.73	1.00	
NSSS*	0.45	0.53	0.48	0.40	0.13	0.27	-0.10	0.05	0.81	0.96	0.05	0.12	0.77	0.47	0.25	0.71	0.69	0.58	0.71	1.00

*NSSS is symbolizing the non sea salt sulfate.

3.4.3. The application of Factor Analysis on the Current Aerosol Chemical Constituent Dataset

The main applications of factor analyses techniques are: to reduce the number of variables and to detect structure in the relationship between variables. Combining two correlated variables into one factor is the basic idea of factor analyses. In this study 'Statistica' program package was used for the factor analysis. Interpretation of the common factors is facilitated by performing varimax rotation. Statistica package program offers two extraction method for factors: Kaiser criterion (eigenvalues larger than 1 are retained) and graphical scree test of Cattel (the place where the smooth decrease of eigenvalues appears). Although factors with eigenvalues less than 1 make no significant contribution to the variance of the data they can be retained if they are physically interpretable.

In atmospheric studies factor anlysis is a powerful technique for characterising aerosols with respect to their sources and may quantify the influence of different sources. However, factor analysis has the disadvantage in that there is no obvious way of obtaining the relative concentrations of the elements that make up each components. It indicates how much of the variance of an element's concentration can be attributed to each factor, but says nothing directly about contributions to its average absolute concentration (Hopke *et al.*, 1976).

The results of varimax-rotated factor anaysis are given in Table 3.8. Only factor loadings larger than 0.30 were included in the table, smaller loadings (< 0.30) were considered to be 'insignificant'.

The data can be interpreted on the basis of three common factors accounting for 70.4% of the total variance in the system. The first factor can be identified as crustal factor, because it included high loadings of crustal elements, namely Al, Fe, Ca and moderate loadings of Mn, Mg, Ca^{2+} and K^+. The crustal factor accounts for 34.3% of the total variance in the system.

The second factor has high loadings of Cl^-, Br^-, Na^+, Mg^{2+} and moderate loadings of Mg, K^+. Factor 2 is strongly dependent on the concentrations of Cl^-, Br^-, Na^+ and Mg^{2+} and is attributed to the sea-salts components in the Erdemli aerosol population. Therefore, this factor is identified as the marine factor and accounts for a further 27.9% of the total variance.

Factor 3 is highly loaded in NO_3^-, nss-$SO_4^=$ and NH_4^+ and moderately loaded with Ca^{2+} and MSA^-. Since factor 3 is strongly dependent on the concentrations of NO_3^- and nss-$SO_4^=$, this factor appears to represent the by-products of the oxidation of SO_2 and NO_x (via homogeneous and heterogeneous reactions), which are from fossil fuel combustion including possible biomass burning. This factor explains 8.3% of the variance. Factor 3 can be identified as aerosols derived from anthropogenic emissions (combustion processes).

The first two factors (crustal and marine factors) accounts for 62.5% of the total variance in the system. Kubilay (1996) has previously argued that the aerosol composition over the Cilician Basen is dominated by natural emissions rather than anthropogenic emissions. Results obtained from factor analysis supports this argument.

Table 3.8. Factor loadings of concentrations of different elements of aerosol (Varimax rotated factor pattern)

Variable	Factor 1	Factor 2	Factor 3	Communality
Al	0.84	-	-	0.81
Fe	0.89	-	0.36	0.90
Zn	0.54	-	0.38	0.54
Mn	0.69	-	-	0.59
Mg	0.58	0.45	-	0.58
Ca	0.78	-	-	0.69
Cl^-	-	0.97	-	0.96
Br^-	-	0.83	-	0.78
NO_3^-	0.39	-	0.81	0.81
nss-$SO_4^=$	-	-	0.92	0.84
$C_2O_4^=$	-	-	-	0.14
Na^+	-	0.98	-	0.96
NH_4^+	-	-	0.79	0.67
K^+	0.51	0.59	0.38	0.79
Mg^{2+}	-	0.92	-	0.91
Ca^{2+}	0.61	-	0.68	0.86
MSA^-	-	-	0.63	0.70
Eigenvalue	5.83	4.75	1.42	
%Variance	34.3	27.9	8.3	70.4
Probable Source	Crustal	Marine	Combustion	

3.4.4. Air Mass Back Trajectories and Their Relation to Biogeochemical Tracers

In general aerosol populations in the eastern Mediterranean basin result from the superimposition of a marine component (sea spray generated from the Mediterranean sea itself), a mineral dust component (outbreaks of Saharan dust, but also local dust resuspension), and an anthropogenic component (local and long-range transported contaminants). Local anthropogenic sources are situated along the Mediterranean Sea, mainly (especially power plants for SO_2 emissions) along the Turkish and Israeli coasts, but also the highly populated and industrialized inland areas of Turkey, Israeli and Greece. Distant sources from Europe and the former Soviet Union also play a contributing role (Foner and Ganor, 1992; Ganor, 1994; Kubilay and Saydam, 1995; Luria *et al.*, 1996; Mihalopoulos *et al.*, 1997; Güllü *et al.*, 1998; Kallos *et al.*, 1998; Özsoy *et al.*, 2000; Ganor *et al.*, 2000).

Results from the current study together with the available literature information reveal that the chemical composition of the eastern Mediterranean aerosols presents two important features. One is the high amount of crustal influence as exemplified by anomolous peaks in time series data or/and high average concentrations of crustal derived elements (Al, Fe, Ca, Si). The Mediterranean is bordered on its southern and eastern shores by arid and desert regions, including the Sahara and Middle Eastern deserts. These deserts act as a source of crust dominated aerosols, which is transported largely in the form of non-continuous dust “pulses”. In the last 20 years, a large effort has been made toward the understanding of African dust transport over the Mediterranean Sea (Ganor and Mamane, 1982; Chester *et al.*, 1984; Alpert and Ziv, 1989; Bergametti *et al.*, 1989b; .Dulac *et al.*, 1987; 1992, 1996; Ganor *et al.*, 1991; Alpert and Ganor, 1993; Ganor, 1991; 1994; Kubilay and Saydam, 1995; Kubilay *et al.*, 1994; 1997; 2000; Chester *et al.*, 1996; Moulin *et al.*, 1998; Hamonou *et al.*, 1999; Özsoy *et al.*, in press).

The other important feature of the chemical composition of the eastern Mediterranean aerosols was that the peak and average concentrations of particulate sulfate where the highest reported worldwide compared to those measured at various surface sites and from aircrafts (Bergametti *et al.*, 1989a; Luria *et al.*, 1989; 1996; Mihalopoulos *et al.*, 1997; . Formenti, 2000; Formenti *et al.*, 2000; Özsoy *et al.*, 2000; Ganor *et al.*, 2000). The concentrations show a clear seasonal cycle with highest measured levels during the summer, when photochemical activity is at its over the background ratio, that a particulate Al concentration > 1000 ng m^{-} of air represents the input of desert-derived dust "pulse" at any site in the Mediterranean Sea. In their study air mass back trajectory information was lacking which could result in misidentification of the events having aerosol Al concentration > 1000 ng m^{-} ^{3} due to local re-suspension of soil as Saharan dust outbreak. This is particularly the case in summer, when wet removal is practically absent, local resuspension of dust cause aerosol Al concentration to become ≥1000 ng m^{-3} (Kubilay and Saydam, 1995). It has been well illustrated that the identification of Saharan dust outbreaks to the region is possible only by utilizing geochemical tracers of mineral dust (e.g. Al, Si) complemented with air mass back trajectories and satellite images (Bergametti *et al.*, 1989b; Martin *et al.*, 1990; Dulac *et al.*, 1992; Kubilay *et al.*, 2000). Similarly, Dulac *et al.* (1987) selected a lower particulate Al concentration (> 500 ng m^{-3}) to separate crust-enriched and background populations in shipboard collected samples across the western Mediterranean. Kubilay *et al.* (2000) selected much higher particulate Al concentration (> 2500 ng m^{-3}) as a threshold to identify major dust events at the Erdemli site. During the transitional seasons of the sampling period (from August 1991 to December 1992) they identified 17 pulses of high dust inputs.

For precipitation, pH values were also used to improve the distinction between non-Saharan and Saharan events, since alkalinisation effect of Saharan dust in rain has been well described , both in Erdemli (Özsoy and Saydam, 2000) and elsewhere (Loye-Pilot *et al.*, 1986; Mamane *et al.*, 1987b; Glavas, 1988; Roda *et al.*, 1993; Le Bolloch and Guerzoni, 1995; Avila *et al.*, 1997). Precipitation in the eastern Mediterranean occurs mostly during the months of November through to April, and is associated with stormy weather. During the winter season, low pressure systems moving along the northern part of the Mediterranean raise large amounts of desert particles (mineral dust) into the air as the cold front sweeps over the North

African regions. At the same time the northern section of the front, which lies in the northeast-southwest direction, passes over the Mediterranean Sea and is assocated with stormy weather: Strong winds, haze, thunderstorms and rain. Thus, before the fronts arrive at the East Mediterranean coast, the air is heavily loaded with mineral dust particles originating from the arid regions of the African continent (Ganor and Mamane, 1982). This would explain the higher concentration of soil components (Ca^{+2}, Mg^{+2} , $SO_4^{=}$) and very large sea salt contribution (Na^{+}, Mg^{+2}, K^{+}, Cl^{-}) in the precipitation of the eastern Mediterranean (Israel) site (Mamane, 1987). Not many sites in the world have a reported high soil influence (continental) coupled with strong sea salt impact (maritime). Spring is the most favorable period for the Saharan depressions (or Sharav cyclones) responsible for major dust storms in the eastern Mediterranean (Alpert and Ziv, 1989). Moulin *et al.* (1998) have shown how the seasonality of the Mediterranean mineral dust transport could be explained by the seasonality of the cyclogenesis inside and around the basin.

Outbreaks of Saharan dust into the eastern Mediterranean region are very frequent in winter and spring and minimal during summer (Ganor, 1994; Kubilay and Saydam, 1995; Kubilay *et al.*, 2000; Moulin *et al.*, 1998). To identify the distant mineral dust outbreaks from Sahara during the winter and spring sampling period of the present study a threshold of aerosol Al concentration of about 1000 ng m^{-3} was utilized. The time series plots of the concentrations of the elements (proxy for mineral dust) of Al, Fe and Ca were reproduced in Figure 3.19 for the aerosol samples collected during the months of November through to May. It has been shown that the elements of Mn and Zn in the Mediterranean aerosol have a mixed origin (anthropogenic+crustal) and behave as completely crust originated during outbreaks of Saharan dust (Kubilay and Saydam, 1995; Guieu *et al.*, 1997). Accordingly the time series of Mn and Zn are also included in Figure 3.19. During the period of the sampling 25 African dust events were clearly identified by an abrupt increase in the Al, Fe, Ca and also Mn and Zn concentration in the atmosphere. The average concentrations of the elements for the identified dates were calculated as 1569, 1146, 5532, 17.9 and 27.9 ng m^{-3} for Al, Fe, Ca, Mn and Zn, respectively. On the other hand the average concentrations of the same elements for the remaining samples (where there was no recorded mineral dust transport) were much lower (262, 255, 2212, 6.8 and 17.5 ng m^{-3} for Al, Fe, Ca, Mn and Zn, repectively).

For each sample (one per day), three-dimensional air mass back trajectories were computed to assess the transport of aerosol particles from their source area. The trajectories were computed over a period of 3 days, arriving at 900, 700 and 500 hPa levels, at mid-time of each sample period (12 00 UT). Variable level air mass trajectories provided the means to study the influence of the altitude of transport on the observed aerosol concentrations at the ground level.

For 25 events the computed horizontal trajectories together with their vertical movements (illustrated in the lower panels) were illustrated in Figure 3.20.The origins of the air masses arriving vary with respect to their arriving levels. The shallower trajectories (900 hPa) identified air masses coming from non-Saharan sources, except for the outstanding three cases (Figure 3.20a). On the other hand, the trajectories arriving at the upper barometric levels (700 or 500 hPa) mostly originated from Africa during all peak events except three cases which originated from the Arabian Peninsula (Figure 3.20b). The slope of the vertical component of trajectories shown in the lower panel of Figure 3.20 provides information on prevailing meteorological conditions during the transport.

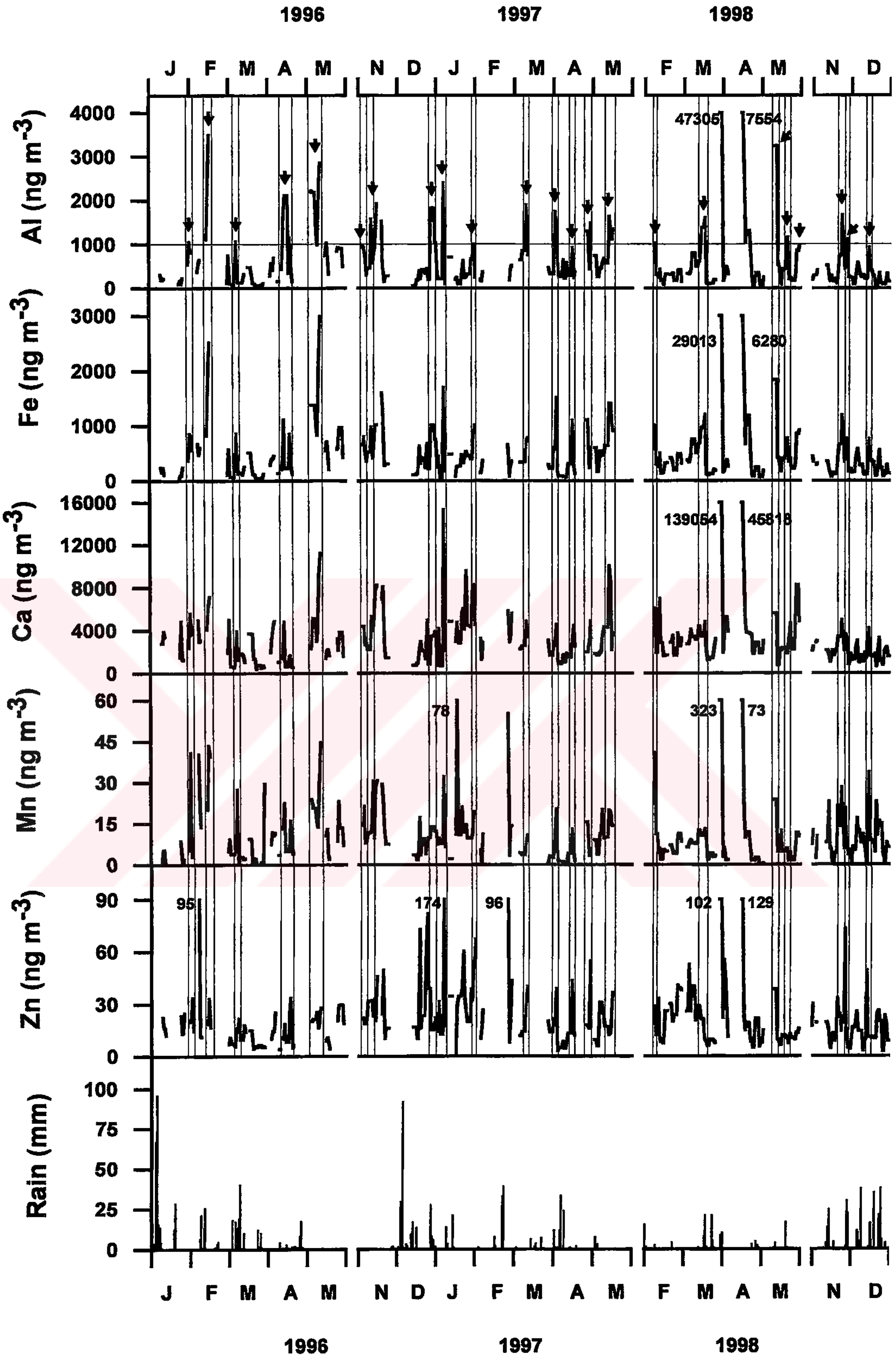
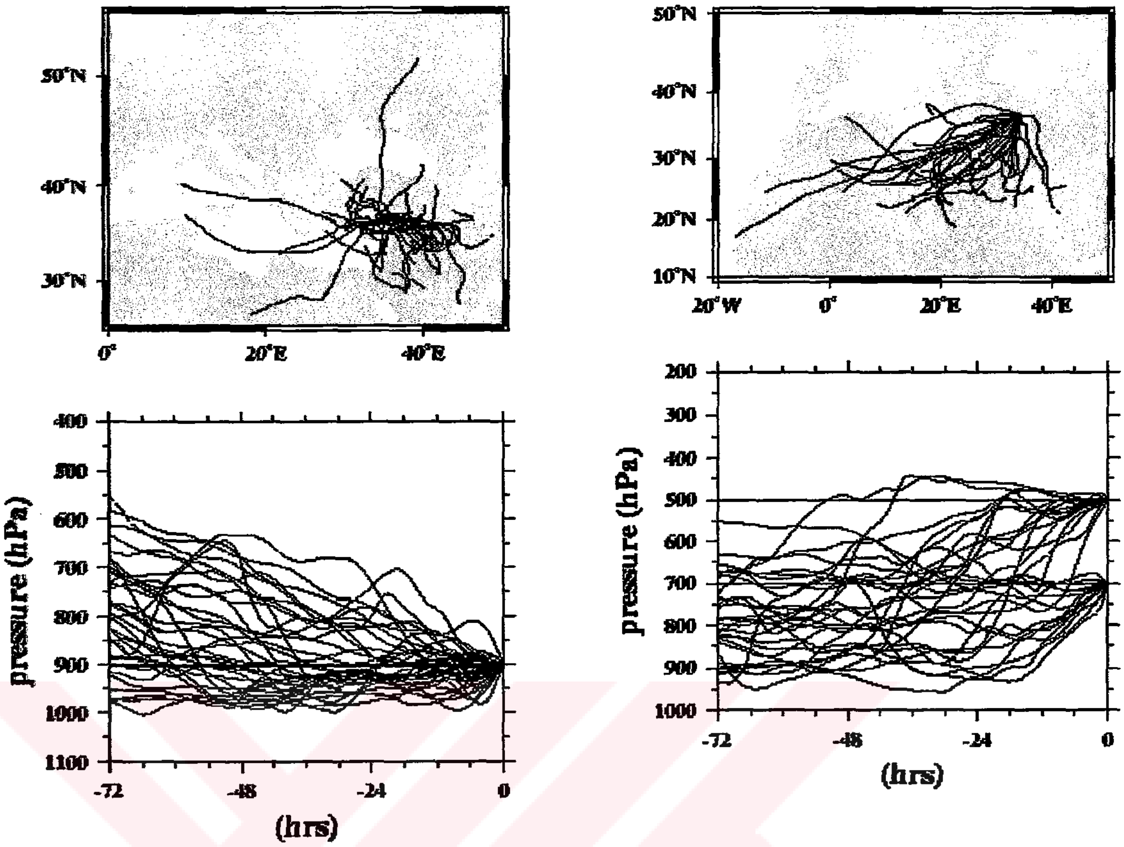


Figure 3.19. Time series concentration of geochemical tracers of mineral dust at Erdemli during the period of November through May. The arrows indicate dust transport from arid regions.



(a) (b)

Figure 3.20. Air-mass back trajectories arriving at Erdemli. Vertical motions along trajectories are given at the lower panels. (a) Trajectories arriving at 900 hPa level. (b) Trajectories arriving at 700 and 500 hPa levels.

There is a significant upward motion for the upper level trajectories and in contrast, a notable downward motion for the lower level trajectories, characterising frontal systems described previously (Bergametti *et al.*, 1989b; Martin *et al.*, 1990; Dulac *et al.*, 1992; Kubilay *et al.*, 2000) in the content of mineral dust transport reaching the western and eastern regions of the Mediterranean. This frontal process induces strong vertical mixing in the frontal zone which leads to the detection of mineral dust at ground level despite its mean transport at higher levels. Dulac *et al.* (1996) have estimated using METEOSAT data an average altitude of the dust layer of 2300 m during a summer transport event in the western Mediterranean region. Moreover, Hamonou *et al.* (1999) have also defined the free tropospheric transport during a Saharan dust event by examining the vertical soundings of the dust outbreak using backscatter lidar system.

The aerosol sulphate levels during summer in the atmosphere over the eastern Mediterranean and coastal stations (Erdemli, Israel and Crete) are much higher than those expected from local anthropogenic sources (Luria *et al.*, 1989; 1996; Mihalopoulos *et al.*, 1997; Ganor *et al.*, 2000; Özsoy *et al.*, 2000). Sulphate levels are comparable to those over industrial areas of continental Europe or the United States. The usual explanation of this phenomenan has been long-range transport of sulphate derived from industrial areas of eastern and central Europe. Marine biogenic production of sulphate from the oxidation of dimethylsulphide (DMS) has been suggested as another possible source of sulfate (Mihalopoulos *et al.*, 1997; Ganor *et al.*, 2000; Özsoy *et al.*, 2000). Although it has been validated by these researchers that there is a definite biogenic component over Israel and eastern Mediterranean, the main source of non-sea salt (nss) sulfate is still attributed to long-range transport from anthropogenic sources. The object of the subsequent section was to investigate the source of anomalously high nss-sulfate concentrations observed at the Erdemli station and also to estimate the relative importance of marine biol ogical emissions.

Sea water has a high sulphate concentration– about 0.3 % by mass- and this “sea salt sulfate” must be accounted for whether aerosols or precipitation samples are collected at coastal stations and/or onboard of the research vessels. Fortunately, the ratios of the major ions, including sulfate, appear to be conserved in the sea salt aerosol production itself. Thus, nss-sulfate resulting from post-production processes can be differentiated from sea salt sulfate by (i) measuring a indicator element for sea salt (sodium), (ii) calculating the amount of sea salt sulfate present based on its ratio to the indicator element in surface sea water, and (iii)subtracting this sea salt fraction from the measured total aerosol concentration of sulfate to yield the non-sea-salt (nss) concentration. The mean contribution of the sea salt sulfate to total sulfate during the sampling period of the present study was calculated from the mean Na and $SO_4^{=}$ concentrations given in Table3.1. The mean sea salt contribution to sulfate level of the Erdemli station is about , 10 %. and show a variation between 1 % to 87 % in the daily time scale. The maximum mean contribution being observed (20 %) during the winter and the minimum sea salt contribution (5 %) being in the summer period.

One of the major sources of nss-sulfate in the marine boundary layer is oxidation of dimethylsulfide (DMS) produced by marine phytoplankton which subsequently diffuses through the sea surface to the atmosphere, where it is oxidized by OH or NO_3 radicals to methane sulfonic acid (MSA) or SO_2. SO_2 undergoes gas to particle conversion to form nss-$SO_4^{=}$ submicrometer aerosol particles or is absorbed into cloudwater and oxidized to $SO_4^{=}$. In the atmosphere, DMS is oxidized on time scales of 1 to 2 days. Most authors assume that it forms SO_2 which is then oxidized to the sulfate aerosol, but may also be directly oxidized to sulfate. A fraction of the DMS (5 to 50 %) becomes MSA. A summary of the processes occuring in the marine boundary layer when DMS escape to the atmosphere is given in Figure.3.21 (taken from Capaldo and Pandis, 1997). The only known source of MSA is the oxidation of DMS, whereas SO_2 and nss-$SO_4^{=}$ have anthropogenic (mainly burning of S-laden fossil fuels) and biogenic sources. If the ratio of MSA to nss-$SO_4^{=}$ was constant in purely marine air masses, MSA would provide a unique biochemical tracer of the amount of nss-$SO_4^{=}$ aerosol attributable to the oxidation product of biogenic DMS emissions from the sea surface (Bates *et al.*, 1992a,b; Huebert *et al.*, 1993 references therein).

The mechanism of DMS conversion to nss-sulfate in the atmosphere is not completely understood. It is a combination of multi-step photochemical reactions likely involving dozens of intermediate species of which only SO_2 and MSA are measured in ambient air (Capaldo and Pandis, 1997; Kerminen *et al.*, 1998).

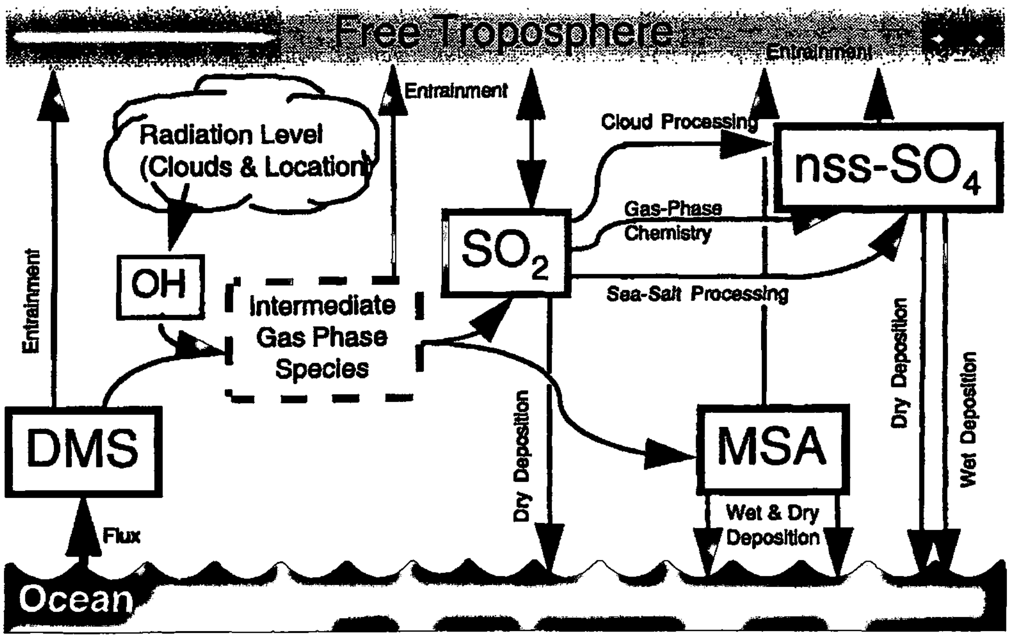


Figure 3.21. Overview of the major processes and species utilized for simulation of the oxidation products of DMS in the marine boundary layer (*after* Capaldo and Pandis, 1997).

It is known that DMS is a hydrolysis product of dimethylsulfoniopropionate (DMSP) a compound produced by phytoplankton, possibly for cellular osmotic regulation or cryoprotection. There have been many studies which have found correlations between DMS and chlorophyll a (chla) concentration or phytoplankton cell concentration. However, there have also been studies where no correlation was found with either phytoplankton cell number or chlorophyll concentration. This has several possible explanations. First, populations of phytoplankton are not homogeneous in the ocean, and second, different species of phytoplankton contain different amounts of DMSP and different concentrations and types of chlorophyll. In most cases wherein there was a high correlation between DMS and chlorophyll concentration, one species of phytoplankton dominated the bloom. Even though DMS is produced by phytoplankton, it is released to the water column by phytoplankton and zooplankton excretion, phytoplankton senescence, zooplankton grazing and possibly by viral infection. In addition, DMS is subject to a number of removal mechanism including bacterial and photochemical degradation, surface outgassing, and downward mixing that vary according to time and place and meteorological conditions. One can therefore not necessarily expect a simple correlation between DMS and phytoplankton cell number or chlorophyll concentration (Kettle *et al.*, 1999 and references therein). It may be seen using the conceptual model of the surface ocean seawater sulfur cycle (Figure 3.22), proposed by Bates *et al.* , 1994) air-sea exchange appears to be only a small sink for oceanic DMS. Instead there exists an active biological sulfur cycle within the ocean surface waters. Owing to the complexity of the sulfur cycle in both sea water and in the marine atmosphere (Figures 3.21 and 3.22) and together with the fact that DMS precursor, DMSP, is higly species specific and the conversion of DMSP to DMS is often associated with the decline of a phytoplankton bloom during the senescence phase. This may also be the case during active zooplankton grazing as opposed to active growth phase. It is appearent, therefore, that reliable parameterization of surface oceanic DMS or/and atmospheric DMS and its precursor MSA with phytoplankton production or biomass will require a better understanding of the processes involved in the cycling of sulfur both in the upper water column and marine atmosphere (Bates *et al.*, 1994 and references therein).

During summer, wet removal is negligible in the eastern Mediterranean and it is minimum in the surrounding European and Asian regions, which are potential sources of anthropogenically derived aerosols (*e.g.* nss-sulfate). As a consequence, the atmospheric lifetime of aerosols is enhanced and can be as long as 10 days (Luria *et al.*, 1996; Kallos *et al.*, 1998). To obtain a first insight in the relationship between air mass transport from distant sources and high non-sea-salt sulfate levels at Erdemli, cases were selected, when air masses advected over Europe before arriving to the sampling station during the summer period (June through to September). As the emission of air pollutants (e.g. SO_2) take place mostly near ground level, the trajectories arriving at Erdemli within the boundary layer have been utilized to examine the impact of long-range transport of distant anthropogenic sulfate sources on the nss-sulfate concentrations.

Dayan *et al.* (1996) has calculated a mean 1500 m height for the boundary layer over the Mediterranean basin. In the present work an average pressure level of 850 hPa have been accepted as the boundary layer height. And the air masses travelling below 850 hPa pressure level assumed to be able to accumulate ground level pollutants and transport them to the receptor regions.

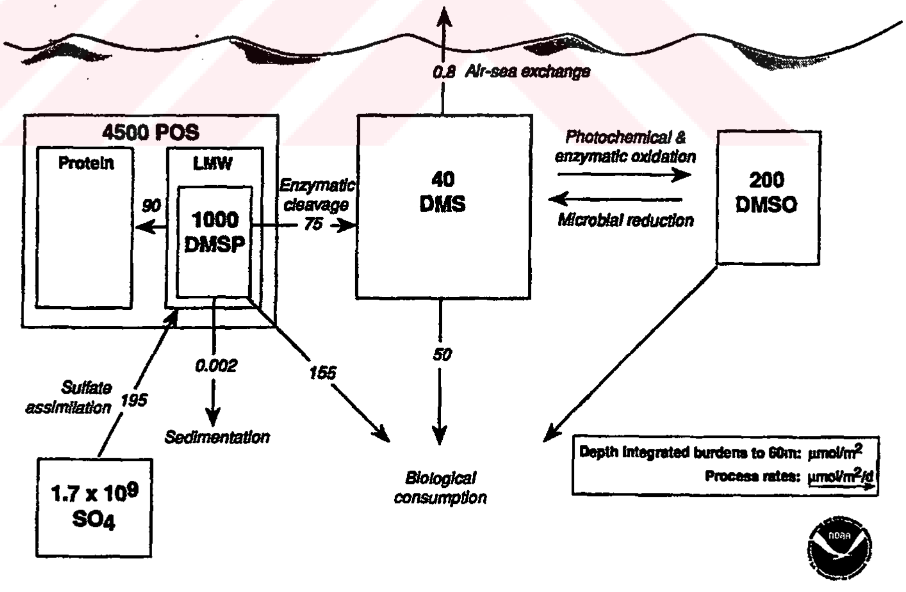
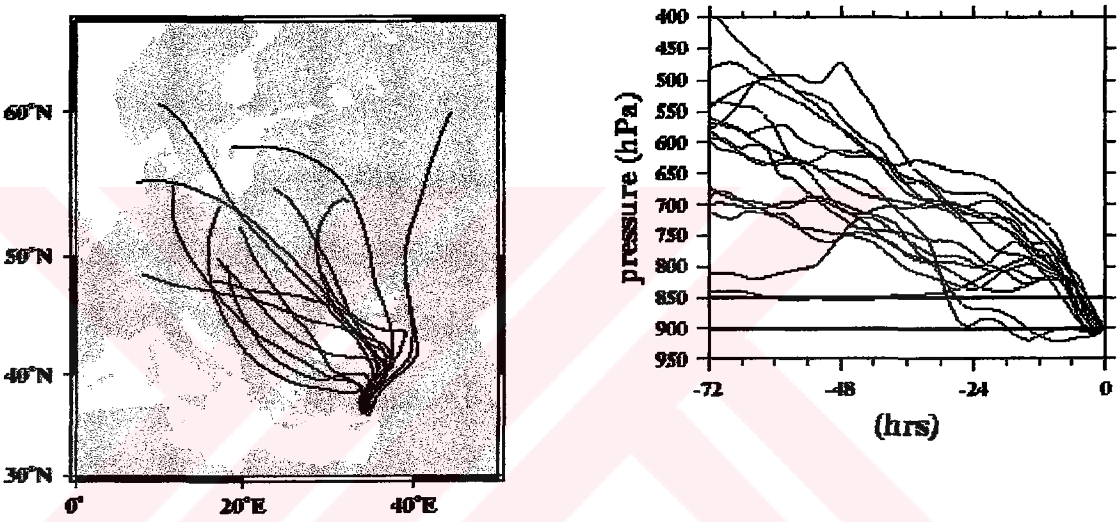


Figure 3.22. The seawater sulfur cycle at the time series station during the third Pacific Sulfur/Stratus Investigation (after Bates *et al.*, 1994).

The air mass back trajectories of the selected cases when air masses advected from Europe and former Soviet Union are presented in Figure 3.23. At the synoptic scale the downward motion for the trajectories arriving at Erdemli (–900 hPa level) were associated with an anticyclonic motion. The air masses were above the boundary layer during their passage over Europe and former Soviet Union (Fig. 3.23b) where they were supposed to pick up ground level pollution (SO_4 particles and/or its gaseous precursor which is SO_2) and advected to the Eastern Mediterranean region. The mean nss-sulfate and MSA concentrations of the days corresponding to air mass back trajectories given in Figure were calculated as 4786 and 43.3 ng m^{-3} respectively.

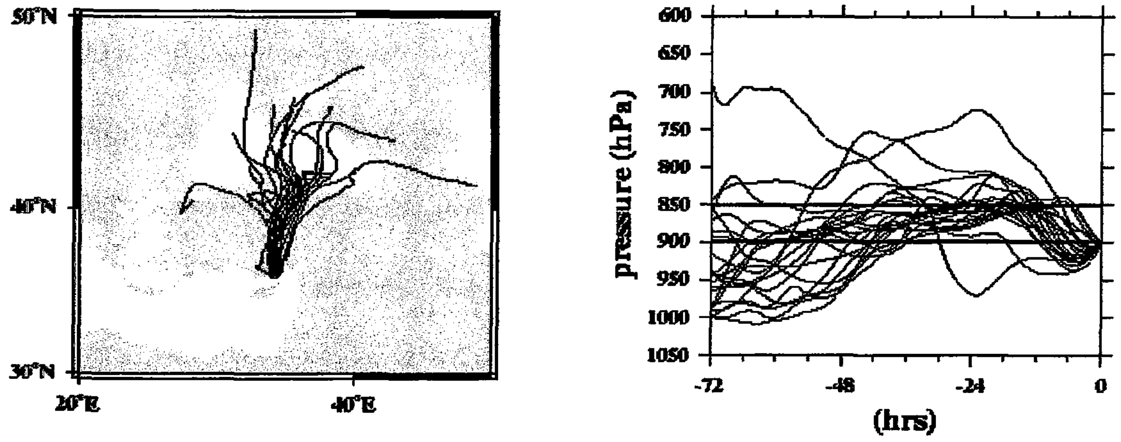


(a) (b)

Figure 3.23. Horizontal (a) and vertical (b) projections of air mass back trajectories originated over Europe and former Soviet Union and arriving at 900 hPa level..

The examples of air mass back trajectories originated from the Black Sea Region are presented in Figure 3.24. The mean nss-sulfate and MSA concentrations (12174 and 97.8 ng m^{-3}) of the corresponding aerosol samples were about two fold higher than the mean concentrations of the samples of which had their air mass origin over Europe and former Soviet Union (see Fig. 3.23)

It can be seen from the vertical projections of air mass back trajectories originated over the Black Sea (Fig. 3.24.b), the air masses started from the surface and were trapped within the boundary layer during the most of their journey time.



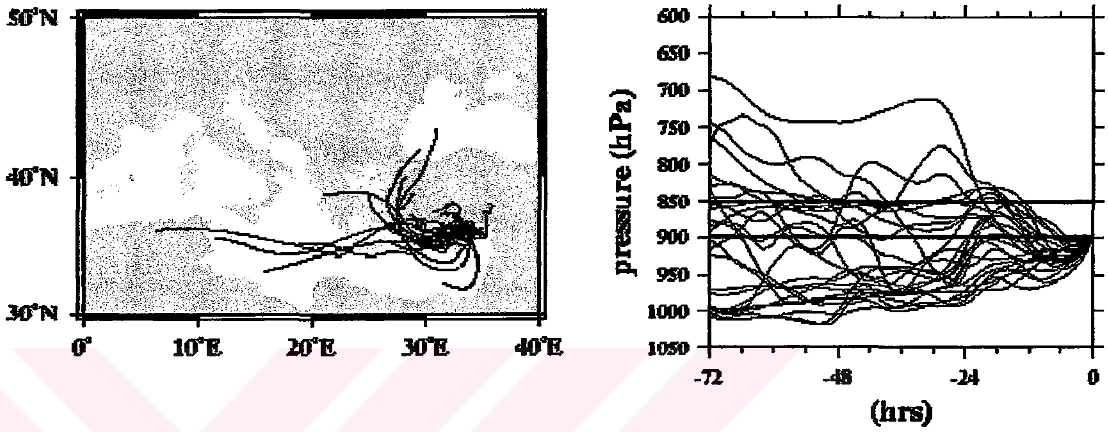
(a) (b)

Figure 3.24. Horizontal and vertical projections of air mass back trajectories originated over the Black Sea and arriving at 900 hPa level.

It has been suggested previously by Özsoy *et al.* (2000) that the relatively lower concentrations of anthropogenic trace elements in Erdemli aerosols, compared with the values in the western Mediterranean basin, would suggest that marine biogenic DMS is the dominant contributor to aerosol nss-sulfate, especially during the summer, when unusually high nss-sulfate levels have been observed. Unfortunately their study did not include simultaneous measurements of MSA, which may have served as a tracer of the biogenic DMS contribution to the nss-$SO_4^{=}$. Based on the analyses of major anionic (NO_3^-, $SO_4^{=}$, Cl^-) concentrations in aerosols, combined with air mass trajectory analysis they have shown an enhanced coccolithophorid bloom in the Black Sea with high levels of nss-$SO_4^{=}$ (July 1992). Biogenic DMS could be the dominant source in aerosols transported from the Black Sea. Despite the absence of the concurrent MSA or atmospheric DMS measurements, by using nitrate concentrations together with EFs as qualitative indicators of anthropogenic influence and by observing coccolithophore blooms taking place in the surrounding marine regions they suggested that the Black Sea is particularly likely to be an important biogenic DMS source on the nss-sulfate budget of the Erdemli aerosols.

The samples which had air mass trajectory sources from the Mediterranean Sea were selected and horizontal and vertical movements of their air mass back trajectories are displayed in Figure 3.25. The mean concentrations of the aerosol nss-sulfate and MSA were 14746 and 109.3 ng m^{-3}, respectively for the selected cases.

The vertical projections of the air masses (Fig. 3.25.b) indicate that air masses originated from the surface levels and were trapped within the marine boundary layer over the Mediterranean Sea before arriving at the sampling station. This type of vertical movements of the air masses suggest that they could be influenced by marine biogenic emission of DMS from the surface waters of the Mediterranean Sea.



(a) (b)

Figure 3.25. Horizontal (a) and vertical (b) projections of air-mass back trajectories originated over the Mediterranean Sea and arriving at 900 hPa.

From the preceding findings it might be suggested that the contribution of distant anthropogenically derived sulfate to the high level of nss-sulfate observed in the summer period could be less significant than the contribution made by natural marine biogenic emission from both the Mediterranean and the Black Seas. Based on the measured MSA concentrations, of the relative contribution of biogenic and anthropogenic sources to sulfate levels measured at the Erdemli station may be estimated. If the molar ratio of MSA/nss-$SO_4^=$ from biogenic source is known then the component of nss-$SO_4^=$ originating from biogenic and anthropogenic sources can be calculated. However, the MSA/ nss-$SO_4^=$ ratio, R, is not constant and varies as a function of latitude and the concentration of the primary oxidants OH and NO_3, and heterogeneous cloud processes (Capaldo and Pandis, 1997; Kerminen *et al.*, 1998). From measurements over the remote South Pacific Ocean, far from pollution sources under oceanic conditions (low NO_x) levels Bates *et al.* (1992) reported a significantly strong relationship between MSA and nss-$SO_4^=$ (derived from marine biogenic DMS emission) ratios, R. Using their results, $R = -1.5\ T\ (°C) + 42.2$, Ganor *et al.* (2000) have calculated a mean 11 % (ranging between 5.6 – 22 %) contribution of biogenic derived material to total nss-$SO_4^=$ during the summer (by using T=20°C) in the atmosphere of Israel and the eastern Mediterranean Sea. Based on the same ratio, Mihalopoulos *et al.* (1997) calculated biogenic nss-$SO_4^=$ contribution to the total nss-$SO_4^=$ measured at a coastal site of island Crete, as 0.6 to 28.3 %. From the empirical formula strong inverse relationship can be observed between temperature and MSA to nss-sulfate molar ratio. Validity of this formula has not been testified at high ambient air temperatures. In fact, at high ambient air temperatures {T>28.2°C} formula loses its validation. The influence of NO_x concentrations on the product distribution of the OH-initiated oxidation of DMS has been studied at room temperature by Patroescu *et al.* (1999). It is shown that the formation yields of MSA increases with increasing NO_x concentrations, whereas yields of SO_2 decrease. As can be seen from the formula, it has not included NO_x species which influences yield production of MSA and SO_2. Ganor *et al.*(2000) testified this formula using an alternative calculation based on DMS date from independent source. Hence, these authors depicted that empirical formula suggested by Bates *et al.* (1992) is quite well convenient for assesing the MSA to nss-sulfate molar ratio resulted from oxidation of DMS.

By utilizing monthly mean air temperature, MSA and nss-$SO_4^=$at Erdemli seasonal variation of biogenic contribution to measured nss-$SO_4^=$ is calculated and presented in Figure 3.26. It may be seen from the figure the biogenic contribution is negligible during the months of January, February, March and December. It starts to increase in April and reachs its maximum in July. The elevated biogenic contributions to nss-$SO_4^=$ in summer period suggest that there is a major source of oceanic emissions of DMS in the eastern Mediterranean or surrounding seas (*e.g.* Black Sea).

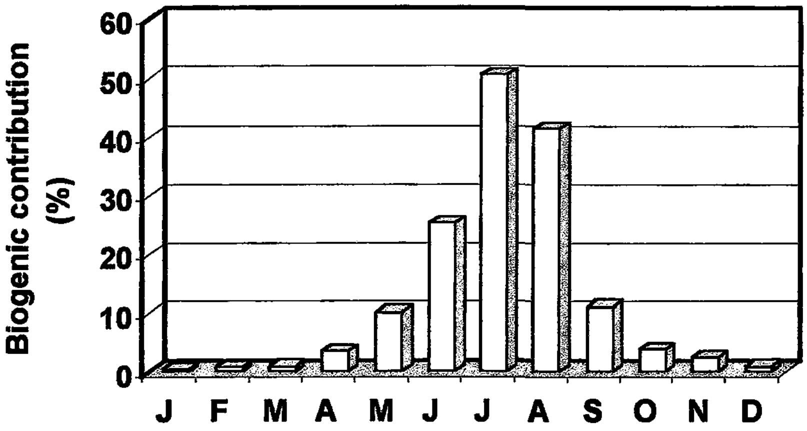


Figure 3.26. Monthly mean variation of the biogenic nss-$SO_4^=$ contribution to total nss-$SO_4^=$ measured at the Erdemli station.

Spring-summer concentrations of the dissolved DMS have been measured and DMS sea-to-air fluxes were estimated from aqueous DMS concentrations, seawater temperatures and wind speeds in western Mediterranean Sea (Simo *et al.*, 1997; Simo and Grimalt, 1998). The reported DMS surface water concentrations vary between 0.1 to 19.3 nM with later high value measured in a summer month (June).

Existing data suggest that oceanic DMS concentrations change both regionally and seasonally. Seasonal studies of oceanic DMS concentrations have shown that average surface seawater DMS concentrations can vary by as much as a factor of 50 between the summer and the winter in the mid and high latitudes. Overall the concentration of DMS in surface seawater varies from approximately 0.2 nM in winter to 10 nM in summer. However, DMS concentrations in excess of 90 nM have been measured in summer plankton blooms in the North Atlantic and Southern Ocean. The starting point in the marine atmospheric sulfur cycle is the air-sea exchange of DMS, which is a function of the gas transfer velocity and surface seawater DMS concentration. The gas transfer velocity is controlled primarily by surface turbulence, seawater temperature and gas diffusivity and can be modeled as a function of wind speed for various trace gases (Bates *et al.*, 1994 and references therein). The amount of DMS fluxes from the surface sea water of the western Mediterranean to the atmosphere have been estimated by Simo and Grimalt (1998). They highlighted the importance of utilising gas transfer velocities as a function of

A more recent study by Simo and Pedros-Alio (1999) explained the highest concentrations of DMS in surface water occcured at a range of subtropical, temperate and subpolar open-ocean areas when surface chlorophyll a levels were lowest with poor vertical mixing of the water column. In winter and early spring mixed waters are characterized by blooms of large diatoms and high chlorophyll a concentrations. During such events high biomass is present but there is a low potential for DMS production, as most of the diatoms are weak DMSP producers. The stratification of surface waters during spring lowers phytoplankton biomass but favours the development of small flagellates, coccolithophores and dinoflagellates, most of them strong DMSP producers. Moreover, phytoplankton succession is accompanied by profound seasonal changes in the food-web structure: in mixed waters during winter-spring, autotrophs and grazers are larger , and part of the primary production sinks and swims out of the photic layer, whereas in strongly stratified waters most of the primary production in the mixed layer is recycled in situ through the microbial loop, thus facilitating a more rapid turnover of phytoplanktonic DMSP. This pattern of phytoplankton succession and changes in the food-web structure should favor an increase in the DMS production as water stratifies, peaking along with the biomass of DMSP producers in spring and summer (Simo and Pedros-Alio, 1999 and references therein).

McArdle and Liss (1995) studied the isotopic composition of aerosol sulphur at two remote European sites to distinguish quantitatively between atmospheric sulphur sources. They showed that DMS derived sulfate concentrations display a strong seasonality with values rising during April and May to a peak in June with little or any occuring during the winter. However even in summer the proportion of biogenic sulphur varied widely (from about 0 to 100 %) from sample to sample.

The intracellular DMSP content in algae and hence their ability for producing DMS, varies largely with species, some groups being more profilic producers than others (Keller *et al.*, 1989). Of particular importance phytoplankters, dinoflagellates and prymnesiophytes (including coccolithophorids) are the most significant DMS producers. This taxon-dependence has been invoked as the main reason for the poor DMS vs chlorophyll correlations usually obtained.

Gotsis-Skretas *et al.* (1999) have shown that there is a seasonal succession of phytoplankton species in the Eastern Mediterranean region. According to their results diatoms dominate in winter and spring and are replaced by dinoflagellates in summer and coccolithophores in autumn. The Black Sea is known to be a region of moderate to high productivity and peaks in primary productivity occuring twice a year, with a major bloom of mainly diatoms in the early spring, followed by a secondary bloom of mainly coccolithophorids in the autumn. Recently, additional summer blooms with the predominance of dinoflagellates and coccoliths have been increasingly observed (Uysal *et al.*, 1998; Moncheva *et al.*, 1998 and references therein). Accordingly the high biogenic contribution to the nss-$SO_4^=$ aerosol in summer months and September at Erdemli could be related to the abundance of the dinoflagellates and coccolithophores in the eastern Mediterranean and the Black Sea waters.

CHAPTER IV

CONCLUSIONS

The results obtained from the current study have shown:

1.That the seasonality of precipitation intensity at the Erdemli is similar to that exhibited for the whole Mediterranean region. The sampling site experiences wet season (in the winter) and a dry season (in the summer season). The local ambient air temperature increases in April (16 °C) and reaches its maximum July-August (28 °C) and decreases to its minimum winter value (8 °C).
Air mass back trajectories are useful tools to show the potential source locations of collected aerosols. Three days back trajectories calculations were performed starting at midday (UT 1200) and arriving at point at 900, 850, 700 and 500 hPa barometric levels. The 10-years database of daily 3-day back trajectories allow a quantification the frequency with which specific source regions (of aerosols) contribute to the material transported across the eastern Mediterranean. The lower layer trajectories indicate that the dominating group of air masses originates from the west, north and east and accounting for 74% at 900 hPa and accounting for 72% at 850 hPa, respectively. The layer trajectories indicate a rapid transport from the south-southeasterly sector (the North African continent) have frequencies of 36% at 700 hPa and 61% at 500 hPa over the 10 year period.

2. The atmospheric concentrations of aerosol associated elements (Al, Fe, Ca, Mg and Zn), water soluble anions (Cl^-, Br^-, NO_3^-, $SO_4^=$, $C_2O_4^=$ and $CH_3SO_3^-$) and cations (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) were measured by Atomic Absorption Spectrometry and Ion Chromatography, respectively. The wide range of concentrations of each element and ion species detected, resulted in calculated high standard deviations from the mean concentrations. Using Na^+ as an indicator element the sea salt contributes 4, 10, 35 and 79% of the observed mean concentrations of Ca^{2+}, $SO_4^=$, K^+ and Mg^{2+}, respectively.

3. Concentrations of crustally derived elements (Al, Fe) observed in this study indicated higher values compare to those stations located at Irish Sea (Liverpool), Black Sea (Amasra), western (Corsica, Sardinia, Blanes, Tour du Valat and Cap Ferrat) and

eastern Mediterranean (Antalya), except Tel Shikmona, which is relatively closer to arid desert regions. Antropogenically derived elemental concentrations (such as those for Zn, Pb and Cd) are approximately two to four times lower than those values reported for Liverpool, Blanes, Tour du Valat and Cap Ferrat. Concentrations of these elements are identical or slightly higher that the values observed sampling sites located at Corsica, Sardinia, Amasra and Antalya.

Sulfate concentrations in the atmosphere at the Erdemli indicates similar values detected over the Mediterranean, however, concentrations of this ionic species is comparably higher than those over continental Europe. Water-soluble nitrate concentration at the Erdemli is higher than those values reported for the Mediterranean and Black Sea coast.

4. The long term average concentration of crustal elements (Al, Fe, Ca and Mn) are much higher in Sde Boker than those detected at Erdemli. The average concentrations of sea spray originated elements (Na, Cl and Mg) are lower than the levels observed at Erdemli. During the summer season sulfate and nitrate concentrations indicate similar values detected at both station.

5. Long-term variations define the average changes at seasonal time scales. These variations are attributed to changes in the emission strengths, local meteorology and transport patterns. Cl^-, Br^-, Na^+ and Mg^{2+} indicate pronounced peaks in the winter season since sea salt generation is more prevalent during this season . The concentrations of crustal elements such as Al and Fe indicate an order of magnitude increase compared to their winter values, due to desert dust transport associated with cyclones originating from North Africa. Nitrate, ammonium, non-seasalt sulfate and methane sulfonate concentrations indicated a winter minimum and summer maximum.

6. Concentrations of all trace species are highly variable on a daily time scale (an order fo magnitude). During the rainy days aerosol constituent concentrations demonstrated drastic decrease, since wet deposition is a very efficiently.

7. Influence of local rain events on aerosol chemical constituent concentrations were highlighted All the trace species, except marine derived elements have lower concentrations during rainy days compare to dry days. Wet removal of particles from

he atmosphere vary significantly from one species to another and elements associated with the largest sized aerosol fraction are scavenged most efficiently. Hence, crustal elements are scavenged from the atmosphere more efficiently by local rain events compared to anthropogenic derived elements.

8. The crustal and marine enrichment factors allow an assessment of the importance of he crust and sea salts. Elements with crustal/marine EF close to unity are likely to have he crust/sea salts as their main source. During the whole sampling period Fe and Mn concentrations are dominated by crustal material. , Sea salt is the dominant source for Br^-, K^+ and Mg^{2+} ions. As would be expected, according to their EF values, Zn and $SO_4^=$ were identified as being of anthropogenic origin. EF value of Cl^- is below unity, especially during summer period. This low value may be attributed to the evaporation of Cl^- or excess Na^+ originating from soil particles.

9. Correlations between variables indicate commonality of cause. The crustal indicator, Al exhibits a strong correlation ($p<0.0001$) with Fe and is moderately correlated with Mn, Mg, Ca, K^+ and Ca^{2+} and Zn. As expected, marine elements (Cl^-, Br^-, Na^+ and Mg^{2+}, $p<0.0001$) have strong correlation coefficient between each other.

The anthropogenically derived ion nss-$SO_4^=$ is strongly correlated with NO_3^- and moderately correlated with MSA. Moderate correlation between nss-$SO_4^=$ and MSA indicate bio-sulfur contribution to the detected sulfate value.

10. Factor analysis identifies three different source groups; crustal, marine and combustion. The crustal factor is highly loaded with Al, Fe and Ca, the marine factor has high loadings of Cl^-, Br^-, Mg^{2+} and Na^+, whereas, the last factor has high loadings of NO_3^-, nss-$SO_4^=$ and NH_4^+. The first two factors (crustal and marine) accounts for 62.5%

ver the sampling period a threshold of aerosol Al concentration of 1000 ng m^{-3} was tilized. During the period of the sampling 25 African dust events were clearly lentified by an abrupt increase in the Al, Fe, Ca and also Mn and Zn concentration in he atmosphere. The average concentrations of the elements for the identified dates were alculated as 1569, 1146, 5532, 17.9 and 27.9 ng m^{-3} for Al, Fe, Ca , Mn and Zn, espectively. The average concentrations of the same elements for the remaining amples (where there was no recorded mineral dust transport) were much lower (262, 55, 2212, 6.8 and 17.5 ng m^{-3} for Al, Fe, Ca, Mn and Zn, repectively). Shallow back trajectories (900 hPa) identified air masses originating from non-aharan sources, except for three outstanding cases. The back trajectories arriving at he upper barometric levels (700 or 500 hPa) mostly originated from Africa during all eak events except three cases which originated from the Arabian Peninsula.

The aerosol sulfate levels during summer in the atmosphere over the eastern Mediterranean and coastal station (Erdemli, Israel and Crete) are much higher than hose expected from local anthropogenic sources. The mean sea salt contribution to ulfate during the sampling period is calculated about 10% and show a variation etween 1% to 87% in the daily time scale. In addition, 3-day back trajectory analysis ndicate that air masses originating from Black Sea Region and Mediterranean Sea have MSA and nss-$SO_4^{=}$ values two times as much as than those calculated for air masses of samples originating from European and former Soviet Union. And elevated biogenic ontributions to nss-$SO_4^{=}$ in summer period (reaches up to 50%) suggest that there is major source of oceanic emissions of DMS in the eastern Mediterranean or surrounding seas (e.g. Black Sea).

CHAPTER V
RECOMMENDATIONS FOR FUTURE RESEARCH

The work presented here is based on studies cofined to aerosol filter samples it have collected from January 1996 to the end of December 1998. The aerosol filter nples were analysed for 11 ion species (Cl^-, Br^-, NO_3^-, $SO_4^=$, $C_2O_4^=$, $CH_3SO_3^-$, Na^+, $_4^+$, K^+, Mg^{2+} and Ca^{2+}) and 6 trace metals (Al, Fe, Mn, Ca, Mg and Zn). Therefore, s study is only include analysis of aerosol filter samples.

Trace metals and nutrients in the air are delivered to the sea surface by a nbination of 'dry' (not involving an aqueous deposition phase) and 'wet' ecipitation scavenging) depositional modes. The two deposition modes are ochemically different. The 'dry' mode is a continuous process in which the fall-out particles is strongly constrained by particle size. In contrast, the 'wet' deposition de is a sporadic, rain event-specific, process which is cosiderably less dependent the particle size of scavenged aerosol. With respect to atmospheric transport and position of particulate material, the Mediterranean Sea has received special interest ice its northern shore is sorrounded by industrialised regions, which act as a ntinuous source of man made aerosols to the atmosphere, whereas, its southern and stern shores is bordered by arid and desert regions, which act as sources of crustal iterial which is transported in the form of non-continuous dust 'pulses'. As a result, th 'dry and 'wet' depositions allow to measure net deposition of these constituents, d to assess the impact of atmospheric fluxes on chemical cycles in the editerranean Sea. Since these two deposition modes are geochemically different, ce metal solubility is controlled by distincly different processes. Trace metal lubility is mainly constrained by particle ↔ sea water during dry deposition. owever, in the wet deposition mode trace metal solubility is initially constrained by rticle ↔ rainwater reactivity then trace metals deposited onto sea surface. Besides, solubilities of trace metals from aerosols are dependent on a number of complex tors, which include the following; (a) the type of the aerosol (crust or urban minated), (b) the pH history of an aerosol, (c) the solution pH, especially in nwaters and (d) the particle concentration (Chester et al.,1999; references therein). erefore, it is essential that further research should be devoted toward the lubilization of the trace metals since deposition and subsequent dissolution of these nstituens may significantly affect the biogeochemical cycles.

DMS is the major volatile sulfur gas in surface marine waters, which is roduced by biological activity in seawater. It has been well known that the vertical istribution of DMS in the euphotic zone follows that the primary production, with a aximum at or near the ocean surface and a decrease with depth (Barnard et al., 982; Andreae and Barnard, 1984). The surface layers are always observed to be uper saturated with DMS, implying a net flux to the atmosphere (Bernard et al., 982; Andrea and Raemdock, 1983). Once DMS escape into the atmospheric ompartment, it is subjected to complex oxidation processes. The main oxidation roducts are MSA (methane sulfonic acid), DMSO (dimethyl sulfoxide), $DMSO_2$ imethyl sulfone) and SO_2 (sulfur dioxide). SO_2 undergoes gas-to-particle conversion o for nss-$SO_4^{=}$. Complex and challenging problem is assessment of bio- sulfate to bserved total sulfate concentrations since this constituent has both natural and nthropogenic sources. By using a biological tracer (MSA) it has been shown that bio-ulfur (especially during summer time) significantly contributes to observed sulfate alues at Erdemli station. In order to clarify this phenomenon it would be useful to ake time series measurements of DMS in water column and in the atmosphere.

The particulate material in the atmosphere arise from natural and nthropogenic (man-made) sources. Particulate material can be emitted directly as articles (primary aerosol) or formed in the atmosphere by gas-to-particle conversion rocesses (secondary aerosol). Generally, atmospheric aerosols have been divided into wo size classes: coarse mode consists of particles with diameters larger than 2μm and ine mode occurs with particle diameters less than 2μm, reflecting the two formation echanisms: primary and secondary. Besides, some aerosol constituents (nitrate) hows bimodal size distribution due to heterogeneous (reaction between gas and pre-xisting aerosol particles) reactions. Therefore, installing size separated sampler ascade impactor) will improve better resolution in the identification of sources of erosols.

In addition, it will be valuable to measure precursors (SO_2, NO_x and NH_3) of itrate, sulfate and ammonium ions in the gas phase. Gas phase measurements ombined with aerosol data will give valuable information about gas to particle onversion processes in the atmosphere of eastern Mediterranean.

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