INVESTIGATION OF THE RELATIONSHIP BETWEEN AEROSOL AND RAINWATER COMPOSITION

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Canan Özgen

Prof. Dr. Canan Özgen
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Filiz B. Dilek
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Prof. Dr. Gürdal Tuncel
Supervisor

Examining Committee Members

Prof. Dr. Kahraman Ünlü	(METU,ENVE)	
Prof. Dr. Gürdal Tuncel	(METU,ENVE)	
Prof. Dr. Mürvet Volkan	(METU, CHEM)	M. Volkan
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Name, Last name : Ahmet TÜRKÜM

Signature :

ABSTRACT

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Türküm, Ahmet

M.S., Department of Environmental Engineering

Supervivor: Prof. Dr. Gürdal Tuncel

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Chemical composition of particles and rain water at three sites in Turkey were extensively compared to determine if there is a relationship between aerosol and rain composition. If such relationship exists, it can allow one to construct rain water composition using aerosol data. This is important because, rain composition data is scarce as sampling and analysis of very low concentrations of elements and ions in rain water is more difficult compared to sampling and analysis of atmospheric aerosol.

Results showed that aerosol composition can be closely reflected in composition of rain water if below cloud processes dominate over the incloud processes. This is clearly observed for crustal elements in all stations and for most of the elements in urban Ankara station.

However, in rural stations there were differences in rain and aerosol that is attributed to significant contribution from in cloud processes.

Seasonal patterns and enrichment factors observed in aerosol composition showed general agreement with corresponding temporal variations observed in rain water concentrations of elements, but short term variations became visible only if data is averaged over a long period of time. These observations suggest that certain features of rain water composition can be constructed from if concentration data is available for aerosols. However it should be noted that there are also significant differences between stations and between elements or element groups, indicating that composition of rain water constructed from aerosol data can only be a crude one. Similarities between rain and aerosol compositions is more pronounced in urban Ankara station compared to rural stations used in this study.

Factor analysis performed to aerosol and rain water data sets showed that source types affecting chemical composition of rain and particles are generally the same, bur contribution of each source type to rain and aerosol composition shows differences.

Similarly, the source regions, defined by potential source contribution function, affecting aerosol and rain compositions are not identical. In Antalya station Source regions affecting chemical composition of rain water are more local compared to source regions affecting composition of aerosol. Same difference is not observed in Amasra station.

Scavenging ratios is found to be a suitable tool to construct rain water composition using aerosol data. Scavenging ratios calculated using paired daily data are more variable both between stations and within a station. Long-term averaged data was found to be more reliable for calculating SRs of elements and ions at all stations.

Key Words: Scavenging ratio, Enrichment factor, precipitation, aerosol, potential source contribution function, Factor analysis

ÖZ

AEROSOL VE YAĞMUR SUYUNUN İÇERİKLERİ ARASINDA Kİ İLİŞKİNİN ARAŞTIRILMASI

Türküm, Ahmet

M.S., Çevre Mühendisliği Bölümü

Tez yöneticisi: Prof. Dr. Gürdal Tuncel

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Yağmur suyunun örneklenip analiz edilmesi aerosollere nazaran çok daha zor olduğundan, yağmur suyunun kimyasal kompozisyonu ile ilglili çalışmalar çok daha az sayıdadır. Aeorollerin ve yağmur suyunun kimyasal kompozisyonları arasında bir ilişki kurulabilmesi halinde, yağmur suyu kompozisyonunu aerosol verileri kullanarak, yaklaşık olarak da olsa, belirleyebilmek mümkün olacağndan, bu belirtilen ilişkinin kurulması önemlidir.

Yapılan çalışmada, Türkiyenin değişik bölgelerinde, daha önceki çalışmalarda ölçülmüş olan, element ve iyonların aerosol ve yağmur suyundaki konsantrasyonları kapsamlı olarak karşılaştırılarak, aerosol ve yağmur suyunun kimyasal kompozisyonları arasında bir ilişkinin olup olmadığı araştırılmıştır.

Element ve iyonların değişik istasyonlarda, yağmur suyu ve aerosollerde ölçülmüş olan ortalama konsantrasyonlarının karşılaştırılması; elementlerin yağmur suyundaki konsantrasyonlarının lokal aerosoller tarafından belirlenmesi halinde konsantrasyonlar arasında bir ilişkinin olduğunu ancak yağmur suyundaki elementlerin uzak mesafelerden taşınması halinde bu ilişkinin zayıf olduğunu göstemiştir. Toprak kökenli elementler, lokal kökenli olduklarından, bütün istasyonlarda gerek yağmur suyunda ve gerekse parçacıklarda benzer eğilimler göstermekteidr. Ancak, deniz tuzundan kaynaklanan elementlerle antropojenik kökenli elementlerin yağmur suyu ve aerosollerdeki ortalama konsantrasyonları arasında bir ilişki bulunamamış, bu da söz konusu elementlerin yağmur suyundaki konsantrasyonların daha ziyade uzun mesafeli taşınım ile belrilenmesine bağlanmıştır.

Element ve iyonların gerek yağmur suyunda ve gerekse aerosollerdeki konsantrasyonlarının benzer mevsimsel değişimler gösterdikleri görülmüş ve aerosol verilerinin olması halinde elementlerin yağmur suyundaki mevsimsel değişimlerinin öngörülebileceği sonucuna varılmıştır. Aynı şekilde, elementlerin yağmur suyu ve parçacıklardaki zenginleşme faktörlerinin de birbirine benzenesi, aerosol ölçümlerinin olması halinde yağmur suyundaki zenginleşme faktörlerinin, yaklaşık olarak da olsa, hesaplanabileceğini göstemektedir.

Yapılan faktör analizi çalışmasında, Gerek Amasra ve gerekse Antalya istasyonlarında yağmur suyu ve aerosol verilerinin aynı kaynak türlerini gösterdiği görülmüştür. Ancak, yağmur suyu ve aersol verielerideki varyansın benzer kaynak türleri tarafından açıklanan miktarları aynı değildir. Bu, farklı türde parçacıkların aerosol ve yağmur suyunda farklı miktartarda bulnmasıyla açıklanmıştır.

Aerosol ve yağmur suyunun kimyasal kompozisyonlarının belirleyen kaynakların nerelerde bulunduğu PSCF (potansiyel kaynak katkı fonksiyonu) tekniği ile belirlenmiştir. Sonuçlar, yağmur suyu ve parçacıkların kimyasal bileşimini belirleyen kaynak bölgelerinin genel olarak birbirine benzediğini ancaka ralarında bire bir bir ilişkinin olmadığını göstermektedir. Antalya istasyonu için yapılan karşılaştırmada, yağmur suyunun kompozisyonunu belirleyen kaynak bölgelerinin aerosollere nazaran çok daha lokal olduğu görülmüştür. Aynı farklılık Amasra istasyonunda görülmemiştir.

Yıkanma oranının (scavenging ratio), aerosol kimyasal kompozisyonunun bilinmesi halinde yağmur suyunda beklenen konsantrasyonların hesaplanması için faydalı bir araç olduğu görülmüştür. Değişik zaman dilimleri için ortalamalar alınarak yapılan değerlendrmelerde, yıkanma oranlarının uzun dönemli ortalamalar alınarak hesaplanması halinde kullanılabileceği ancak günlük aerosol ve yağmur suyu konsantrasyonları kullanılarak hesaplanan yıkanma oranlarının, çok değişken olması nedeniyle, güvenilr olmadığı sonucuna varılmıştır.

Anahtar Kelimeler : Yıkanma oranı, zenginleşme faktörü, yağmur, aerosol, potansiyel kaynak katkı fonksiyonu, faktör analizi

To My Parents…

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INTRODUCTION

1.1. Character of the Atmosphere

The atmosphere composes the thin layer of mixed gases covering Earth's surface. Exclusive of water, atmospheric air is 78.1% (by volume) nitrogen, 21.0% oxygen, 0.9% argon, and 0.03% carbon dioxide. Normally, air is 1–3% water vapor by volume. In addition, air contains a large variety of trace level gases at levels below 0.002%, including neon, helium, methane, krypton, nitrous oxide, hydrogen, xenon, sulfur dioxide, ozone, nitrogen dioxide, ammonia, and carbon monoxide (Williamson, 1973). The concentrations are remaining nearly constant or vary slowly. The following are variable in their concentration: Water > variable 1.0% by volume, pollen, meteoric dust, bacteria, sodium chloride, spores, soil, condensation nuclei, NO_2 formed by electric discharge, O_3 formed by electric discharge, SO_2 volcanic oxygen, HCl of volcanic origin, HF of volcanic origin.

The atmosphere is divided into several layers on the basis of temperature. Figure 1.1. illustrates the layers of the atmosphere.

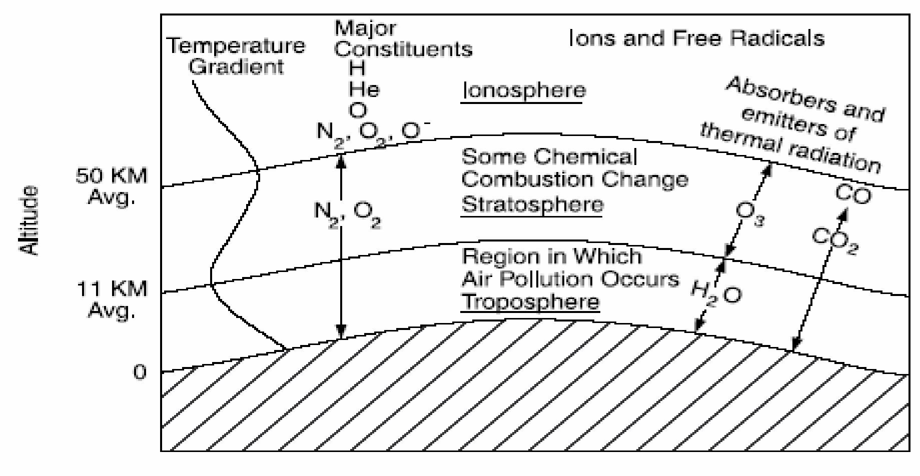


Figure 1.1. Layers of the atmosphere (Schnelle and Brown, 2002)

- Ionosphere (above 50 km) is the highest lying layer in the atmosphere. It consists of ions and activated molecules produced by photolysis of O_2 + N_2 molecules, such as the one shown in equation 1.1.

$$O_2 = hv \rightarrow O^- + O^- \tag{1.1}$$

- Stratosphere (11 to 50 km) is an intermediate layer in the atmosphere. It is important because ozone layer occurs in stratosphere. Temperature in the stratosphere increases from - 56^0C at 11 km to -2^0C at 50km due to ozone reactions shown in equations 1.2 – 1.4. These reactions consumes high energy UV photons coming from the sun, thus prevents this harmful radiation to reach the surface of the earth.

$$NO_2 + hv \rightarrow NO + O^- \tag{1.2}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{1.3}$$

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (1.4)$$

- Troposphere (0 to 11 km) is the lowest lying layer in the atmosphere. Temperature decreases from + 13^0C at the surface to - 56^0C at 11 km. It is the most important laye in terms of air pollution, because most of the anthropogenic and natural emissions occur in this layer. Troposphere is divided into two compartments, namely boundary layer and free troposphere. Boundary layer is the first 5 km of the atmosphere and free troposphere is the rest (5-11 km). Most of the emissions and meteorological events occur in the boundary layer. Residence time of pollutants are shorter in the boundary layer owing to meteorological processes(Schnelle and Brown, 2002).

1.2. Air Pollution

Air pollution is defined as the presence in the outdoor atmosphere of one or more contaminants (pollutants) in quantities and duration that can injure human, plant, or animal life or property (materials) or which unreasonably interferes with the enjoyment of life or the conduct of business (Boubel et al, 1994). Table 1.1. compares concentrations of what could be considered pure air to concentrations in polluted air.

Examples of traditional contaminants include sulfur dioxide, nitrogen oxides, carbon monoxide, hydrocarbons, volatile organic compounds (VOCs), hydrogen sulfide, particulate matter, smoke, and haze. This list of air pollutants can be subdivided into pollutants that are gases or particulates. Gases, such as sulfur dioxide and nitrogen oxides exhibit diffusion properties and are normally formless fluids that change to the liquid or solid state only by a combined effect of increased pressure and decreased temperature. Particulates represent any dispersed matter, solid or liquid, in which the individual aggregates are larger than single small molecules (about 0.0002 mm in diameter) but smaller than about 500 micrometers (mm) (Goldsmith, 1977). Of recent attention is particulate matter equal to or less than 10 mm in size, with this size range of concern relative to potential human health effects. More recently, epidemiological studies demonstrated that health effects of particles are primarily due to ones with diameters < 2.5 mm ($PM_{2.5}$) (Englert, 2004). Development of regulatory standards for this group of particles is now in progress (Sloss and Smith, 2000).

Table 1.1. A Comparison of pure air and a polluted atmosphere (Schnelle and Brown, 2002)

Component	Considered to Be Pure Air	Typical Polluted Atmosphere
Particulate matter	10–20 $\mu g/m^3$	260–3200 $\mu g/m^3$
Sulfur dioxide	0.001–0.01 ppm	0.02–3.2 ppm
Carbon dioxide	300–330 ppm	350–700 ppm
Carbon monoxide	1 ppm	2–300 ppm
Oxides of nitrogen	0.001–0.01 ppm	0.30–3.5 ppm
Total hydrocarbons	1 ppm	1–20 ppm
Total oxidant	0.01 ppm	0.01–1.0 ppm

To have an air pollution incident, there are three factors that must occur simultaneously. There must be sources, a means of transport, and receptors. Figure 1.2. illustrates these three process. Air pollution sources are relatively common knowledge. Their strength, type, and location are important factors. By transport, reference is made to the meteorological conditions, and the topography and climatology of a region, which are the important factors in dispersion — that is, in getting the material from the sources to the receptors (Liu et al., 1999). The receptors include human beings, other animals, materials, and plants. We also know that air pollution can affect visibility and can endanger our lives simply by making it difficult to travel on the highways and difficult for planes to land (Sloane, 1984).

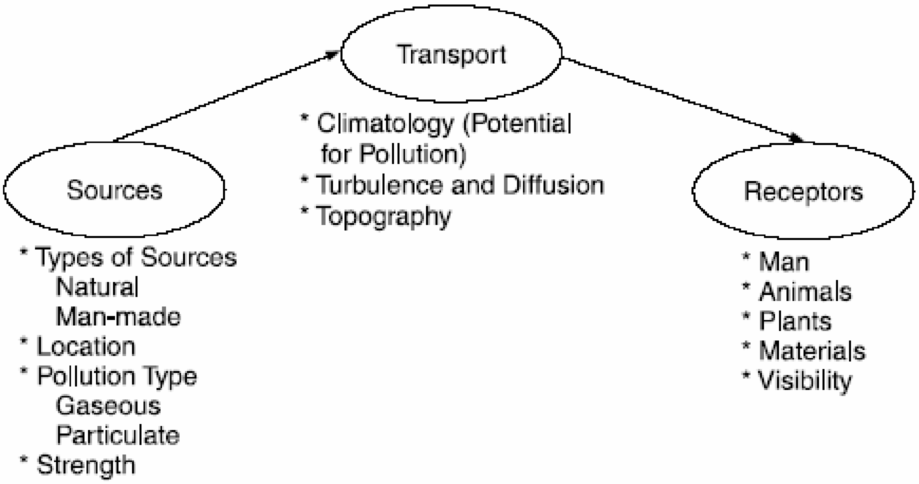


Figure 1.2. The trilogy: Sources — Transport — Receptors
(Liu et al., 1999)

Pollutants enter the atmosphere primarily from natural sources and human activity. This pollution is called primary pollution, in contrast to secondary pollution, which is caused by chemical changes in substances in the atmosphere. Sulfur dioxides, nitric oxides, and hydrocarbons are major primary gaseous pollutants, while ozone is a secondary pollutant, the result of atmospheric photochemistry between nitric oxide and hydrocarbons (Liu et al., 1999).

Urban air pollution has evolved into a significant worldwide problem with many urban areas attaining levels above the World Health Organization (WHO) guidelines (Faiz, 1993). Motor vehicular transport is a primary cause of the observed decline in urban air quality and the significance of motor vehicle use is increasing in many urban areas (Anderson et al., 1996) through rising traffic volumes (Kirby, 1995), despite vehicle emission controls and/or stabilizing or declining industrial emissions (Faiz, 1993; Anderson et al., 1996). This is particularly significant for developing countries, where the rapid rates of both urbanisation (White and Whitney, 1992) and growth in vehicle fleet (Faiz, 1993) are expected to be the highest in the world (World Health Organization/United Nations Environment Programme, 1992).

1.3. Aerosols

Particulates is a term that has come to stand for particles in the atmosphere, although particulate matter or simply particles, is preferred usage. Particulate matter makes up the most visible and obvious form of air pollution. Atmospheric aerosols are solid or liquid particles smaller than 100 µm in diameter (NRC, 1983). Atmospheric reactions are strongly affected by the number of suspended solid particles and their properties. Atmospheric particles have numerous effects. The most obvious of these is reduction and distortion of visibility (Sloane, 1984). Particles also provide active surfaces upon which heterogeneous atmospheric chemical reactions can occur and nucleation bodies for the condensation of atmospheric water vapor, thereby exerting a significant influence upon weather and air pollution phenomena (Aloyan, 2004). Moreover, solid particles can react with industrially emitted gases in common chemical reactions (Warner et al., 1997). Some chemical and physical aspects of atmospheric particles are illustrated in Figure 1.3.

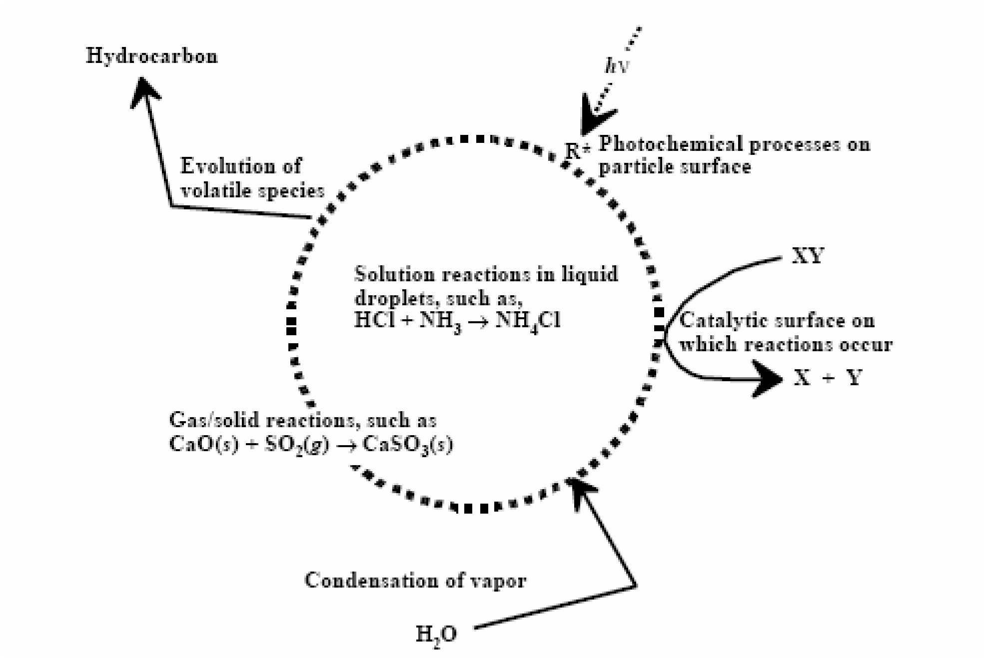


Figure 1.3. Aspects of particle reactions and effects in the atmosphere (Manahan, 2001)

Combustion, volcanic eruptions, dust storms, and sea spray are a few processes that emit particles. Many particulates in the air are metal compounds that can catalyze secondary reactions in the air or gas phase to produce aerosols as secondary products (Lantzy and Mackenzie, 1974).

The chemical composition of atmospheric particulate matter is quite diverse (Beim et al. 1997). Figure 1.4. illustrates the basic components that determine the composition of inorganic particulate matter.

Among the constituents of inorganic particulate matter found in polluted atmospheres are salts, oxides, nitrogen compounds, sulfur compounds, various metals, and radionuclides. In coastal areas, sodium and chlorine get into atmospheric particles as sodium chloride from sea spray (Harrison, 2004). The major trace elements that typically occur at levels above 1 $\mu g/m^3$ in particulate matter are aluminum, calcium, carbon, iron, potassium, sodium, and silicon; note that most of these tend to originate from terrestrial sources. Lesser quantities of copper, lead, titanium, and zinc, and even lower levels of antimony, beryllium, bismuth, cadmium, cobalt, chromium, cesium, lithium, manganese, nickel, rubidium, selenium, strontium, and vanadium are commonly observed (Warner et al., 1997) . The likely sources of some of these elements are given below:

- **Al, Fe, Ca, Si**: Soil erosion, rock dust, coal combustion

- **C**: Incomplete combustion of carbonaceous fuels

- **Na, Cl**: Marine aerosols, chloride from incineration of organohalide polymer wastes

- **Sb, Se**: Very volatile elements, possibly from the combustion of oil, coal, or refuse
- **V**: Combustion of residual petroleum
- **Zn**: Tends to occur in small particles, probably from combustion
- **Pb**: Combustion of leaded fuels and wastes containing lead

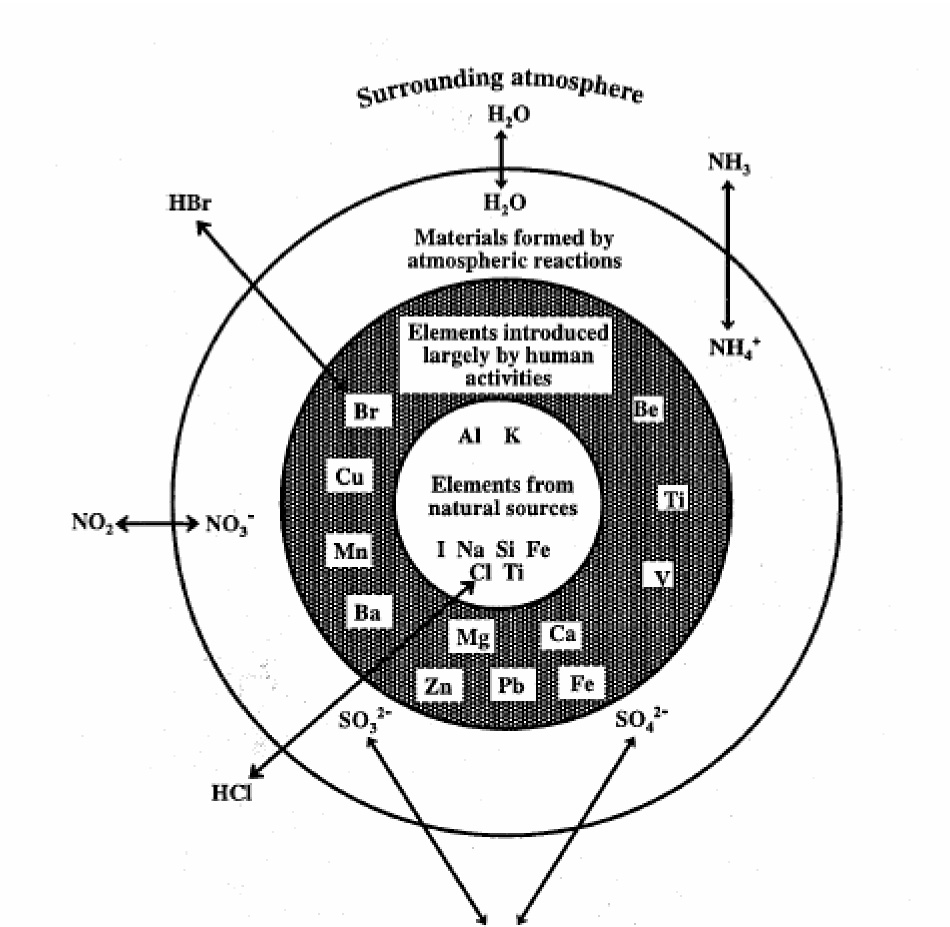


Figure 1.4. Some of the components of inorganic particulate matter and their origins (Manahan, 2001)

Particulate carbon as soot, carbon black, coke, and graphite originates from auto and truck exhausts, heating furnaces, incinerators, power plants, and steel and foundry operations, and composes one of the more visible and troublesome particulate air pollutants. Because of its good adsorbent properties, carbon can be a carrier of gaseous and other particulate pollutants. Particulate carbon surfaces may catalyze some heterogeneous atmospheric reactions, including the important conversion of SO_2 to sulfate (Manahan, 2001).

1.4. Sulfur Species in Atmosphere

Main aspects of global sulfur cycle is depicted in Figure 1.5. There are many uncertainties regarding the sources, reactions, and fates of these atmospheric sulfur species. Approximately 100 million metric tons of sulfur per year enter the global atmosphere through anthropogenic activities, primarily as SO_2 from the combustion of coal and residual fuel oil (Lantzy and Mackenzie, 1979). The greatest uncertainties in the cycle have to do with nonanthropogenic sulfur, which enters the atmosphere largely as SO_2 and H_2S from volcanoes, and as $(CH_3)_2S$ and H_2S from the biological decay of organic matter and reduction of sulfate (Kubilay, 2002). Any H_2S that does get into the atmosphere is converted rapidly to SO_2 The primary source of anthropogenic sulfur dioxide is coal, from which sulfur must be removed at great expense to keep sulfur dioxide emissions at acceptable levels (Bertine and Goldberg, 1971). Approximately half of the sulfur in coal is in some form of pyrite, FeS_2, and the other half is organic sulfur (Maynard, 1998).

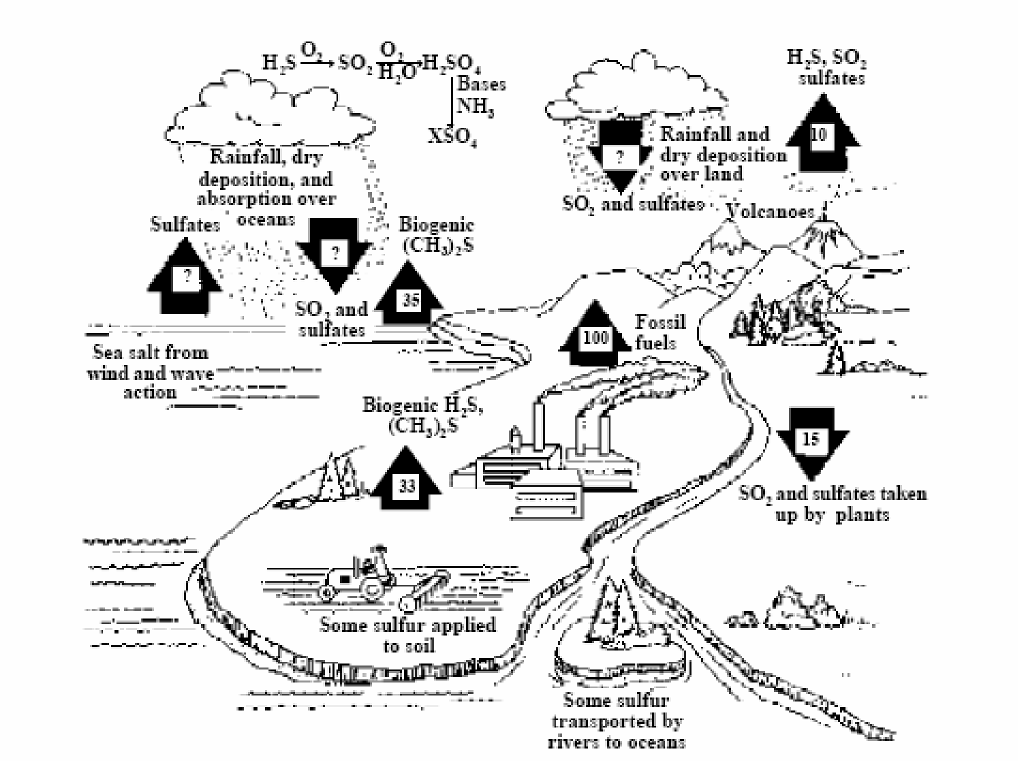


Figure 1.5. The global atmospheric sulfur cycle. Fluxes of sulfur represented by the arrows are in millions of metric tons per year. Those marked with a question mark are uncertain, but large, probably of the order of 100 million metric tons per year (Manahan, 2001)

Oxidation of sulfur dioxide to particulate sulfate has gained increasing importance due to the effects of acid deposition, global climate change, and possibly, increased human mortality rate. The sulfate aerosols are thought to be a major source of cloud condensation nuclei, which effect the radiactive proberties of clouds and cause visibility degradation (Gebhart and Malm, 1994; Malm, 1984; White, 1990). Particulate sulfate also affects global solar radiation balance by scattering the short-wave region (Bolin and Charlson, 1976; Shaw, 1983; Charlson et al. 1990, 1992). Reduction in total solar radiation was reported by Stanhill and Moreshet (1994). The effect of SO_4 aerosol is one of the least known areas in global warming issue, and because of this very extensive research is underway. Exposure to acidic aerosols may also pose a potential treat to health (Liang and Waldman, 1993; Waldman et al., 1993).

1.5. Nitrogen Oxides in the Atmosphere

The three oxides of nitrogen normally encountered in the atmosphere are nitrous oxide (N_2O), nitric oxide (NO), and nitrogen dioxide (NO_2). Microbially generated nitrous oxide is relatively unreactive and probably does not significantly influence important chemical reactions in the lower atmosphere. Its levels decrease rapidly with altitude in the stratosphere due to the photochemical reaction and some reaction with singlet atomic oxygen (Rogers and William, 1991). These reactions are significant in terms of depletion of the ozone layer.

Increased global fixation of nitrogen, accompanied by increased microbial production of N_2O, could contribute to ozone layer depletion. Colorless, odorless nitric oxide (NO) and pungent red-brown nitrogen dioxide (NO_2) are very important in polluted air. Collectively designated NO_x, these gases enter the atmosphere from both natural sources, such as lightning and biological processes, and from anthropogenic sources. The latter are much more significant because of regionally high NO_2 concentrations, which can cause severe air quality deterioration, particularly photochemical smog formation. Practically all anthropogenic

NO_2 enters the atmosphere as a result of the combustion of fossil fuels in both stationary and mobile sources (Stevens, 1998).

Contribution of gasoline powered motor vehicles on urban NO_x levels is more pronounced than emissions from stationary sources. Atmospheric chemical reactions convert NO_x to nitric acid, inorganic nitrate salts, organic nitrates, and peroxyacetyl nitrate. The principal reactive nitrogen oxide species in the troposphere are NO, NO_2, and HNO_3. These species cycle among each other, as shown in Figure 1.6. Although NO is the primary form in which NO_x is released to the atmosphere, the conversion of NO to NO_2 is relatively rapid in the troposphere (Manahan, 2001).

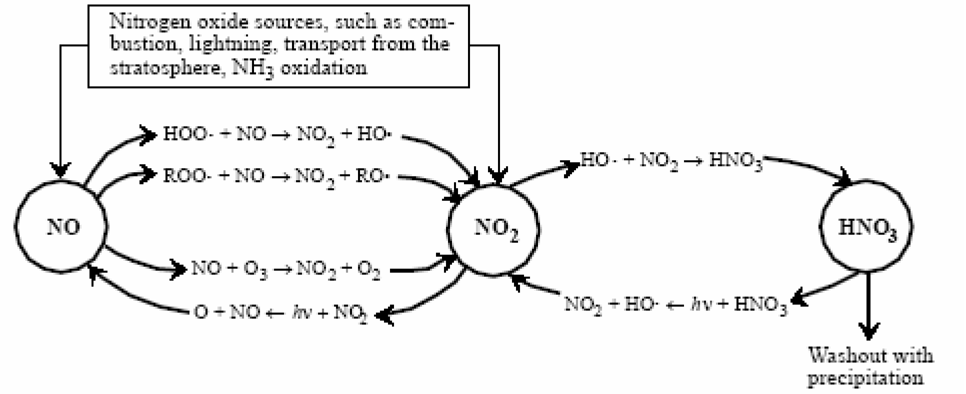


Figure 1.6. Principal reactions among NO, NO_2, and HNO_3 in the atmosphere. ROO• represents an organic peroxyl radical, such as the methylperoxyl radical, $CH_3OO\bullet$ (Manahan, 2001)

1.6. Ammonia in the Atmosphere

Ammonia is present even in unpolluted air as a result of natural biochemical and chemical processes. Among the various sources of atmospheric ammonia are microorganisms, decay of animal wastes, sewage treatment, coke manufacture, ammonia manufacture, and leakage from ammonia-based refrigeration systems (Krupa, 2003). High concentrations of ammonia gas in the atmosphere are generally indicative of accidental release of the gas. Ammonia is removed from the atmosphere by its affinity for water and by its action as a base. It is a key species in the formation and neutralization of nitrate and sulfate aerosols in polluted atmospheres (Munger, 1982; Rodhe et al., 2002; Lee et al., 2000; Schuurkes et al., 1967).

In a very short time, the ammonia released from the source is transformed to ammonium (NH_4^+) containing aerosols, $(NH_4^+)_2SO_4$ and NH_4NO_3 by giving reaction with H_2SO_4 and HNO_3, respectively (Al-Momani, 1995). Due to its high concentration near the source and high deposition velocity ammonia is removed from the atmosphere locally. However, ammonium aerosols are transported over long distances due to their small size and low deposition velocity (Singles et al., 1998).

1.7. Removal of Pollutants from Atmosphere

Even though understanding of chemical constituents in the atmosphere has emerged only within the past three decades, acquisition of this knowledge has accelerated in part because of public concern regarding air pollution and also in part because of a greatly expanded interest in chemical interactions with the biosphere. Particularly, sulfur oxides and nitrogen oxides have received much attention since the 1970s because of concern about not only human health and atmospheric visibility impairment but also a number of other effects. Ecological effects, including acidification of lakes and streams with effects on fish and interference with forest productivity, is believed to be geographically widespread (Driscoll et al., 2003; Bini and Bresolin, 1998; Ghosh, 2003; Lawrence, 2002; Calace et al. 2001). The vulnerability of aquatic and terrestrial ecosystems to deterioration results from exposure to acidic pollution depends on a complicated set of circumstances. These involve the natural waters, soil, and bedrock chemistry of acid neutralization, as well as the presence of leachable potentially toxic chemical species (Park, et al., 1999).

The concentration of sulfate in precipitation is a consequence of Brownian motion, inertial impaction, phonetic attachment and nucleation. All serve to remove the sulfate aerosol from the air and attach it to the cloud and precipitation elements. The sulfate deposited in precipitation originates from either nucleation of pre-existing sulfate particles or from aqueous-phase conversion of SO_2 occurring within the precipitating cloud. The conversion rates for in-cloud transformation of SO_2 to SO_4^{2-} depended upon the ambient level of ingested sulfate and precipitation efficiency. These rates could increase as the level of ingested sulfate aerosol concentration and precipitation efficiency decrease and they found to be about 10% h^{-1} in both winter and summer storms (Luria, 1996). More than 80% of the ingested sulfate aerosol in-cloud was removed from precipitation and a high-level source of sulfate that was not removed by precipitation was attributed to in-cloud conversion of SO_2. Thus, the primary removal mechanism of sulfate from atmosphere is believed to be nucleation of sulfate aerosol followed by collection with large falling precipitation particles (Maynard, 1998). Therefore, the sulfate deposited in precipitation represents the scavenging of pre-existing sulfate during the lifetimes of individual cloud elements and the impaction scavenging below clouds. This does not imply that aqueous-phase oxidation of SO_2 is unimportant in the production of sulfate. It implies that the rate constants are (or the concentration of oxidants is) insufficient to produce appreciable quantities of sulfate during the lifetime of the cloud particles contributing to precipitation (Maynard, 1998).

1.7.1. Wet and Dry Deposition

There are two main mechanisms by which pollutants are removed from the atmosphere to the sinks such as soil, vegetation, structures and water bodies, especially the oceans (Galloway, et al, 1982). The first mechanism, namely dry deposition occurs through direct transfer of both gases and particles from the atmosphere to the water, soil and plants surfaces through physical processes excluding the removal by rain and snow. On the other hand, wet deposition takes place when the atmospheric pollutants are deposited to the surfaces of the earth in the form of precipitation through rain and snow. It includes two main processes, namely rainout and washout. Rainout (or in-cloud scavenging) occurs when the pollutant material is incorporated into the cloud water droplets or ice crystals, which eventually grow to sufficient size to overcome gravity and fall to the ground. Whereas, washout (or below-cloud scavenging) occurs when the pollutant material below the cloud is swept by rain or snow as it falls (Sienfield and Pandis, 1998).

Dry deposition of an agent refers to the combined effects of three transfer steps:

1- Transfer through the turbulent layer of the atmosphere,

2- Molecular transfer through the viscous layer close to the surface,

3- Transfer to the surface as a result of adsorption, dissolution in water or other processes.

Wet and dry depositions, monitored on a large scale across Europe and North America over the past decade, have been shown to be the most important processes by which the airborne pollutants impact terrestrial and aquatic ecosystems (Van Leeuwen et al., 1996; Sanusi et al., 1995). Qualitative and quantitative assessment of atmospheric depositions are essential for understanding regional variations, for determining when critical loads are exceeded, and for demonstrating, by analysis of pluri-annual trends, the efficiency of emissions reduction policies on the regional scale. Precipitation is the major pathway of anthropogenic and natural species from the atmosphere to oceanic and terrestrial ecosystems (Losno R., 1991).

1.8. Scavenging Ratio

Precipitation plays an important role in determining the fluxes of many elements and species at atmosphere-ecosystem interfaces (Galloway et al., 1982; Settle et al., 1982; Slinn, 1983). However, field studies show that the concentrations in wet depositions are highly variable, which make it difficult to quantify these fluxes without long-term campaigns.

Most of the elements found in rainfall come from the aerosol and gas phase, either incorporated directly in the clouds (in-cloud scavenging) or washed-out by the precipitation itself (below-cloud scavenging). A better understanding of the rainfall phenomena therefore can only be achieved by studying the relationship between aerosol and rain water media (Jaffrezo and Colin, 1987).

Part of the concentration variations in rain can be associated with that in the aerosol due, in particular, to the effect of the source zones traversed by the cloud system. By classifying the precipitation collected at a given site according to the back-trajectories of the associated air-masses it is possible to distinguish more homogeneous groups than the entire initial sample (Colin et al., 1986; Duysing et al., 1986; Slanina et al., 1983).

But this type of classification is not enough to account for the diversity of the concentrations observed. It does not describe the magnitude of the exchanges between the two phases, rain and aerosol, the variations of which also contribute to this diversity. To a first approximation, this characteristic depends on the meteorological conditions (cloud type, phase contact time, precipitation intensity, etc.) and also on the microphysical conditions (size and hygroscopy of the particles, number of condensation nuclei, etc.) (Slinn, 1983). The effects of some of these factors have been studied theoretically, but in practice, the coupling is expressed by the "scavenging ratio" (Chamberlain, 1960; Engelmann, 1970).

SRs were first developed to estimate the rate of wet deposition for radioactive bomb test debris (Engelmann, 1971). They have been applied subsequently to estimate wet deposition fluxes for a number of other atmospheric species (Varhelyi and Gravenhorst, 1983) However, in addition to its role in the study of precipitation and aerosol relationship, the scavenging ratio potentially constitutes a tool for evaluating the wet deposition of species if the concentrations in the aerosol are known (Arimoto et al., 1985; Uematsu et al., 1985; Davidson et al., 1985; Keene et al., 1986; Jaffrezo et al., 1990).

Factors that influence the magnitude and variability of SRs have been the focus of numerous studies. These factors include: particle-size distributions and solubilities (Buat-Menard and Duce, 1986; Jaffrezo and Colin, 1987; Gatz, 1977; Eder and Dennis, 1990), precipitation rates (Scott, 1981; Krey and Toonkel, 1977) and amounts (Savoie et al, 1987), droplet accretion processes (Scott, 1981), air mass trajectories (Jaffrezo et al., 1990), and the importance of gas-phase scavenging (Harrison and Pio, 1983; Wolff et al., 1987; Stedman 1991). Barrie (1985) thoroughly reviews some of the processes impacting the magnitude of SRs and more recently assesses the usefulness of SRs (Barrie, 1991). Models have been developed to predict the magnitude of SRs (Scott, 1978; Hegg, 1983).

Precipitation volume has been the factor most often studied in relation to scavenging ratio variation. This is due partly to the avaibility of this datum, easily measured during sampling. But, more importantly, it is known that the concentrations generally decrease with the amount of rain for a single event, because of a dilution effect (Junge, 1963; Dawson, 1978; Hicks and Shannon, 1979; Jaffrezo et al., 1990). Independently of the relation with the volume or the rain-rate, the nature of the precipitation system can also affect the scavenging ratios by modifying the incorporation mechanisms. Convection, which causes more rapid and extensive exchanges between the cloud and the underlying air, plays an important role. In addition to this, increased mixing efficiency, the effect of convection is found in several theoretically described processes (Jaffrezo et al., 1990). These processes include: turbulence associated with convection (Glower and Pruppacher, 1985), faster growth of the cloud droplets by collision and coalescence (Pruppacher and Klett, 1980) and super saturation reached within clouds increases in parallel with the updraft speed (Jaffrezo et al., 1990).

Modeling exercises showed that, aerosol particle size seems to be one of the chief factors determining scavenging efficiency (Slinn, 1983; Pruppacher and Klett, 1978), depending on the diameter of the particle, the collection efficiency between a raindrop and a particle is predicted to vary over three orders of magnitude (Jaffrezo and Colin, 1987). The values of Radke et al. (1980) obtained from measurements of the aerosol size at the base of a cloud before and after precipitation are in good agreement with model results although they cover a smaller range. Several researchers have found that, due to more efficient removal of larger particles by precipitation, species that occur on larger particles can have larger SRs than those occur on smaller particles (Gatz, 1977; Jaffrezo and Colin, 1988). In contrast, Buat-Menard and Duce (1986) found no dependency of SR with particle size in their studies in marine environment.

Differences in the vertical and horizontal dimensions of cloud systems and the duration, intensity and droplet size of the precipitation will certainly affect the precipitation scavenging efficiency of aerosol particles and the relation between scavenging ratio and the mass-size distribution of the materials associated with these particles. As shown by Scott (1978), large variations in scavenging ratio can be expected at different latitudes. For example, smaller SRs would be expected in 'cold clouds', where a much greater fraction of the precipitation occurs as a result of vapor-phase growth rather than droplet coalescence (Buat-Menard and Duce, 1986). The concentration of sea salt aerosol decreases rapidly with altitude. For species such as NO_3^-, which are associated primarily with sea salt aerosol in the near surface marine boundary layer, the decrease in sea salt with increasing altitude can alter the partitioning between the vapor and particulate phases as well as the size distribution in the particulate phase (Hastie et al., 1990; Galloway et al., 1992).

The interspecies variations in the SRs may also reflect differences in the partitioning of the constituents between the vapor and particulate phases. In addition to particulate NO_3^- and SO_4^{2-}, HNO_3^- and SO_2 exist in significant concentrations in the marine boundary layer. These species can be directly scavenged by precipitation to yield aqueous-phase NO_3^- and the SO_4^{2-}. By comparison, the vapor-phase lifetime of $CH_3SO_3^-$ appears to be relatively short and hence precipitation scavenging of gaseous $CH_3SO_3^-$ is probably an insignificant influence on corresponding SRs.

This coefficient is generally defined as the dimensionless ratio of the concentrations of the element in the precipitation and in the aerosol:

$$SR = \left({}^{C_p}\!\big/_{C_a} \right) \rho_{air} \tag{1.5}$$

Where C_p is the concentration of the species in precipitation (pbb), C_a is the concentration of the species in the aerosol (µg/m^3) and ρ_{air} is the density of air (1.170 kg/m^3).

However, the definition of this ratio imposes very restrictive assumptions, amongst which are:

- The aerosol measured (generally at ground-level) is vertically homogeneous (up to cloud level) and constitutes a faithful image of that which enriched the air mass throughout its history,

- The linearity of this relationship implies that there are no limiting factors upon exchanges (saturation, short contact time, etc.).

Implicit in the estimation of SRs is the underlying assumption that the concentration of a species in precipitation is directly related to its particulate-phase concentration in air at the same site. In this content, the time scales over which concentrations in the two phases are interpreted are of crucial importance. Because factors which influence SRs may vary independently not only from one event to another, but also within a single event, event-averaged SRs can range over several orders of magnitude even for a single species at a single location (Galloway et al., 1992).

Because of the large degree of variability, a measure of central tendency is required to make the SRs useful. Many investigators use the geometric mean for rain samples because of the log-normal distribution of paired SRs (Whelpdale, 1981; Barrie, 1985; Jaffrezo and Colin, 1988). Other investigators used the arithmetic mean or the median of the paired data set (Galloway et al., 1992). İn this study volume weighted average is used for the calculation of SRs. Precipitation volume has been the factor most often studied in relation to scavenging ratio variation. This is due partly to the avaibility of this datum, easily measured during sampling. Since the concentrations of elements are expected to be inversely related with the precipitation amount, variations in their measured concentrations are partly due to different precipitation volume in each sample. Volume weighted arithmetic averages (VWA) are frequently used in the literature to avoid the contribution of precipitation amount on the annual average concentrations at the receptor (Kaya and Tuncel, 1997; Seto, et al., 1999; Saxena, et al., 1996; Baez, et al., 1996; Fujita, et al., 2000). By the use of volume weighted average a better description of the data is obtained and the large variations in the data are lowered.

Volume weighted average concentration of elements and ions in rainwater could be calculating using the following relation (Acker K., et al., 1998; Valenta P., 1986):

$$C_w = \frac{\sum(C_i V_i)}{\sum V_i} \qquad (1.6)$$

where C_w volume weighted average. V_i is the precipitation amount of a given i^{th} day, C_i is the concentration of a given specie

1.9. Objectives of the Study

Atmospheric aerosol and rainwater both provide media to understand state of air pollution at a receptor and potential impacts on ecosystem. Mass and chemical composition of atmospheric particles had been extensively used to understand health effects of particles and pollutants associated with them, to understand mechanisms of transport from source to receptor, to understand reasons for visibility degradation, to understand light scattering characteristics of the atmosphere, which is important as a feedback mechanism in global warming issue, to determine sources and source regions affecting atmospheric composition at the receptor. Chemical composition of rainwater, on the other had, is being used to understand transport of pollutants, particularly acidity, persistent organic compounds and heavy metals, from atmosphere to terrestrial and marine ecosystems and to assess the effect of such transport in deterioration of various ecosystem components.

As can be easily appreciated, these two areas of research are complementary to each other; in other words, questions addressed by analyzing atmospheric particles and rain water are not the same, but complement each other. But unfortunately, sampling and analysis of rain water is much more difficult compared to sampling and analysis of atmospheric aerosol. Because of this, data on chemical composition of rain water are not as abundant as data on chemical composition of particles, not only in Turkey, but also in everywhere in the world. Since, questions that can be answered by using chemical composition of rain water are important and should not be given up, then it is worthwhile to attempt to deduce, or approximate rainwater composition from chemical composition of aerosol collected at a given location. If such a relationship, which allows constructing rainwater composition from aerosol data can be established, then questions about deposition fluxes of pollutants, acidification of environment, forest deterioration etc. can be answered without undertaking difficult task of sampling and analysis of very low levels of pollutants in rain water.

The main objective of this study is to establish such a relationship, if any exists, between chemical compositions of aerosol and rain water, using data sets generated in different parts of Turkey, so that difficult rain water sampling and analysis can be avoided in the future.

Studies performed in other parts of the work demonstrated that the relationship between chemical compositions of rain water and aerosols is generally complex and highly variable from sampling site to another. Some of the variability observed in these studies can be due to limited aerosol and/or rain water composition data used. Fairly long-term data (2 – 5 years) on chemical compositions of both aerosols and rain water is available at three stations located at the Mediterranean, Black Sea coasts and at the Central Anatolia. These relatively long-term data allowed more statistically reliable assessment of the similarities and differences between aerosol and rain water composition, compared to many studies reported in the literature. Limited Aerosol and rain water composition data generated at Ankara is also included in the study to evaluate the differences imposed by high emissions on this relationship.

In this study, the following questions were answered at each measurement site:

Is the state of pollution of the measurement point found from aerosol and rainwater data the same?

Do the aerosol and rain water data show the same temporal variability?

Do the aerosol and rain water data indicate same source types when multivariate apportionment techniques are applied?

Do the aerosol and rain water data suggest the same source regions when trajectory statistics are applied?

If answers to all of these questions are “yes” than one can conclude that chemical composition of rain water is determined by below cloud scavenging processes at the sampling point and there should be a relation between chemical compositions of particles and rain at that particular site. But if the answer to some or all of the above questions are “no” then, incorporation of pollutants into clouds during the transport of clouds to the receptor site (in-cloud mechanism) can be more important than below cloud processes and a very clear relation may not exist between the rain water and particles.

CHAPTER 2

MATERIALS AND METHODS

Aerosol and rainwater data used in this study are generated previously in other studies. Aerosol composition data at Antalya station is generated by Güllü (1996), rainwater data at the same station is generated by Al-Momani (1995); Aerosol data at Amasra station is generated by Karakaş (1999); Aerosol and rainwater data at Çubuk station is generated by the Ministry of Health, through EMEP program; Aerosol data at Ankara station is generated by Yatın (1994), rain data in Ankara is generated by Kaya (1997).

Since data generation is done in previous studies, only a brief description of experimental techniques will be presented in this thesis, as detailed description of methods used for sampling and analysis of both aerosols (Yatın, 1994; Güllü, 1996; Karakaş 1999; Yörük, 2004) and precipitation (Al-Momani, 1995; Kaya, 1997; El-Agha, 2000; Tunçer, 2000) are given elsewhere. However, stations at which aerosol and rainwater samples were collected are described in fair detail, because characteristics of sampling sites are an important factor in some of the conclusions derived in this study.

2.1. Sampling Site

Data used in this study are generated in four stations in different parts of Turkey, as pointed previously characteristics of the stations are presented in following sections.

2.1.1. Amasra

The station was implemented approximately 20 km east of Amasra town and 3.5 km far from the Black Sea (32.29 longitude east of Greenwich and 41.47 latitude north of Equator). The location of the sampling station is depicted in figure 2.1.

The station was consisted of 2 components that were the platform and the field laboratory. The platform was containing a Hi-Vol PM-10 aerosol sampler, a wet and dry deposition collector, had a ground filled with large sand stones. The field laboratory was a container with the dimensions of 3 m × 2 m × 2 m, which was including a storage area, a refrigerator and a sample change area.

The station was established in February 1993. In this study, the aerosol (Karakaş 1999) data (345 samples) collected between 1995 and 1997 and precipitation (El-Agha, 2000) data (177 samples) collected between 1995 and 1999 are used.

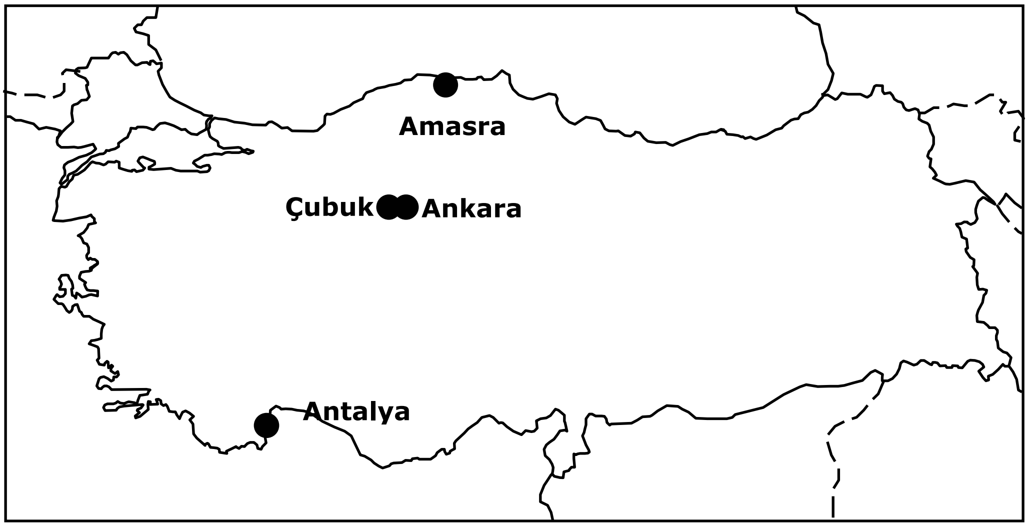


Figure 2.1. Locations of Sampling Stations

2.1.2. Ankara

The station was implemented in the Middle East Technical University, which is located at a suburban area that is situated 10 km to the heavily populated districts in the city. The location of the sampling station is depicted in figure 2.1.

The station was consisted of a dichotomous sampler and two cascade filtration samplers for parallel sampling. They were installed on the roof of Environmental Engineering Department in METU and run for 24 hours at the same time in order to compare the size fractionation efficiency of the three samplers used in this study.

The station was established in February 1993. In this study, the aerosol data (108 samples) collected at 1993 (Yatın, 1994) and precipitation data (71 samples) collected between 1993 and 1994 (Kaya, 1997) are used.

2.1.3. Antalya

The station, was implemented approximately 20 km away from the city of Antalya, in a land owned by the Ministry of Forestry. The location of the sampling station is depicted in figure 2.1.

The station, as in the Black Sea station, was consisted of 2 components that were the platform and the field laboratory. The platform was composed of a 4 m × 4 m concrete base that was surrounded 2 m high fence. It was constructed on a rock structure which was 20 m above the sea level. A Hi-Vol sampler, a Hi-Vol impactor, a wet and dry deposition sampler and a wet only precipitation sampler were attached to the base of the platform. The field laboratory was a container with the dimensions of 3 m × 2 m × 2 m, which was including a storage area, a refrigerator and a sample change area.

The station was established in December 1991. In this study, the aerosol data (597 samples) collected between 1992 and 1993 (Güllü, 1996) and precipitation data (115 samples) collected between 1992 and 1993 (Al-Momani, 1995) are used.

2.1.4. Çubuk

The station was implemented approximately 50 km away from the city of Ankara and 12 km away from Çubuk town (33.10 longitude east of Greenwich and 40.10 latitude north of Equator). The location of the sampling station is depicted in figure 2.1.

Sampling station was a rectangular cabin with a surface area of about 12 m^2. It was consisted of an air intake, a high volume sampler, a precipitation meter and a stack filter unit which were placed on a gravel platform with a height of 2.50 m, 2.00 m, 1.60 m, and 2.00 m, respectively above the ground level.

The station was established in 1992 and it has been collecting air and precipitation samples since then Çubuk station is the only certified EMEP station in Turkey. The station is operated by the Ministry of Health using strict sampling and analytical protocols common to all EMEP network. Between 1992 and 2000 1341 aerosol and 320 precipitation samples were collected and subsequently analyzed at Ministry of Health laboratories. Precipitation data generated in the station is evaluated by Tunçer (2000) and aerosol data by Yörük (2004).

2.2. Sampling and Analysis

At Çubuk, aerosol samples were collected with Digitel, model DHA-80 Hi-Vol sampler and at all the other stations they were collected with

Andersen Hi-Vol sampler as pointed out earlier in the text, only a brief description of experimental techniques will be presented in this thesis, as detailed description of methods used for sampling and analysis of both aerosols (Yatın, 1994; Güllü, 1996; Karakaş 1999; Yörük, 2004) and precipitation (Al-Momani, 1995; Kaya, 1997; El-Agha, 2000; Tunçer, 2000) are given elsewhere.

Aerosol samples were collected on cellulose filters (Whatman-41), for 24 hour periods at Amasra and Antalya using an Andersen Hi-Vol sampler. At Ankara, aerosol samples were collected with a stacked filter unit and dichotomous sampler. By using these samplers, particles in atmosphere were collected on different Teflon membrane filters depending on their diameter as fine (<2.5 µm) and coarse 2.5 µm<d< 10 µm) fractions. As both fine and coarse fraction of collected samples were analyzed separately, aerosols at Ankara were also measured as PM-10. At Çubuk station, samples were collected with Hi-Vol sampler for 24 hour periods (Yörük, 2003). As sampler at Çubuk was not a equipped with PM-10 preimpactor, collected samples were total particulate matter (TSP) instead of PM-10. However, previous studies on particle dimension indicate that difference between PM-10 and TSP is <%10 for crustal elements, and for anthropogenic elements it is even smaller (Kuloğlu, 1997). Because of this, aerosols collected at Çubuk were included to comparisons in this study.

Rain water samples were collected with Andersen wet – dry sampler at Antalya (Al-Momani, 1995), Amasra (Al Agha, 2000) and Ankara (Kaya, 1997). With this sampler it was possible to collect wet and dry deposition samples into different containers. With a modification made to the sampler, rain water was collected with a funnel, then passed through a filtration unit and ended up in the sampling bottle. By the help of a filtration apparatus, placed between the funnel and the sampling flask, rain water was collected in sampling flask after passing from a 0.47 µm pore sized cellulose acetate membrane filter. By analyzing the solution in the sampling bottle, and on residue filter, fractions of elements and ions, that are in particulate phase and dissolved in rain water were determine separately. In this study, total concentrations (dissolved + particulate) of elements and ions were used in statistical treatment of data. Sampling period was 24 hours.

Samples were collected at Çubuk station using a Walter Eigenbrodt NSA 181 wet-only sampler for 24 hour periods. Sampler used at Çubuk was different than that used in other stations as it was collected only wet deposition samples. The sampler sensed the rain, at the beginning of the event, through a sensor, which opened the lid to collect the rain in a sampling bottle. The end of the rain event was again sensed by the sensor and the lid is closed. Since dry deposition samples were not into the consideration in this study, rainwater samples collected at Çubuk station were identical with the samples collected in other stations. Rain water sampling at Çubuk station was discussed in detail by Tuncer (2000).

Samples collected at Antalya, Amasra and Ankara stations were digested with a HNO_3 – HF mixture, then were analyzed for elements Al, Fe, Pb, Mg, , Zn, Cu, Ba, Mn, Na, K, Ca Ni, Cr, Cd, Pb and V using a a Perkin Elmer 1100B Atomic absorption spectrometry (AAS). Concentrations of SO_4^{2-}, NO_3^-, Cl^- ve NH_4^+ in collected aerosol and rain water samples were measured with ion chromatography (IC) and spectrometric methods. Aerosol samples at Antalya, Amasra and Ankara stations were also analyzed with instrumental neutron activation analysis (INAA), in this way, concentrations of approximately 30 additional elements were determined. Used analytic methods were discussed by Yatın (1994) (Ankara), Güllü (1996) (Antalya) and Karakaş (1999) (Amasra) in detail.

Data at Çubuk station was not as complete as those measured at Antalya and Amasra, because INAA measurements were not performed at Çubuk station and AAS measurements were applied to only a few samples. Ion measurements , as in other stations, were performed with IC (Yörük, 2004; Tunçer, 2000).

As it is mentioned above, samples of aerosol and rain collected at Antalya, Amasra, Çubuk and Ankara stations are analyzed for trace elements and ions. Since the objective of sampling in these stations was not to establish a relation between rain and particle composition, different elements and ions were measured at each station, consequently, data generated at each station were not completely identical. Elements and ions measured at stations, and analytical methods used are depicted in Table 2.1. As it can be seen from the table, ions are generally measured in both aerosol and rain water in all stations. Likewise, Ca, K, Mg and Ca, except Çubuk station, were measured at every station. These elements measured only in rain water at Çubuk but not in particles. Trace elements, measured with AAS and INAA, were measured at Antalya, Amasra and Ankara stations and not measured at Çubuk Station. Ion concentrations, measured at Çubuk station were included in statistical data treatment as it has the highest number of samples in both aerosol and rain water. However, it was not possible to include Çubuk station to statistical studies like factor analysis as many elements and ions were needed. In this kind of evaluations, data obtained from Antalya, Amasra and Ankara stations were used.

Table 2.1. Elements and ions measured at stations, and used analytical methods

		Aerosol				Rain water			
		Antalya	Amasra	Ankara	Çubuk	Antalya	Amasra	Ankara	Çubuk
SO_4^{2-}	IC	✓	✓	✓	✓	✓	✓	✓	✓
NO_3^-	IC	✓	✓	✓	✓	✓	✓	✓	✓
Cl	IC	✓	✓	✓	✓	✓	✓	✓	✓
NH_4^+	S	✓	✓		✓	✓	✓	✓	✓
Ca	AAS	✓	✓	✓		✓	✓	✓	✓
K	AAS	✓	✓	✓		✓	✓	✓	✓
Mg	AAS	✓	✓	✓		✓	✓	✓	✓
Na	AAS	✓	✓	✓		✓	✓	✓	✓
Pb	AAS	✓	✓	✓		✓	✓	✓	
Ni	AAS	✓	✓	✓		✓	✓	✓	
Cr	AAS	✓	✓	✓		✓	✓	✓	
Cd	AAS	✓	✓	✓		✓	✓	✓	
Mn	AAS	✓	✓	✓		✓	✓	✓	
V	AAS	✓	✓	✓		✓	✓	✓	

Table 2.1. Cont’d.

Al	AAS	✓	✓	✓		✓	✓	✓	
Fe	AAS	✓	✓	✓		✓	✓	✓	
Zn	AAS	✓	✓	✓		✓	✓	✓	
Cu	AAS					✓	✓	✓	
Ti	INAA	✓	✓	✓					
Sc	INAA	✓	✓	✓					
Co	INAA	✓	✓	✓					
As	INAA	✓	✓	✓					
Se	INAA	✓	✓	✓					
Br	INAA	✓	✓	✓					
Mo	INAA	✓	✓	✓					
In	INAA	✓	✓	✓					
Sb	INAA	✓	✓	✓					
Ba	INAA	✓	✓	✓					
Cs	INAA	✓	✓	✓					
La	INAA	✓	✓	✓					
Ce	INAA	✓	✓	✓					

Table 2.1. Cont'd.

Nd	INAA	✓	✓	✓					
Sm	INAA	✓	✓	✓					
Yb	INAA	✓	✓	✓					
Lu	INAA	✓	✓	✓					
Hf	INAA	✓	✓	✓					
Au	INAA	✓	✓	✓					
Th	INAA	✓	✓	✓					
Hg	INAA	✓	✓	✓					
Hg	INAA	✓	✓	✓					

2.3. Statistical Methods Used

Since, statistical data treatment is the most important part of this study, statistical tools used in data treatment are briefly discussed in the following sections.

Since emissions from different source categories occur at different heights within the atmosphere, their impact on airborne concentrations is not directly proportional to their relative source strengths. Numerical methods are extensively used in literature to apportion sources contribution to particular receptor. The alternative approach to quantification of the impact of individual source types upon ambient air pollutant concentrations, which bases on application of statistical tools to concentrations measured at the receptor, is called receptor modelling (Hopke and Glover, 1991; Thurston and Spengler, 1985; Hopke and Thurston, 1984; Watson, 1979; Harrison et al.).

Receptor oriented models have been employed to identify possible sources of pollution, to resolve the elemental composition of sources and to determine the contributions of each source to the measured pollution level (Cooper and Watson, 1980, Hopke, 1985). In air pollution studies, among all multivariate statistical approaches, Factor Analysis (FA) (Hopke, 1985), Chemical Mass Balance (CMB) (Miller et al., 1972), Principle Component Analysis (PCA) (Thurston and Spengler, 1985), and Positive Matrix Factorization (PMF) (Paatero and Tapper, 1994) have been most commonly applied to arrays of pollution variables, to aerosol and precipitation elemental composition data, or to the spatial pollution distributions in order to derive information about pollution sources influencing the data.

In general, receptor models use the chemical and physical characteristics of ambient gases and particles to both identify the presence of and to quantify source contributions to the receptor site. In this modeling, the chemical and physical characteristics must be such that:

- They are present in different proportions in different source emissions,

- These proportions remain relatively constant for each source type,
- Changes in these proportions between source and receptor sites are negligible or can be predicted.

First generated receptor models like PCA, FA and CMB have limited abilities to locate regional sources of air pollutants as only chemical information is used and the regional pollutants are often secondary in their chemical nature and these receptor models can not determine the specific location of sources. Malm et al., (1986) presented the potential source contribution function (PSCF) to identify geographical regions that may have a higher probability of being source areas of pollutants. PSCF overcome these problems by integrating meteorological information with the receptor models.

2.3.1. Factor Analysis

Factor analysis (FA) is a multivariate statistical technique which is used frequently in atmospheric pollution research to obtain information on pollution sources that affect chemical composition of aerosol and precipitation at a given sampling site (Plaisance H., 1997, Karakaş D., 1999, Güllü G., 1996, Al-Momani I., 1995). Factor analysis separates elements into smaller number of groups or factors depending on their fluctuation and common variance. The produced groups or factors represent a definite source or mixed sources of the analyzed elements. FA produces a simplified representation of the data that permits the identification of the nature of the factors by computing the correlation coefficients or 'Loadings' between the original variables and the factors (Plaisance H., 1997).

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

One drawback of the factor analysis is that concentrations of elements found in a sample are the result of the combined influences of several sources. In order to separate the effects of different sources, the method calculates the communalities of the variation of the variables.

Another disadvantage is that despite the usage of a large data set, the method may not always separate the sources sufficiently. In cases that the sources are located close to each other, even if they have different types of emissions, it becomes difficult to distinguish between them, since the identification of sources by Factor Analysis from receptor samples is entirely dependent on the transport of species. Hence, the sources, which are located far from the sampling site, can be blended together. Local wind patterns may further urge the mixing of air from different directions. Additionally, sampling durations, which are longer than the temporal changes in the wind patterns, can also result in aggregation of different sources into one factor. Furthermore, if there is a force, which is not measured but affects two or more elements equally then this might lead an inference that some elements are related as if they were originated from a common source (Tunçer, 2000).

When FA is applied to a data set the first result obtained is a factor matrix which relates each of the elements or variables. The numbers in the matrix are referred to as the factor loadings and indicate how much of the variance of the given element can be explained by the given factor. Though the complete square matrix would exactly transform the data points between the two representations, the factors in the matrix are given in order of decreasing ability to describe the variance of the whole system. Usually only the higher order factors are retained for further analysis (generally factors having eigen values greater and equal to 1.0). The physical meaning of the factors must be interpreted by observing which elements or variables display high (> 0.25) loading within the factor. Although many elements may display high loadings, a particular source type is usually assigned to a factor by the presence of high loadings of a few marker species which are characteristics of that source type (Karakaş, 1999).

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

In this study, factor analysis was performed, for Antalya and Amasra stations, using the Statgraphics Statistics Software with varimax rotation to improve the orthogonality of resolved factors. The Statgraphics Statistics Software first normalizes the data set before performing factor analysis. It first subtracts the mean from the individual value of any element in the data set. After, this normalization, the new data set is used in the FA to compute the factors. When data is normalized, the mean vale becomes zero, and factor scores affected heavily by the pollution sources have positive values and the factor scores which are affected by the pollution source less than the average contribution of sources have negative values. The software then extracts the factors having the eigen values greater or equal to one and rotate the matrix and gives the rotation statistics. In the varimax rotation process the software simplies the factor matrix by maximizing the variance of the squared loadings in each column (Statgraphics Manual, 1977).

The factor scores for each factor were inspected and the factor score values higher than 7 were excluded just for running of factor analysis in order to avoid shielding of samples which have low factor scores (Hopke, 1980). FA was then run again until reasonable factor scores were obtained.

2.3.2. Potential Source Contribution Function (PSCF)

Several methodologies using trajectory analyses have been used to study emitter-receptor relationships for pollutants in aerosol and rain. In local scale, since sources are well known, source-receptor relationship refers to finding contirbution of each source on observed concentrations of pollutants. However, in regional scale, neither source types, nor locations of sources are known. Consequently, source-receptor relation in the regional scale refers to finding the source regions affeting observed levels of pollutants in the first step and estimating, if possible, contribution of those source regions in the second step.

Chemical information obtained by measurements at the receptor must be combined with geographical information to find source regions of pollutants measured at a particular receptor. In this type of source apportionment studies, measurements at the receptor provides chemical information. Geographical information, on the other hand, is provided by backtrajectory modeling. The methods that combine this two different types of information are commonly known as “trjectory statistics”.

Different techniques in trajectory statistics are in use today and rewiewed by Stohl (1996). The one that is used to determine source areas affecting chemical composition of particles and precipitaiton in this study is potential source contribution function (PSCF). Potential source contribution function calculations was first performed in 1986 by Malm et al. (1986), than succesfully used to determine source regions affecting pollutant concentrations at various receptors (Polisar et al., 1998; Stohl et al., 2002; Song et al., 2001; Liu et al., 2003).

In this study, PSCF calculations were performed to assess if the source regions affecting chemical composition of particles and rain at Antalya, Amasra and Çubuk stations are the same or different.

In PSCF calculations, study area must be defined. The area in which calculations were performed is assigned as 15^0 N – 75^0 N latitudes and 20^0 W – 60^0 E longitudes. This study area was then divided into 4800 grids (1^0 X 1^0) and PSCF values were calculated at each of these grids. Calculation of PSCF at each grid bases on calculating back trajectories using an appropriate model. In this study trajectories that goes for 5.5 days backward in time were calculated using ECMWF 3D, isentropic model. Calculated back trajectories were divided into 1 hour long segments then segments in grids were counted.

Suppose N represents the total number of trajectory segment endpoints for the whole study period, T. If the number of endpoints that fall in the j^{th} cell for trajectory i is n_{ij}, the overall residence time of air masses in cell j in entire study period is given by;

$$P\left[A_{ij}\right] = \frac{n_{ij}}{N} \qquad (2.1)$$

For the same cell, if there are m_{ij} endpoints whose arrival times of air parcels correspond the events with pollutant concentrations higher than a given value observed at the site, residence time of pollutant events in the study period is given by;

$$P\left[B_{ij}\right] = \frac{m_{ij}}{N} \qquad (2.2)$$

Then the PSCF for j^{th} cell can be calculated as:

$$\mathrm{PSCF} = \frac{P\left[B_{ij}\right]}{P\left[A_{ij}\right]} = \frac{m_{ij}}{n_{ij}} \tag{2.3}$$

PSCF values calculated for each grid were then transferred to Map Info Professional 7.0, which is a GIS software. Finally, thematic maps showing distribution of PSCF values in the study are prepared using an interpolation technique.

There are two sources of uncertainty in PSCF calculations. First of these is the horizontal uncertainty in trajectory segments. The uncertainty in trajectory calculations increase with distance (time) from receptor. Studies performed showed that horizontal uncertainty in back trajectories is between 140 km and 300 km after 24 hours backward in time and between 350 and 500 km after 72 hours backward in time (Kuo et al., 1985; Kahl and Sampson, 1986; 1988; Drexler, 1987). Since back trajectories calculated in this study extends to 5.5 days backward in time, horizontal uncertainty in the segments located in grids that lies at outer parts of the study area can be as large as 500 km.

The second source of uncertainty is due to small number of segments in each gird. As expected, uncertainty in calculated PSCF values increase as the number of segments in the grid decrease. This second source of uncertainty also depends on the distance between the grid and the receptor. Since all trajectories ends at the receptor, grids around receptor have large number of trajectory segments. Statistical uncertainty in PSCF values in these grids is fairly low. But number of grids decrease with the distance from the receptor and hence the statistical uncertainty increase proportionally. Since uncertainty due to horizontal error in trajectory segments and statistical uncertainties are both high for grids that are located at the edges of the study area, PSCF values calculated for these grids can be very large. Because of this, statistical significance of PSCF scores obtained from all grids should be evaluated in a certain confidence interval.

In all the PSCF calculations made in this study, statistical significance of PSCF values obtained from grids are evaluated by Bootstrapping method (Lupu and Maenhaut, 2002) and only PSCF scores that are statistically significant at statistically %95 confidence interval are shown in dispersion maps.

In order to identify the high PSCF values that might have arisen purely by chance, it is necessary to test these values against the null hypothesis that there is no association between concentrations and trajectories (Vasconcelos et al., 1996). The statistical significance of the spatial distribution of the PSCF values is examined by making use of a non-parametric bootstrap method (Wehrens et al., 2000). The method assumes that the concentration values are independent and identically distributed. Replacement from the original concentration data set is drawn, $C = (c_1, c_2, \ldots, c_N)$, B random sub samples of size equal to the data set, $C^* = (c_1^*, c_2^*, \ldots, c_N^*)$. For each bootstrapped sample k, the corresponding PSCF spatial distribution, $P^*_{k;ij}$, is calculated. Let $P^*_{1;ij} < \ldots < P^*_{B;ij}$ be the ordered values $(P^*_{k;ij})$, $k = 1, \ldots, B$, and let α be the chosen significance level. If

$$P_{ij} \geq P^*_{((B+1)(1-\alpha/2));ij} , \qquad (2.4)$$

The null hypothesis is rejected at (1- α) 100% confidence level. Then it is decided to retain, for further analysis, only the PSCF values satisfying the above relation (Lupu and Maenhaut, 2002).

2.3.3. Enrichment Factors (EF)

The chemical composition of the aerosols in the atmosphere is controlled by the mixing of various natural and anthropogenic components and the extent to which the mixing occurs will vary both in space and time. EF provide qualitative information on the natural and anthropogenic components in the aerosol (Zoller et al., 1974).

Enrichment factor of an element can be calculated as follows;

$$EF = \frac{(C_X/C_R)_{sample}}{(C_X/C_R)_{reference}} \qquad (2.5)$$

where, C_X, corresponds to the concentration of the element in the sample and in the reference material. C_R corresponds to the concentration of reference element in the sample and in the reference material. There are two types of EF, which are crustal (EF_c) and marine (EF_m) enrichment factors. In this study, only EF_c is calculated.

As a reference element Al is used as it is the most abundant element in earth crust. For that reason it is considered as representative for the soil composition, since soil is the only source for lithophilic elements. Mason’s soil composition (Mason, 1966) is used in this study as the reference soil composition, concentrations are given in Table 2.2.

Table 2.2. Mason’s soil composition (mg/m^3)

SO_4^{2-}	780	Cl	130	Ni	75
Na	28	Al	81300	Cu	55
K	25.9	V	135	Zn	70
Mg	20.9	Cr	100	Cd	0,2
Ca	36300	Mn	950	Pb	13
Ba	425	Fe	50000		

CHAPTER 3

RESULTS AND DISCUSSIONS

3.1. Comparison of Annual Concentrations

3.1.1. Comparison of Median Concentrations

Median concentrations of elements and ions (SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, Na, K, Mg, Ca, Al, Fe, Cr, Ni, V, Pb, Cd and Zn) in rain water and aerosols at Antalya, Amasra, Ankara and Çubuk stations are given in Table 3.1.

Similarities in spatial patterns in concentrations of elements can provide information on similarities and differences of sources affecting composition of particles and precipitation. Spatial patterns of elemental concentrations in rain and particles are given in Figure 3.1.

Concentrations of Cl, Na, Fe, Pb, Mg and K show approximately similar spatial variation in both aerosols and rain water, indicating concentrations of these elements in aerosol and precipitation can be controlled by the same source. Sodium and chlorine are elements associated with sea salt, in both aerosol and rain.

Table 3.1. Median concentrations of elements and ions in aerosol and rain water at Amasra, Antalya, Ankara and Çubuk stations (Rain concentrations are in μg L^{-1} and aerosol concentrations are in ng/m^{-3})

	Amasra		**Antalya**		**Ankara**		**Cubuk**	
	RAIN	Aerosol	RAIN	Aerosol	RAIN	Aerosol	RAIN	Aerosol
SO_4^{2-}	2740	4124	3130	4282	2080	2370	2759	1573
NO_3^-	1660	809	2198	1076	1159	730	1527	317
NH_4^+	380	1260	599	1250			902	441
Cl	1110	230	7505	973	587	8		
Na	2000	302	2869	667	324	45		
K	172	141	263	254	76	75	361	170
Mg	88	116	798	275	111	28	113	114
Ca	180	286	1543	1694	2143	49	1349	408
Al	337	226	269	346	208	56		
Fe	282	228	389	281	131	65		
Cr	0.90	0.98	3.92	2.97	0.98	2.82		
Ni	0.99	1.13	15	1.92	1.80	2.74		
Mn	70	9.25						
V	0.35	2.05			1.16	3.03		
Pb	5.57	13	5.83	18	8.45	50		
Cd	3.57	0.22			3.74	0.08		
Zn	80	10	26	7.66	20	13		

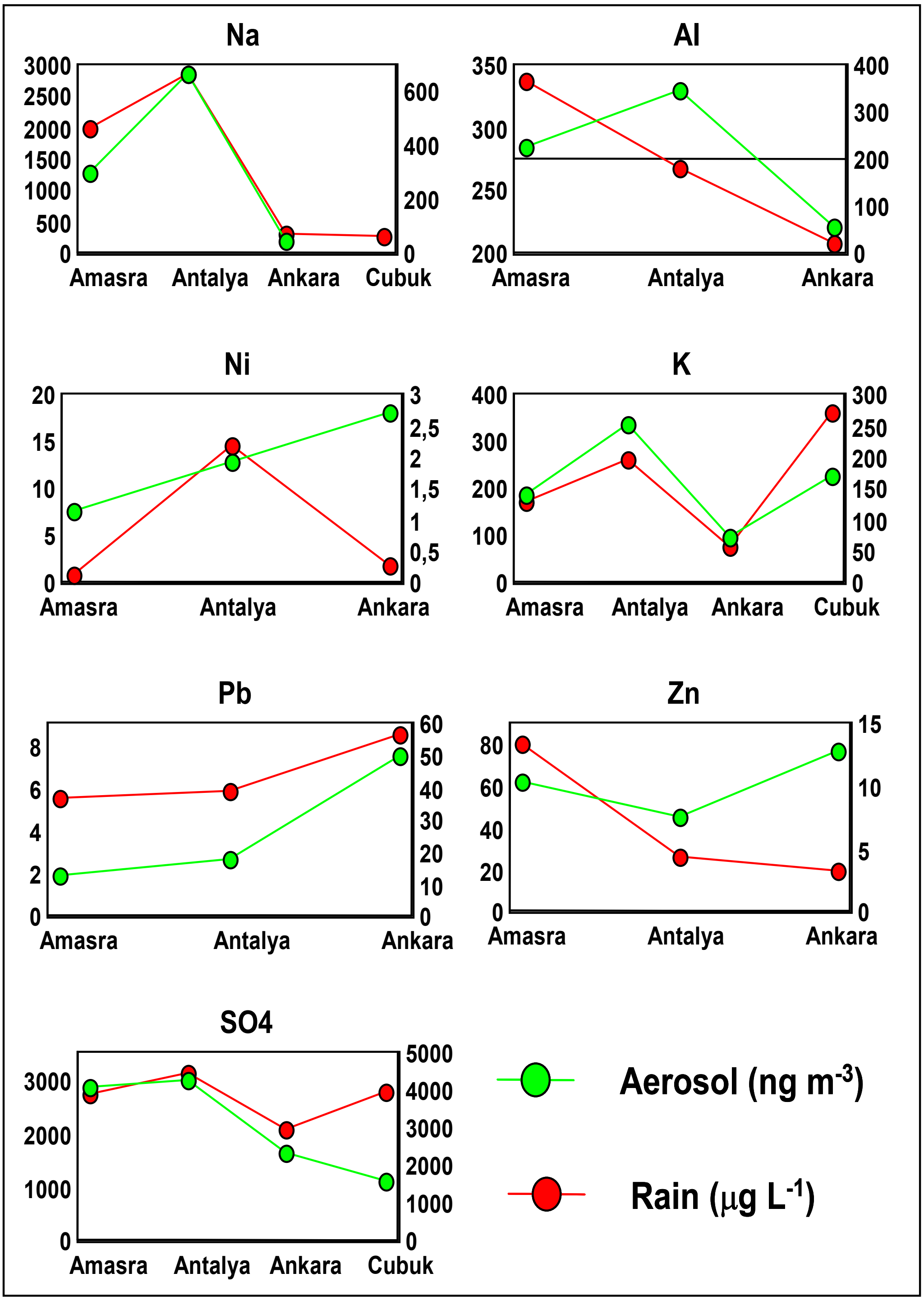


Figure 3.1 Spatial patterns of elemental concentrations in rain and particles

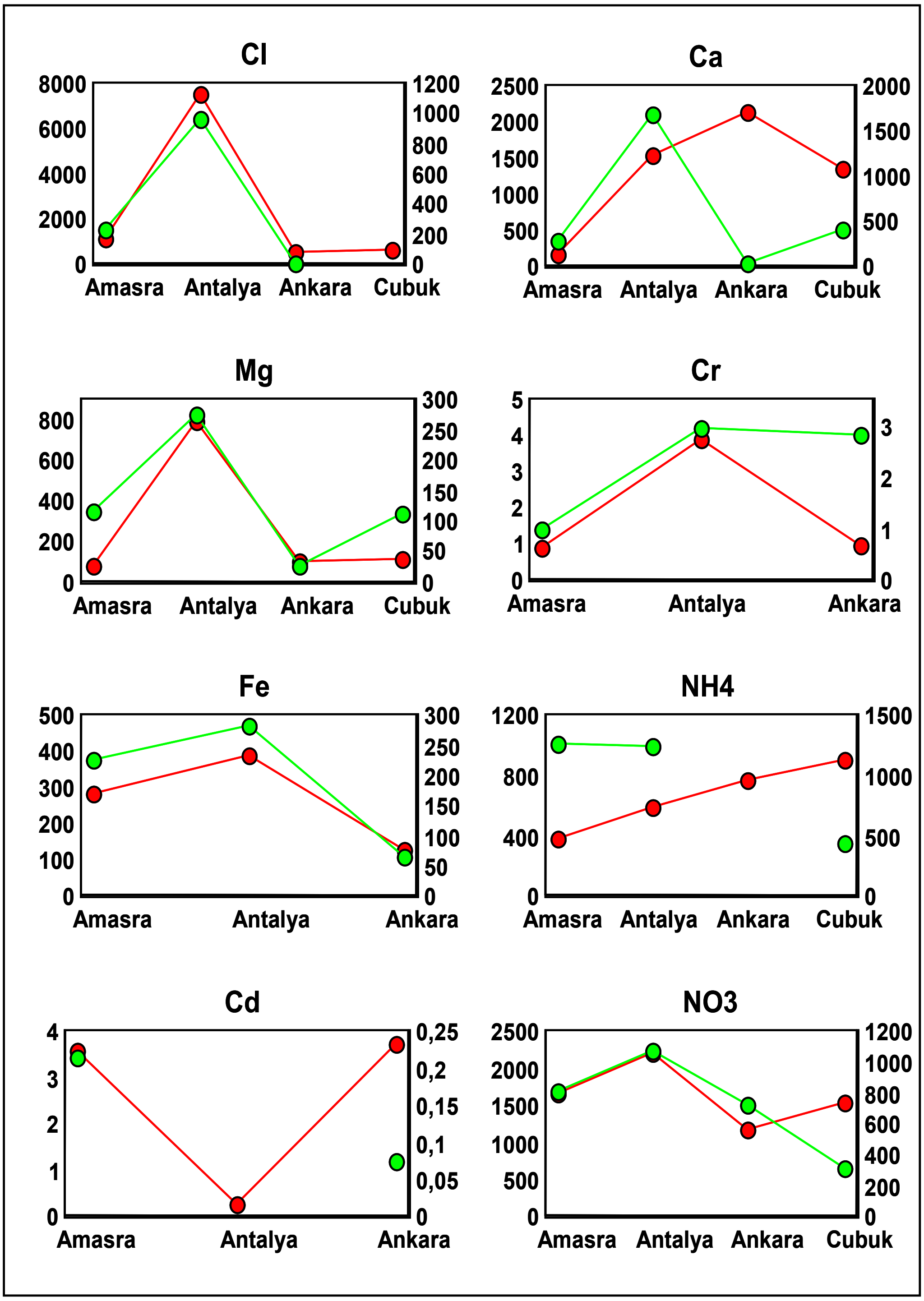


Figure 3.1. Cont'd.

Their concentrations at different stations depend on relative distance to coast. This is true for both matrices. Other elements, except for Pb, are crustal and their concentrations in both aerosol and rain are controlled by abundance of re-suspended soil particles in the atmosphere.

All of these elements (Cl, Na, Fe, Mg and K) are known to be associated with coarse particles, which are scavenged approximately three times more efficiently than fine particles bearing anthropogenic elements (Gesamp, 1990; Galloway et al., 1993; Güllü, 1996). Coarse particles are effectively removed by below cloud scavenging (washout) which is a local process. Consequently, coarse particles incorporated in rain represent local aerosol collected at the receptor, suggesting good agreement between aerosol and rain concentrations.

Concentrations of anthropogenic elements such as Cr, Ni, NH_4, Zn and SO_4^{2-}, which are associated with fine atmospheric aerosols, have different spatial patterns in aerosol and rain water. For these elements wet deposition with incloud processes can be important. These elements can be incorporated into cloud droplets in any source region, and then are transported to other locations with in the cloud. (El-Agha, 2000, Al-Monami, 1995). Consequently these elements are brought to the receptor site by clouds from other locations and falls from cloud droplets with rain. Composition of rain water in this sense are not expected to be the same with composition of the aerosols sampled. The only exception for this scenario is Pb. Lead is also an anthropogenic element associated with fine particles and it is expected to show similar spatial pattern with other anthropogenic elements. However, rainwater and aerosol show similar spatial variation as shown in the Figure 3.1.

This is probably due to the fact that Pb has also relatively local contributions from roads around stations and decrease in Pb concentrations in European atmosphere in recent years increased the relative contributions of local sources on Pb concentrations at receptors such as Amasra and Antalya. Due to this reasons lead behaves like locally generated parameters.

Al and Ca are crustal elements and expected to depict similar spatial pattern with other crustal elements (Fe, K, Mg), but spatial variation in Al and Ca concentrations in rain and aerosol are significantly different. The reasons for this pattern are not known.

Fingerprints of elements and ions at each station (abundance of elements relative to each other) also provide information on relative contributions of incloud and below cloud processes on concentrations of measured species. If rain water composition is derived entirely from local aerosol, (i.e. if below cloud mechanism dominates over in cloud mechanism), elemental fingerprints in rain and aerosol should be identical. Differences between aerosol and rain fingerprints indicate regional nature of observed concentrations. Fingerprints (elemental profiles) at each station are depicted in Figure 3.2. As it can be seen from the figure several species have higher than expected concentrations in rain relative to aerosol. These species are Na, Cl, NO_3^-, Mn, Cd and Zn for Amasra station; Na, Cl, NO_3^-, Zn and Ni for Antalya station; Na, Cl, Cd, Ca and Mg for Ankara station and NO_3^- for Çubuk station.

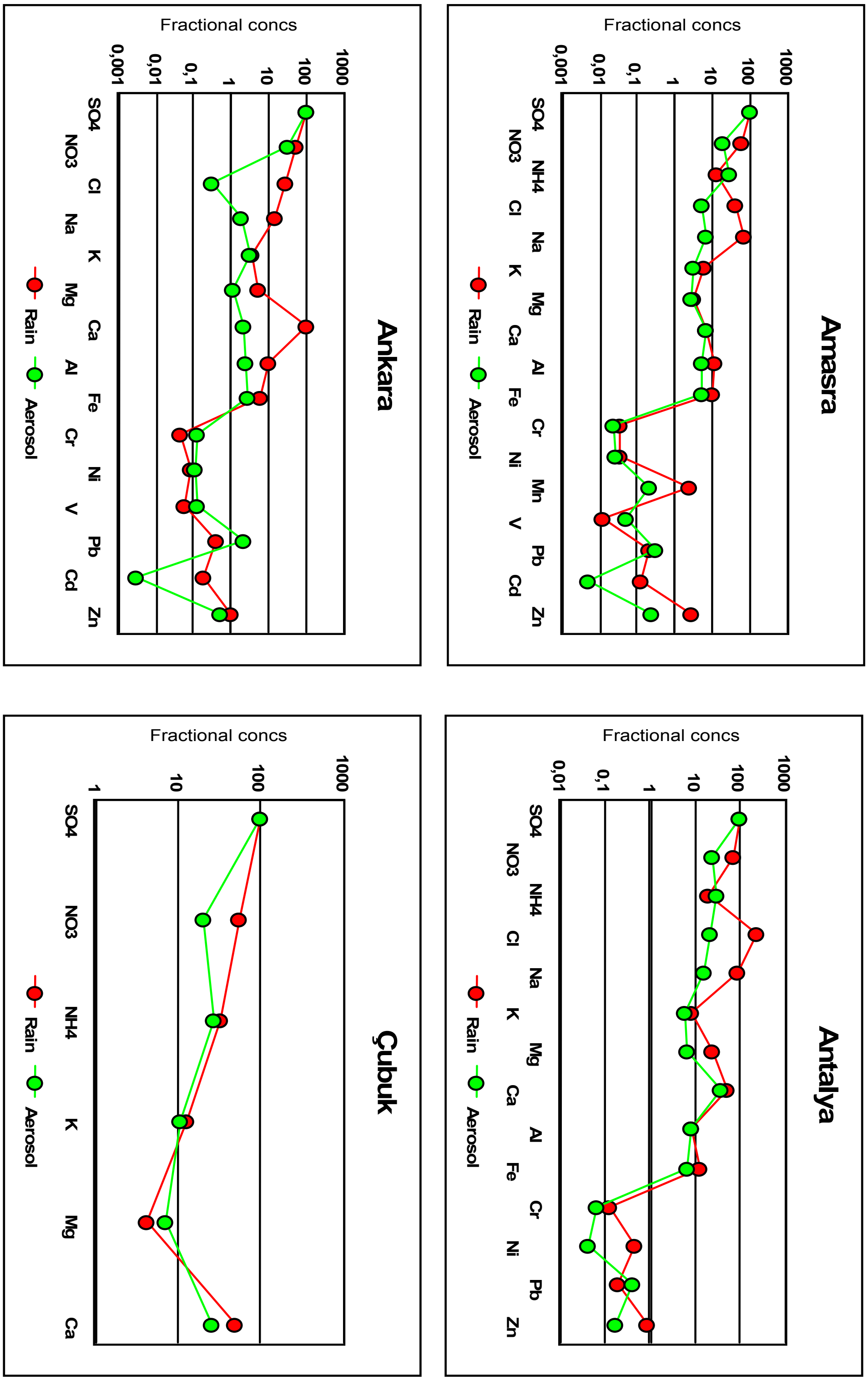


Figure 3.2. Elemental patterns in rain and aerosols

In none of the stations rain concentrations are less than expected relative to aerosol concentrations. This is because washing of local aerosol forms a baseline for rain water concentrations then material transported in clouds from distant sources adds to this baseline.

Na, Cl, NO_3^- , Mn, Cd and Zn commonly differs from expected pattern in all stations, suggesting that observed concentrations in rain cannot be explained only by local washout. All air masses that ends up in any part of Turkey has to cross seas. Sea salt particles are generated by the bubble bursting on the sea surface. These sea salts are picked up by the air masses, which are passing through the sea, and carried to the sampling stations. Marine elements like Na and Cl are associated with sea salts that are brought to the sampling sites. Consequently some additional sea salt is carried by clouds from distant regions over the sea and rains out at the station, while it is raining, it also washes out local sea salt at the station. Higher Na and Cl in rain relative to aerosol indicate sea salt transported from distant ocean is significant. NO_3^- is an anthropogenic specie, but in most studies it is well correlated with Na and Cl, and it is suggested that correlation is due to reaction between gaseous HNO_3^- and NaCl which forms $NaN0_3$ and HCl (Savoie and Prospero, 1982). Consequently, mechanisms that bring additional sea salt to station also bring NO_3^- that is associated with coarse sea salt particles. This explains additional NO_3^- observed in rain water at Antalya, Amasra and Çubuk stations. There is no source for anthropogenic elements such as Cd, Zn and Mn in the vicinity of Antalya and Amasra stations, the significant fraction of them are transported from distant sources and this explains higher concentrations of these elements in rain water than aerosol. Contributions of incloud processes on observed concentrations of these groups of elements are probably higher than contribution of below cloud processes. Since these elements are all anthropogenic, higher contribution of incloud processes on their observed concentrations agrees with the conclusions reached by comparing spatial variations in concentrations of measured species in the previous section.

In Ankara, most anthropogenic elements fits to same pattern (with exception of Cd), suggesting that these elements are more influenced from local sources. This is because, Ankara is an urban site and there are strong local anthropogenic sources of these elements which dominate over long-range transported sources. Lead fits to the pattern in all stations, indicating strong local sources, which are most probably local roads.

3.1.2. Comparison of Fractional Concentrations

If rain water concentrations reflect aerosol composition then fractional concentrations in aerosol and rainwater should be identical. Fractional concentrations of elements and ions in rain water and aerosols are calculated for Amasra, Antalya and Ankara data sets. To calculate fractional concentrations, median concentrations of SO_4^{2-}, NO_3^-, Cl, Na, K, Mg, Ca, Al, Fe, Cr, Ni, Pb and Zn in aerosol and rain are separately summed up and percent contribution of each element to this total concentration is calculated at each station for rain and particles.

Only the ions that are measured in both aerosols and precipitation at Antalya, Amasra and Ankara stations are included in calculations.

Çubuk data were not included in calculations as only few elements are measured in that station. Although NH_4^+ is an important ion, it is not included in this calculation, because it is not measured in Ankara station. But its fractional concentration is calculated for Antalya and Amasra data sets and included in discussions. Results are given in Table 3.2 and Figure3.3.

Table 3.2. Comparison of fractional concentrations of elements in rain water and aerosols

	Amasra		**Antalya**		**Ankara**	
	Rain	Aerosol	Rain	Aerosol	Rain	Aerosol
SO_4^{2-}	31,65	63,59	16,46	43,34	30,37	67,81
NO_3^-	19,18	12,47	11,56	10,89	16,92	20,89
Cl	12,82	3,54	39,47	9,84	8,57	0,22
Na	23,10	4,65	15,09	6,75	4,73	1,28
K	1,99	2,17	1,38	2,58	1,11	2,14
Mg	1,02	1,79	4,20	2,78	1,62	0,81
Ca	2,08	4,40	8,11	17,15	31,28	1,40
Al	3,89	3,48	1,41	3,50	3,04	1,60
Fe	3,26	3,51	2,05	2,85	1,91	1,86
Cr	0,010	0,015	0,021	0,030	0,014	0,081
Ni	0,011	0,017	0,077	0,019	0,026	0,078
Pb	0,064	0,198	0,031	0,182	0,123	1,443
Zn	0,92	0,16	0,14	0,08	0,29	0,37

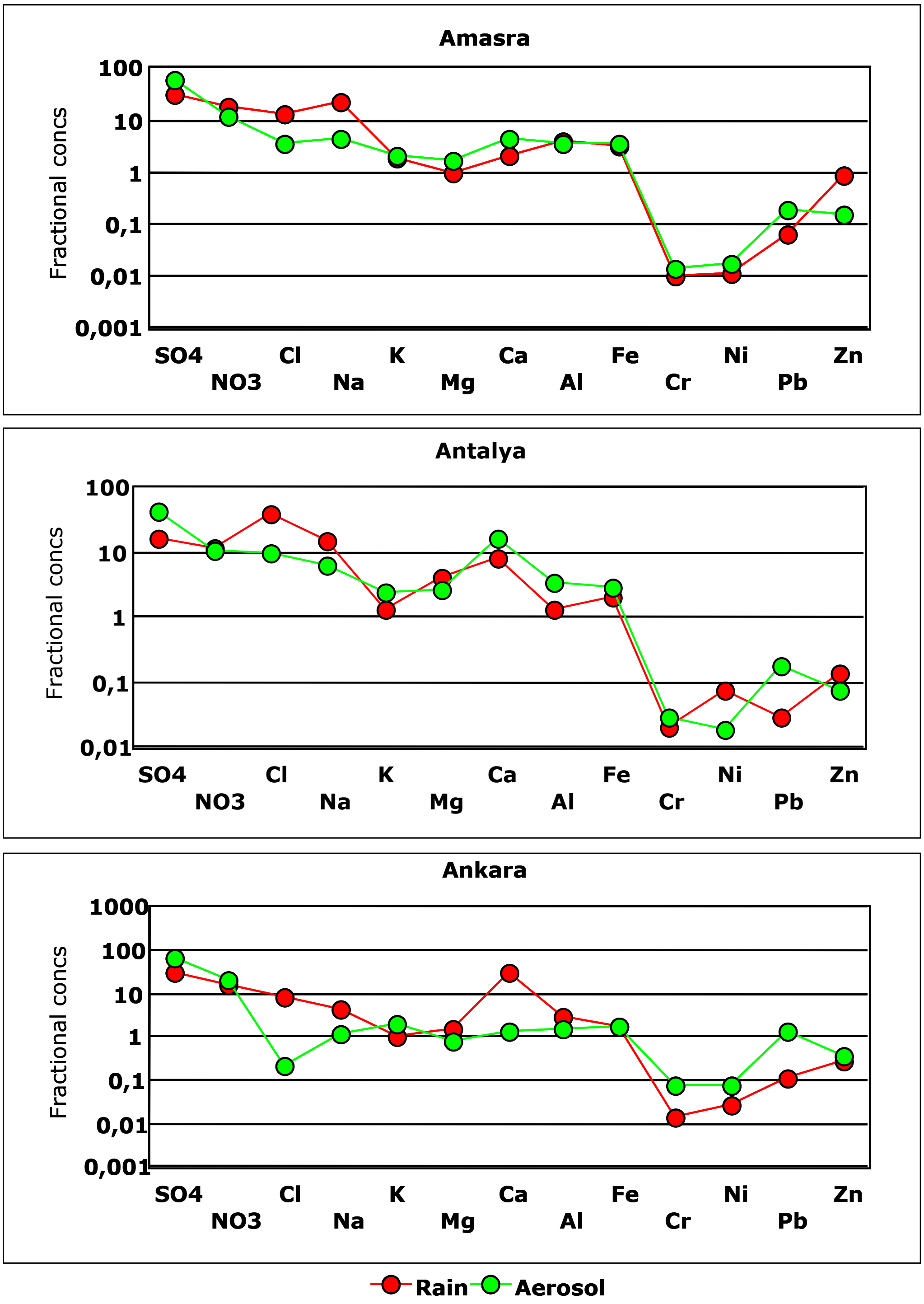


Figure 3.3. Fractional fingerprints

Highest contribution to total elemental and ionic mass is by SO_4^{2-}, NO_3^-, Cl and Na. Calcium has high contribution in Ankara station but not in others. This trend is consistently observed in both aerosols and precipitation at all three stations.

In all stations contribution of SO_4^{2-} to total mass in aerosols is higher than that in rain. The same trend is also observed for Pb and NH_4^+ (in Antalya and Amasra, not measured in Ankara). Higher contribution of these ions and elements in aerosol mass is owing to their association with fine particles. Fine particles are scavenged out less efficiently compared to coarse particles. Since scavenging is incomplete for these fine fraction elements, their contribution to total mass is higher in atmospheric particles than in rain.

Na and Cl have higher contribution to mass in rain in all stations. As it is discussed before, significant fraction of Na and Cl intercepted at stations are brought there from the seas surrounding Turkey, not necessarily from immediate surrounding of the stations.

Comparison the concentrations of elements and ions in aerosol and rain suggests that, the composition of rain water in different parts of Turkey do not directly reflect the composition of aerosol at that particular site. For some elements (particularly with crustal elements, such as Al, Fe and elements associated with coarse particles, such as NO_3^-) rain water composition seem to be similar to aerosol fingerprints. However, for marine element and for anthropogenic, the agreement between rain and aerosol profiles are not identical.

There are two reasons for this, firstly, aerosols samples at a particular location reflects local composition. Contribution of local and distant aerosol to composition of precipitation changes from one specie to another. Lastly, elements and ions that are associated with fine particles are not scavenged out as efficiently as the elements and ions associated with coarse particles. These two factors seem to explain observed patterns of annual median concentrations in rain and aerosol.

3.2. Temporal Variation in Concentrations of Rainwater and Aerosol Concentrations

Temporal variations of ion concentrations are generally studied for different time-scales. Short-term variations are the episodic changes in concentrations, while long-term variations are the average changes in the time scales of seasons or years.

3.2.1. Short-Term Variations

Concentrations of ions show large variations from one day to another due to daily changes in emission strengths, local meteorology and transport patterns. Episodic changes can be pronounced for both soil and anthropogenic elements for different reasons. Investigation of short-term variations can provide useful information on the point sources, source regions and transport patterns and specific meteorological patterns that give rise to elevated levels of elements and ions (Tunçer, 2002). Daily variation in concentrations of selected species in rain and aerosol at Çubuk station are given in Figure 3.4.

The same behavior is also observed for all species in other stations as well.

For all the species shown in the Figure 3.4, generally concentration maxima in rain water correspond to a minimum in aerosol data. This indicates a relation between aerosol composition and rain water composition. The relation is complex. Every dip in aerosol concentrations does not correspond to a rain event. This can be seen better in Figure 3.5. Where aerosol and rainwater concentrations are plotted for Çubuk and Antalya stations. There is no statistically significant correlation between aerosol and rain water SO_4^{2-} concentrations with 95% confidence. This is not true only for SO_4^{2-}, similar lack of correlation is observed for all other elements as well.

Some relation between short term variations in aerosol composition can be obtained if data on variability is averaged over long periods of time. Concentrations of elements and ions in atmospheric particles are scavenged out by rain and because of this concentrations decrease during rain events. If this is the case then during rain atmosphere is depleted in particles (also elements and ions associated with these particles) and it is expected to be reloaded gradually with particles after the rain. This behavior is plotted in Figures 3.6, 3.7 and 3.8 for crustal, marine and anthropogenic elements. Ankara data set is not included in this discussion, because rain and aerosol is not sampled simultaneously.

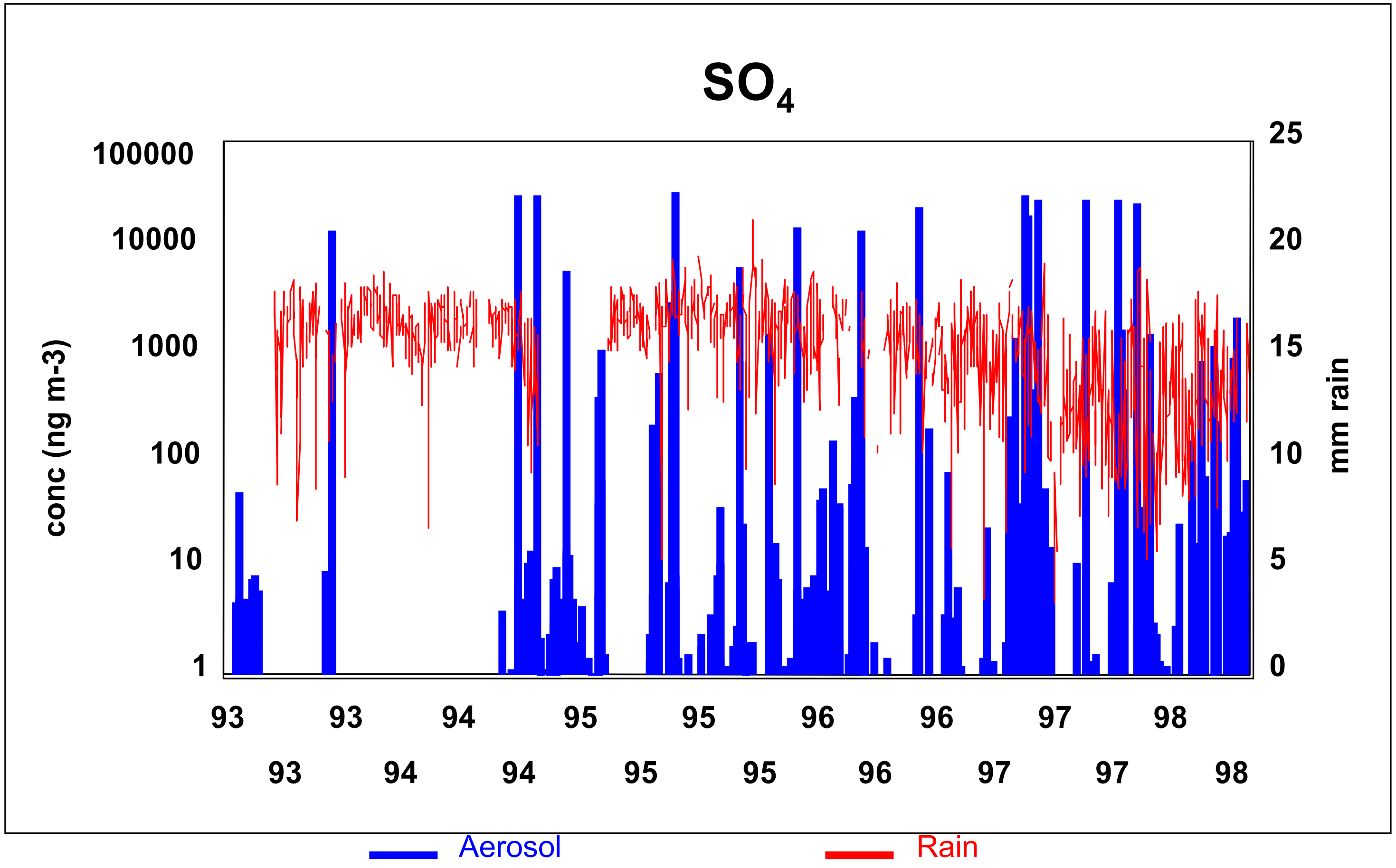
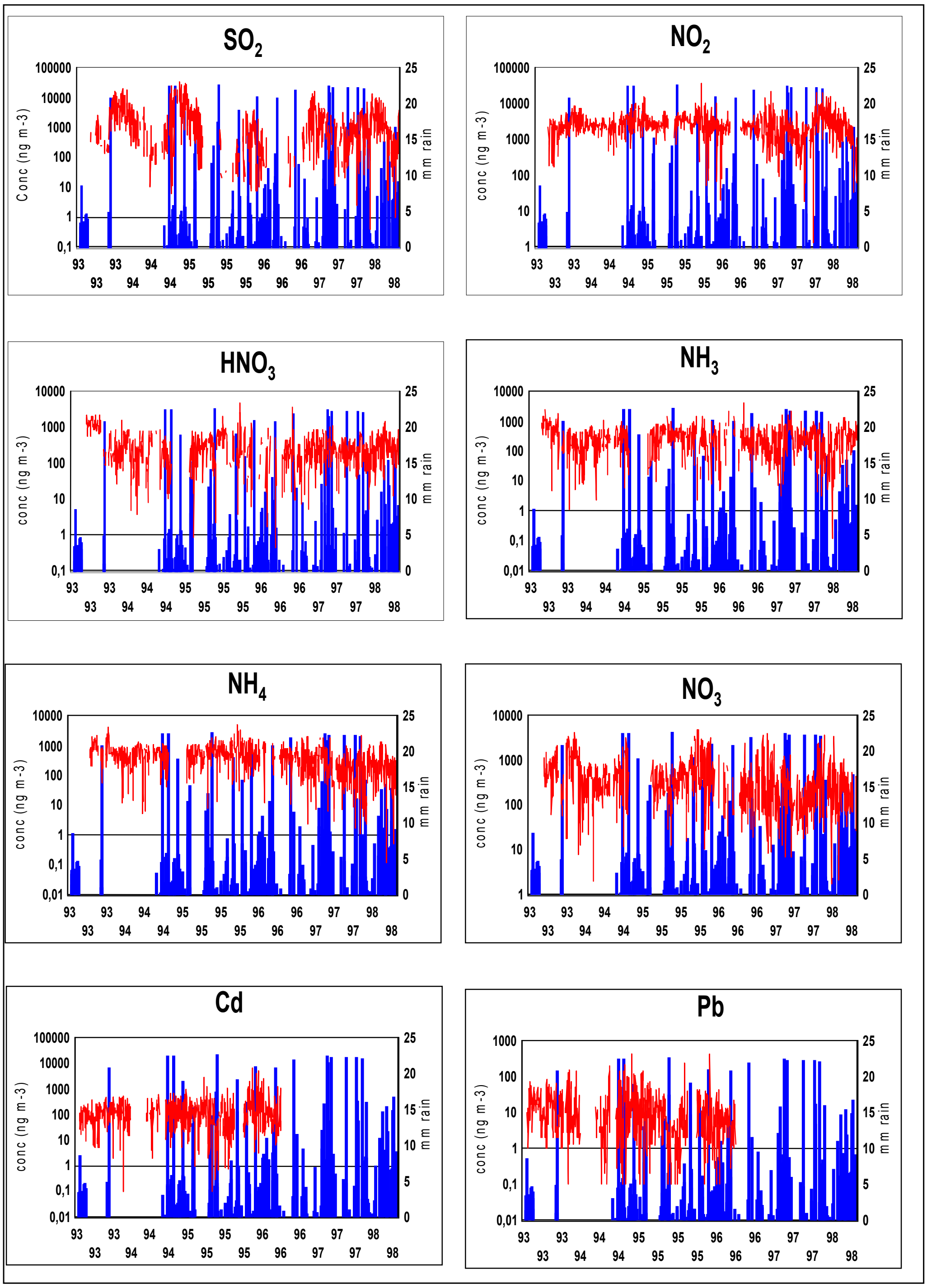


Figure 3.4. Daily variation in concentrations of selected species in rain and aerosol at Çubuk station



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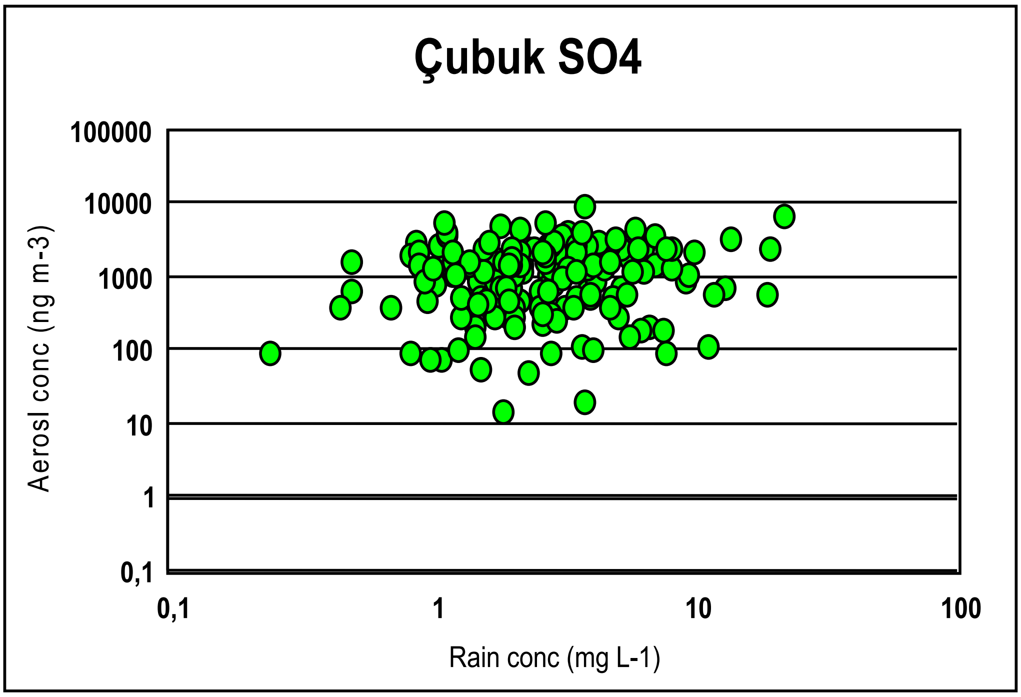

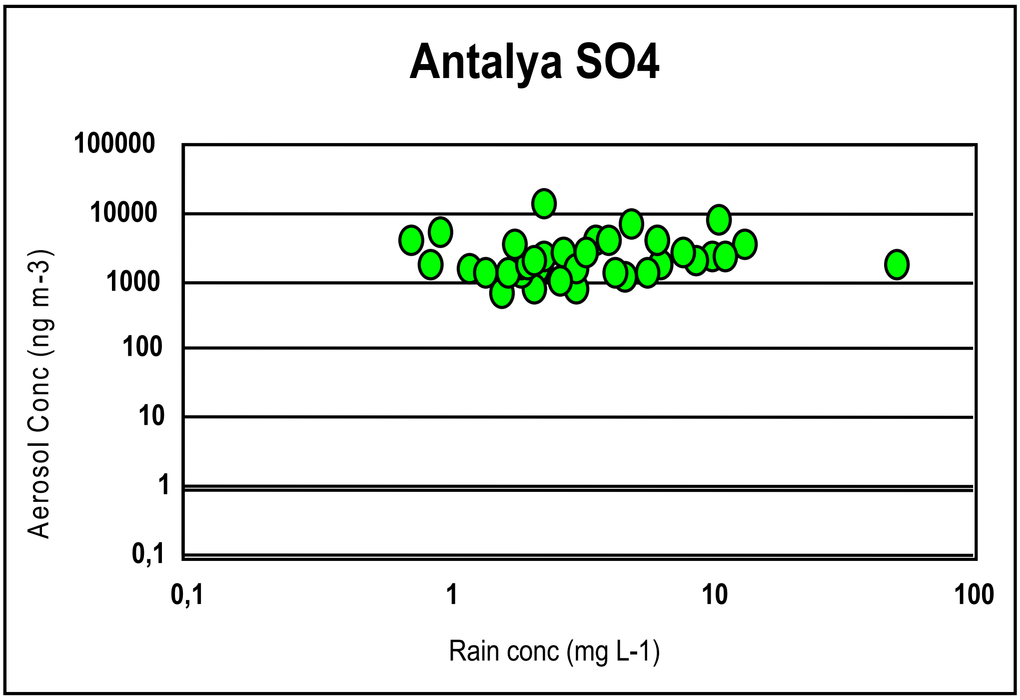

Figure 3.5. Relation between aerosol and rain water compositions

3.2.1.1. Crustal Elements

Variations in concentrations of crustal elements as a function of time from rain event are depicted in Figure 3.6. Figure for crustal elements are prepared for Amasra and Antalya but not for Çubuk data sets, because crustal elements Al and Fe are not measured in Çubuk data set.

The crustal particles are generated in situ and their generation rate depends on wind velocity and dryness of the soil. A rain event not only removes crustal particles from the atmosphere, but also it wets the soil and hinders the generation of dust particles. In the event of rain, certain fractions of crustal particles in the atmosphere are scavenged out. The concentrations of soil related elements in the day following rain inevitable low, because no matter what the wind velocity is since the soil is still wet, resuspension is low. As the soil gets dryer in the following days generation of dust particles start to increase (Güllü, 1996). Behaviors observed in Antalya and Amasra are more or less the same. Concentrations of Al and Fe in Antalya station are less than 100 µg m^{-3} during rain and increase to more than 200 µg m^{-3} within a week in Antalya and more gradual in Amasra.

From the figure, even though there are some exceptions, it can be depicted that the general trend is in accordance with the suggested scenario; concentrations are the lowest during rain and gradually increase. Two exceptions are Mg and K, as concentrations of Mg and K are higher during rain days than the first day after rain in Antalya. Concentrations of these two elements in atmospheric particles are determined by both crustal material and sea salt. This behavior of K

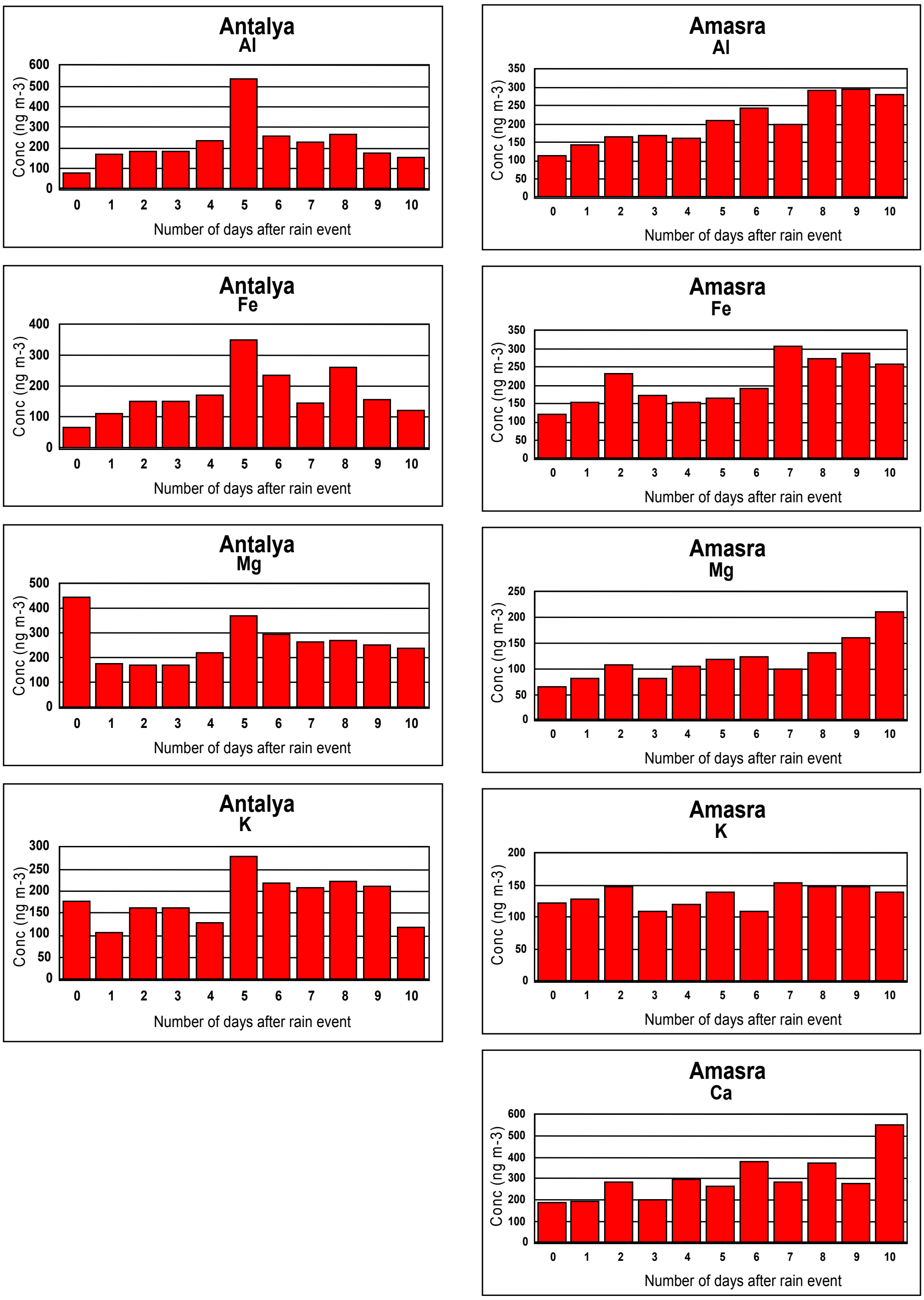

Figure 3.6. Concentrations of crustal elements measured after rain event

and Mg in Antalya aerosol data agrees with the pattern observed in marine elements in Antalya station as will be discussed in the next section.

3.2.1.2. Marine Elements

Figure for marine elements are prepared for Amasra and Antalya data set, because marine elements like Na and Cl are not measured in Çubuk aerosol data set. Variations for marine elements can be seen in Figure 3.7.

Unlike crustal elements, concentrations do not increase after rain events. Rains are generally associated with storm activity as the storm activity over the sea generates large quantities of sea salt, consequently in the first day concentration of sea salt particles in the atmosphere and rain are high. After the rain, with cessation of strong winds associated with storms, atmosphere clears out resulting with a decrease for subsequent days. This is clearly observed in concentrations of Na and Cl in Antalya station.

The pattern observed in Amasra station is different. Concentrations of Na and Cl observed in aerosols during the rain are not higher than concentrations observed in subsequent days. Concentrations observed in day-0 is comparable to concentrations observed in subsequent days. Slight increase observed in the first few days in Cl unlike Na. That can be explained as Cl also occur in gas phase as HCl, which subsequently condenses on particles or adsorbed on filters. The increase in Cl

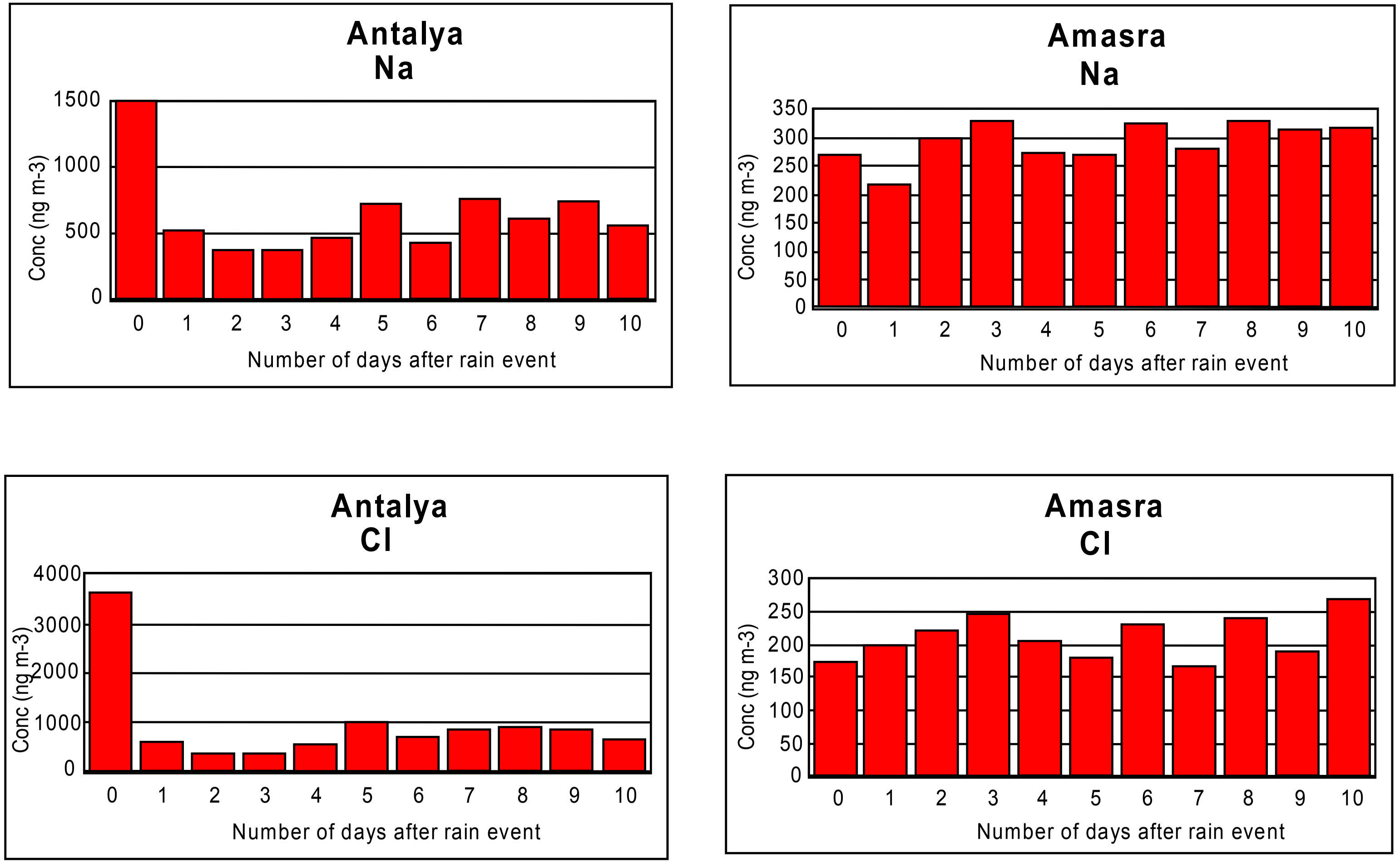

Figure 3.7. Concentrations of marine elements measured after rain event

concentration within few days after the rain suggests built up of gaseous Cl.

The difference between Antalya and Amasra stations is their relative distances to the sea. Antalya station is at the coast, it is under strong influence of sea spray (although it is approximately 20 m from sea surface, during strong storms it occasionally gets sea water splashes), Amasra station is approximately 3 km from the coast, consequently large spray droplets generated during storm activity over the sea can not be transported to the station as easily as they do in Antalya. Direct influence of sea spray generated by the storm in the immediate vicinity of Antalya station most probably explains very high aerosol Na and Cl concentrations observed in Antalya station.

3.2.1.3. Anthropogenic elements and ions

Figure for anthropogenic elements and ions prepared for Amasra, Antalya and Çubuk data sets are given in Figure 3.8. Anthropogenic elements are brought to the receptor site from distant sources. When precipitation occurs in an air mass, certain fraction of the fine particles which contain anthropogenic elements in the air mass are scavenged. The concentration of the anthropogenic elements in the next day depends on whether the same air mass still stays in the region or a new air mass arrives. If the atmosphere is still under the influence of the air mass in which the precipitation occurred, then the low concentration of the anthropogenic elements prevail, but if a new air mass starts to affect the region, concentration of the anthropogenic elements start to

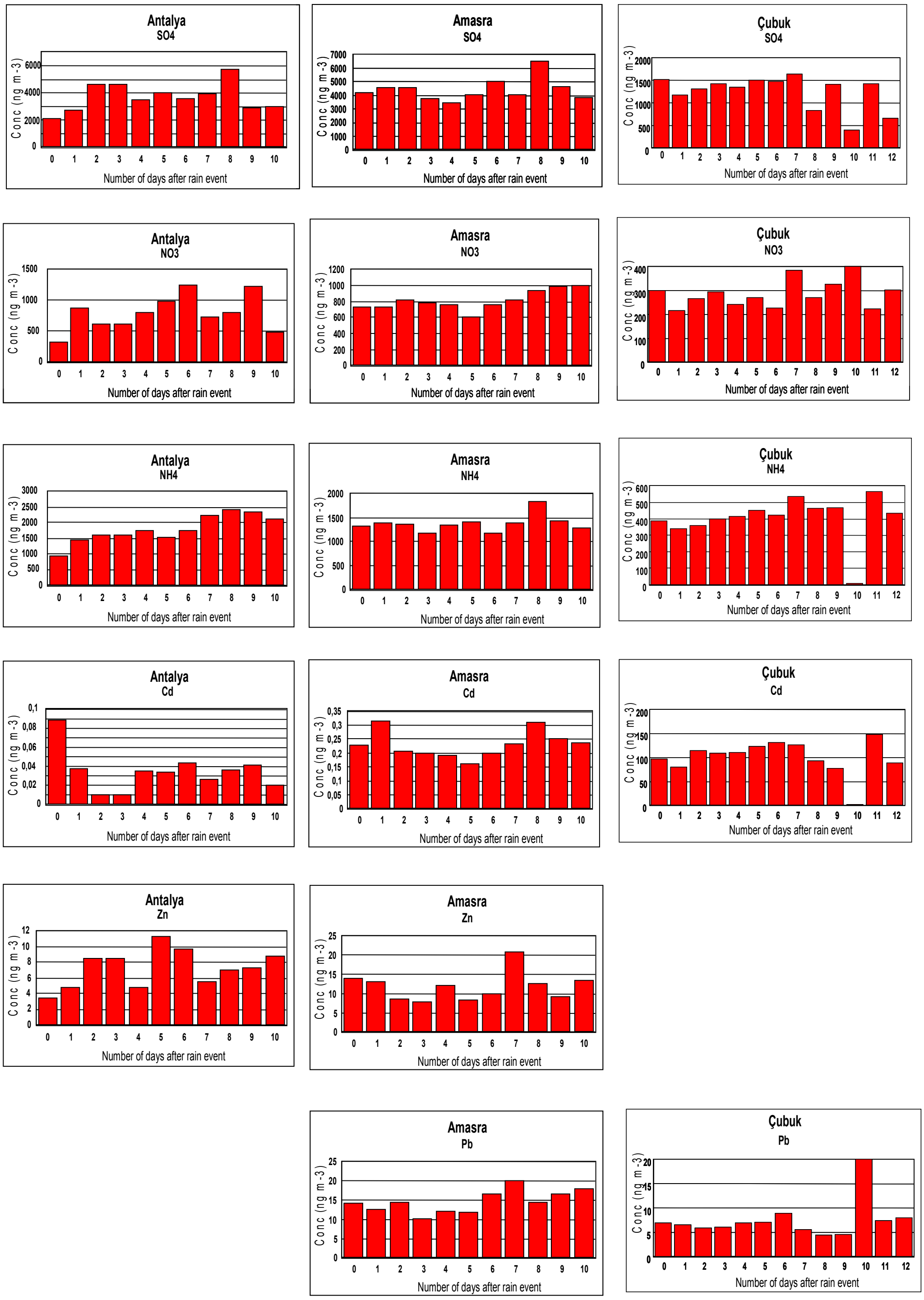

Figure 3.8. Concentrations of anthropogenic elements measured after rain event

increase (or further decrease, depending from where the air mass originates) (Güllü, 1996).

In all stations anthropogenic elements and ions show rather different behavior. In Antalya there is a clear increase in concentrations of most anthropogenic species, except for Cd, in the first few days after rain, then they level off. This behavior is similar with that observed for crustal elements and ions. Except atmospheric loading times are shorter for anthropogenic elements.

A similar increase is also observed in Çubuk station, but the increase is more gradual than that observed in Antalya and also difference between concentrations of elements measured during rain and concentrations measured in subsequent days is not as large as that observed in Antalya. It should also be noted that concentrations of elements and ions measured in Çubuk Station is approximately a factor of two smaller than concentrations measured at Antalya. There are also significant differences in annual rainfall and rain intensity between the two stations (Tuncer et al., 2002). There is an efficiency difference of stripping the atmosphere from particles and subsequent reloading is significantly different between the two stations. In Amasra station, concentrations of anthropogenic elements do not show a consistent change within 10 days after the rain events. The reason is not clear, but suggests a significantly different size distribution or vertical profile (both of which were not measured in this study) of anthropogenic particles at Amasra.

3.2.2. Long-Term Variations

Long term variations in the concentrations of ions can provide information on factors affecting ion compositions at the receptor site. Such variations were shown to be due to factors such as seasonal and systematic variations in the source strengths, seasonal changes in transport patterns and seasonal changes in particle scavenging in the atmosphere (Güllü et al., 1998; Al Momani et al., 1998). For example, more frequent transport of anthropogenic ions such as SO_4^{2-} and NO_3^- from a specific wind sector covering a polluted region during a particular season may well lead to an increase in the concentrations at the sampling site at that period. As an other example, more extensive dust generation in the dry season causes the concentrations of crustal ions to increase (Tuncer, 2000).

As pointed out in the previous section daily variations in aerosol composition after rain events can be detected if the data is averaged over a long period of time, probably due to high variability of the processes in a single event. This also suggests that any relationship between aerosol and rain composition can be better demonstrated using long-term averaged data.

Monthly variation in concentrations of anthropogenic elements in rain water and particles in Antalya, Çubuk and Amasra stations are shown in Figure 3.9. Although there is no one-to-one respondance, general features in the monthly variations in anthropogenic element concentrations in rain and aerosol agrees fairly well suggesting a relation do exists in monthly time scale. As a general trend, concentrations of anthropogenic elements have higher concentrations

Figure 3.9. Monthly variation of concentrations in rain water and aerosols: anthropogenic species

in summer due to more extensive scavenging of these pollutants during winter. Their seasonality can only be explained by long range transport as these elements are transported to the site in clouds.

Similar monthly patterns in aerosol and rain water concentrations are also observed in crustal and marine elements and they are shown in Figures 3.10 and 3.11. Consequently for most of the elements monthly averages seems to be related with each other. This can be seen better in Figure 3.12. where regression lines are prepared for selected elements in the three stations. For most of the anthropogenic and crustal species in Antalya and Amasra stations, shown in the Figure 3.12., there is an easily detectable relation between monthly average concentrations in rain water and aerosol. However, there are some exceptions, marine elements such as Na is not correlated. The reason for this is sea salt, which is picked up by storms while they travel over the sea before they reach to receptor. What is deposited in the receptor depends on the history of the storm tack as well as atmospheric loading of sea salt at the receptor.

SO_4^{2-} and Ca at Çubuk station are not correlated as much as the rain – aerosol correlation at Amasra and Antalya stations, the reason is not very clear, but it should be noted that concentrations of most of the elements at Çubuk is approximately a factor of two smaller than concentrations measured at coastal stations, consequently contribution of aerosols on concentrations of elements and ions are expected to be smaller at Çubuk than other two stations and relative proportions of in cloud processes is expected to be higher.

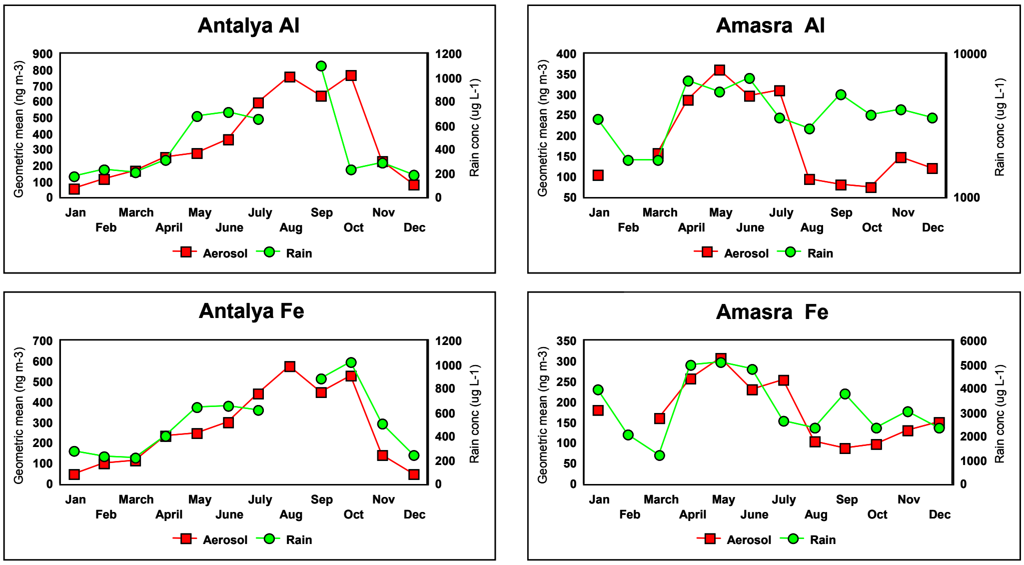

Figure 3.10. Monthly variation of concentrations in rain water and aerosols: Crustal elements

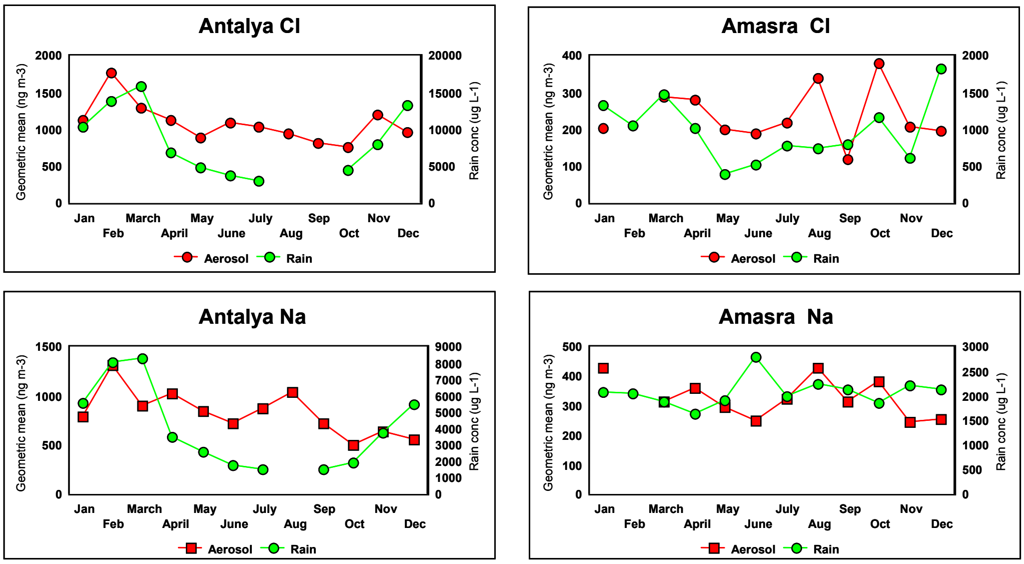

Figure 3.11. Monthly variation of concentrations in rain water and aerosols: Marine elements

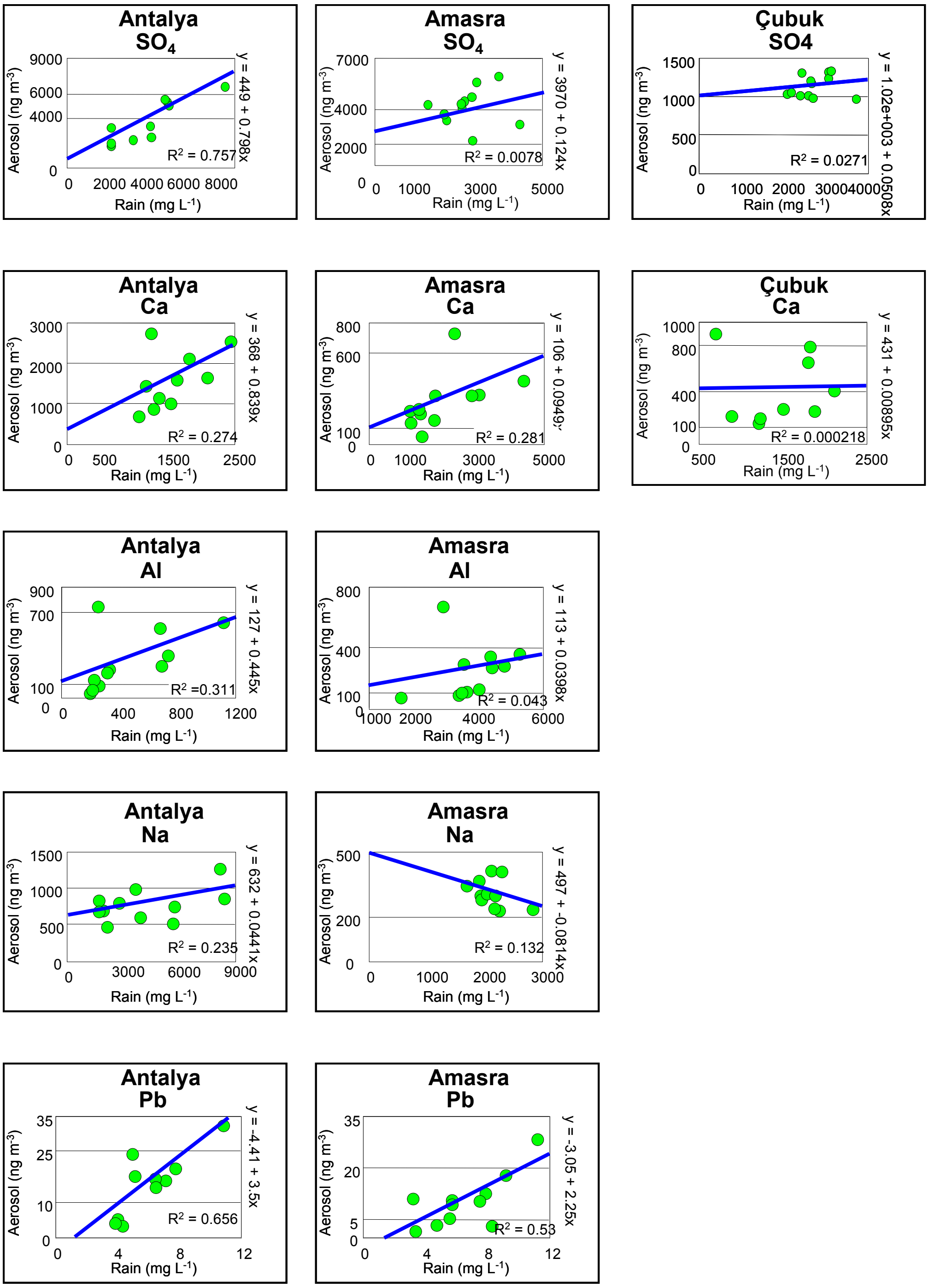

Figure 3.12. Correlations between monthly average rain and aerosol data

The quantitative relation between the rain water and aerosol composition will be discussed in subsequent section (scavenging ratios).

So as the short term variations, with some exceptions, general characters in the monthly variations for all kinds of elements in rain and aerosol are same.

3.2.3. Effect of Aerosol on Rain Composition

Up to this point the effect of rain on aerosol composition is discussed. But the process operates in two ways, not only aerosol are affected by scavenging of particles by rain, but also rain composition is effected when particles area captured by cloud or rain droplets. It is clear from the regression plots given in the previous section that, on a monthly time scale rain composition is affected from the concentrations of elements and ions in atmospheric particles at the receptor site. But, no clear relation was found for a shorter time scale.

For a detectable contribution of aerosol composition on concentrations of elements in rain, the quantity of elements captured from particles at the receptor should be higher than or at least comparable to the elements that are carried to the receptor from elsewhere in cloud droplets. To assess this, the expected concentrations of elements and ions in rain water are calculated assuming all of the particles in the atmosphere at the receptor are scavenged out during rain events.

While performing this calculation, “mm” unit, measured in rain water, is taken as “kg/m^3”. It is assumed as an air column, which has a height 5000 m (also this calculation performed for 1000 m height) and an area of 1 m^2, is washed with unit kg of rain. Volume of air in this colon is calculated. Since aerosol concentrations provide information on how much element exists in 1 m^3 of air, how much mg of element washed in 1 m^2 is calculated. Finally, the rainwater concentration that this quantity corresponds to is calculated..

Clouds in the atmosphere generally occur between 1000 m and 5000 m. Therefore the calculations are performed for these two cloud base altitude. Calculations assuming 1000 cloud base is more realistic as precipitating clouds are generally closer to the surface. The results are compared with measured concentrations of elements in rain in Table 3.3.

Concentrations given in the table should be considered as an upper limit, because these are fairly crude estimates due to a number of factors. Firstly, all of the particles are not scavenged during rain events. Discussion in the previous section indicated that concentrations of elements at day 0 (rain day) are approximately half of the concentrations that is reached in 10 day period following the event. The other factor is, in calculations concentrations of elements are assumed to be homogeneous in the atmosphere between the ground and cloud base, but most studies indicated that concentrations decrease with altitude. This factor cannot be taken into account in calculations, because for the time being, decrease in elemental concentrations with altitude is very uncertain and composition of particles sampled at any station represent the particles at the surface only.

Table 3.3. Concentrations of elements in rain water calculated by assuming complete scavenging of aerosols in 5000 m and 1000 m column of air.

	Measured	Calculated 5000 m cloud base	Calculated 1000 m cloud base
ANTALYA			
SO_4^{2-} (mg/l)	5.02 ± 7.40	4.70 ± 4.12	0.94 ± 0.82
NO_3^-	3.70 ± 2.98	0.69 ± 0.58	0.14 ± 0.11
NH_4^+	1.64 ± 1.52	1.71 ± 1.40	0.34 ± 0.28
Na	10.96 ± 16.16	5.00 ± 5.46	1.00 ± 1.09
Mg	1.46 ± 1.44	0.87 ± 0.75	0.17 ± 0.15
Al	532 ± 646	280 ± 372	56 ± 74
Cl	18.4 ± 25.3	8.35 ± 9.79	1.67 ± 1.96
K	0.81 ± 1.50	0.29± 0.25	0.06 ± 0.05
Cr	5.29 ± 6.10	3.44 ± 2.86	0.69 ± 0.57
Zn	241 ± 692	8.25 ± 8.28	1.65 ± 1.66
ÇUBUK			
SO_4^{2-}	3.85 ± 3.88	6.16 ± 15.19	1.23 ± 3.04
NO_3^-	2.73 ± 4.12	1.99 ± 6.14	0.40 ± 1.23
NH_4^+	1.70 ± 2.28	1.98 ± 6.54	0.40 ± 1.31
Mg	0.17 ± 0.16	0.18 ± 0.20	0.04 ± 0.04
Ca	1.97 ± 2.95	1.13 ± 1.15	0.23 ± 0.23
K	0.55 ± 0.77	0.22 ± 0.18	0.04 ± 0.04
ANKARA			
SO_4^{2-}	2,503	11,05	2,21
NO_3^-	3,198	3,57	0,71
Cl	1,46	0,05	0,01
Na	0,53	0,22	0,04
K	0,14	0,44	0,09
Mg	0,24	0,13	0,03

Table 3.3. Cont'd.

Ca	2,64	0,16	0,03
Al	0,98	1,35	0,27
Fe	749	863	172
Cr	1,46	5,50	1,10
Ni	4,11	5,36	1,07
V	2,26	6,77	1,35
Pb	19,08	121,87	24,37
Cd	9,54	0,19	0,04
Zn	0,03	26,77	5,35

With all these uncertainties, the table provides some useful information. For most of the elements in Çubuk and Antalya stations concentrations calculated assuming 5000 m cloud base are comparable to concentrations actually measured in rain water samples. However, concentrations calculated using 1000 m cloud base level are significantly smaller than measured concentrations. Since calculated values are upper limits of aerosol contribution due to reasons described previously, in these two stations concentrations of elements and ions in rain is determined primarily by components transported from distant source regions, except in rain events associated with unusually high clouds.

The variation in cloud altitude, together with variation in vertical profiles of elements in the atmosphere from one event to another is probably the main reason for why a clear relation between aerosol and rain water compositions is not observed in every event.

3.3. Receptor Oriented Models

3.3.1. Comparison of Crustal Enrichment Factors of Elements and Ions in Aerosol and Rain Water

The enrichment factors of elements and ions in rain and particles are calculated for Antalya, Amasra and Ankara stations are presented in Figure 3.13.

In all three stations enrichment patterns in aerosol and rain are the same, the elements that are considered as non enriched in aerosol are also non enriched in rain. Even though this may indicate that rain composition is affected from aerosol composition at the receptor, this is not a conclusive evidence as with few very exceptions aerosols are enriched almost everywhere in the same way. Even if the particles are incorporated to rain in some distant location, the enrichment fingerprints are expected to be fairly similar.

The general similarity in EF_c's of elements in rain and particles indicates that, if there is enrichment data on aerosols it can be used to deduced information on enrichment of elements in rain. Relative enrichments of elements and ions in aerosol and rain at each station can be seen in Figure 3.14.

With few exceptions the agreement between aerosol and rain water enrichments of measured parameters are reasonably good.

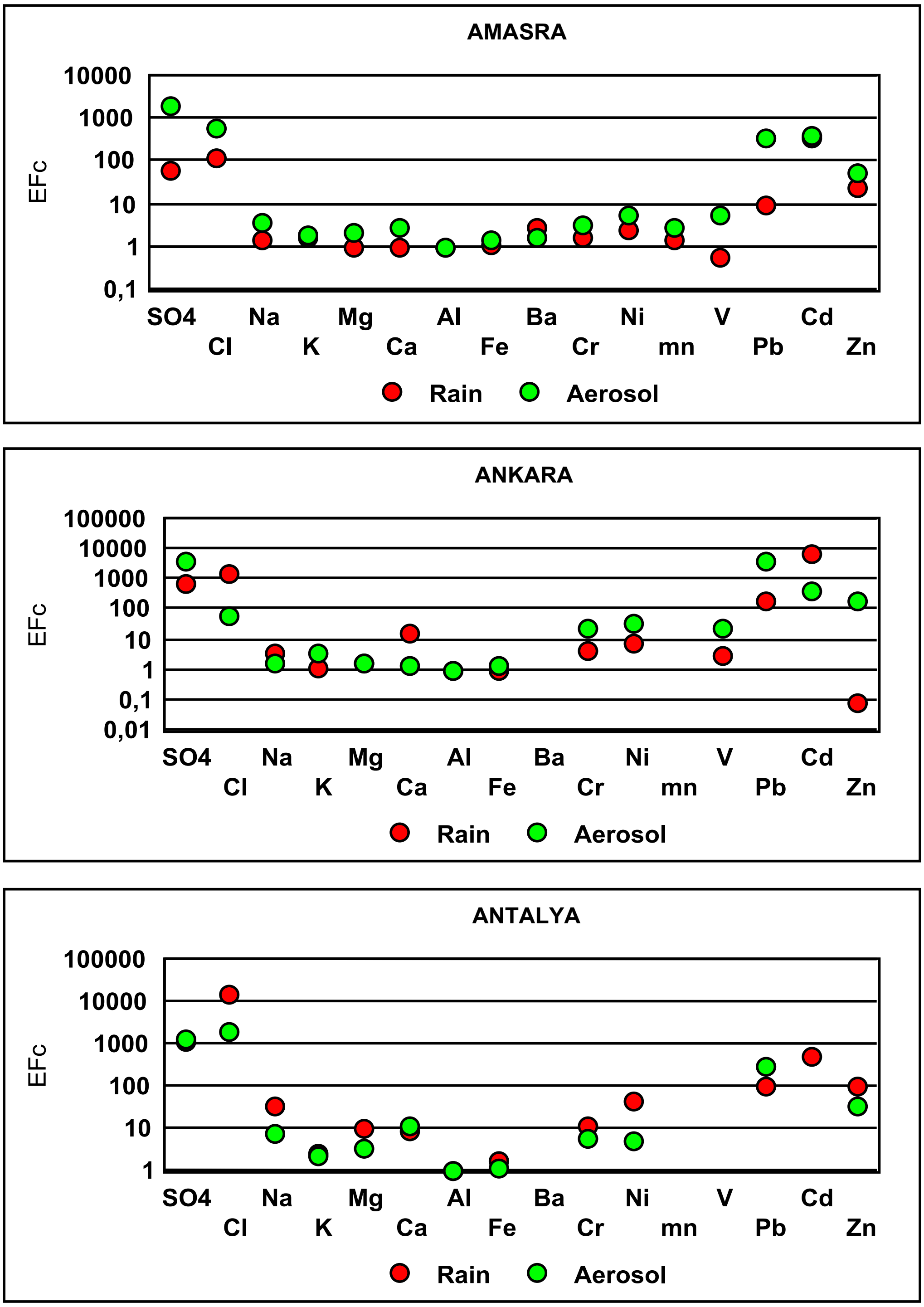

Figure 3.13. EFc of elements and ions in rain and aerosol

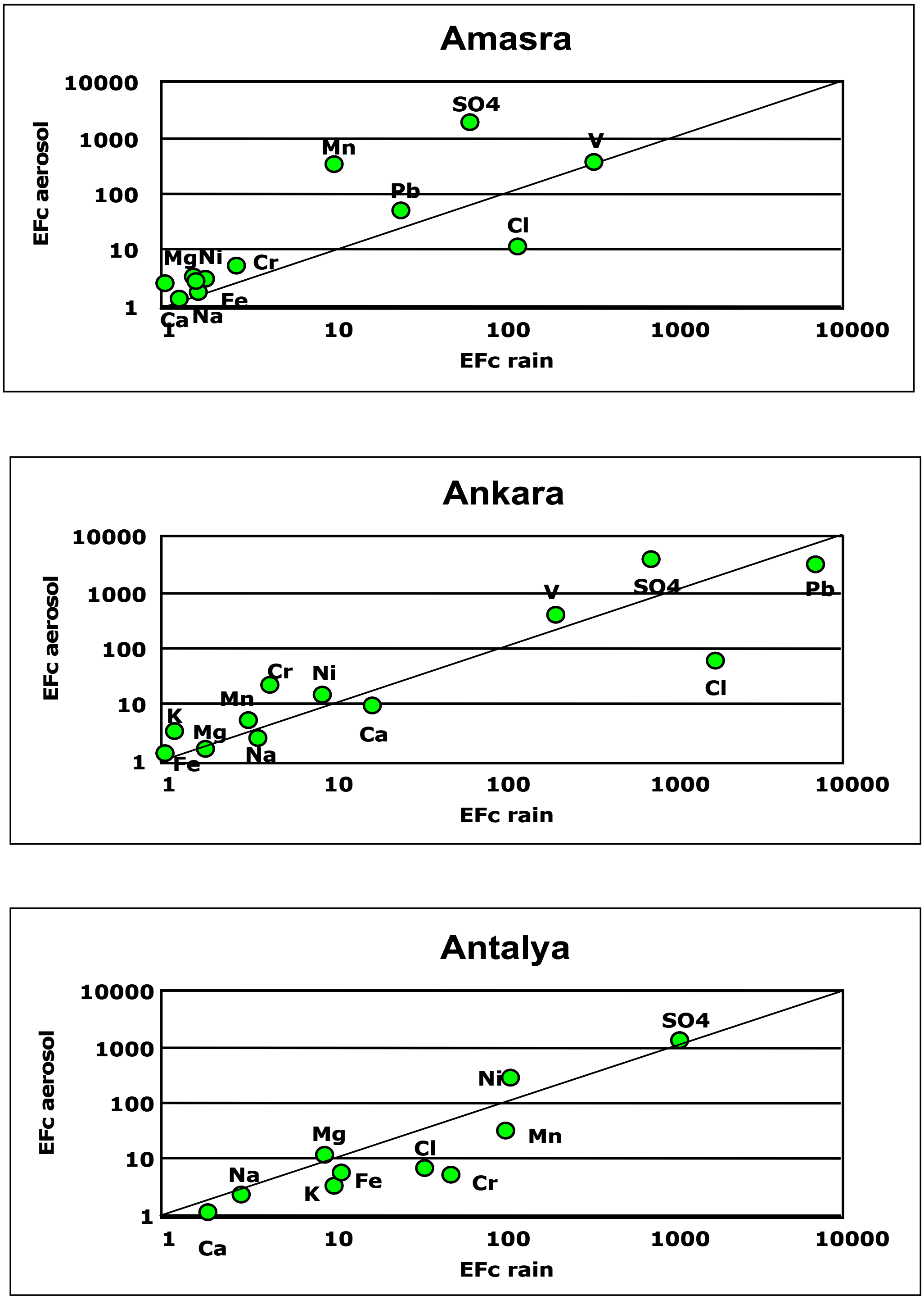

Figure 3.14. Relative enrichments of elements and ions in aerosol and rain

SO_4^{2-} ion is more enriched in aerosol, particularly in Amasra and Ankara data, this is an expected result as SO_4^{2-} is associated with the smallest size particles (MMD in Antalya is 0.7 µm) which are least efficiently scavenged by rain.

The best agreement between aerosol and rain enrichments of elements is observed in Ankara station. As Ankara is a polluted urban area, rain water composition is affected by high local concentrations of elements and effect of incloud processes (transport of pollutants from distant sources incloud droplets) is not important. On the contrary, the agreement between rain and aerosol enrichments of elements are not good in rural stations, because there is no local emissions in these sites and pollutants transported from distant locations within cloud, contribute significantly to their observed concentrations at the rural sampling point.

It can be concluded that composition of rain water is more affected from local aerosol composition in polluted urban and industrial locations and relationship is weaker in rural areas where particle concentrations in the atmosphere is not very high.

3.3.2. Factor Analysis

3.3.2.1. Factor Analysis Results of Antalya

The elements included in factor analysis calculations are Al, Cl, Cr, K, Mg, Na, NH_4^+, Ca, Ni, Pb, NO_3^- and SO_4^{2-}. After several run four factors were retained were retained for both rain and aerosol FA, two of them are anthropogenic components, and the other two is marine and crustal components. The results are given in Table 3.4. and Table 3.5. for aerosol and rain respectively. Factor loadings for both aerosol and rain in Antalya is also ploted in Figure 3.15., for visual inspection.

In aerosol factor analysis, factor 1 is a clear crustal factor which is loaded with Al, Cr, K, Mg, Ca, Ni, NO_3^- and SO_4^{2-}. NO_3 and SO_4 are anthropogenic components, but in earlier studies it was shown that some of these are in the forms of $CaSO_4$ and $Ca(NO_3)_2$ (Güllü et al., 1998) and some of the fine SO_4^{2-} and NO_3^- particles sticks on coarse crustal particles (Kuloğlu, 1999). This factor explains 35% of system variance.

In rain FA crustal factor is factor 2 which is loaded with Al, Ca, Cr, K, Mg, Ni. There are some differences between crustal factors in rain and aerosol FA. In aerosol FA crustal factor accounts for 35% of variance, whereas in rain FA it acounts for a smaller fraction of the system variance (15%). This is because sea salt has stronger influence on the composition of rain water, whereas crustal particles has stronger influence on composition of aerosol.

Another important difference is that, SO_4^{2-} and NO_3^- are associated with crustal factor in aerosol FA, but they are not in rain FA. In aerosol FA there is another factor (factor 4) in which these two speices are also loaded together with NH_4^+. But in rain FA SO_4^{2-} and NO_3^- appears in two seperate factors. SO_4^{2-} is loaded in factor 3 together with NH_4^+ and NO_3^- is loaded in Factor 4 again with NH_4^+ and Pb. Presence of SO_4^{2-} and NO_3^- together with crustal component can be explained by sticking of fine SO_4^{2-} and NO_3^- particles onto coarse crustal particles in the

Table 3.4. FA results of Antalya aerosol

	Factor 1	Factor 2	Factor 3	Factor 4	Communality
Al	**0.81**				0.74
Ca	0.36	0.19	**0.66**		0.61
Cl		**0.94**			0.90
Cr	0.60		**0.49**		0.62
K	0.76	**0.50**			0.84
Mg	0.39	**0.77**			0.84
Na		**0.87**			0.78
NH_4^+			**0.70**	0.24	0.58
Ni	0.84				0.73
NO_3^-	0.78			0.32	0.72
Pb				**0.81**	0.72
SO_4^{2-}	0.75			**0.42**	0.81
Eigenvalue	4.22	2.37	1.39	0.92	
% variance	35.13	19.74	11.62	7.64	74.14

Table 3.5. FA results of Antalya rain

	Factor 1	Factor 2	Factor 3	Factor 4	Communality
Al		**0.70**			0.56
Ca	**0.55**	**0.49**	**0.36**		0.73
Cl	**0.92**				0.89
Cr		**0.55**	**0.30**		0.51
K	**0.86**	0.31			0.84
Mg	**0.84**	0.20			0.80
Na	**0.90**				0.85
NH4			**0.81**	0.22	0.71
Ni		**0.74**			0.56
NO3				**0.65**	0.45
Pb				**0.68**	0.47
SO4			**0.64**		0.55
Eigenvalue	3.68	1.89	1.25	1.11	
% variance	30.67	15.78	10.40	9.23	66.08

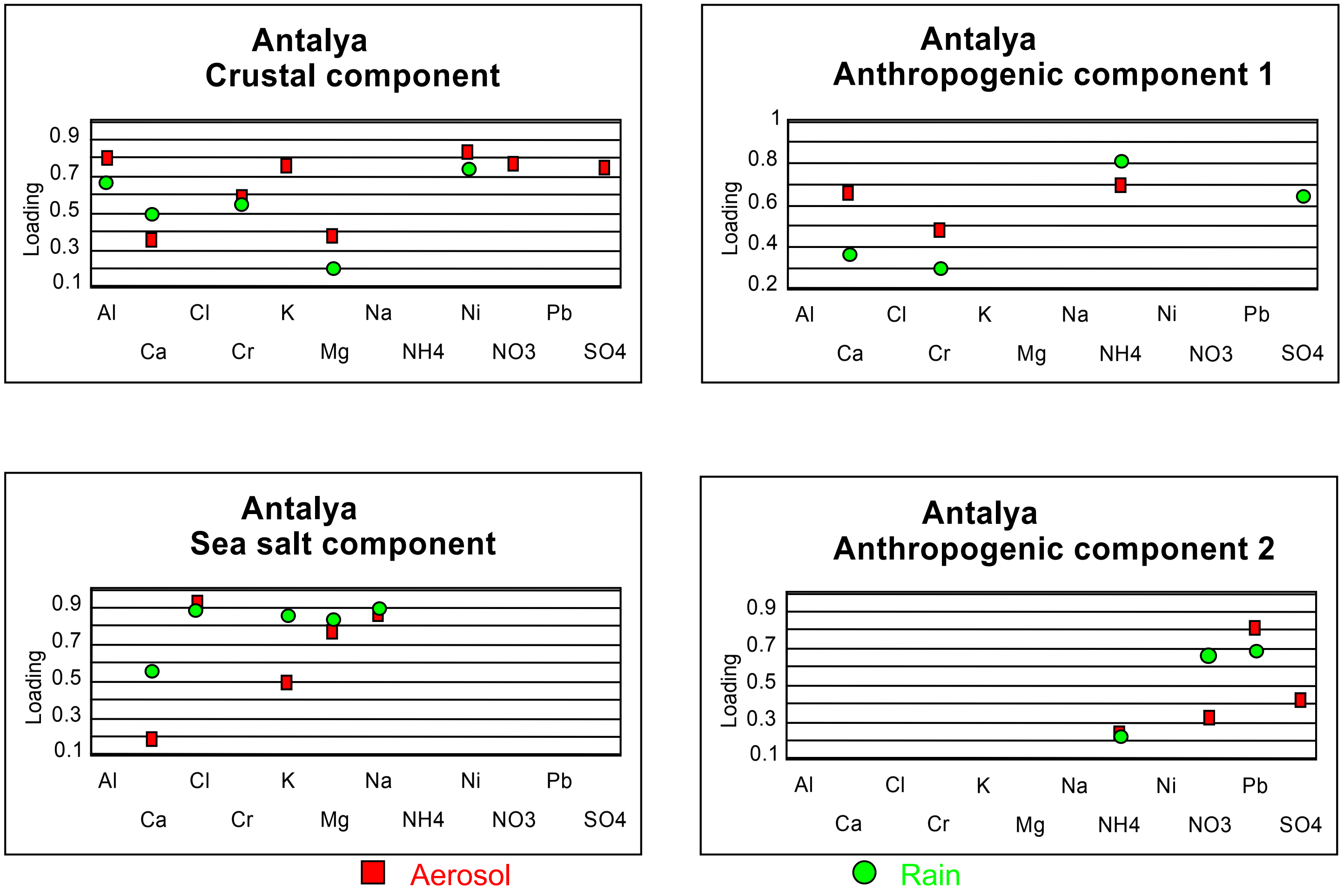

Figure 3.15. Components for both aerosol and rain in Antalya

atmosphere, but lack of similar association in rain water FA indicates that crustal component in rain water is not generated by washout process. As washout is a local process and if it was determining factor in the crustal composition of rain water, than crustal components (and other components) in aerosols has to be completely identical with the corresponding factors in rain.

Factor 2 in aerosol FA, and Factor 1 in rain FA represent marine factor which loaded with Na, Cl, Mg, K and Ca. These factors explains approximately 20% of system variance of aerosol FA and 31% of system variance of rain FA .

The most important difference for rain and aerosol FA is that the marine factor explains a significantly greater fraction of system variance in rain water as it accounts for a larger fraction of the ionic mass in rain. This suggests that amount of sea salt in rain can not be explained by washing of sea salt in particles at station site as rain brings in additional sea salt while clouds are being transported to eastern Mediterranean.

Factors 3 and 4 in both aerosol and rain FA are anthropogenic factors. Unlike crustal and marine components, composition of these two factors are fairly similar. Factor 3, in both aerosol and rain FA, is loaded with Ca, Cr, NH_4^+ and factor 4 is loaded with NH_4^+, NO_3^- and Pb. The only difference is the loading of SO_4^{2-} as SO_4^{2-} is loaded in factor 3 in aerosol FA whereas in rain FA it is loaded in factor 4. These two factors are probably identical and represent similar anthropogenic components in aerosol and rain. In Antalya aerosol and rain factor analysis, crustal and marine components, which has strong local sources are different. The ones that are transported from distant sources, anthropogenic components, are similar.

3.3.2.2. Factor Analysis Results of Amasra

The complete set of total concentrations of ions measured in rain and aerosol samples used in factor analysis calculations includes, Al, Cd, Cl, Cr, K, Mg, Na, NH_4^+, Ca, Ni, Fe, V, Zn, Pb, NO_3^- and SO_4^{2-}. After several run six factors were retained for both rain and aerosol FA, three of them are anthropogenic, and the other three is crustal, marine and a mixed crustal-anthropogenic components. The results are given in Table 3.6 and Table 3.7. for aerosol and rain, respectively. Factor loadings are also plotted in Figure 3.16 for visual comparison.

Table 3.6. FA results of Amasra aerosol

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Comunality
Al		**0.87**			**0.33**		0.88
Ca		0.19			**0.86**	0.12	0.80
Cd	**0.48**		**0.40**		0.11	**0.42**	0.59
Cl				**0.92**			0.87
Cr	**0.82**	0.13					0.70
Fe	0.19	**0.88**			0.23		0.88
K		0.25		0.13		**0.83**	0.79
Mg	0.14	**0.38**		0.29	**0.80**		0.90
Na				**0.91**			0.85
NH_4^+	0.15		**0.82**		0.17		0.74
Ni	**0.63**	**0.38**	0.11			0.14	0.61
NO_3^-	0.16	**0.39**	**0.40**	**0.54**		0.21	0.67
Pb	**0.72**		**0.33**		0.23		0.71
SO_4^{2-}		0.20	**0.86**				0.78
V	**0.51**	**0.37**	**0.53**			0.19	0.72
Zn	**0.39**		0.15		0.17	**0.68**	0.69
Eigen value	4.36	27.23	1.63	1.41	1.25	1.07	
% variance	2.47	15.46	10.16	8.84	7.82	6.71	76.21

In aerosol Fa Factor 2 is a crustal factor, it is highly loaded with (loadings > 0.5) Al and Fe and moderate loadings of Ca, Cr, K, Mg, Ni, NO_3^-, SO_4^{2-} and V. Factor 2 explains approximately 15% of the system variance. Corresponding crustal factor in rain FA is factor 1, it is mainly loaded with Al, Fe, K, Mg, Na and moderately loaded with Ca, Cd and V and explains approximately 28% of system variance.

Table 3.7. FA results of Amasra rain

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Communality
Al	**0.92**		0.15				0.88
Ca	**0.46**	0.13		**0.64**		0.13	0.66
Cd	0.18	**0.54**	**0.34**			**0.34**	0.58
Cl		0.13		0.11	**0.78**		0.66
Cr						**0.45**	0.29
Cu	0.21				0.10	**0.77**	0.65
Fe	**0.93**			0.13		0.18	0.92
H	0.11						0.39
K	**0.91**		0.11			0.14	0.86
Mg	**0.87**		0.22				0.82
Mn	**0.46**			0.27	0.21	**0.53**	0.61
Na	**0.52**				**0.34**	0.26	0.47
NH4		**0.65**		**0.36**			0.62
Ni			**0.43**	0.18	**0.58**	0.25	0.62
NO3		**0.81**			0.18		0.70
Pb	**0.35**		**0.72**				0.65
SO4	0.14	**0.59**			**0.43**		0.64
V	0.16		**0.80**				0.68
Zn				**0.78**	0.23		0.68
Eigen value	4.93	1.99	1.63	1.48	1.27	1.08	65.22
% variance	25.94	10.49	8.59	7.80	6.70	5.70	

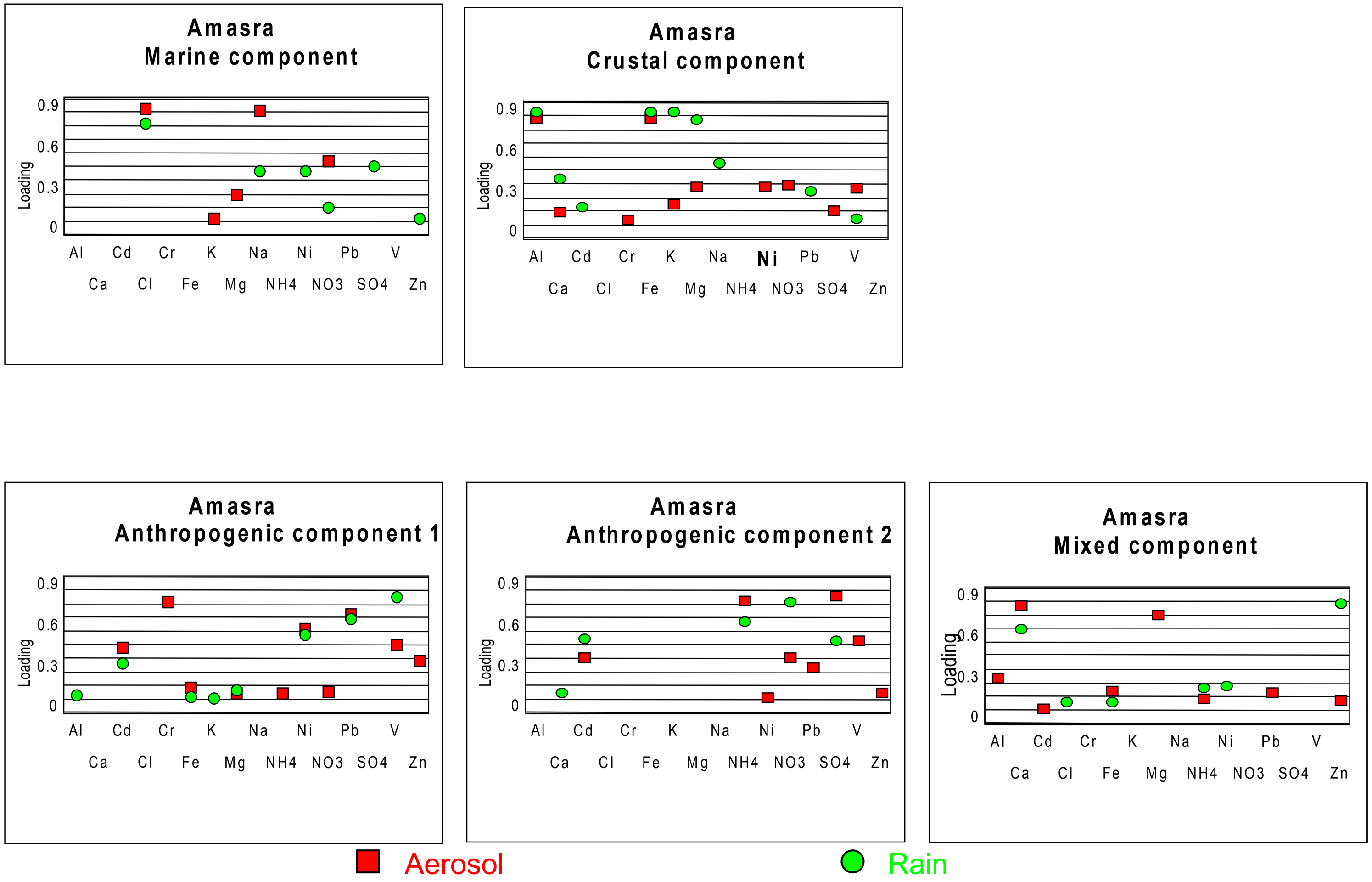

Figure 3.16. Components for both aerosol and rain in Amasra

These factors in rain and aerosol are clearly represent crustal component in Amasra atmosphere, even though there are some differences. Firstly, SO_4^{2-} and NO_3^- have moderate loadings in aerosol crustal component, but are not loaded at all in rain crustal component. The reason is not very clear, but suggests that crustal component in aerosol and rain water is not necessarily the same. Since they both represent crustal material chemical composition is similar, but in fine details, like presence of SO_4^{2-} and NO_3^- they are not the same. Secondly, crustal component accounts for a larger fraction of system variance in rain water (28% vs 12%). This is probably due to stronger correlation of crustal elements with each other in rain samples; this in turn is due to presence of a second crustal component in aerosol as will be discussed later.

Factor 3 in aerosol and Factor 2 in rain water are an anthropogenic components with similar basic composition. In aerosol FA this factor is loaded with NH_4^+, SO_4^{2-}, NO_3^- and other anthropogenic elements Cd, Pb and Zn. In rain FA it is loaded with NH_4^+, SO_4^{2-}, NO_3^- and Cd. In both rain and aerosol FA factors explains approximately 10% of system variance. As a matter of fact, in both aerosol and rain this factor is a neutralized acidity factor.

Factor 4 in aerosol FA is clear marine factor loaded with Na, Cl, Mg, K and NO_3^- corresponding to factor 5 in rain FA which is also a marine factor with similar loadings. This marine factor explains 9% of system variance in aerosol FA and 8% in rain FA.

Factor 5 in aerosol FA is another crustal factor loaded with Al, Ca, Cd, Fe, Mg, NH_4^+, Pb and Zn and explains 8% of system variance. Presence of Cd, NH_4^+, Pb and Zn suggests mixing of some anthropogenic component (air masses that brings this component to Amasra also brings anthropogenic particles). This factor corresponds to factor 4 in rain FA which is loaded with Ca, Cl, Fe, NH_4^+, Ni and Zn and explains 8.5% of system variance. These two factors resemble each other, but they are not completely identical. Al is loaded in this second crustal in aerosol FA, but not in rain FA . Although factor 4 in rain FA is loaded with Zn and NH_4^+, other anthropogenic elements, namely Cd and Pb, which is loaded in factor 5 in aerosol FA do not appear in rain FA factor 4.

These two factors probably represent the same component in aerosol and rain a mixed crustal-anthropogenic component. This component is clearly identified in aerosol FA, but it is not as clear in rain FA, this is probably due to smaller number of rain water samples included in the analysis compared to aerosol.

Factor 6 in rain water and aerosol FA are different, they are both anthropogenic components, but loaded with different elements and ions. This could either indicate a component brought to station from distant sources or an artifact in statistical tool used.

It can be concluded that, generally similar components are identified in rain and aerosol FA in both Antalya and Amasra stations, which is suggesting that washing of local aerosol particles has a profound influence on the composition of rain water in both stations. But lack of exact match between crustal and marine factors in Antalya and anthropogenic components in Amasra indicates that the fraction of natural anthropogenic species brought by clouds to sampling site can not be totally ignored in explaining chemical composition of rain in these two stations.

Another possibility for the observed similarity between factors obtained in aerosol and rain FA exercises is that the composition of rain may be totally independent of aerosol composition at the sampling location. But the source types not necessarily affecting chemical composition of rain water and aerosol sampled at the stations may be very similar. In such a case factors obtained in aerosol and rain FA would be similar as observed in this study. This issue will be discussed in subsequent section where source regions that affect chemical composition of rain and particles at our stations is determined using spatial distribution of calculated potential source contribution function (PSCF) for each factor.

3.3.3. Potential Source Contribution Function

Potential source contribution function (PSCF) is a technique in trajectory statistics that is frequently used to determine source regions affecting observed levels of pollutants measured at a receptor. Details of PSCF calculations and Bootstrapping method which is used to test the statistical significance of calculated PSCF values are given in Section 2.3.2.

In this study, PSCF calculations applied for both SO_4^{2-} concentrations that are measured both in rain water and aerosol and factor scores, which are discussed in previous section, obtained from FA at Antalya and Amasra stations.

As it is discussed in previous section, factor scores of FA at Antalya and Amasra for rain and aerosol imitate each other. At every station, similar factors represent similar components in aerosol and rain. Even it could be concluded that factors which have similar compositions are composed from same sources, it is hard to say this sources are in the same regions. For instance, a factor composition defined as ‘crustal’ at a receptor point would be similar both in rain and aerosol, but the regions contribute to crustal components in aerosol could be similar or different in rain.

In this study, PSCF calculations are applied to factor scores obtained from FA at Antalya and Amasra stations, and source regions of similar factor components of rain and aerosol are compared.

However similarities of factors and their representation of same component is an evaluation and involve a particular uncertainty. Reason for different source regions obtained from the application of PSCF to similar factors in rain and aerosol could be different source regions determining the similar components in both media or as it mentioned above, incorrect identifying the factors due to uncertainty. PSCF calculations are applied to SO_4^{2-} concentrations measured at Antalya and Amasra both in rain and aerosol, in order to reduce the uncertainties to minimum.

In order to present the distribution of principal sources in Map Info, highest %40 factor scores obtained from FA and highest %40 concentration values of SO_4^{2-}, both for Antalya and Amasra stations, taken into account.

3.3.3.1. PSCF Results of Antalya Data Set

Factor 1 in aerosol FA and factor 2 in rain water FA represents crustal component. Distribution of PSCF calculated for factor 1 in aerosol FA and Factor 2 in rain water FA are depicted in Figure 3.17.

Source regions for crustal components in rain water and aerosols in Antalya station are not exactly the same. The main difference is that sources of crustal component are more local in rain water. Crustal material that forms this component in rain are located in the western parts of Turkey, where as crustal particles that arrive from regions in Europe also contribute crustal component in Eastern Mediterranean aerosols.

Distribution of PSCF values for rain water and aerosol factor 4 scores are given in Figure 3.18.

Factor 4 has the same composition in both aerosol and rain FA, suggesting that rain water and aerosol composition are affected from similar source types, but there are significant variations in the source regions identified by PSCF calculations. As observed in crustal component, source regions for factor 4 in rain FA are more local. Aerosol PSCF suggests that sources responsible for factor 4 are located in the western part of Turkey, but rain PSCF calculations suggests that sources located at the central Anatolia are more responsible for species associated with this factor. There are significant source areas in central Europe (Romania, Bulgaria, Ukraine) in aerosol

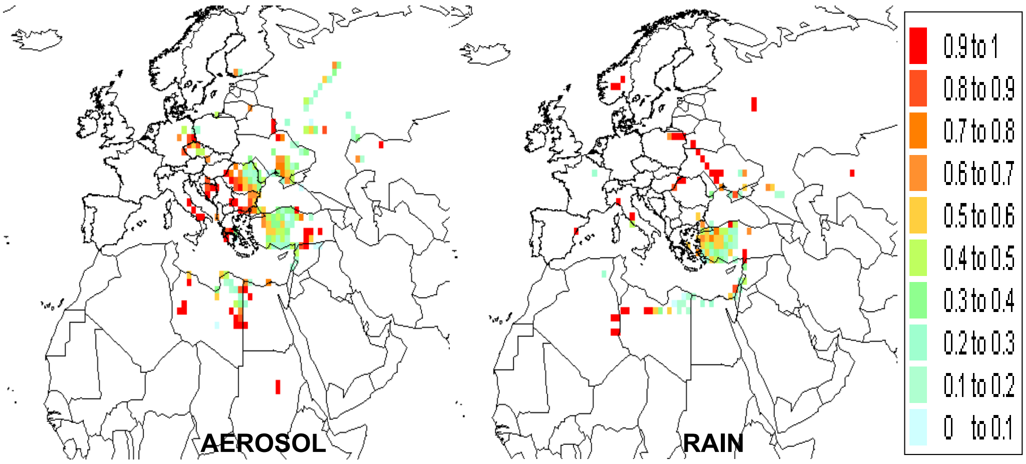

Figure 3.17. Distribution of PSCF calculated for factor 1 in aerosol FA and Factor 2 in rain water FA at Antalya

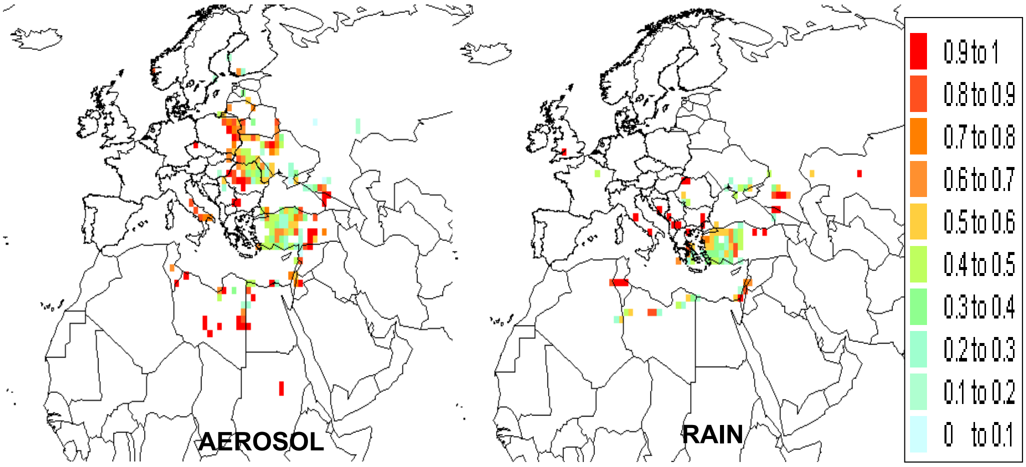

Figure 3.18. Distribution of PSCF calculated for factor 4 in aerosol and rain water FA at Antalya

PSCF for factor 4, but these distant source areas do not appear when PSCF is calculated for rainwater Factor 4.

It should not be forgotten that similar factor composition in FA suggests same type of sources, but do not imply that sources should be in the same location. Similar source types in different parts of Europe and Turkey seem to generate factor 4 in aerosol and rain water. But locations of sources are different. Sources that generated factor 4 in aerosol mass are located farther away from Antalya than sources that generate factor 4 in rain.

3.3.3.2. PSCF results of Amasra Data Set

Factor 1 in aerosol and factor 2 in rain water was found to represent anthropogenic component in rain water and aerosol. Distribution of PSCF values for these components are given in Figure 3.19. There is no one-to-one correspondence between source regions for this anthropogenic component in aerosol and rain water. General appearance is not as different as observed in Antalya. Source regions for both aerosol and rain are located to the north of the Black Sea. Also generally closer nature of rain water source regions observed in Antalya is not observed.

Factor 2 in aerosol and factor 1 in rain represent crustal component in Amasra atmosphere. Distribution of PSCF in rain and aerosols are given in Figure 3.20. Commonly, comments made for the anthropogenic

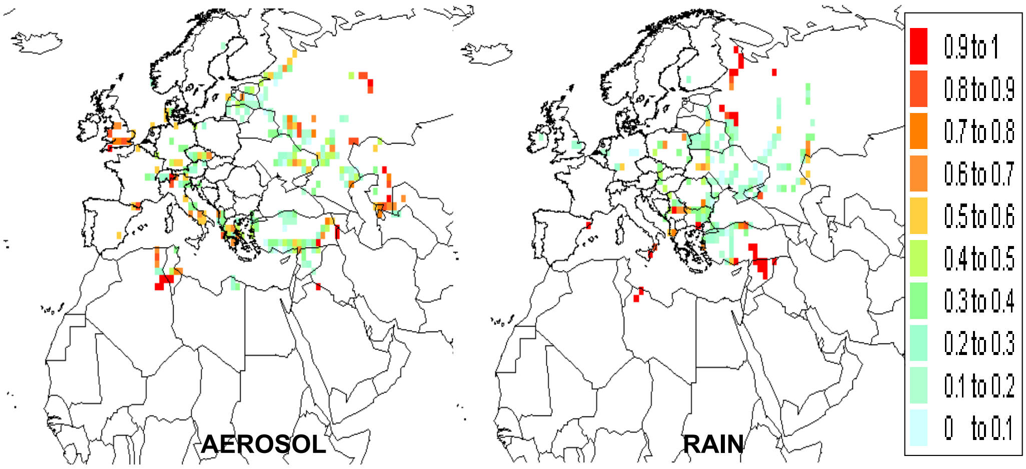

Figure 3.19. Distribution of PSCF calculated for factor 1 in aerosol FA and Factor 2 in rain water FA at Amasra

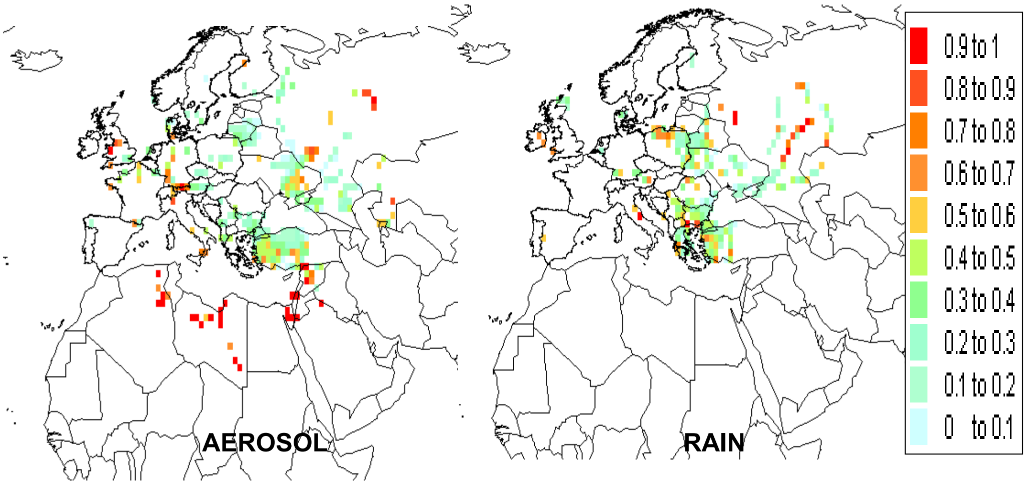

Figure 3.20. Distribution of PSCF calculated for factor 2 in aerosol FA and Factor 1 in rain water FA at Amasra

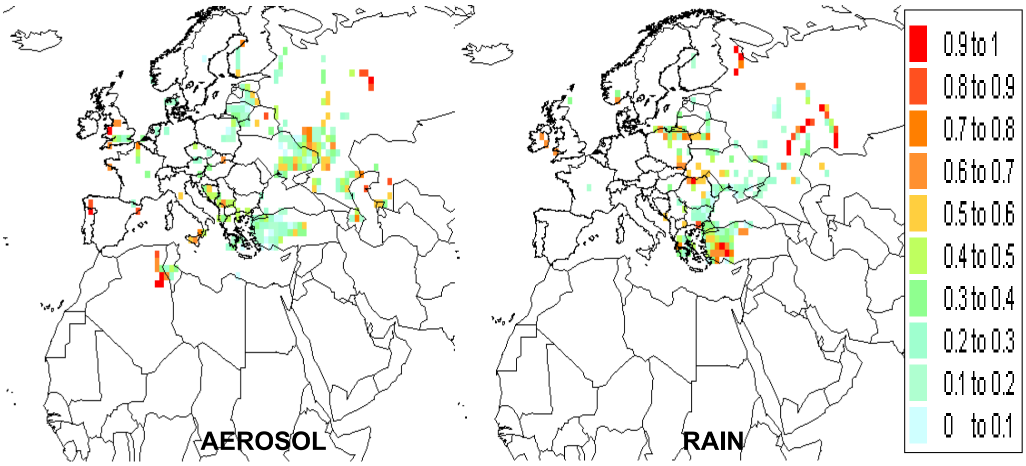

Figure 3.21. Distribution of PSCF calculated for factor 3 in aerosol and rain water FA at Amasra

component is also valid for this crustal component. Source regions of the crustal component, that is determined from aerosol and rain FA, are generally in agreement with each other, but there is no one to one relation between them. Source regions of crustal component for rain are located to the north of the station. Source regions of crustal component for aerosol have sources generally at Balkan countries in addition to sources at north. But, unlike in Antalya, there is no indication that source regions affecting rain factor is more local compared to source regions assigned to this factor in aerosol FA.

In previous section, it is concluded that, factor 3 obtained from aerosol and rain FA represents the same anthropogenic component. Distribution of PSCF scores of these factors can be seen in figure 3.21.

When distribution of PSCF scores of rain and aerosol compared, similar distributions can be seen with the results of the previous factors. Source regions are generally located at north of Blacksea for both aerosol and rain, but, just like the other factors, no one to one relation could be seen. West of Aegean and even Africa coasts are observed as source regions for anthropogenic component of aerosols. These source regions could not be observed in the anthropogenic component of rain.

3.3.3.3. PSCF results for Sulfate

The main conclusion reached in the previous section was that source regions of a given component in rain and aerosol at sampling points are not the same. This conclusion was based on the assumption that factors for which PSCF distributions are compared, represent the same component (or the same type of source) in rain and aerosol at the same station. The similarities between factors in rain and aerosol FA was interpolation based on the similarities in factor profiles. Any error in this assignment would directly reflect to interpretation of PSCF distributions. In other words, if factors, for which PSCF distributions are compared, do not represent the same component in aerosol and rain, then it is normal to observe different source regions in aerosol and rain. To avoid this uncertainty, PSCF calculations were also performed for SO_4^{2-} concentrations in rainwater and aerosol at Antalya and Amasra stations. Results are depicted in Figure 3.22 and 3.23, respectively. Distribution of PSCF values of Antalya SO_4^{2-} concentrations in rain and aerosol is given in Figure 3.22.

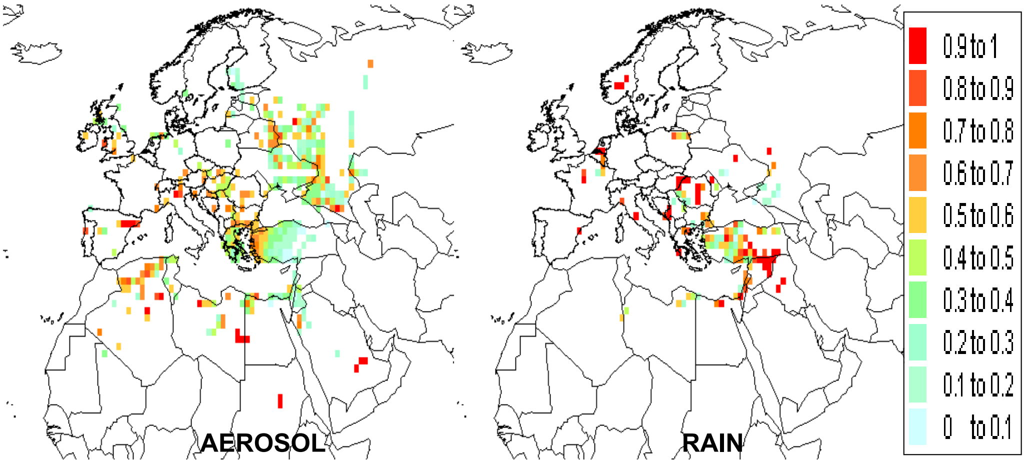

Figure 3.22. Distribution of PSCF applied to rain water and aerosol Sulfate concentrations obtained at Antalya

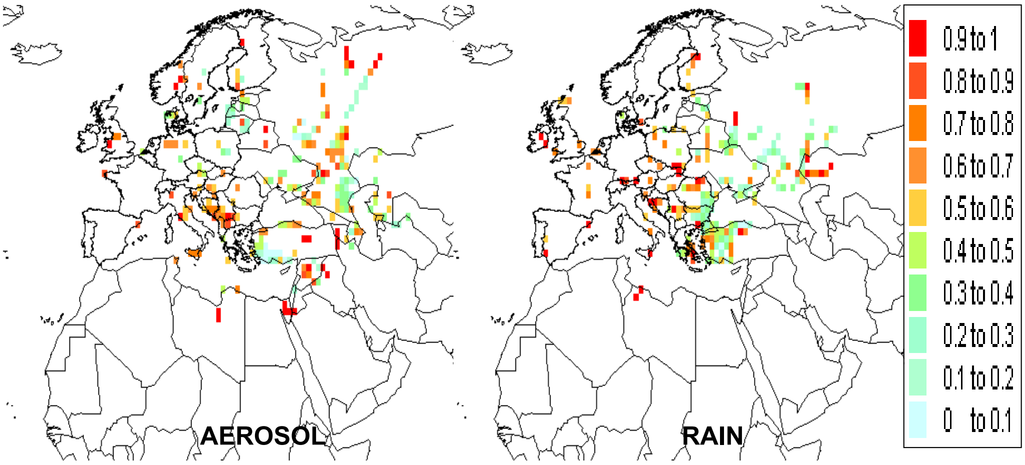

Figure 3.23. Distribution of PSCF applied to rain water and aerosol Sulfate concentrations obtained at Amasra

Distributions of PSCF scores calculated for SO_4^{2-} give the same spatial distribution variations observed with the factor scores obtained in FA. Aerosol SO_4^{2-} values are contributed from farther locations than rain SO_4^{2-} values. It is very clear that, rain at Antalya influenced much more from local sources. West of Turkey, Balkan countries are considerable source regions for both rain and aerosol. On the other hand, countries located at further north such as Ukraine and Russia, and Middle European countries such as Hungary, Czech Republic, have a high contribution to the concentration of SO_4^{2-} in aerosol, however, the same source regions do not contribute to rain water SO_4^{2-} concentrations.

Distribution of PSCF values obtained from rainwater SO_4^{2-} concentrations measured at Amasra aerosol and rain is given in Figure 3.23.

As at Antalya, at Amasra distributions of PSCF values calculated for SO_4^{2-} have similar spatial distribution observed in the PSCF values obtained from FA. It is observed that, SO_4^{2-} concentrations measured from both rain and aerosol are generally affected from the sources located north of Europe. Some parts of Turkey, Ukraine, Russia and some regions at Balkan's have a contribution to the SO_4^{2-} concentrations measured both in rain and aerosol. However, beside these common regions, there are other source regions affecting the SO_4^{2-} concentrations in aerosol and rain water. Consequently, it can be easily said that, source regions of SO_4^{2-} concentrations for rain water and aerosol are not the one to one same.

Furthermore, evaluations that are made at Antalya and Amasra station giving fairly different results. PSCF calculations applied for both SO_4^{2-} concentrations and factors obtained from FA at Antalya, clearly indicating that rain water compositions are affected from local sources more than aerosol. On the other hand, there is no sign of higher local source impact on rain water than aerosol at Amasra. It is not possible to explain the reason of the variation between stations by current knowledge. Most probably, this variation is due to the differences of air flow climatology's at different heights and seasons. In order to understand this mechanism completely, a comprehensive model study on this issue is needed.

It is concluded after these evaluations, if there is only aerosol data, one can not made any comment about source regions of rain water compositions and wet depositions.

3.4. Scavenging Ratio

Scavenging ratio is a mean of calculating concentrations of species in rainwater if there is aerosol data. Details of SR calculations are given in Section 1.8. Three different calculation procedures were used. In the firrst calculation method, overall averages of wet precipitation concentrations were divided by the overall averages in aerosol samples .In the second procedure only paired samples, i.e. days with airborne and precipitation data, were considered. And in the end monthly SR averages are calculated.

3.4.1. Annual Average Scavenging Ratios

Annual average scavenging ratios are calculated from volume weighted average concentration of elements and ions in all precipitation samples collected during one year period and the average concentration from all aerosol samples collected during the same period for Antalya, Ankara, Amasya and Çubuk stations. Annual SRs are given in Figure.3.24. and Table 3.9. Scavenging ratios are in general agreement with values reported in literature. There are significant differences for some elements between stations.

In antalya station, even though annual SRs show significant variations from one constituent to another, in general the order of SRs is seasalt elements > anthropogenic elements > crustal elements. This ordering of SRs is due to sizes of particles in the atmosphere which determine their scavenging efficiencies. Sea salt particles are the largest ones with mass median diameter (MMD) between 4.5 – 5 µm (Kuloğlu, 1997). These particles are scavenged out most effectively resulting in the highest SRs. Crustal particles are known to be in the coarse mode but their MMD are smaller than that of marine particles (3 – 3.5 µm) (Kuloğlu, 1997). Consequently SRs for crustal elements are smaller than SRs for marine elements. Atmospheric particles are the smallest with MMD varying betveen 1.5 – 0.5 µm and their SRs are the smallest. Even though Mg and K are marine elements, their SRs are lower than the major sea salt elements Na and Cl. This is due to the contribution of crustal material in addition to sea salt. SRs for anthropogenic elements show significant variations, as SRs for Pb and Zn vary from 443 to 12643. SRs for Zn is higher around factor of 30. if all

Table 3.8. Scavenging ratios caculated for anual averages

	Amasra	Ankara	Antalya	Cubuk
Ca	6971.776	26927.5	1256.675	2723.464
Al	35757.81	5513.221	1141.99	
Fe	30760.01	4024.407	1635.573	
Ni	14133.7	1212.622	10279.5	
Cl	5282.741	62488.4	12695.68	
Na	10724.88	6830.295	11974.64	
K	26764.02	888.8679	3120.249	1223.581
Mg	16178.86	2644.692	6024.632	792.3214
V	3742.6	454.5503		
Pb	889.0942	209.6892	443.0672	
Cd	22233.62	67659.86		
SO4	664.9737	470.9669	1279.073	1725.267
NO3	2310.884	1145.024	4337.633	3909.854
NH4	821.078		870.7335	2497.214
Zn	21199.58	1.653517	11643.69	
Cr	11631.36	424.2215	2144.448	

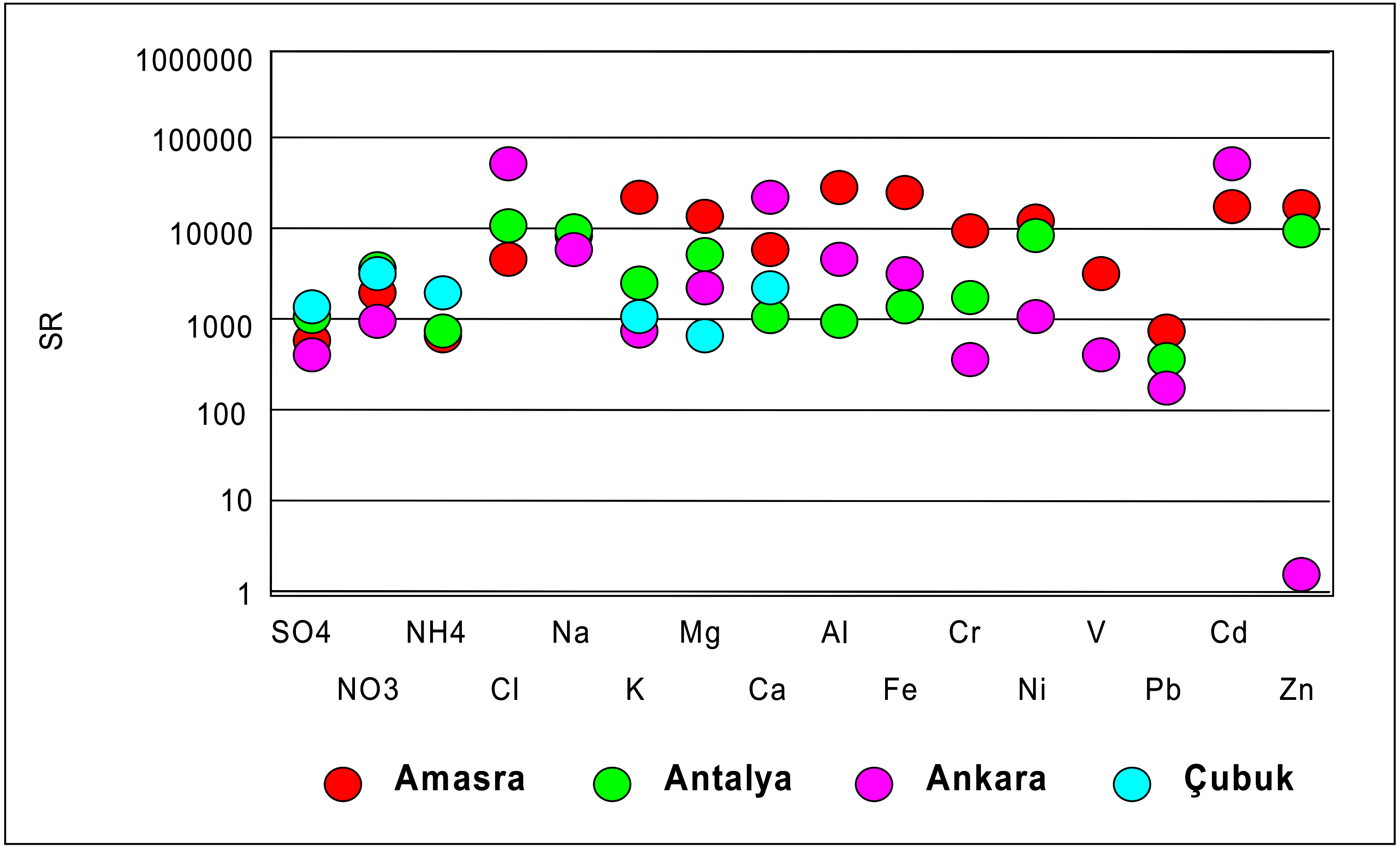

Figure 3.24. Scavenging ratios caculated for anual averages

anthropogenic elements are originated at distant locations, during long transit times, particles in air mass would be an aged, internally mixed aerosol. Observed variability in calculated SRs of anthropogenic elements is probably, fairly wide range of MMD's of these elements. Srs of NO_3^- is larger than other pollutant elements and sulfate. This is due to the incorporation of gaseous HNO_3^- and coarse particle NO_3^- formation on sea salt particles (Wolff, 1987).

At Amasra station, in general the order of SRs is crustal elements > seasalt elements > anthropogenic elements. At Amasra all crustal elements have higher SRs than Antalya, whereas at Antalya marine elements have higher SRs than at Antalya. This could be the result of the position of Antalya station, as it is near to the sea and local sources contribute to marine elements higher. Acidity forming species NO_3^- and SO_4^{2-} have lower SRs at Amasra than Antalya, these species are associated with fine fraction of aerosol, that is why they have low scavenging ratio (El-Agha O ., 2000).

At Ankara station, even though annual SRs show significant variations from one constituent to another, in general the order of SRs is seasalt elements > crustal elements > anthropogenic elements. Anthropogenic elements have very low values compared to marine and crustal elements. The reason could be the local contribution like industry and transport.

3.4.2. Paired Scavenging Ratios

Paired SRs are calculated for days only rain event occurs, in order to see whether they show similar patterns with the annual averages. Values of paired SRs for Antalya, Ankara, Amasra and Çubuk stations can be seen in Figure3.25and Table 3.10.

SRs of paired samples are much more variable when it is compared with SRs calculated using annual average. It has large variety both at each site and among all stations. This differences are due to a wide variety of factors: precipitation rate, vertical distribution of relative humidity, droplet size distribution, total evaporation during fall, precipitation interaction with sub-cloud and in-cloud aerosols, vertical distribution of aerosols and reactive gasses, vertical distribution of the air which is being processed in the cloud taking into account entrainment, detrainment, updrafts and downdrafts etc. When one considers how rapidly and how radically each of these can change independently each other, it quickly becomes clear that estimates of SRs for individual events will retain a large degree of uncertainty (Galloway et al., 1992).

More specific comparison of annual average and paired SRs of species are depicted in figure 3.26. With a few exceptions general trend for annual average SRs and paired SRs are the same. But paired SRs have larger values for a few factors. These large variations reflect the different conditions prevailing during the single precipitation events, and the limitations of scavenging ratios to describe single precipitation events .

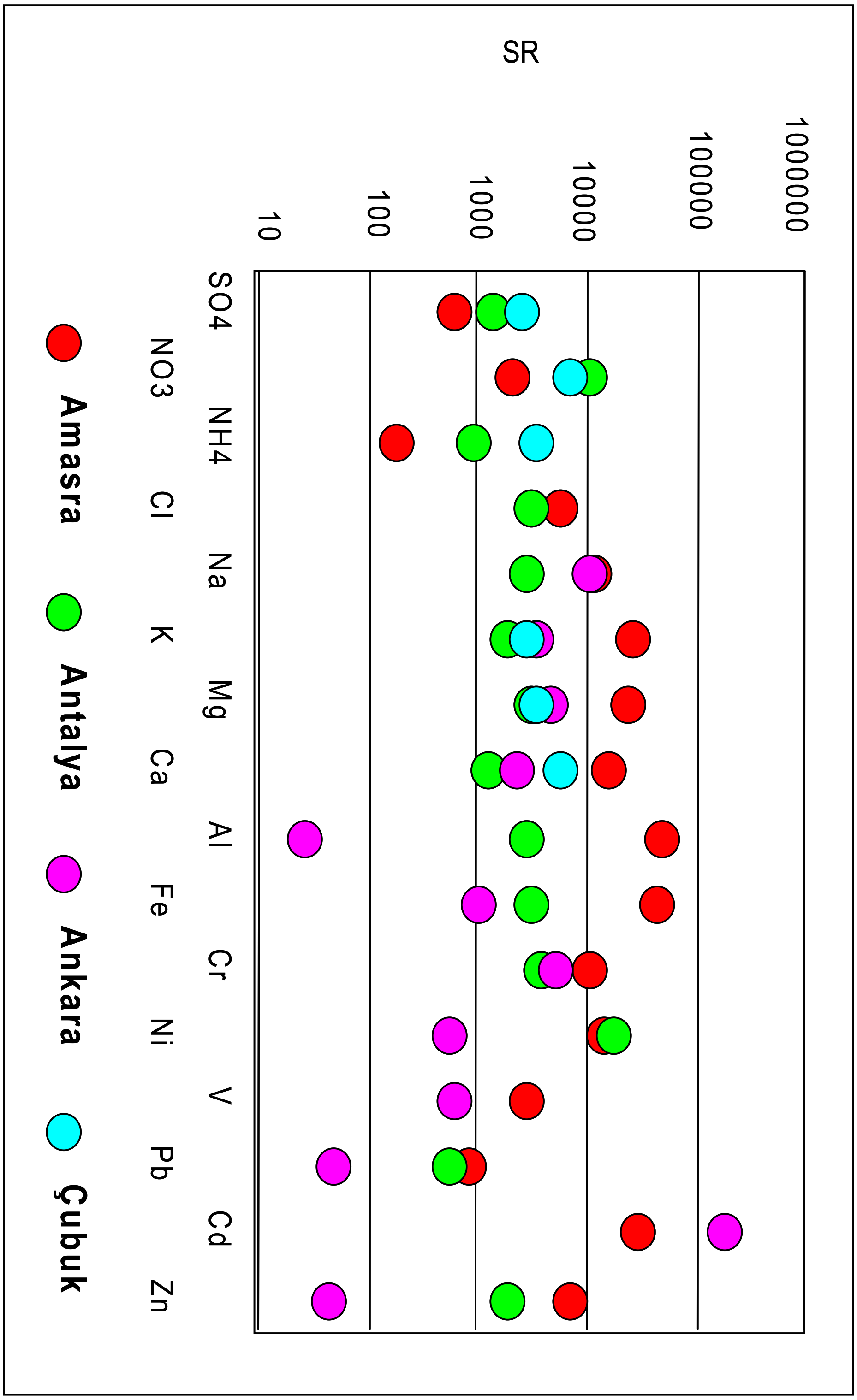

Figure 3.25. Scavenging ratios calculated in rainy days

Table 3.10. Scavenging ratios calculated in rainy days

	Amasra	Antalya	Ankara	Cubuk
Ca	17980.26	1343.554	2701.933	6372.198
Al	53066.4	3182.914	28.28513	
Fe	47783.14	3662.868	1093.833	
Ni	16723.82	19744.93	647.875	
Cl	6133.229	3414.36		
Na	13611.14	3147.527	12059.23	
K	31224.27	2000.421	3976.146	3252.474
Mg	27730.54	3329.872	5063.584	3689.81
V	3063.629		656.0674	
Pb	941.289	639.9986	51.05889	
Cd	33956.22		197774.8	
SO4	674.3757	1558.973		2986.68
NO3	2437.764	12404.45		8244.766
NH4	198.9912	989.1744		3925.46
Zn	8296.897	2057.461	47.59244	
Cr	12327.75	4124.044	5642.528	

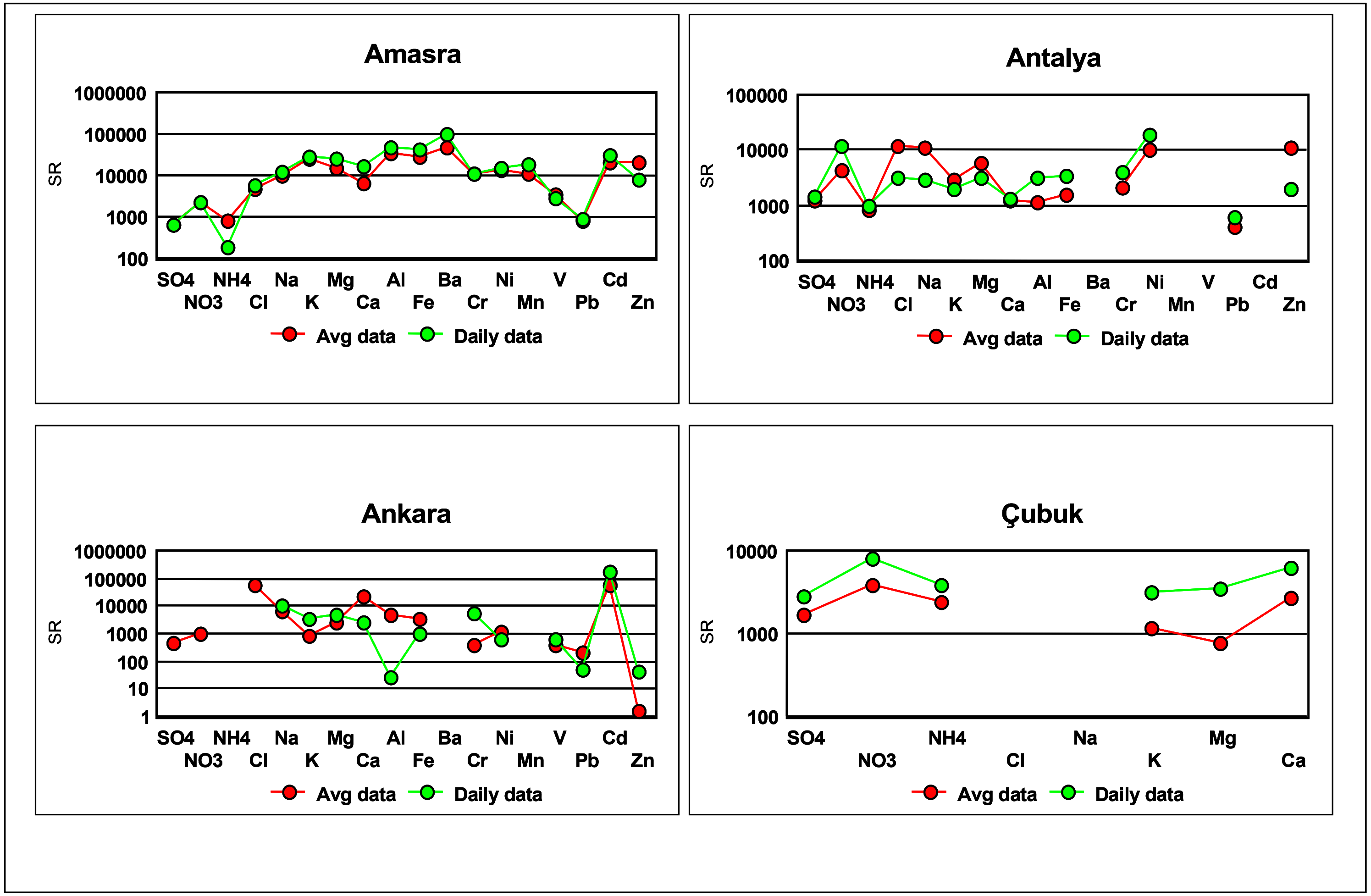

Figure 3.26. Comparison of annual average and paired SRs

A comparison between overall and 'paired' monthly averages of SRs, is also given by Savoie et al. (1987) for nitrate, non-sea-salt sulfate and sea-salt. For their measurements scavenging ratios for nitrate and NSS sulfate are about 20-25% lower in the 'paired' samples. Comparing the advantages and disadvantages of the two calculation methods, 'paired' averages might be more instructive for physical processes. However, the main reason of calculating SRs in this study is to relate the concentration in wet precipitation to the mean concentration of their airborne precursors. This mean concentration of airborne precursors would be better reflected by the overall anual averages than by summarizing the days with precipitation only. Another point favoring the use of annual averages is that most aerosol data sets are not segregated into samples which span and samples which do not span rain events (Savoie et al., 1987).

3.4.3. Monthly Average Scavenging Ratios

Variability of SRs assessed further on a monthly basis. The monthly average SRs are presented in two different formats. To show the effects of variations in the respective components of the SRs, the monthly SRs for each species at Antalya and Amasra stations are plotted along with the monthly average concentrations in aerosols and precipitation in Figure 3.27 and Figure 3.28.

As it can be depicted from figures, aerosol data show more pronounced seasonal signals relative to those for precipitation, and SRs varies significantly month to month. The most probable reasons for this could

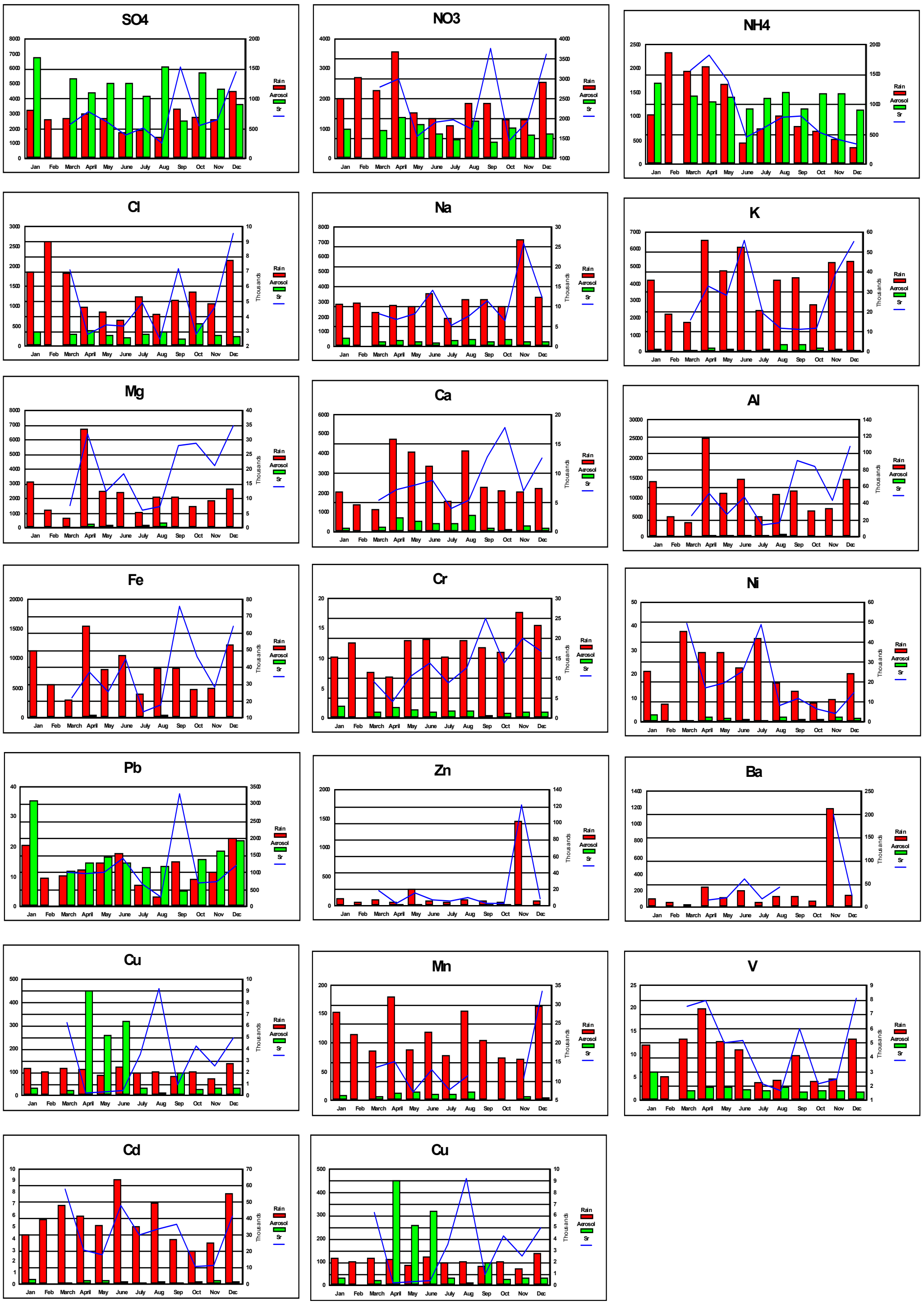

Figure 3.27. The monthly SRs, VWA of rain (μg L^{-1}) and arithmetic mean of aerosol (ng/m^{-3}) at Amasra station

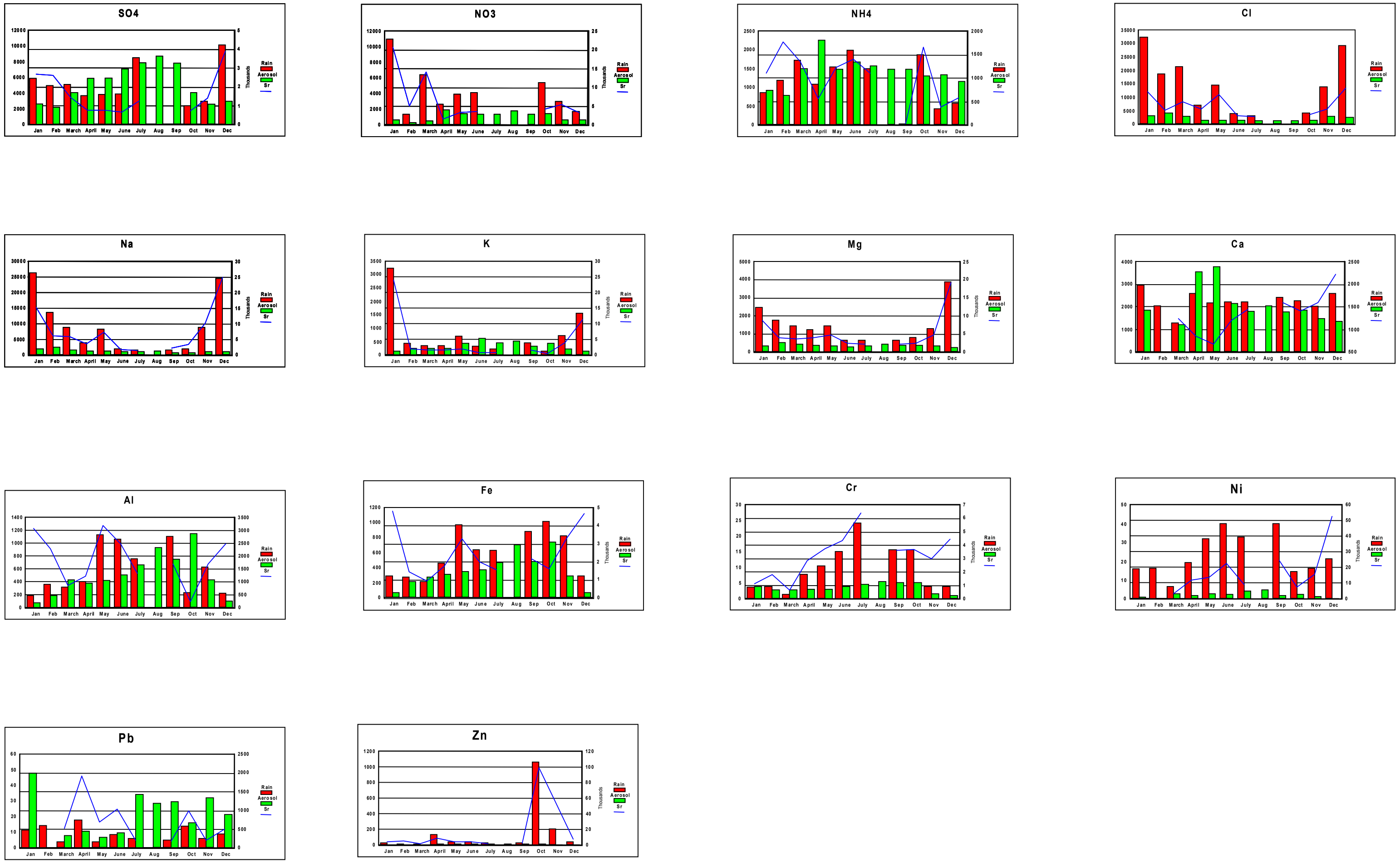

Figure 3.28. The monthly SRs, VWA of rain (mg L-1) and arithmetic mean of aerosol (ng/m^{-3}) at Antalya

be additional sulfate sources (DMS), influence of precipitation amount on concentrations. To illustrate any commonalities and differences between the variations in the SRs of the constituents, The monthly SRs in Antalya and Amasra stations, are plotted in figure 3.29.

Monthly SRs of seasalt elements show same seasonal variations at both station. In winter months SRs values for these elements are higher than those in summer. This is most probably, because of the increases in precipitation concentration, and vertical turbulence in the lower troposphere during storm activities in winter. Especially, in winter concentration of sea salt elements increase in precipitation much more than aerosols.

Despite the marine elements, crustal elements do not follow a general trend. There are significant variabilities between crustal elements in a station and among the stations. While at Antalya, generally there is a increase in SRs of crustal elements in winter, whereas this is contrary in Amasra, at Amasra Station SRs are increase in summer.

Anthropogenic elements do not show any seasonal behavior, at both stations high variabilities are calculated for anthropogenic species.

It can be concluded that, scavenging ratios calculated for the stations are in agreement with the SR’s in literature, but there are differences between stations and depending on integration time. The most useful SRs are based on average aerosol and VWA precipitation data. Annual average SRs are more reliable than paired SRs as variability of SRs are increased when paired SRs used, in stead of annual average SRs.

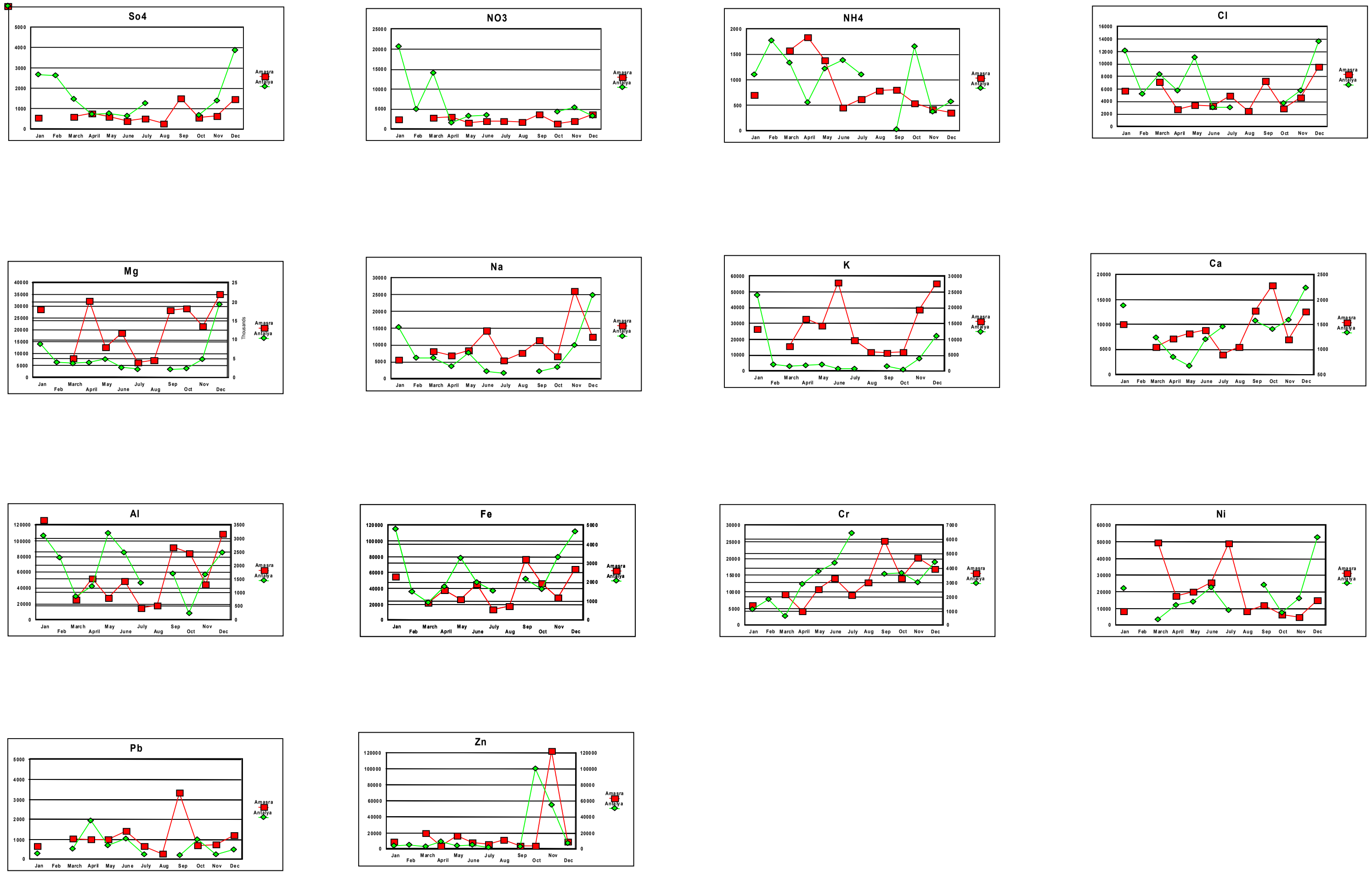

Figure 3.29. Monthly distribution of scavenging ratios for same species

CHAPTER 4

CONCLUSIONS

In this study, relationship between chemical composition of atmsopheric aersol and rain water collected at the same location is investigated using data generated at Antalya, Amasra and Ankara stations. Data generated in these stations are suitable for to establish such a relationship, becasue in all three stations chemical composition of particles and rain water were simultaneously determined for relatively long periods of time.

Spatial varations of elemental concentrations (variation of concentrations from one station to another) demonstrated similarities for crustal elements indicating that crustal elements measured in rain water represents the aerosol population at the receptor. However, such similarities were not observed for marine and anthropogenic elements, suggesting that composition of rain for these gropups of elements are also affected from transport of these speceis from distant source regions in cloud droplets.

Comparison of annual average concentrations in rain and particles, both in absolute terms and as fractional concentrations revealed similar conclusions. Elemental fingerprints and fractional concentrations were simlar in rain and particles for for soil ralted elements and ions, but differences existed for marine and anthropogenic elements.

One point that worth noting is that elemental fingerprints and fractional concentrations of elements and ions in rain water and aerosols at Ankara station were more similar than that observed in Antalya and Amasra stations. Ankara station is an urban station whereas the other two are rural staions. This observation probably suggests that chemical composition of rain reflets the local aerosol population in locations that are strongly affected from strong local emissions.

Short term (episodic) variations in rain amount influences chemical composition of particles. But there is no one-to-one relation between concentrations of elements in aerosol and concentrations in rain water. Effect of rain on aerosol composition can be seen fairly clearly if concentrations are averaged over a reasonably long periods of time. Atmospheric reloading times were found to show differences between different element groups and between different stations.

Comparision of seasonal variaitons in concentrations of elements in rain and particles at three stations showed that seasonal variation in concentrations of elements and ions in rain water closely reflects sesonal pattern in aerosols, suggesting that if there is sesasonal variation data in aerosol, this can be used to construct seasonla variations of elements in rain water.

Similar conclusion was also reached in comparison of crustal enrichment factors of elements and ions in aerosols and rain. Elements that are enriched in aersosols are also enrihed in rain water and elements that are not enriched in particles are also not enriched in rain. This pattern is consistent in all three stations suggesting that if there is data on concentrations of elements in aerosols, enrichment factors calculated closely reflets the enrichments of elements in rain.

Not anly concentrations of elements in aerosols are affected from rain events, but also composition of rain is affected from aerosol population. Calculation of elemental concentrations in rain water, assuming that all particles in 1 m2 column with a dapth of 5 km and 1 km depicted showed that Concentrations of elements calculated assuming 5000 m cloud base would be comparable to concentrations actually measured in rain in rural stations (Antalya nd Amasra). However calculated concentrations were found to be significantly smaller than measured concentrations if the cloud base is assumed to be only 1000 m. Indicating that influences of pollutants transported from distant locations in cloud drpolets would be significant in rural sites.

A different pattern emerged in Ankara station. In this heavily polluted urban site, measured concentrations of elements in rain were found to be comparable to concentratiosn calculated assuming 1000 m cloud base, suggesting that in locations where atmosphere is loaded with anthropogenic particles, influences of local aerosol on rain composition is more pronounced than influences of distant sources. This means aersol rain water relationship can be established more reliably in rural atmosphere.

Factor analysis which is a tool to identify types of sources affecting a receptor was applied to aerosol and rain composition data at Antalya and Çubuk stations to determine if the source types affecting chemical composition of rain and particles are the same at each station. Results showed that same source types can be identified in both aersol and rain data in each station. But the agreement is rather approximate and not one-to-one. Natural crustal and marine components were identified both in aerosol and rain water FA, but fractions of variance explianed were not the same, which is attributed to different degree of contribution of rain water and and crustal particles on chemical compositon of particles and rain.

Elemental composition of anthropogenic factors were also approximately same in aerosol and rain water FA. Differences in elemental profiles may arise from neutralization chemistry in ran water.

Potential source contribution calculations were performed using both aerosol and rain composition data at Antalya and Amasra, to determine if the source regions affecting chemical composition of rain and particles are the same or different.

Significant differences were observed in results obtained for Antalya and Amasra stations. The general pattern observed in distribution of source regions in rain and aerosol showed some similarities in both stations, but there were substantial differences in detail.

The most notable difference between PSCF results in Antalya and Amasra is that source regions affecting composition of rain water in Antalya are much more local compared to source regions affecting composition of particles. Such difference is not observed in Amasra.

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