CHEMICAL COMPOSITION OF PRECIPITATION IN DIFFERENT PARTS OF TURKEY

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

GÜL AYAKLI

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
ENVIRONMENTAL ENGINEERING

FEBRUARY 2014

Approval of the thesis:

CHEMICAL COMPOSITION OF PRECIPITATION IN DIFFERENT PARTS OF TURKEY

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ABSTRACT

CHEMICAL COMPOSITION OF PRECIPITATION AT DIFFERENT PARTS OF TURKEY

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February 2014, 147 pages

In this study major ion composition of rain water samples collected at General Directorate of Meteorology Antalya, Balıkesir and Trabzon rain sampling stations were analyzed. The major ions SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, Ca^{2+}, K^+ and Na^+ were analyzed by ion chromatography. Data generated in these stations are compared to evaluate how chemical composition of rainwater changes as air masses travel on the Anatolian plateau. Data also demonstrate how rainwater composition varies seasonally at different parts of Turkey. Reasons behind these variations are investigated using statistical tools. Multivariate statistical tool Positive Matrix Factorization was used to understand types of sources affecting precipitation composition at different locations in Turkey. As a result, four types of factors were resolved as long range transport, crustal emissions, sea salt and fertilizer usage. Similarly, trajectory statistics are used to understand locations of sources. Data evaluation heavily base on back trajectory information. Back trajectories, arriving the stations at the mid day of every sample, were collected using HYSPLIT trajectory model. HYSPLIT is 3D isentropic trajectory model developed by the US National Oceanic and Atmospheric Administration (NOAA). The model will be run at NOAA computers and results are transferred to our computers.

Keywords: Wet deposition, rain water composition, IC, acid rain, back trajectory.

ÖZ

TÜRKİYE'NİN ÇEŞİTLİ BÖLGELERİNDEKİ YAĞIŞLARIN KİMYASAL BİRLEŞİMİ

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Tez Yöneticisi: Prof. Dr. Gürdal Tuncel

Şubat, 2014, 147 sayfa

Bu çalışmada Meteoroloji Genel Müdürlüğünün Antalya, Balıkesir ve Trabzon illerindeki yağmur örnekleme istasyonlarından toplanan yağmursuyu örneklerinin iyon birleşimleri analiz edilmiştir. SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, Ca^{2+}, K^+ ve Na^+ gibi iyonların analizleri iyon kromatografisi ile yapılmıştır. Bu ölçümlerden elde edilen sonuçlar ile hava kütlelerinin Anadolu platosunda taşınması ile yağmur suyunun kimyasal birleşiminin nasıl değiştiği karşılaştırılmıştır. Bunun yanı sıra bu sonuçlar Türkiye'nin değişik bölgelerindeki yağmursuyu birleşiminin dönemsel olarak nasıl değiştiğini de göstermektedir. Bu değişimlerin arkasında yatan sebepler istatistiksel hesaplamalarla incelenmiştir. Türkiye'nin farklı lokasyonlarındaki yağış birleşimini etkileyen kaynakları anlayabilmek için çok-değişkenli istatistiksel bir yöntem olan Pozitif Matris Faktorizasyonu kullanılmış ve dört kaynak ayrıştırılmıştır. Bunlar uzun mesafeli kirleticiler, toprak emisyonları, deniz tuzu ve tarımda kullanılan gübreleme faktörüdür. Aynı şekilde kaynakların lokasyonlarının tayininde yörünge istatistikleri kullanılmıştır. İstasyonlara her gün ortasında gelen geri yörünge bilgileri, National Oceanic and Atmospheric Administration (NOAA) tarafından geliştirilmiş, 3D, eş entalpili bir yörünge modeli olan HYSPLIT yörünge modeli kullanılarak toplanmaktadır. Bu model NOAA bilgisayarlarında çalıştırılır ve sonuçlar bizim kullandığımız bilgisayarlara aktarılır.

Anahtar Kelimeler: Yaş çökelme, Yağmur suyu kompozisyonu, İyon kromatografisi, Asit Yağmurları, Geri-yörünge

To My Beloved Family

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to the following people for their tremendous help and support.

First, I would like to express my greatest appreciation to my thesis supervisor Prof. Dr. Gürdal Tuncel for his guidance, patience, support, enthusiasm, and valuable comments.

I would also like to thank to my committee members Prof. Dr. Dilek Sanin, Assist. Prof. Dr. Tuba Hande Ergüder, Assist Prof. Dr. Barış Kaymak and Assist. Prof. Dr. Seda Aslan Kılavuz for their insightful comments, valuable suggestions and time spent in evaluating my dissertation.

I would like to extend my gratitude to the financial support from The Scientific and Technological Research Council of Turkey (TUBITAK) and General Directorate of Meteorology for the collection and analyses of the rain water samples.

I am truly indebted to Deniz Genç Tokgöz, Güray Doğan, Sema Yurdakul. Without their technical and moral support, and guidance, I would never been able to realize this work.

I would like to thank to our air pollution group members; Ebru Sarıkaya, İlker Balcılar, İlke Çelik, Sena Uzunpınar, Tuğçe Bek, and my roommates; Cansu Karakaş, Engin Koç for their friendship and motivation.

I am also very thankful to my colleagues Cansu Yazıcı, Duygu Dinçer, Gizem Güngör, Nilsu Affan, Onur Atak and Elif Küçük, they are really helpful to me during the writing and auditing part.

I would particularly like to thank Zeynep Malkaz for her help and friendship from the beginning to the end of this study.

Moreover I would like to thank İrem Baysal, Gizem Taner and Gizem Baysal for being with me whenever I need and sharing my feelings warmly. I am also thankful to Yiğit Özkılıç for his sincere encouragement during my hard working days.

Finally I would like to express my deepest appreciation to my family for their love, understanding, encouragement and endless patience. But I am especially thankful to my mother, who primarily supports me to get a master’s degree.

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LIST OF ABBREVIATIONS

BDL	Below Detection Limit
DL	Detection Limit
EC	Elemental Carbon
EMEP	The European Monitoring and Evaluation Program
EPA	Environmental Protection Agency
GIS	Geographical Information Systems
HYSPLIT	HYbrid Single Particle Lagrangian Integrated Trajectory Model
IC	Ion Chromatography
LOD	Limit of Detection
MGM	General Directorate of Meteorology
NOAA/A	National Oceanic Atmospheric Administration, Air Resources
RL	Laboratory
NILU	Norwegian Institute for Air Research (Norsk Institutt for Luftforskning)
OC	Organic Carbon
OGM	General Directorate of Forestry
PM	Particulate Matter
PMF	Positive Matrix Factorization
PSCF	Potential Source Contribution Function
QA/QC	Quality Assurance/Quality Control
SRM	Standard Reference Material
UNC	Uncertainty
UTC	Coordinate Universal Time

CHAPTER 1

INTRODUCTION

1.1. Introduction

Acid rain is one of the important environmental pollution problems due to its adverse effects on the health of the ecosystem. It can damage natural resources such as lakes, streams, forests and plants; unbalance atmospheric stability and consequently adversely affect human health. Because of this concern, it has been a significant subject of environmental studies conducted worldwide (Alagha and Tuncel, 2003; Al-Momani, 1995; Avila and Alarcon, 1999; Losno et al., 1991; Al- Khashman, 2005; Zhang et al., 2006)

Chemical composition of precipitation plays an important role in scavenging soluble components from the atmosphere and helps to identify the relative contribution of possible natural and anthropogenic emission sources of atmospheric pollutants. Therefore, it is an important research area of environmental pollution field.

In order to investigate the effects of acid rain on natural and artificial environments, it is necessary to monitor the components of rain continuously. In this study, precipitation samples were collected at three stations of General Directorate of Meteorology which are located at Antalya, Balıkesir and Trabzon, between years 2010 and 2012. Major ion concentrations; which consist of the cations H^+, NH_4^+, Na^+, K^+, Mg^{2+}, and Ca^{2+}, and the anions NO_3^-, Cl^-, and SO_4^{2-} were measured by using

Ion Chromatography device in the laboratory of GDM which will be explained in chapter three. Incorporation of those ions and acidic levels of the precipitation samples of the sampling stations were determined.

The composition of rain water varies from site to site due to meteorological conditions of the receptor area such as temperature, humidity, wind direction and intensity; location of the station and closeness of pollution sources.

In order to estimate the source regions of pollutants, measured ion composition results at the receptor sites were combined with the geographical information method which is known as back trajectory analysis. In addition to that, positive matrix factorization of the measured ions was conducted. As a result of these source apportionment methods, the responsible pollution sources are determined as: (1) anthropogenic sources (Western Europe, Western part of Turkey and local sources), (2) crustal sources (Northern Africa, Saharan desert and local soil), (3) agricultural sources (Local cultivated areas) and (4) marine sources (Surrounding Seas).

1.1.1. Objectives of the Study

In this study, the chemical composition of precipitation samples, which were collected at three different regions of Turkey, was investigated. The main purposes of the study are:

- To investigate the chemical composition of precipitation in terms of major ion concentrations in Mediterranean, Black Sea and Marmara regions of Turkey.
- To determine the background concentrations in Mediterranean, Black Sea and Marmara regions.
- To study the level of acidity of rainwater, analyze the factors affecting the acidity and explain the neutralization processes.
- To understand the short and long term variations of the concentrations of measured ions.

- To identify the potential source regions contributing to the observed concentrations by using back trajectory statistics.
- To quantify the relative contribution of identified pollution sources.
- To determine the general flow climatology of Mediterranean, Black Sea and Marmara regions respectively by analyzing the back trajectories between years 2010-2013.
- To evaluate the relation between measured concentrations of ions and general flow patterns of back trajectories.

CHAPTER 2

BACKGROUND

2.1. Atmospheric Removal Mechanisms

Precipitation is the most effective scavenging factor for removing particulate and dissolved gaseous pollutants from the atmosphere. This scavenging mechanism occurs either by wet or dry deposition (O.Al-Khashman, 2005).Wet and dry depositions are two pathways by which the pollutants and particulate matters removing from the atmosphere to oceanic and terrestrial ecosystems (Das et al., 2005).

The term wet deposition occurs when the weather is wet and the atmospheric pollutants are trasported to the ground in the form of rain, snow, fog, or mist. Wet deposition includes two processes; 1-rainout and 2-washout. Rain-out means incorporation of pollutants to water droplets and subsequent deposition when droplets form a raindrop. Wash-out means, on the other hand, washing the atmospheric particles by rain or snow that are formed below the cloud.

In areas where the weather is dry, the particles may become incorporated into dust or smoke and settle to the ground through dry deposition (URL 1). The velocity of dry deposition depends upon particle size, meteorological conditions (temperature, wind, etc.) and the receiving medium (Al-MOMANI, 1995).

2.2. Acid Deposition

Acid deposition, which is an important environmental problem, caused by the emission or atmospheric formation of sulfuric acid, nitric acid, or hydrochloric acid and occurs when these acids deposits to soils, lakes, farmland, forests, or buildings. (Mark Z. Jacobson, page 254)

Deposition of acid gases is indicated by dry acid deposition, and deposition of acid liquids is indicated by wet acid deposition. Wet acid deposition can be through rain (acid rain), fog (acid fog), or aerosol particles (acid haze), whereas dry acid deposition occurs when dust settles out of the atmosphere during dry periods. The term acid deposition defined as the combination of acid rain plus dry deposited acid. (O. EL-AGHA, 2000)

2.2.1. Chemical Composition of Acid Precipitation

Precipitation chemistry is an important subject of atmospheric acid precipitation research (Fujita et al., 2000).The relative acidity or alkalinity of precipitation is affected by the presence of acid-producing and alkaline-producing species. These species may present in either the gaseous or particulate forms and can be derived from natural and anthropogenic sources (Cooper, 1975).

In the absence of major anthropogenic pollutants, the pH of the rainwater is expected to be around 5.6 due to carbonate buffer observed with dissolved CO_2 in rain droplets (Charlson and Rodhe, 1982).

In atmosphere CO_2 reacts with water and form HCO_3 which is a weak acid with an acidity constant of pKa=6.8. Carbonic acid then dissociates to give the H^+ ion and the HCO_3^- (bicarbonate) ion:

CO_2 (gas) $+H_2O \leftrightarrow HCO_3$

$H_2CO_3 \leftrightarrow H^+ + HCO_3^-$

$HCO^{3-} \leftrightarrow H^+ + CO3^{2-}$

If CO_2 concentration is assumed to be equal to 350 ppm in the atmosphere, pH is found to be (as Granat, 1972):

$p[HCO_3^-]=-\ln([HCO_3^-)]=11.24- pH$

However, CO_2 is not the only atmospheric specie that influences the pH of rain water. The processes controlling the composition of rain water are complex and influenced by both natural and anthropogenic sources (Gülsoy, 1988). The pH of the rainwater differs from one region to other in accordance with the presence of acidic precursors (CO_2, H_2SO_4, HNO_3, and HCOOH) or neutralizing species (HN_3, $CaCO_3$) (Al-Momani, 1995).

2.2.1.1. Principal Precursors of Acidification

The principal precursors of acid rain are; anthropogenic sources, mainly emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) resulting from combustion, and natural sources such as volcanoes and decaying vegetation (URL 1).

Sulfur is the main constituent of the anthropogenic sources. The sulfur is converted to sulfur dioxide during combustion, and then it becomes sulfuric acid as it joins with hydrogen atoms in the air. The sulfuric acid formed either by hydrolysis of sulfur trioxide or oxidation of sulfurous acid.

The stochiometric equations for the sulfuric acid formation are:

$S + O_2 \rightarrow SO_2$
$SO_2 + H_2O \rightarrow H_2SO_3$

$H_2SO_3 + 1/2O_2 \rightarrow H_2SO_4$

$2SO_2 + O_2 \rightarrow 2SO_3$

$SO_3 + H_2O \rightarrow H_2SO_4$

Nitrogen oxides are other precursors of acid rain, which are emitted from combustion processes. Nitric oxide is formed at elevated temperatures by reaction of nitrogen and oxygen. After that it can be oxidized to form nitrogen dioxide in either the combustion zone or the atmosphere. The nitrogen dioxide can be hydrolyzed in the presence of water to form both nitrous and nitric acids. The stochiometric equations for the nitric acid formation are:

$N_2 + O_2 \rightarrow 2NO$
$2NO + O_2 \rightarrow 2NO_2$
$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$
(Cooper, 1975)

The pH of rain water is expected to be lower than 5.6 at the areas are exposed to strong influence of SO_2 and NO_x gases.

2.2.1.2. Principal Agents of Neutralization

Sulfuric acid (H_2SO_4) and nitric acid (HNO_3) are subjected to neutralization before being deposited from the air (Tunçer, 2000). Therefore, the acidity of precipitation depends on the neutralization capacity of the alkaline components such as NH_3, Ca^{2+}

($CaCO_3$ or Ca $(OH)_2$), Mg^{2+} and Na^+ (Tsitouridou et al., 2006). In regions where the atmosphere has high alkaline capacity, majority of the rain water acidity can be neutralized. Therefore, high pH values will be observed.

The alkaline particles in the air are originated from both anthropogenic and natural sources. Natural sources of alkaline particles are associated with wind erosion of arid soils, volcanic eruptions, natural forest-fires and biological mobilization (e.g. pollen, weathered-leaf cuticle, leaf hairs). Especially soils on calcareous bedrock may emit large amounts of Ca^{2+} ions to the air (Draaijers et al., 1997). Therefore climate conditions, topography of the area and the elevation above sea level are the factors affect composition of the natural sources. Anthropogenic sources, on the other hand, include industrial and agricultural activities. The ammonium, for example, comes from agricultural practices, livestock breeding and biomass burning (Migliavacca et al., 2005).

2.2.2 Studies of Acid Precipitation

Acid precipitation problems have existed since coal was first combusted, but with the Industrial Revolution in eighteenth century, it was intensified. The problem has become an important issue of international interest in all over the world with the growth of industrial processes. Since then, numerous studies on acid rain have been carried out. As a result of these studies, control methods were specified (Mark Z. Jacobson, page 257).

2.2.2.1. Studies of Chemical Composition

Rainwater has been an important subject of environmental studies, and many studies have been conducted on the chemical composition and long term trends in many urban and rural areas (Leeuwen et al., 1996; Avila and Alarcon, 1999; Al-Momani, 1995; Losno et al., 1991; Güllü et al., 1998; Alagha and Tuncel, 2003; Lazaridis et al., 2002). Most of the current acid deposition research rely on wet deposition maps based on the results of both long-range transport models and actual measurements.

These measurements showed that in the certain parts of Central Europe the levels of acid precursors are high, which were attributed to industrial activity. Very high SO_4^{2-} levels and fluxes were found in the Black Triangle region, which is the border area between Germany, Checz Republic and Poland (Leeuwen, et al., 1996).

The Europe is the strongest potential source region of ions and elements (Al-Momani et al., 1995). Therefore, long-range transport of gaseous air pollutants has been studied extensively in Europe during the last decades. The European Monitoring and Evaluation Program (EMEP), which is an acronym for the Co-operative Program for Monitoring and Evaluation of the Long-range Transmission of air Pollutants in Europe, is the responsible organization for the conducted studies

Main objectives of the EMEP program are to provide quantitative information on the transport of air pollutants across national boundaries and the deposition concentration levels caused by this transport. EMEP's work in the past has been related to acid precipitation and photochemical oxidant formation, and lately heavy metals and persistent organic compounds have been included (Lazaridis et al., 2002).

Wet deposition of alkaline particles was studied in relation to the issue of acidification through their neutralization ability. In large parts of southern Europe, more than 50 % of the potential acid deposition was neutralized by deposition of alkaline species. However, in central and northwestern Europe, alkaline emissions usually amounted to less than 25 % of the acid input (Draaijers, et al., 1995). In this respect, transport of Saharan dust is an important source of neutralizing agents in precipitation of Southern Europe (Draaijers et al., 1997). Another study was conducted in Spain, which is in the Southern part of Europe (Calvo et al., 2010). According to this study, back-trajectory data were divided into nine groups as Mediterranean (M),Tropical Maritime (Tm), Polar Maritime (Pm), Local (L), Continental (C), Arctic (A) and Saharan (S) at three different altitudes (500 m, 1500 m and 3000 m a.g.l.). Results show that the Saharan 1500 m and 3000 m back trajectory groups seem to have an important influence on chemical rain composition.

In Northern Central Europe, on the other hand, NH_3 is the dominating neutralizing agent (Glavas, 1988; Mamane and Gottlieb 1995). While Mediterranean data show clear distinction between Saharan and non-Saharan cases, the separation in Hungarian data groups is weak, sometimes even disappearing, as a consequence of poorer regional air quality (Borberly-Kiss et al., 1999). According to the 1989 EMEP database, NH_3 fluxes were largest in Central Europe and large Ca^{2+} fluxes were observed in the Black Triangle and Ukraine, which could be attributed to the intensive industrial activity (Leeuwen, et al., 1996).

Extensive studies were conducted on Mediterranean region to explain chemical composition of wet and dry deposition, acidifying compounds and neutralizing agents (Avila and Alarcon, 2003; Al-Momani,et al., 1995; Al-Momani,et al., 1998; Güllü et al.,1998; Guerzoni et al., 1995; Herut et al., 1999; Glavas et al., 2002). As a result of those studies it is obtained that Mediterranean atmosphere is under the influence of three general source types: (1) anthropogenic sources, which are located to the north and northwest of the basin; (2) a strong crustal source located in North Africa; and (3) a marine source, which is the Mediterranean Sea itself (Güllü et al., 1998).

The most important characteristic of the precipitation of the eastern Mediterranean region is the extensive neutralization capacity of acidity by the airborne $CaCO_3$ particles from soil. Although concentrations of NO_3^- and SO_4^{2-} were high, not significantly differences are observed of the high pH of samples. That is why neutralization of acidity determines the pH of the rain water in the Mediterranean region. Results represent that more than 70 % of the acidity were neutralized by $CaCO_3$ which originate both from airborne local soil and dust transported from North Africa (Al-Momani et al., 1995).

In western Mediterranean region, similar results have been observed (Losno et al., 1991; Camarero and Catalan, 1993; Sotirios et al., 2002; Avila and Alarcon, 1999).

They all find that Saharan dust has a great influence on neutralizing acidic acidity in the western Mediterranean precipitation.

Acidic and alkaline rains have also been studied in Israel and the large Ca^{2+} concentrations were observed in rain water (Mamane and Gottlieb, 1995). While the marine originated ion concentrations were approximate values with worldwide coastal areas; pH, Ca and SO_4 concentrations were found to be relatively higher than them. The chemical composition of rain water in northern Israel is dominated by Ca^{2+}, Na, Cl^- and SO_4^{2-}, central Israel is dominated by Na^+, Ca^{2+}, Cl^-, SO_4^{2-} and HCO_3^-, and in the south, Ca^{2+} and HCO_3^-. The regional pH variations of contemporaneous rain events demonstrate a similar trend with other Mediterranean studies, and as a result it was obtained that the main parameter that affect the pH is not local anthropogenic source, but the regional neutralizing capacity for each rain event. The overall regional effect on chemical composition of rain was related to the transitional zone from large deserts to Mediterranean climate.

In Turkey, several studies have been carried out on major ion compositions of wet and dry deposition subject. Chemical composition, acidifying and neutralizing compounds and source types of these compounds were analyzed in different parts of Turkey (Al-Momani et al., 1995; Kaya and Tuncel, 1997; Tunçer, 2000; Gülsoy, 1998; Topçu, 2002; Okay, 2002). In the light of these studies, maximum SO_4^{2-} and NO_3^- concentrations, which are acidifying ions, appeared in winter or autumn seasons, due to heating demand, whereas minimum concentrations in spring or summer seasons when heating demand lessens. Results indicated that SO_4^{-2} concentrations in precipitation were quite high; however, significant neutralization of acidity was observed.

The neutralizing agents are primarily $CaCO_3$ and NH_3. One of the main reasons of not having high acidity in the precipitation is the alkaline nature of the soil which is rich in calcium. Another reason is the fertilizers containing high amounts of NH_3^- and NH_4^+.

Long term trend analysis is the other important subject of wet deposition and acidification studies, since the relation between time and ion concentrations helps us making future predictions about environmental issues.

2.3. Receptor Oriented Models

Receptor modeling approaches such as positive matrix factorization (PMF), flow climatology and wind sector analysis are effective tools in source identification of urban and regional scale pollution. In this work, these models were applied to identify categories and locations of sources of compounds in precipitation samples.

2.3.1. Trajectory Statistics

Trajectory is defined as the path of an air parcel followed in the atmosphere until it reaches the receptor site. Atmospheric trajectory analysis is frequently used to identify the source areas and the direction of detected pollutants at a receptor site (José et al., 2005; Rousseau et al., 2004). The model uses long term air pollution measurements and movement of air mass (Castillo et al., 1983; Kelly et al., 1984; DeFelice and Saxena, 1990; Lin and Saxena, 1991; Kim and Aneja, 1992).

In most of the trajectory models, while observed or analyzed winds are used to compute horizontal advection component, vertical components are computed assuming that they are isobaric, isentropic or kinematic (Doğan, 2005)

In isobaric trajectory modes, trajectory is assumed to follow a constant pressure surface. Isobaric models were used extensively in the past; however it has been found that the significant vertical motions were ignored in isobaric assumption (Harris and Kahl, 1994). Isentropic trajectory models are widely used in trajectory calculations in recent years. In isentropic models trajectory is assumed to follow a constant potential temperature. Isentropic models are advantageous due to not requiring vertical motion data. The vertical air motions occur implicitly as air parcel move along sloping isentropic surfaces (Fuelberg et al., 1996).

Five-day back trajectories computed using the HYSPLIT model (Draxler and Rolph, 2003; Rolph, 2003). The HYSPLIT model is a system that calculates air mass back trajectories at the National Oceanic Atmospheric Administration, Air Resources Laboratory (NOAA/ARL) of the United States (URL 2).

Long-range transport of pollutants through the troposphere is a significant interest due to its potential impact on regional climate. Back trajectory analyses provide an explanation on how, when, and where potentially harmful materials are atmospherically transported, dispersed, and deposited.

There are various statistical methods that have been developed to compute the trajectories. In this study; flow climatology and wind sector analyses were used to identify the source regions affecting chemical compositions of precipitation.

2.3.1.1. Flow Climatology

Statistical analysis of air mass back trajectories combined with long-term ambient air pollution measurements are useful methods for source identification. Back trajectory analysis is frequently used to point out the direction and sources of air pollution at a receptor site (José et al., 2005; Rousseau et al., 2004).

Flow climatology is a backward trajectory-using-technique that helps to understand air flow patterns during sampling years. It counts the trajectory which passed through a given cell and plots a distribution map. Higher density means more trajectories passed through that grid square.

2.3.1.2. Wind Sector Analyses

Wind sector analysis is a kind of receptor modeling approach in which meteorological measurements such as wind direction is accounted for in the analysis of the data. This technique can be helpful for identifying possible air emission sources.

Air mass back trajectories were calculated for all analyzed samples and classified into categories depending on the path followed by the air masses. In this study domains were divided into eight directional sectors as North, North East, East, South East, South, South West, West and North West.

Residence times of air masses passing through each wind sector are calculated for different trajectory starting altitudes separately and their combinations (Genç Tokgöz, 2013). Therefore, origin of the air masses was understood by wind sector analysis. In other words, the wind sector analysis gives an idea about the direction of potential sources of pollutants.

In recent literature studies, flow climatology and wind sector analysis were conducted together to identify the pollution source regions.

2.3.2. PMF

PMF is a commonly used receptor model in which sample data are decomposed into two sub-matrices as the factor profiles and factor contributions. It solves the factor analysis problem by using least square analysis with data weighting. In the data matrix, the weights are determined depending on the experimental uncertainty (error) estimates of each individual data value (Paatero and Tapper, 1994; Paatero, 1997).

Analysis of the precipitation samples using PMF resulted in a successful partitioning of variance into sources related to pollution factors (Paatero and Tapper, 1994; Paatero, 1997).

The model used in this study was EPA PMF 3.0, developed by U.S. EPA based on the ME-2 algorithm. According to PMF 3.0, the problem under study is treated as a 2-dimensional factor analytic model. The method of PMF is shown in equation (2.1),

$$Xij = \sum_{k=1}^{p} gik\ fkj + eij\ , \qquad i=1,...,m \quad j=1,\ldots,n \qquad (2.1)$$

where X is the concentration of jth species on the ith day at a receptor, i is the number of the sample and j is the number of the measured species; p is the number of independent sources; fkj is the concentration of the jth species emitted from the kth source; gik is the contribution of the kth source to the ith sample. eij is the residual, defined as the sum of differences between observed and modeled concentrations. The model is solved by minimizing the object function Q, the sum of the squared, scaled residuals, shown in equation (2.2):

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{xij - \sum_{k=1}^{p} gik\ fkj}{uij} \right]^2 \qquad (2.2)$$

where i = 1,..., m elements; j = 1,..., n samples; k=1,. . ., p sources; u_{ij} is the uncertainty of x_{ij}. (Gu et al., 2011)

Positive Matrix Factorization has been successfully used in different studies with different data types such as; major ions and trace elements in PM2.5 (particulate matter ≤ 2.5 µm in aerodynamic diameter) at Washington, USA (Kim et al., 2003) ; trace elements in PM10 (particulate matter ≤ 10 µm in aerodynamic diameter) atmospheric particles in the highly industrialized harbor of Dunkirk, France (Alleman et al., 2010); major ions in water-soluble atmospheric particulate matter at Corun˜a city, Spain (Prendes et al., 1999); secondary inorganic ions, trace elements, carbonaceous species and light absorption data to investigate sources of PM2.5 in Rochester, New York (Wang et al., 2012); PM2.5, elemental carbon (EC), organic carbon (OC), organic and inorganic source markers are reported from residential indoor, residential outdoor, and ambient microenvironments from a nine home pilot study conducted in Tampa, Florida (Olson et al., 2007);and major and trace elements of respirable suspended particulates (RSP) in Hong Kong (Lee, Chan, & Paatero, 1999).

Moreover, the PMF model results in several factors. The various factor types refers different pollutant sources, such as marine source, industrial activities, motor vehicle, vegetative burning, a soil dust, wood combustion, biogenic emissions and coal power plant/secondary aerosols.

2.4. Geography and Climatology of Study Area

The first station of the study is at Antalya which is in the Mediterranean region of Turkey. The Mediterranean region is surrounded by the Central Anatolia Region in the north, the Aegean Region in the west, the Eastern Anatolia Region in the northeast, the Southeastern Anatolia Region in the east, Syria to the southeast, and the Mediterranean Sea in the south.

It has two different climates: Coastal part has Mediterranean climate which is hot and dry in summers and mild and wet in winters. The interior parts, on the other hand, has semi-arid continental climate, which is hot, dry summers and cold, snowy in winters.

Second station is at Balıkesir, which is in the southern part of Marmara region. The region is bordered by the Aegean Region in the South, Black Sea Region in the east and Central Anatolian Region in the South West. The Marmara region has three different climates. The Aegean Sea coast and the south Marmara Sea coast have a hybrid Mediterranean climate/humid subtropical climate, the Black Sea coast has an oceanic climate and the interior parts have a humid continental climate. Summers are warm to hot, humid and moderately dry whereas winters are cold and wet and sometimes snowy.

The third sampling station is at Trabzon, which is in Eastern part of Black Sea region of Turkey. Black Sea region is surrounded by the Marmara Region in the west, the Central Anatolia Region in the south, the Eastern Anatolia Region in the southeast, the Republic of Georgia in the northeast, and the Black Sea in the north. Black Sea region has an oceanic climate which means the region has high and evenly distributed rainfall the year round. At the coastal part, summers are warm and humid, and winters are cool and damp. The eastern part of Black Sea coast is the highest precipitation receiving part of Turkey.

All sampling regions are under the influence of three general sources as anthropogenic sources, crustal sources, and marine sources (Al-Momani, 1995; Güllü et al, 1998; Isıkdemir, 2006). Using detailed meteorological station data, Table 1.1 was prepared for years 1960-2012 average temperature values.

Table 1.1 Monthly average temperatures (1960-2012)

Months	**Average Temperatures**		
	Antalya	Balıkesir	Trabzon
January	9.8	4.7	7.4
February	10.3	5.7	7.3
March	12.7	8.3	8.5
April	16.1	13.1	11.8
May	20.5	17.8	15.9
June	25.4	22.6	20.4
July	28.4	24.8	23.2
August	28.2	24.5	23.3
September	24.7	20.6	20.3
October	20.0	15.8	16.5
November	14.9	10.4	12.7
December	11.4	6.7	9.6

According to the table 1.1 for Antalya and Balıkesir, the hottest month is July with average temperatures 28.4 °C and 24.8 °C respectively, and the coldest month is January with temperatures 9.8 °C and 4.7°C. For Trabzon, on the other hand, the hottest month is August with average temperature 23.3 °C and the coldest month is February with average temperature 7.3°C (URL 3)

CHAPTER 3

MATERIAL AND METHODS

3.1. Sampling Site

Data used in this study is generated by the General Directorate of Meteorology (MGM). General Directorate of meteorology has approximately 10 rainwater sampling stations operating at different locations of the country. Data generated in three of these stations, namely the Balıkesir, Antalya and Trabzon stations were used in this study. Locations of sampling stations are given in Figure 3.1. Data were generated from samples collected between years 2010 to 2013. Although sampling procedures were identical in all MGM stations, sampling durations were not exactly the same.

Figure 3. 1 Locations of precipitation sampling stations (Google Earth, 2013)

MGM rainwater network was initiated with bulk sampling point established in the central Anatolia (Çamkoru, Ankara) in 90's. Then a second station, wet only sampling station was established in Amasra in 1995. The procedures and the sampling strategy used in Amasra station formed basis for all later stations. First several stations in the network were located at the premises of General Directory of Forestry units, as most of the meteorological stations, where they can be installed are now surrounded by settlement areas and are not suitable to collect regionally-representative samples. Both Antalya and Trabzon stations used in this study are these types of stations. Operating manual stations with the help of a different organization is not easy. Although this type of operation strategy proved to be successful in some of the stations, like Antalya station, MGM suffered from substantial difficulties in collecting systematic samples in some of these stations, including Trabzon station which is one of the stations we used in this work.

MGM is now reorganizing their stations. They understood the difficulty of running a large network with the help of other organizations. Stations that are controlled by the General Directorate of Forestry are gradually being moved to meteorological radar sites, which are operated by the MGM them. There are several advantages of stations being at the radar sites; (1) they are controlled and operated by the MGM, thus they have complete control on technicians who change samples, (2) most of the radar sites are excellent locations to collect regionally representative samples. Radars are located at high altitudes and far from settlement areas, which are also the requirements for regional aerosol or rain water monitoring stations, (3) There are highly trained people at radars, which is essential to collect rain samples reliably. In most of the stations operated by our group, local people who change samples are guards of the General Directorate of Forestry (OGM). These people are at most elementary school graduates. All sampling procedures are designed to be very simple, so that they collect samples without making mistakes all the time. But Guards at Meteorological Radar sites are at least high school graduates and there are also university graduates among them, because their only function is not to protect the equipment, they also are expected to solve simple problems of very sophisticated instruments and (4) there is uninterrupted and voltage regulated power available. This last item may look de facto from Ankara, but is serious luxury in most of the rural locations.

The first sampling station is established in Antalya, in the Mediterranean region of Turkey. The coordinates are 39°44’25’’ latitude north of Equator and 27°37’10’’longitude east of the Greenwich. The height of the sampling location is 460 m above sea level. Antalya station is located at an experimental forest area operated by the Western Mediterranean Forest Research branch of the Ministry of the Forestry and Waterworks. Pictures of the station are given in Figure 3.2.

Figure 3. 2 Antalya Sampling Station

The second station is in Balikesir, in the Marmara region of Turkey. The coordinates of the station are 40°41’22.93” latitude north of Equator and 39°39’21.38” longitude east of the Greenwich. The height of the sampling location is 642 m above sea level. Sampler was placed at the Meteorological Radar located at approximately 25 km to the northwest of the city of Balıkesir. The station is far from all local emission sources and thus an excellent site to collect rainwater and aerosol samples. Some pictures of the radar is given in Figure 3.3.

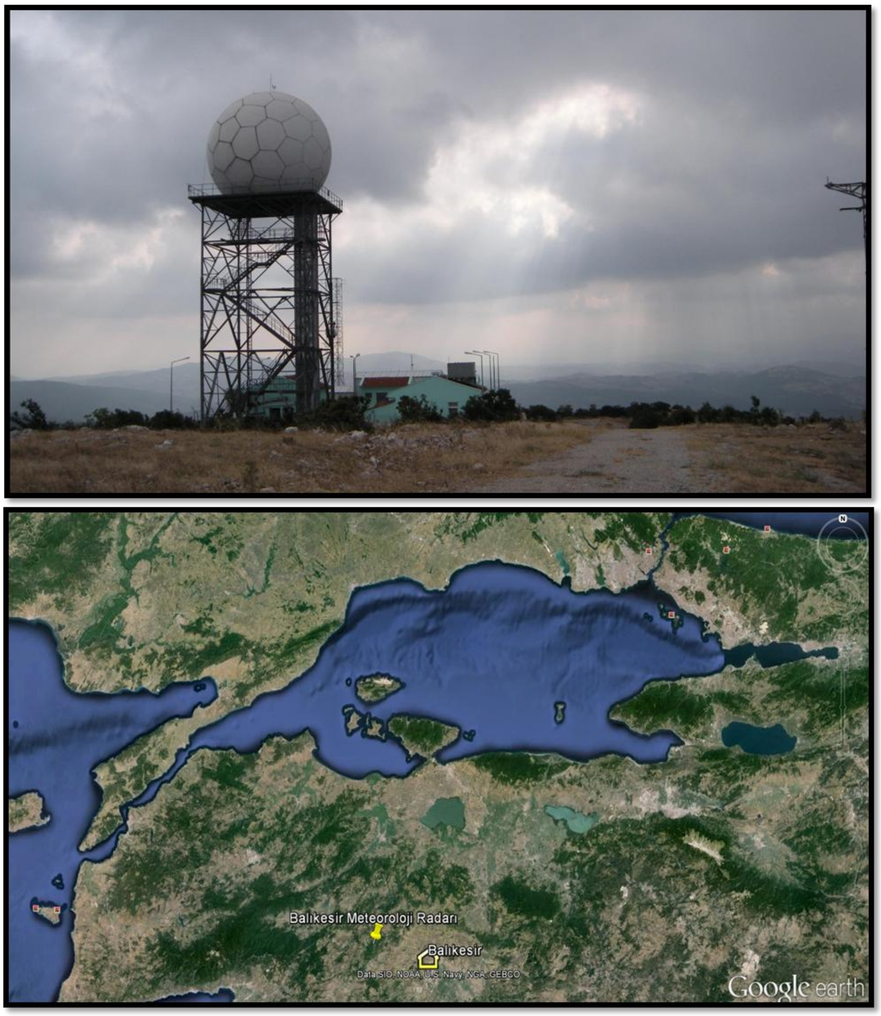


Figure 3. 3 Balıkesir Sampling Station

The third station is in Trabzon, in the Black Sea region of Turkey. The coordinates of the station are 40°41’22.93” latitude north of Equator and 39°39’21.38” longitude east of the Greenwich. The height of the sampling location is 578 m above sea level. Rain sampler was located at the premises of the Sümela Monstir at the Maçka district of the city of Trabzon. Some pictures of the station are given in Figure.3.4. We were not as lucky in Trabzon station as we were in the other two stations used in this study. Sampling at Trabzon station was initiated in December 2010. Sampling went smoothly in the beginning, after few months, General Directory of Forestry appointed the technicians who were changing samples to another location, which was 30 km from Sümela. Since no one else was appointed instead, that technician had to travel 30 km to change the sample every day (and also had to travel another 30 km to go back). It was obvious that this strategy would not work and it did not.

Figure 3. 4 Trabzon Sampling Station

Only 30 samples were collected since December 2011, when operation of the station was terminated. Considering that most of the data evaluation performed at Antalya and Balıkesir stations involved approximately 140 samples, 30 samples collected at

Trabzon station was too little to reach statistically significant conclusions. This was particularly true for statistical treatments where data is divided into several sections, such as for calculating monthly average concentrations to understand seasonal variations in data set. In such cases data from Trabzon station is not included in the statistical treatment.

All three stations are also on the top of 20 m height platform which contains sampling equipments and field laboratory. The stations consist not only of the wet only precipitation sampler. There are also a wet and dry deposition sampler, a Hi-Vol sampler and a Hi-Vol impector. The platform also has a field laboratory with dimensions of 3m x 2m x 2m.

3.2. Sampling Procedures

3.2.1. Preparation of Sampling Bottles

Polyethylene bottles were used to collect wet deposition samples. Before using, bottles were rinsed off with 30% HNO3 solution and steeped in the solution for 24 hours. Then they were washed with double distilled deionized water 5 times and kept in the clean room for 1 day to dry. After drying, bottles were sent to the sampling stations in polyethylene bags and a new storage bottle was set up.

3.2.2. Collection of Wet Deposition Samples at the Station

Rainwater samples in this study and in MGM monitoring network in general, are collected using wet–and-dry samplers. One interesting point about this sampler is that they are constructed at Ankara. Since MGM was planning to establish a large number of monitoring stations and since automated wet and dry samplers in international market are very expensive they decided to encourage companies to construct it in the country. The model constructed were identical to ANDERSEN wet and dry sampler, which were reliably used in many networks around the world. The manufacturing of that particular rain samples is stopped after Andersen Co. Merged to Thermo international. Many small manufacturers around the world copied this popular sampler, and because of that, different versions are now in use in different countries.

The constructing this sampler in Turkey was also very successful as MGM is using them, without a serious problem in last fifteen years. Very strong mechanical background available in the MGM is essential in this success story.

The sampler contains two 30 cm diameter of buckets having an activated rain sensor. One of the buckets is used to collect wet deposition samples and the other one is used to collect dry deposition samples. When start of the rain is sensed y the sensor, it moves to lid onto the dry deposition bucket. In this way no rain enters the dry bucket. When the rain ends sensor moves the lid onto the wet deposition bucket. Thus no dry deposition particles enter the rain bucket when it does not rain. With this system both rain and dry deposition samples can be collected. We used data from wet deposition samples only.

Different versions of this sampler are being used in different countries. In the US acid deposition networks, two buckets on the sampler were replaced with fresh ones at the end of the sampling period. Both buckets were shipped to the central laboratory. In our group the sampler was modified such that rain was first passed through a funnel and then directly collected in 1 L capacity high density polyethylene bottles. However, MGM developed their own system. They placed a 10 L capacity polyethylene bag (like a trash bags used in our houses except transparent one) to both buckets. At the end of the sampling period these bags are replaced with new ones and bags that contain rain water was shipped to the central laboratory at Ankara. This was an easy and effective system, which was also relatively contamination free.
Wet deposition samples were event based. Poly ethylene bags were left on the sampler and investigated every day. If there is rain in it, it is removed and sent to laboratory. If it did not rain that day, the bag was left on the sampler.

Dry deposition samples were collected on a weekly basis. Poly ethylene were placed on the dry deposition bucket and replaced with a new at the end of the week. As pointed previously, data from dry deposition samples were not used in this study.

The funnel, filtration unit and sampling bottle are connected by high-density polyethylene tubing. Filtration units and polyethylene tubing were replaced with clean fresh ones after the collection of each rain sample. The used tubing was discarded, and filtration units were sent to cleaning; and the sample bottle is removed from the container and brought to the laboratory.

Figure 3. 5 Original ANDERSEN Wet and Dry sampler (a) and home-made wet and dry sampler (b) used in MGM network

3.3. Sample Handling

There was minimum handling of polybags used to collect both wet and dry deposition samples. The bags were not reused and thrown away after sampling. However, they were rinsed first with 5% solution of HNO3 and then several times with distilled de-ionized water to ensure that any impurities in the bag that comes from manufacturing process are not transferred to samples.

In the field, at the end of the sampling period, bags in the buckets that contain wet and dry deposition samples are removed from the sampler using polyethylene bottles and carefully sealed, placed in another polyethylene bag and shipped to the laboratory.

In the laboratory, rain samples in the polyethylene bag were transferred to high density polyethylene bottles using a high density polyethylene funnel. An aliquot of that sample was filtered and analyzed for ions H^+, NH_4^+, Na^+, Mg^{2+}, K^+, Ca^{2+}, SO_4^{2-}, NO_3^-, NH_4^+ and Cl^- ions.

3.3.1. Determination of Volume and pH

Volumes and pH of the samples were measured at the laboratory. To measure volume, calibrated sampling bottles were used. Heights of sampling bottles were compared by the calibrated bottle. To measure pH, a Radiometer PHM 80 portable pH meter equipped with a combination glass electrode. pH meter is calibrated before measurements using standard buffer solutions at pH 4.0 and 7.0. The pH was determined immediately when the samples came to the laboratory.

3.3.2. Preparation of Samples for Ion Chromatography

Collected precipitation sampling bottles were then sent to the General Directorate of Meteorology laboratory for analysis. There were not extensive sample treatments for ion measurements. However precipitation samples may include some fine particulate matter. Therefore, samples were first filtered through 0.2µm pore size cellulose acetate membrane filter and the IC column is avoid clogging problem. Ions, SO_4^{2-}, NO_3^-, NH_4^+, Na+, Cl^- are almost 100% soluble in all rainwater samples. Consequently, these ions were not affected significantly from filtration process. However, ions like Ca^{2+}, K^+, Mg^{2+} largely, but not 100% soluble ion rain samples. Their solubility may change from one sample to another depending on the acidity of rainwater and soil content in rain. Earlier studies in our group demonstrated that solubility of these ions were higher than 50% in all pH values. Nevertheless only water soluble fractions of these ions were measured in this study.

3.4. Analysis of Samples

Analytical techniques and devices used in determination of chemical composition of precipitation samples are shown in Table 3.1. Analysis of major species was conducted by Ion Chromatography technique. Ion chromatography is a technique that applied to identify the chemical composition of liquid samples. Inorganic anions, cations, transition metals, and low molecular-weight organic acids and bases of a sample can be determined by IC. Working principles of IC is based on the injection of a filtered aliquot of sample, an analyte, into an eluent stream. Pumping system of the device transports the mixture of sample and eluent to the separator column. In the column, analyte species are separated based on their affinities relative to the functional group. If the affinity of a species is high, it will take more time to separate it from the column; if the affinity of a species is low, then its separation will be easy and it takes shorter time to leave the column. The relative amounts of species are measured by detector as they leave the separator column. Electrochemical and spectroscopic detection methods have been applied in IC (Landsberger and Creatchman, 1999).

Table 3. 1 Analytical techniques and devices used in determination of chemical composition of precipitation samples

Measured Species	**Analysis Technique**
SO_4^{2-}, NO_3^-,Cl^-	Dionex 120 Ion Chromatograph
NH_4^+, Mg^{2+}, Na^+,Ca^{2+},K^+	Dionex 120 Ion Chromatograph
pH	Radiometer PHM 80 Portable pH meter

In this study water soluble fractions of ions in our samples were analyzed, at the MGM laboratories, using a Dionex 120 Ion Chromatograph. Anions and cations were measured with different columns. Anion column used was Dionex model AS9-HC and cation column was CS12A. In addition to these separation columns, Suppressor columns ASRS-ULTRA and CSRS-ULTRA were used for anion and cation analysis, respectively. 10 mM Na2CO3 and 18 mM MSA solutions were used as eluent in anion and cation analysis, respectively. In both cases eluent flow rate was 1.0 mL min-1. Sample injection volumes for anion and cations analysis were 75 µL and 10 µL, respectively. Usually, batch of 100 samples were selected. Anions SO_4^{2-}, NO_3^- and Cl^- were measured in all 100 of them. Then column was changed and cations Na^+, Mg^{2+}, K^+, Ca^{2+} and NH_4^+, in the same samples, were measured with the cation column (Jackson, 2000).

3.5. Quality Assurance and Quality Control

3.5.1. Field Operations

Contamination is a very important and possible problem in precipitation sampling processes as sampling, transportation and analysis because of the low ion concentrations of precipitation. In order to control any potential contamination and guarantee the cleanness of the sampling material field and laboratory blanks were analyzed along with the collected samples.

Field blanks were collected by pouring distilled deionized water in polyethylene bags after they are placed in the sampler. Then these polyethylene bags and water poured in them were treated exactly like samples. Lab blanks on the other hand included in the analysis of water and acids used in washings, and filter digestion etc. Blank concentrations of species is very important in the analysis of trace elements in rain water samples, because their concentrations are very low (low μg L-1) levels. Ion blanks were below the detection limit of the instrument for all ions measured in this study.

3.5.2. Calculation of Detection Limits

Detection limit is a theoretical concept to express the precision of the instrumental method used. Although there are different definitions of limit of detection (LOD), the most commonly used definition, namely, the concentration that corresponds to three times the standard deviation (σ) of ten replicate measurements at the blank level. To determine detection limit values of major ions measured in this study, one of the blank samples were injected to IC ten times, concentration which corresponds to 3σ of these 10 replicate measurements were found from the calibration curve and reported as the detection limit of the instrument for that anion or cation. Detection limits of major ions found with this approach is given in Table 3.2 (URL 4).

Table 3. 2 Detection Limits of Ions (μg/L)

Ion	**Detection Limit**
$\mathbf{SO_4^{2-}}$	0.021454
$\mathbf{NO_3^-}$	0.022668
$\mathbf{Cl^-}$	0.076439
$\mathbf{NH_4^+}$	0.081163
$\mathbf{Mg^{2+}}$	0.007738
$\mathbf{Na^+}$	0.018494
$\mathbf{Ca^{2+}}$	0.044752
$\mathbf{K^+}$	0.020703

3.5.3. Quality Assurance

Proper calibration of the instrument is an integral part of the analytical system, but calibration check is part of the QA/QC protocol.

Dionex-120 ion chromatograph used in this study is calibrated by using commercial Dionex Seven Anion Standard-II and Dionex Six Cation-II Standard for anions and cations, respectively. Accuracy of the calibration was occasionally tested by prepearing and analyzing known concentrations of ions from Merck high purity salts (NaCl, K_2SO_4, $NaNO_3$, KCl, $CaCl_2$ and NH_4Cl) in nanopure water. Results of this test are given in Table 3.3 (Genç Tokgöz, 2013). Reasonable agreement was obtained between the calculated and measured concentrations for ions ensures that calibration of the instrument with commercial solutions is reliable.

Usually this type of calibration checks are performed using certified reference materials, but Rainwater SRM is not commercially available.

Table 3. 3 Calculated and IC measured concentrations of Merck high purity salts

Ion	**Unit**	**Calculated conc.**	**Measured conc.**
Cl^-	mg/L	6.0 ± 0.3	6.26 ± 0.05
NO_3^-	mg/L	6.0 ± 0.3	6.36 ± 0.12
SO_4^{2-}	mg/L	6.0 ± 0.3	6.25± 0.1
Na^+	mg/L	3.01 ± 0.15	2.96 ± 0.27
NH_4^+	mg/L	2.94 ± 0.15	3.1 ± 0.28
K^+	mg/L	3.05 ± 0.15	2.93 ± 0.3
Ca^{2+}	mg/L	3.1 ± 0.16	3.04 ± 0.24

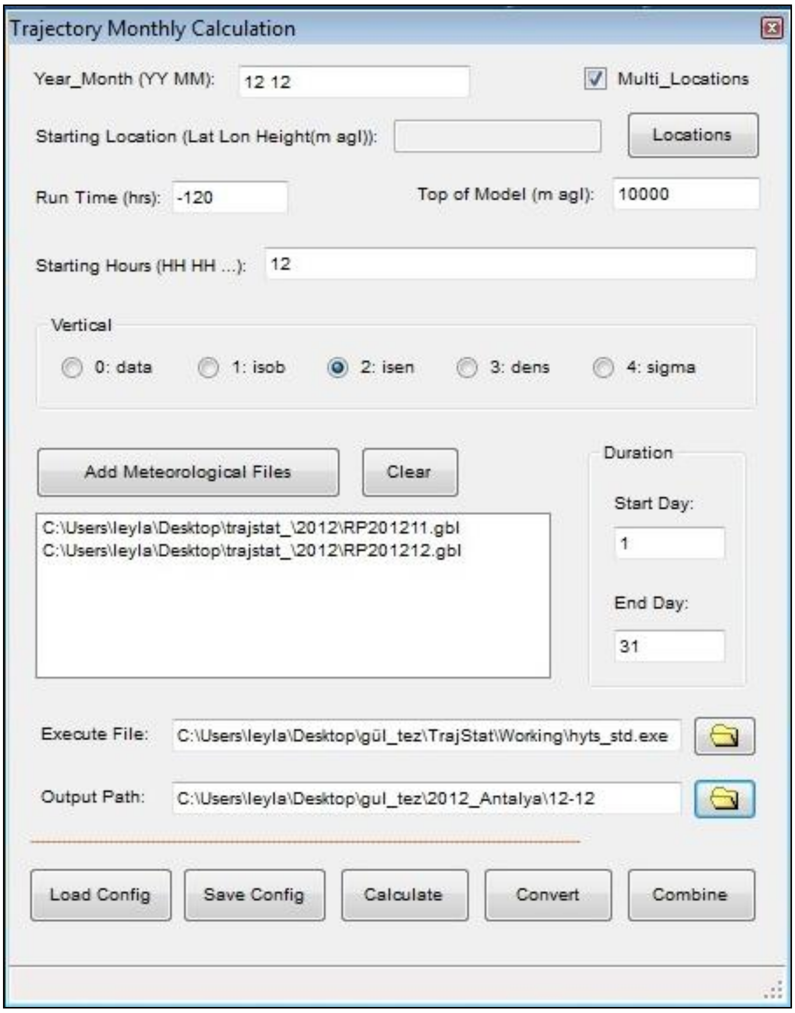
3.6. Computation of Back-trajectories

Back trajectory calculation is a model that has been used in combination with air quality measurements to identify potential source areas of pollutant species in atmosphere and to determine the transport pathways of the chemical constituents before they arrive the receptor site. Therefore the model helps us to evaluate the origin of the air pollutants (Stohl, 1995).

In this study back trajectories were calculated using HYSPLIT, which is a three dimensional, isentropic trajectory model (URL 5 available at May 2013). Since computation of back trajectories require huge quantities of input data, it was not practical to run the model in our own computers. Instead HYSPLIT is run at NOAA computers and outputs of the model, which consisted of hourly trajectory coordinates, were transferred to our own computer system. A Geographical Information System (GIS) based software known as TrajStat was also used to compute trajectories in batches (Wang et al., 2009).

Trajectories were calculated for every sampling day in each station. Calculations were performed for five-day backward time. For each sample three trajectories were calculated with different starting altitudes. These starting altitudes were 100 m, 500 m and 1500 m above the ground level. Latitude and longitude coordinates of each station were converted from degrees, minutes, and seconds to decimal degrees before running the model (URL 6, available at June 2013). The starting time was chosen as 12:00 UTC (Coordinate Universal Time), run time was chosen as 5 days, which corresponds to 120 hours, and model was run for each day in the years 2010, 2011 and 2012. Reanalysis meteorological data archive (horizontal resolution of 2.5 degree latitude) of the NOAA was used as input data to TrajStat software. The model is chosen to be isentropic trajectory type which assumes air parcels to move along constant potential temperature and then hourly position of air masses with latitude, longitude and pressure coordinates along the trajectory’s path was calculated for sampling years by TrajStat.

After calculations, information about every hourly trajectory segments is entered to GIS software, Map Info. All questioning and counting were performed in the GIS program. A screenshot of TrajStat software is shown in Figure 3.6.


Trajectory Monthly Calculation

Year_Month (YY MM): 12 12

☑ Multi_Locations

Starting Location (Lat Lon Height(m agl)):

Run Time (hrs): -120

Top of Model (m agl): 10000

Starting Hours (HH HH ...): 12

Vertical: ○ 0: data ○ 1: isob ● 2: isen ○ 3: dens ○ 4: sigma

C:\Users\leyla\Desktop\trajstat_\2012\RP201211.gbl
C:\Users\leyla\Desktop\trajstat_\2012\RP201212.gbl

Duration

Start Day: 1

End Day: 31

Execute File: C:\Users\leyla\Desktop\gül_tez\TrajStat\Working\hyts_std.exe

Output Path: C:\Users\leyla\Desktop\gul_tez\2012_Antalya\12-12

Figure 3. 6 Trajectory monthly calculation window of Trajstat software

3.6.1 Flow Climatology

Flow climatology refers to the calculation of the fraction of the time air masses spend time in each wind sector. Such a calculation provides information on pollution input from distant sources to the sampling station and also allows understanding of airflow patterns in the study area.

Since we are interested in regional transport of pollutants, we are more concerned with upper atmospheric transport of air masses, which are represented by back trajectories. Back trajectories, computed using HYSPLIT model, were entered to the MapInfo GIS software Version 10.0). MapInfo is a comprehensive computer mapping tool that enables you to perform complex geographic analysis and create thematic maps that emphasize patterns in the data. In this study, MapInfo was used to determine the frequency of air mass trajectories that reach sampling stations through identified domain.

Flow climatology calculations were performed in two different ways. In the first approach, the study domain was divided into 1°x1° girds and trajectory segments in each grid was counted. Results were converted to a segment distribution map by interpolation. These counting was performed for different starting altitudes separately and combined. Since each trajectory segment represents 1-hr part of the trajectory, number of segments in each grid is the number of hours air masses spend in that grid in the years 2010, 2011 and 2012.

In the second approach, calculated back trajectories were assigned to one of the into eight sectors as North (N), North East (NE), East (E), South East (SE), South (S), South West (SW), West (W) and North West (NW). In the second step, and number of trajectories in each wind sector were counted.

Unfortunately it was not that simple to assign trajectories to one of the wind sectors, because each back trajectory generally it travelled through more than one sector before it reaches to station point. An example of this situation is depicted in Figure 3.7. As can be seen from the figure, the trajectory in this particular day spent time in SW, W and NW sectors. Assigning it to one of these factors is not straightforward. In such cases trajectories were assigned to the wind sector in which it spent more time than the other sectors. In another approach that also base on wind sectors, trajectories were not assigned to a sector. Instead, trajectory segments in each sector were counted and thus residence times of air masses in each sector were computed. The last approach was adopted in this study as it was straightforward and avoids us from assigning trajectories to wind sectors.

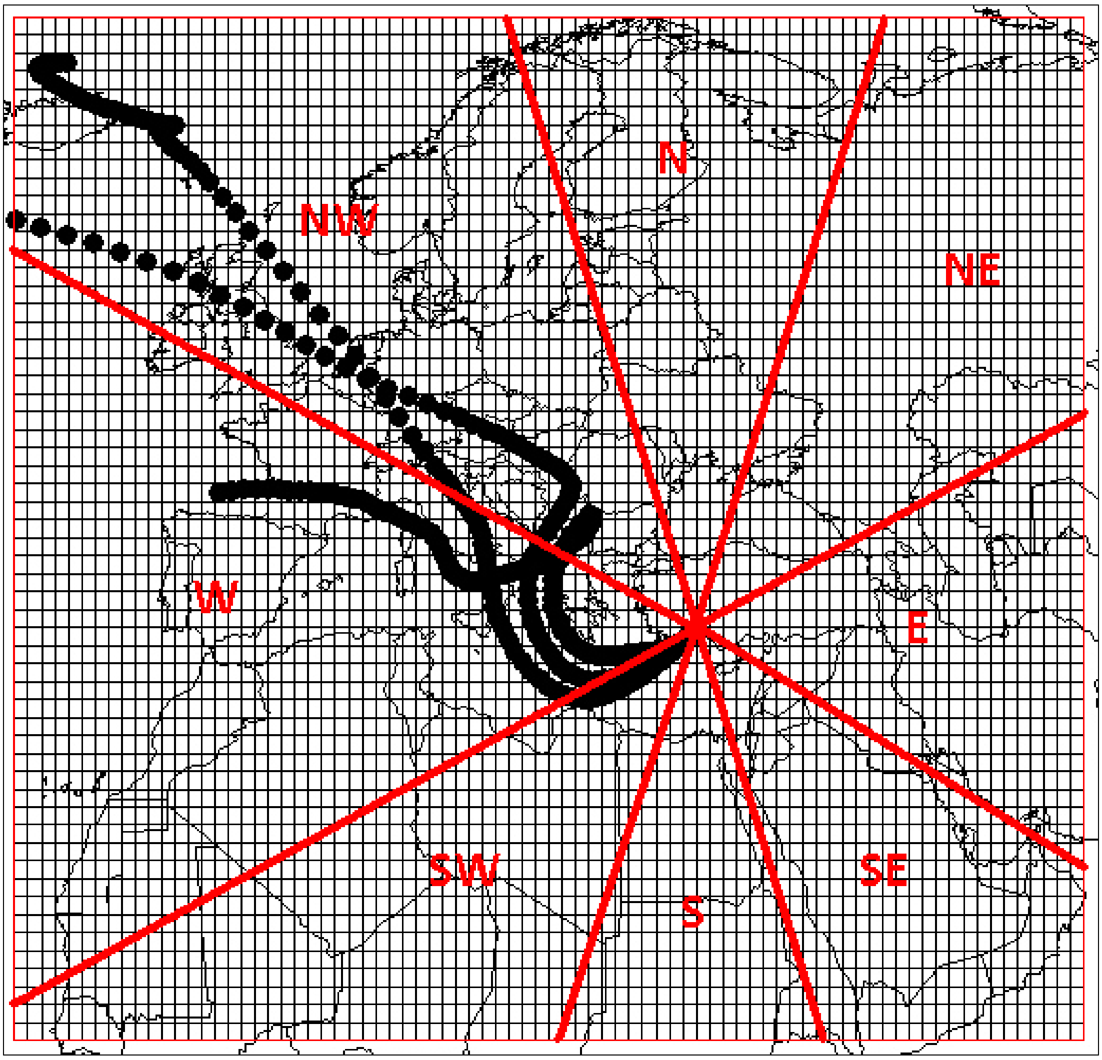


Figure 3. 7 An example plot of a single trajectory on assigned sectors for wind sector analysis

Flow climatology is a source apportionment technique that used to determine the pollution input from distant sources to the sampling station and also allows understanding of airflow patterns. While performing flow climatology whole three years' trajectory dataset were used.

For flow climatology analysis, MapInfo Professional software version 10.0 was used. MapInfo is a comprehensive computer mapping tool that enables you to perform complex geographic analysis and create thematic maps that emphasize patterns in the data (User Guide). In this study, MapInfo was used to determine the frequency of air mass trajectories that reach sampling stations through identified domain.

The movement of an air parcel was described as series of segment end points defined by their latitude and longitude. In this study, flow climatology analyses were applied for the years between 2010 and 2012 by using 100 m, 500 m and 1500 m starting altitudes' trajectories separately and the combined form. Residence times of air masses were calculated for all of them and a distribution graph was achieved. Grid cell size used in the analysis was 1 ° latitude by 1 ° longitude. Results were displayed in the form of maps in a color scale (URL 7).

3.7. PMF

Positive Matrix Factorization (PMF) is the other model that was performed to identify categories and locations of sources by using long-term air pollution measurements, developed by Paatero and Tapper (1993, 1994) and Paatero (1997). PMF was used as a receptor model to separately show the pollution factors.

In this study EPA PMF version 3.0.2.2 was applied to characterize the pollutant source in a set of precipitation samples taken from sampling stations. Each station dataset consists of eight major ions as $S0_4^{2-}$, $N0_3^-$, Cl^-, NH_4^+, Ca^{2+}, Mg^{2+}, K^+, Na^+ concentrations but different numbers of sampling days. To use the model, concentrations in each sample and their corresponding uncertainties of all ions were inserted and an output file was prepared. Before inserting the concentration and uncertainty files, some calculations were done by the below equations:

$$If\ Ci > DLi\ \ \rightarrow Use\ Ci\ as\ concentration\ value\ \ and\ \ UNCi = DLi + 0{,}1 \times Ci \tag{3.1}$$

$$If\ Ci \leq DLi\ \ \rightarrow Replace\ Ci\ with\ \frac{DLi}{2}\ \ and\ \ UNCi = DLi \times \frac{5}{6} \tag{3.2}$$

$$If\ Ci\ is\ missing\ \ \rightarrow Use\ Geo.mean\ as\ Ci\ \ and\ \ UNCi = 4 \times Geo.mean \tag{3.3}$$

Where Ci is concentration and DLi is the detection limit of the ion and UNCi is the uncertainty of the ion.

The model was developed by U.S. EPA based on the ME-2 algorithm. According to PMF 3.0, the problem under study is treated as a 2-dimensional factor analytic model. The method of PMF is shown in equation (3.x),

$$\mathrm{Xij} = \sum_{k=1}^{p} \mathrm{gik\ fkj} + \mathrm{eij}\ , \qquad i=1,...,m \quad j=1,\ldots,n \tag{3.4}$$

where X is the concentration of j^{th} species on the i^{th} day at a receptor, i is the number of the sample and j is the number of the measured species; p is the number of independent sources; f_{kj} is the concentration of the j^{th} species emitted from the k^{th} source; g_{ik} is the contribution of the k^{th} source to the i^{th} sample; e_{ij} is the residual, defined as the sum of differences between observed and modeled concentrations. The model is solved by minimizing the object function Q, the sum of the squared, scaled residuals, shown in equation (2):

$$\mathrm{Q} = \sum_{i=1}^{n}\sum_{j=1}^{m}\left[\frac{\mathrm{xij} - \sum_{k=1}^{p} \mathrm{gik\ fkj}}{\mathrm{uij}}\right]^{2} \tag{3.5}$$

where i = 1,..., m elements; j = 1,..., n samples; k=1,. . ., p sources; u_{ij} is the uncertainty of x_{ij} (Gu et al., 2011).

After inserting the concentration and uncertainty files, according to the S/N ratio values, each ion assigned as “strong”, “weak” and “bad”. Ions with the ratio higher than 2.0, are assigned as strong; between 2.0 and 0.2 are assigned as weak; less than 0.2, are assigned as bad (Paatero and Hopke, 2003). By making categorization, overweighting to weak and bad species is prevented and the strong species gain the importance.

Number of factors was determined by trial and error. Each factor number gives Q robust and Q true values. Q robust refers to Q value calculated when data points having large outliers are excluded; Q true, on the other hand, refers to Q value when all data points are included to the calculation. Those Q values calculated by PMF should be equal or close to the theoretical Q value. Q theoretical is the number of data points in the input concentration file. Thus, factor number and corresponding ion groups are determined.

As a result of PMF, ions emitted from similar sources were shown similar distributions among the different factors. Therefore one can make a judgment about which factor refers which kind of source.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. General Characteristics of the Data

In this study, rain water samples were collected between years 2010 and 2013 from three different parts of Turkey and characteristics of rain waters from those regions were determined. While at Antalya station 90 rain water samples were collected, at Balıkesir station 79 rain water samples were collected and at Trabzon station only 30 rain water samples were collected. The reason of the Trabzon samples are few in number is the problems occurred during sampling period that was mentioned in methodology part. The deficiency of number of samples in Trabzon station causes lack of confidence in statistical evaluations, thus it affects the results.

All collected samples were analyzed and nine major ion concentrations were determined (H^+, NH_4^+, Na^+, Mg^{2+}, Ca^{2+}, K^+, SO_4^{2-}, NO_3^-, Cl^-). General statistical characteristics of measured major ion samples are given in tables 4.1, 4.2 and 4.3 for three stations respectively. By using concentration values and precipitation volumes, volume weighted arithmetic average, geometric mean, median, standard deviation, and minimum and maximum values were calculated. There is a relation between concentration of an ion and precipitation amount. Whether there are same amount of ion exists in the atmosphere, the more precipitation event results in less concentration value because of the dilution. In order to eliminate the contribution of precipitation volume into concentration value, volume weighted arithmetic average of each concentration value was calculated.

Formula of precipitation weighted arithmetic average:

$$Cp = \frac{1}{\sum_x px} \times \sum_x (Cx \times px) \qquad (4.1)$$

Where Cp is precipitation weighted concentration, px is the precipitation volume of day x and Cx is the concentration of an ion in that sampling day.

Table 4. 1 Summary statistics of ionic composition of Antalya Rainwater (concetrations are mg L^{-1})

	Number of Samples	Volume Weighted average ± σ	Geometric Mean	Median	Range
pH	140	5.92 ± 0.63	5.93	6.14	4.15 - 7.26
H^+	140	3.48 ± 9.79	1.09	0.73	0.05 - 70.24
SO_4^{2-}	140	15.28 ± 23.43	13.66	13.7	0.95 - 135.87
NO_3^-	139	8.80 ± 13.98	8.39	7.8	0.82 - 70.11
NH_4^+	135	20.36 ± 26.13	14.39	17.50	0.47 - 135.32
Na^+	140	16.23 ± 21.76	13.53	13.99	1.51 - 113.86
Mg^{2+}	138	8.75 ± 8.11	3.42	3.36	0.45 - 48.60
Ca^{2+}	134	63.22 ± 127.25	32.46	32.77	1.26 - 846.62
Cl^-	138	15.72 ± 18.44	11.00	10.15	1.11 - 128.82
K^+	137	7.40 ± 31.98	7.39	5.66	0.69 - 259.75

Table 4. 2 Summary statistics of ionic composition of Balıkesir Rainwater (concetrations are mg L^{-1})

	Number of Samples	Volume Weighted average ± σ	Geometric Mean	Median	Range
pH	134	5.46 ± 0.84	5.37	5.35	3.83 – 6.99
H^+	134	11.91 ± 25.87	3.65	4.43	0.10 – 146.75
SO_4^{2-}	131	36.22 ± 80.06	46.44	42.85	5.98 – 400.73
NO_3^-	130	16.38 ± 36.09	20.82	20.82	1.62 – 212.36
NH_4^+	129	19.95 ± 40.20	20.56	19.27	0.60 – 187.59
Na^+	134	19.08 ± 27.16	18.78	21.44	1.94 – 111.74
Mg^{2+}	133	7.92 ± 14.89	7.89	8.21	0.71 – 111.91
Ca^{2+}	134	51.98 ± 104.59	42.72	40.19	3.68 – 700.77
Cl^-	133	23.66 ± 83.08	23.69	22.61	3.71 – 663.03
K^+	133	1.71 ± 3.09	2.00	1.91	0.27 – 13.54

Table 4. 3 Summary statistics of ionic composition of Trabzon Rainwater (concetrations are mg L^{-1})

	Number of Samples	Volume Weighted average ± σ	Geometric Mean	Median	Range
pH	30	6.72 ± 0.47	6.92	7.03	5.55 – 7.62
H^+	30	0.75 ± 0.52	0.11	0.09	0.02 – 2.78
SO_4^{2-}	30	196.60 ± 284.58	61.69	57.37	5.63 – 1367.73
NO_3^-	28	44.11 ± 48.96	33.93	38.07	2.20 – 171.85
NH_4^+	15	6.48 ± 19.45	6.28	6.37	0.17 – 76.46
Na^+	30	60.99 ± 48.63	18.93	19.32	0.17 – 223.43
Mg^{2+}	30	53.82 ± 57.96	27.49	34.55	0.45 – 287.08
Ca^{2+}	30	655.06 ± 532.74	241.02	296.74	3.80 – 2525.58
Cl^-	30	50.60 ± 44.65	28.59	35.16	3.90 – 169.28
K^+	30	16.68 ± 11.66	5.31	5.10	0.08 –50.61

According to the tables above, the highest concentrations for all stations were observed in Ca^{2+} and SO_4^{2-} ions, the lowest concentrations were H^+ and K^+ ions. There are consistent differences between stations ion concentrations but it will be discussed in following parts.

4.1.1. Distribution Characteristics of the Data

Distribution of data is identified in terms of frequency distributions of measured ions in the dataset. According to the frequency distribution graphs of ions in three stations; whereas Antalya and Balıkesir stations show similar distributions, Trabzon stations' distributions are different. The main reason for the difference is that few numbers of samples collected from Trabzon station.

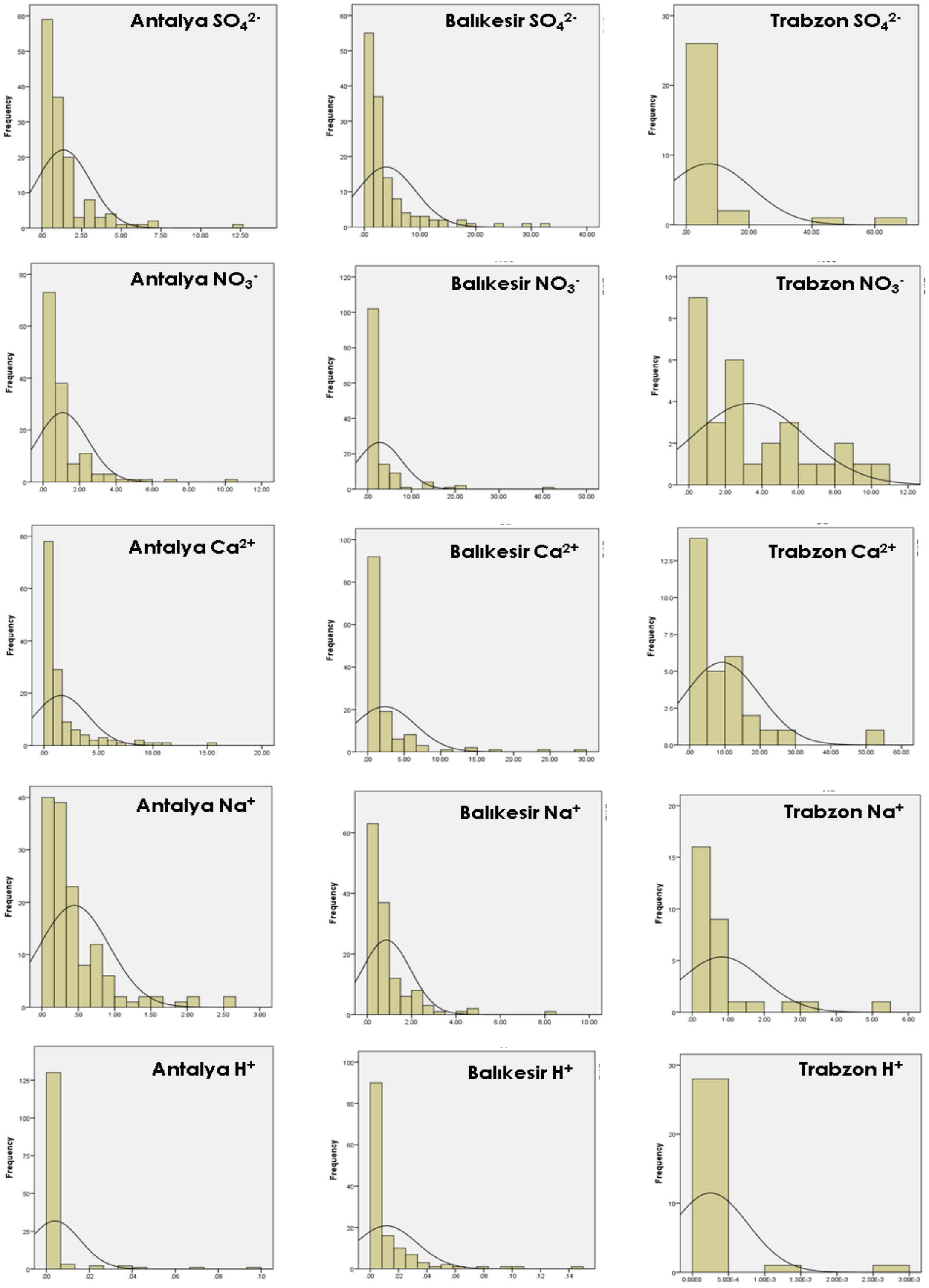


Figure 4. 1 Frequency distributions and best fit curves for SO_4^{2-}, NO_3^-, Ca^{2+}, Na^+, H^+ ions for Antalya, Balıkesir and Trabzon stations

It is clearly seen from the Figure 4.1 that all frequency graphs have right-skewed distribution. However it doesn’t mean that they have log-normal distribution. Therefore, in order to assign the distributions as log normal or not, chi-square test was applied. Although all distributions are not log normal, right-skewed distribution is a better representation way for geometric mean and median of a dataset.

Apart from Trabzon station, the similarity between Antalya and Balıkesir stations is because of the similarity of mechanisms that cause increases and decreases in ion concentrations. H^+ concentration distribution is different than others; it is more right-skewed. It is because H^+ ion concentration does not only depend on air movement and meteorological events. H^+ ion concentration also depend on other concentrations; such as acidic SO_4^{2-} and NO_3^- ions and basic NH_3 and $CaCO_3$ ions concentrations and their relative relationships. Therefore its frequency distribution may be different from other ions.

4.1.2. Comparison of Precipitation Data with the Literature and the EMEP Network

Comparing data with literature is important in scientific studies in order to assess the pollution level of the study and understand the importance of results observed through the study. For a rational comparison, studies should be selected carefully. Sampling site characteristics, applied procedures and analyzed species should be known and results should be definitely reliable.

The EMEP (European Monitoring and Evaluation Programme) is the co-operative programme based on monitoring and evaluation of the long range transmission of air pollutants in Europe (URL 8). The EMEP network data were used for comparison because; (1) all stations in the network have the same site selection, sampling and analytical protocols which are fairly similar to the stations used in this study, (2) the network of stations covers the Europe fairly well and hence the ranges used in comparison are representative for both polluted and unpolluted regions in the continent and (3) the data are easy to access through internet.

General characteristics of the EMEP stations: Stations are located in rural areas. Urban and industrial areas are not allowed. Minimum distances to large pollution sources (such as towns, power plants, major motorways) is 50 km, to small scale domestic heating with coal, fuel oil or wood is 100 m, to minor roads is 100 m, to main roads is 500 m, to manure application and stabling of animals is 2 km and to grazing by domestic animals on fertilized pasture is 500 m.

Valleys or other locations which are subject to formation of stagnant air under inversion conditions, should be avoided, also mountaintops and passes (cols).
The collector should not be exposed to strong winds, but should also not be sheltered by tall trees or buildings. Distance between stations is 150-200 km in central Europe and about 300 km in areas which are influenced by emissions more than 500 km away (URL 9).

Table 4. 4 The location and classification of the EMEP Stations used for the comparison

Station Code	**Country**	**Location**	**Latitude**	**Longitude**	**Altitude**
AM01	Armenia	Amberd	40 23 4 N	44 15 38 E	2080
BY04	Belarus	Vysokoe	52 20 0 N	23 26 0 E	163
CH02	Switzerland	Payerne	46 48 47 N	6 56 41 E	489
CH04	Switzerland	Chaumont	47 2 59 N	6 58 46 E	1137
CH05	Switzerland	Rigi	47 4 3 N	8 27 50 E	1031
CZ01	Czech Republic	Svratouch	49 44 0 N	16 3 0 E	737
CZ03	Czech Republic	Kosetice	49 35 0 N	15 5 0 E	534
DE02	Germany	Waldhof	52 48 8 N	10 45 34 E	74
DE03	Germany	Schauinsland	47 54 53 N	7 54 31 E	1205
DE04	Germany	Deuselbach	49 45 53 N	7 3 7 E	480
DE05	Germany	Brotjacklriegel	48 49 10 N	13 13 9 E	1016
DE07	Germany	Neuglobsow	53 10 0 N	13 2 0 E	62

Table 4.4 (Continued)

Station Code	**Country**	**Location**	**Latitude**	**Longitude**	**Altitude**
DE08	Germany	Schmücke	50 39 0 N	10 46 0 E	937
DE44	Germany	Melpitz	51 31 48 N	12 55 48 E	86
DK05	Denmark	Kendsnor	54 44 0 N	10 44 0 E	10
DK08	Denmark	Anholt	56 43 0 N	11 31 0 E	40
DK12	Denmark	Risoe	55 41 36 N	12 5 8 E	3
DK22	Denmark	Sepstrup Sande	55 5 0 N	9 36 0 E	60
DK31	Denmark	Ulborg	56 17 0 N	8 26 0 E	10
EE09	Estonia	Lahemaa	59 30 0 N	25 54 0 E	32
EE11	Estonia	Vilsandi	58 23 0 N	21 49 0 E	6
ES01	Spain	San Pablo de los Montes	39 32 52 N	4 20 55 W	917
ES06	Spain	Mahón	39 52 0 N	4 19 0 E	78
ES07	Spain	Víznar	37 14 0 N	3 32 0 W	1265
ES08	Spain	Niembro	43 26 32 N	4 51 1 W	134
ES09	Spain	Campisabalos	41 16 52 N	3 8 34 W	1360
ES11	Spain	Barcarrola	38 28 33 N	6 55 22 W	393
ES12	Spain	Zarra	39 5 10 N	1 6 7 W	885
ES13	Spain	Penausende	41 17 0 N	5 52 0 W	985
ES14	Spain	Els Torms	41 24 0 N	0 43 0 E	470
ES16	Spain	O Saviñao	43 13 52 N	7 41 59 W	506
ES17	Spain	Doñana	37 1 49 N	6 19 54 W	5
FI17	Finland	Virolahti II	60 31 36 N	27 41 10 E	4
FI22	Finland	Oulanka	66 19 13 N	29 24 6 E	310
FI36	Finland	Pallas (Matorova)	68 0 0 N	24 14 23 E	340
FI37	Finland	Ähtäri II	62 35 0 N	24 11 0 E	180
FR08	France	Donon	48 30 0 N	7 8 0 E	775
FR09	France	Revin	49 54 0 N	4 38 0 E	390
FR10	France	Morvan	47 16 0 N	4 5 0 E	620
FR13	France	Peyrusse Vieille	43 37 0 N	0 11 0 E	200
FR14	France	Montandon	47 18 0 N	6 50 0 E	836
FR15	France	La Tardière	46 39 0 N	0 45 0 W	133
FR16	France	Le Casset	45 0 0 N	6 28 0 E	1750
FR17	France	Montfranc	45 48 0 N	2 4 0 E	810

Table 4.4 (Continued)

Station Code	Country	Location	Latitude	Longitude	Altitude
FR18	France	La Coulonche	48 38 0 N	0 27 0 W	309
GB02	United Kingdom	Eskdalemuir	55 18 47 N	3 12 15 W	243
GB06	United Kingdom	Lough Navar	54 26 35 N	7 52 12 W	126
GB13	United Kingdom	Yarner Wood	50 35 47 N	3 42 47 W	119
GB14	United Kingdom	High Muffles	54 20 4 N	0 48 27 W	267
GB15	United Kingdom	Strath Vaich Dam	57 44 4 N	4 46 28 W	270
GB48	United Kingdom	Auchencorth Moss	55 47 36 N	3 14 41 W	260
HR02	Crotia	Puntijarka	45 54 0 N	15 58 0 E	988
HR04	Crotia	Zavizan	44 49 0 N	14 59 0 E	1594
HU02	Hungary	K-puszta	46 58 0 N	19 35 0 E	125
IE01	Ireland	Valentia Observatory	51 56 23 N	10 14 40 W	11
IE05	Ireland	Oak Park	52 52 7 N	6 55 29 W	59
IE06	Ireland	Malin Head	55 22 30 N	7 20 34 W	20
IE07	Ireland	Glenveagh	55 3 7 N	7 56 24 W	44
IE09	Ireland	Johnstown Castle	52 17 56 N	6 30 39 W	62
IS02	Iceland	Irafoss	64 5 0 N	21 1 0 W	66
IT01	Italy	Montelibretti	42 6 0 N	12 38 0 E	48
IT04	Italy	Ispra	45 48 0 N	8 38 0 E	209
LT15	Lithuania	Preila	55 21 0 N	21 4 0 E	5
LV10	Lativa	Rucava	56 9 43 N	21 10 23 E	18
MD13	Republic of Moldova	Leova I	46 30 0 N	28 16 0 E	156
NL09	Netherlands	Kollumerwaard	53 20 2 N	6 16 38 E	1
NL10	Netherlands	Vredepeel	51 32 28 N	5 51 13 E	28
NO01	Norway	Birkenes	58 23 0 N	8 15 0 E	190
NO02	Norway	Birkenes II	58 23 18 N	8 15 7 E	219
NO15	Norway	Tustervatn	65 50 0 N	13 55 0 E	439
NO39	Norway	Kårvatn	62 47 0 N	8 53 0 E	210
NO42	Norway	Spitsbergen, Zeppelinfjell	78 54 0 N	11 53 0 E	474
NO55	Norway	Karasjok	69 28 0 N	25 13 0 E	333

Table 4.4 (Continued)

StationCode	**Country**	**Location**	**Latitude**	**Longitude**	**Altitude**
NO56	Norway	Hurdal	60 22 20 N	11 4 41 E	300
PL02	Poland	Jarczew	51 49 0 N	21 59 0 E	180
PL03	Poland	Sniezka	50 44 0 N	15 44 0 E	1603
PL04	Poland	Leba	54 45 0 N	17 32 0 E	2
PL05	Poland	Diabla Gora	54 9 0 N	22 4 0 E	157
RS05	Serbia and Montenegro	Kamenicki vis	43 24 0 N	21 57 0 E	813
RU01	Russia	Janiskoski	68 56 0 N	28 51 0 E	118
RU13	Russia	Pinega	64 42 0 N	43 24 0 E	28
RU18	Russia	Danki	54 54 0 N	37 48 0 E	150
RU20	Russia	Lesnoy	56 31 48 N	32 56 24 E	340
SE11	Sweden	Vavihill	56 1 0 N	13 9 0 E	175
SE12	Sweden	Aspvreten	58 48 0 N	17 23 0 E	20
SE14	Sweden	Råö	57 23 38 N	11 54 50 E	5
SI08	Slovenia	Iskrba	45 34 0 N	14 52 0 E	520
SK02	Slovakia	Chopok	48 56 0 N	19 35 0 E	2008
SK04	Slovakia	Stará Lesná	49 9 0 N	20 17 0 E	808
SK06	Slovakia	Starina	49 3 0 N	22 16 0 E	345
SK07	Slovakia	Topolniky	47 57 36 N	17 51 38 E	113

In this study, mean concentrations of ions measured at Antalya, Balıkesir and Trabzon stations were compared with the 91 EMEP stations for year 2011 (see Table 4.4) and the locations are represented in Figure 4.2. The results are given in Figure 4.3.

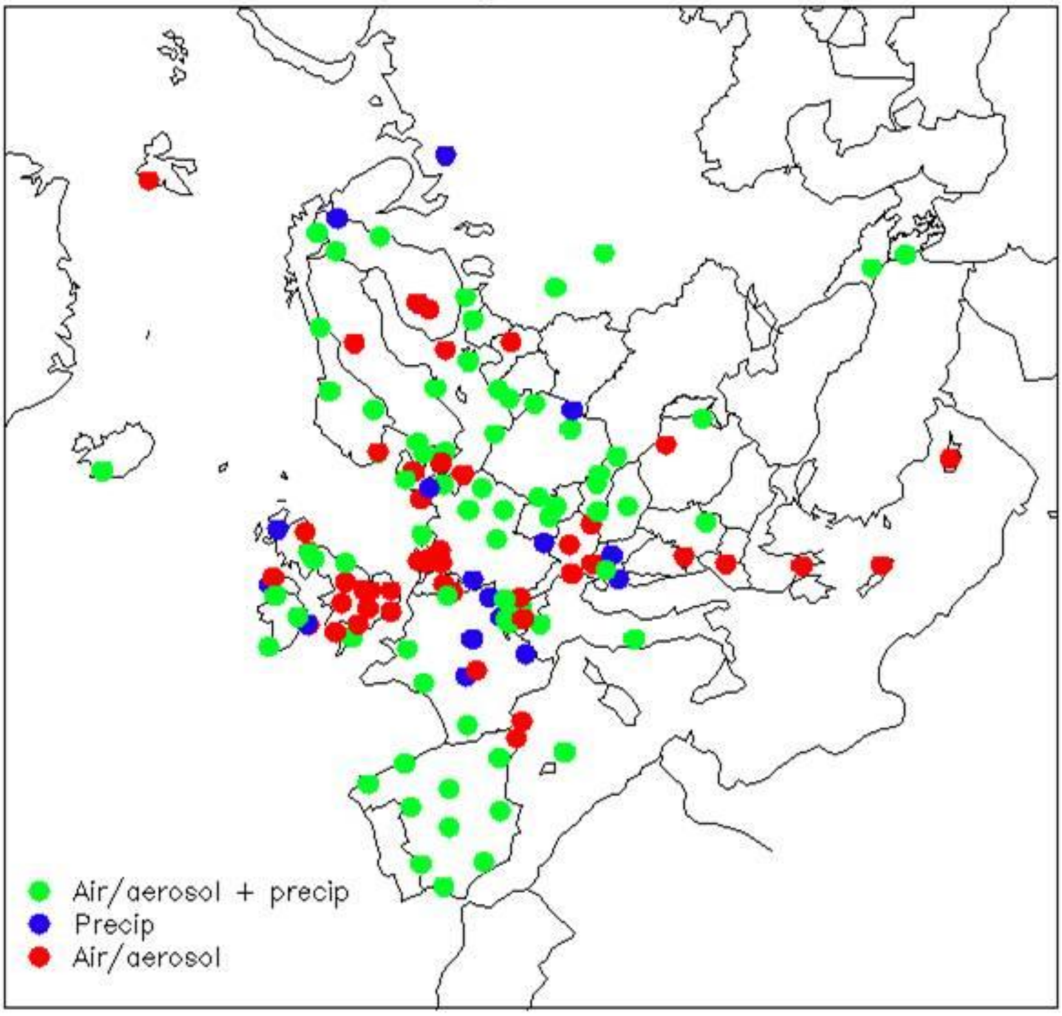


Figure 4. 2 Locations of the EMEP Stations used for the comparison

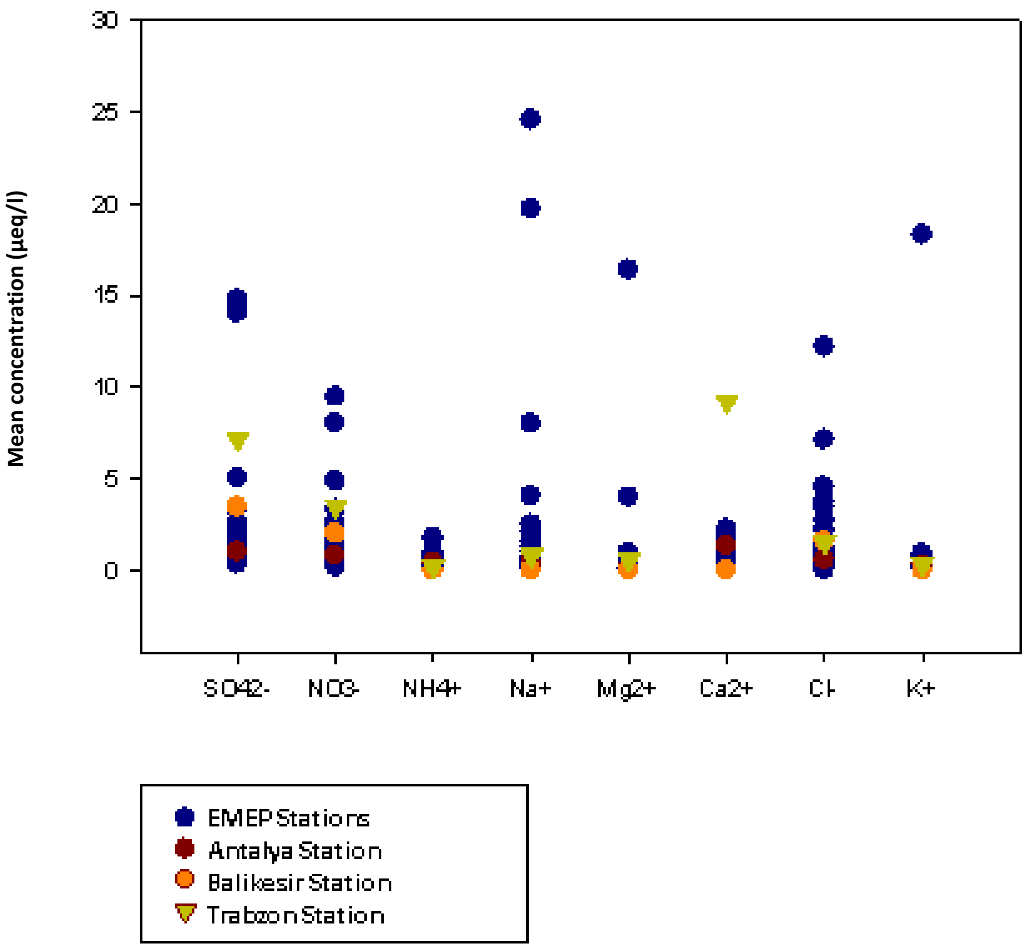


Figure 4. 3 Comparison of volume weighted average concentrations of major ions of Antalya, Balıkesir and Trabzon Stations with the results of EMEP Stations

In this comparison figure, all 91 EMEP stations concentration values are represented with blue dot, Antalya station is represented with red dot, Balıkesir is represented with orange dot and Trabzon station is represented with yellow triangle. In consequence of close concentration values observed in EMEP stations, some dots overlapped and all dots cannot be noticed. However median SO_4^{2-} value for EMEP stations is 0.96, whereas it is 13.7 for Antalya station, 42.85 for Balıkesir station and 57.37 for Trabzon station. Similarly median NO3- value for EMEP stations is 1.28, while for Antalya station it is 7.8, 20.82 for Balıkesir station and 38.07 for Trabzon station. By taking into account that SO_4^{2-} and NO_3^- concentrations measured at Antalya, Balıkesir and Trabzon stations are higher than EMEP stations.

It was referred in chapter 3 that for aerosols measured in Eastern Mediterranean region, SO_4^{2-} concentration is the highest values over the world (Luria et al., 1996; Güllü et al., 1998; 2005). The rainwater samples also show a similar trend. Balıkesir and Trabzon stations concentrations are especially high.

Ca^{2+} ion is also high in Eastern Mediterranean region because the soil is calcareous, rich in Ca^{2+}. Crustal ions, except from Ca^{2+}, the trend is different.

This study is important for anthropogenic based ions. Therefore it is important to observe that the SO_4^{2-} and NO_3^- concentration measured in this area are higher than European concentrations. It is already discussed in several studies that SO_4^{2-} and NO_3^- concentration measured in Eastern Mediterranean aerosol samples are higher than concentration measured in Europe. However it is the first time that same results are observed by analyzing rainwater samples. In this study, it is obviously seen that SO_4^{2-} and NO_3^- concentrations are higher than EMEP stations concentration values.

4.1.3. Flow Climatology

Flow climatology is an important method to identify the detection frequency of an ion at the sampling station. In this study, flow climatology was applied on the basis of two parameters; grid and wind sectors. On the grid basis analysis, all trajectories were counted in each grid for 3 year data. Each segment is 1 hour part of a trajectory; therefore, number of segments of one grid represents the residence time of air mass during three year in terms of hour.

In wind sector analysis, segment numbers were separately grouped in different sectors. Flow climatology studies were performed in terms of wind sector analysis. According to their residence times, each trajectory was assigned to a sector. This method, unfortunately, is not very reliable method. Because trajectories spent their time on different sectors during its 5 days travel, not only one sector. As a result, it is hard to assign a trajectory into one sector.

Residence times of air mass on segments for Antalya, Balıkesir and Trabzon stations are presented in Figure 4.4. Study domain extends from West of UK to middle of Asia in East – West direction (20°W - 60°E) and from Siberia to Middle of Africa in North-South direction (74°N - 14°N). This region is divided into 1°x1° grids, using the MapInfo software. Both source apportionment studies and flow climatology analysis were conducted by using that grid system.

For all three stations regions at which residence time of air mass is high, are different from each other. In flow climatology maps, grids on which air mass spent its 5000 and more hours were represented with claret red. Those grits consist of the grid that sampling station located in and a second grid near it. Each trajectory that was measured at the station has to pass through the grid on which station located. Therefore monitoring high residence time of a trajectory on that grid is not important.

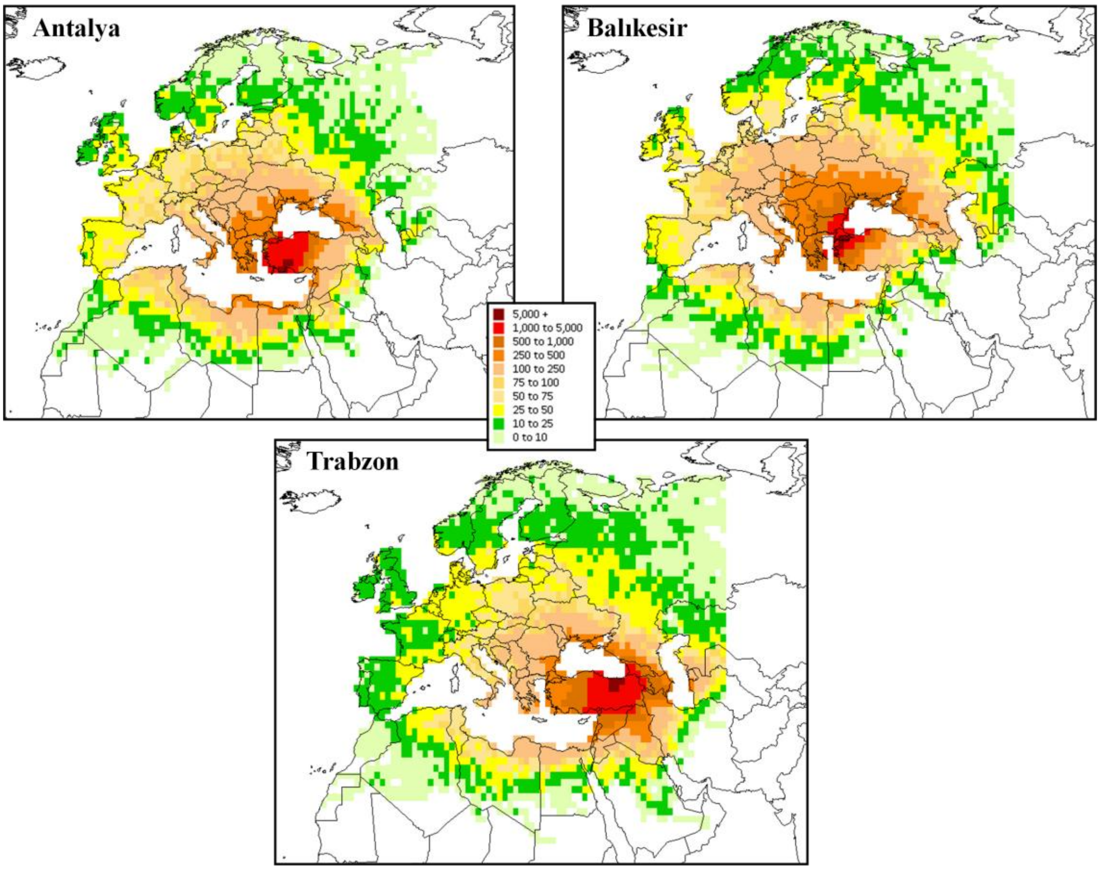


Figure 4. 4 Three year flow climatology for Antalya, Balıkesir and Trabzon stations

During three years between 2010-2012, grits that air mass spent its 250 to 5000 hours were represented with different tones of brown. Those grits are important because air mass spent it majority of time on them and they are many in number and cover wide area. Those grits are different for each station. For Antalya station, Western part of Turkey, Greece, Bulgaria and some parts of Romania and Ukraine consists of that color group. For Balıkesir station, this region reaches up to Southern part of Poland and contains only Western part of Turkey, Greece and Ukraine. For Trabzon station, this region mostly contains Turkey, because air masses coming from West have to pass through Turkey.

Air masses measuring in our stations spend its lesser time on Middle and Western Europe regions and Russia. The residence time analysis also gives an idea about the regions which stands a change to transport polluted species. In the light of the residence time distribution, it is possible that the ions detected at Trabzon station originate from Turkey itself. On the other hand, ions detected at Antalya and Balıkesir stations may come from the Balkans, Middle Europe and Western part of Turkey.

Studies conducted up until now some source regions were identified. Those are Balkan countries Greece in particular, Eastern part of Ukraine, Georgia and part of Russia, which is at border with Northern Georgia. With this residence time analysis, it is realized that those are source regions that affect whole parts of Turkey.

As the starting altitude of a trajectory increases, trajectories lengthen. Therefore, trajectories, which come from more distant regions, have higher residence times. Distributions of residence times of 100 m, 500 m and 1500 m trajectories for each station are calculated. The distribution graphs are shown in Figures 4.5, 4.6 and 4.7.

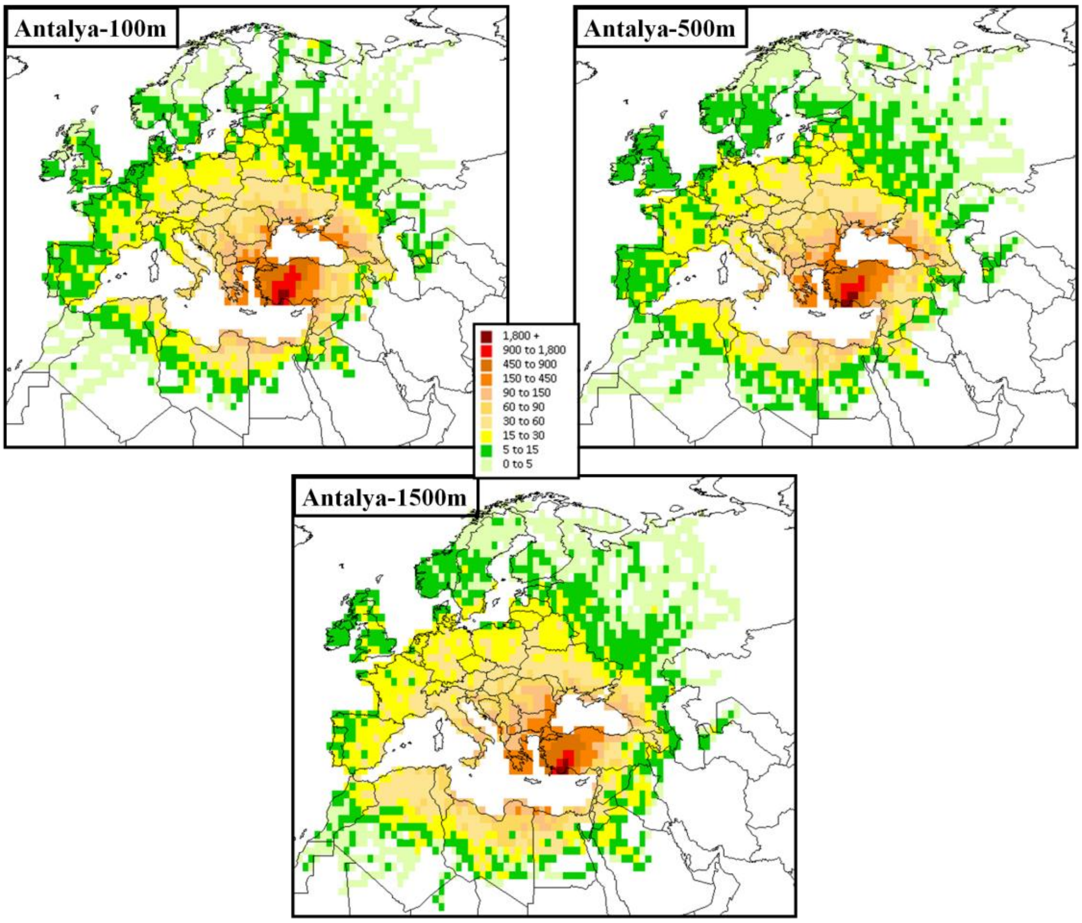


Figure 4. 5 Distributions of residence times of 100 m, 500 m and 1500 m trajectories for Antalya Station

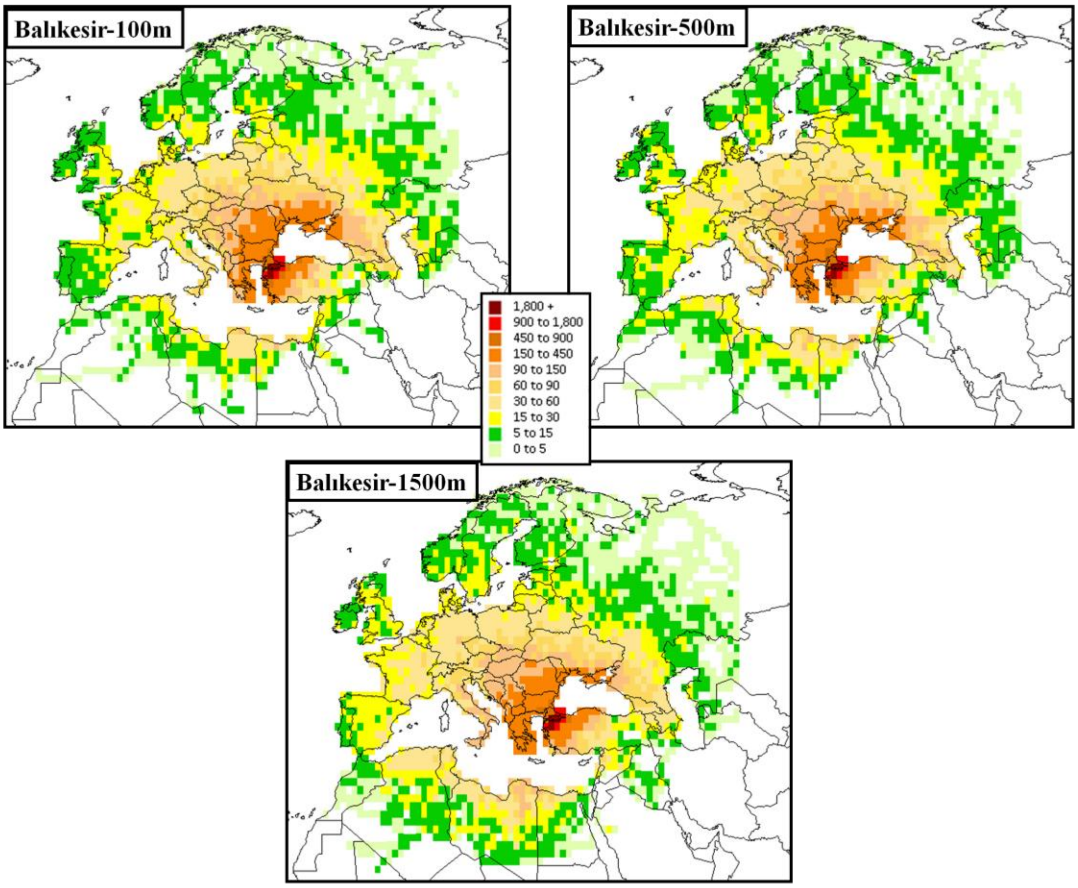


Figure 4. 6 Distributions of residence times of 100 m, 500 m and 1500 m trajectories for Balıkesir Station

Changes on distributions of residence times with respect to altitude are similar with each other for all stations. Moreover, trajectories with starting altitudes 100m and 500 m are exactly the same. Distribution of residence times of trajectories with 1500 m starting altitude are little different than others.

If we look at Balıkesir distribution graphs calculated for different starting altitudes, it can be seen that residence times of trajectories calculated at 1500 m starting altitude are higher than those at 100 m and 500 m altitudes at regions far away from sampling stations such as United Kingdom and Scandinavia. However at regions near the sampling stations, residence time of trajectory for 1500 m starting altitude is not so different from 100 m and 500 m values.

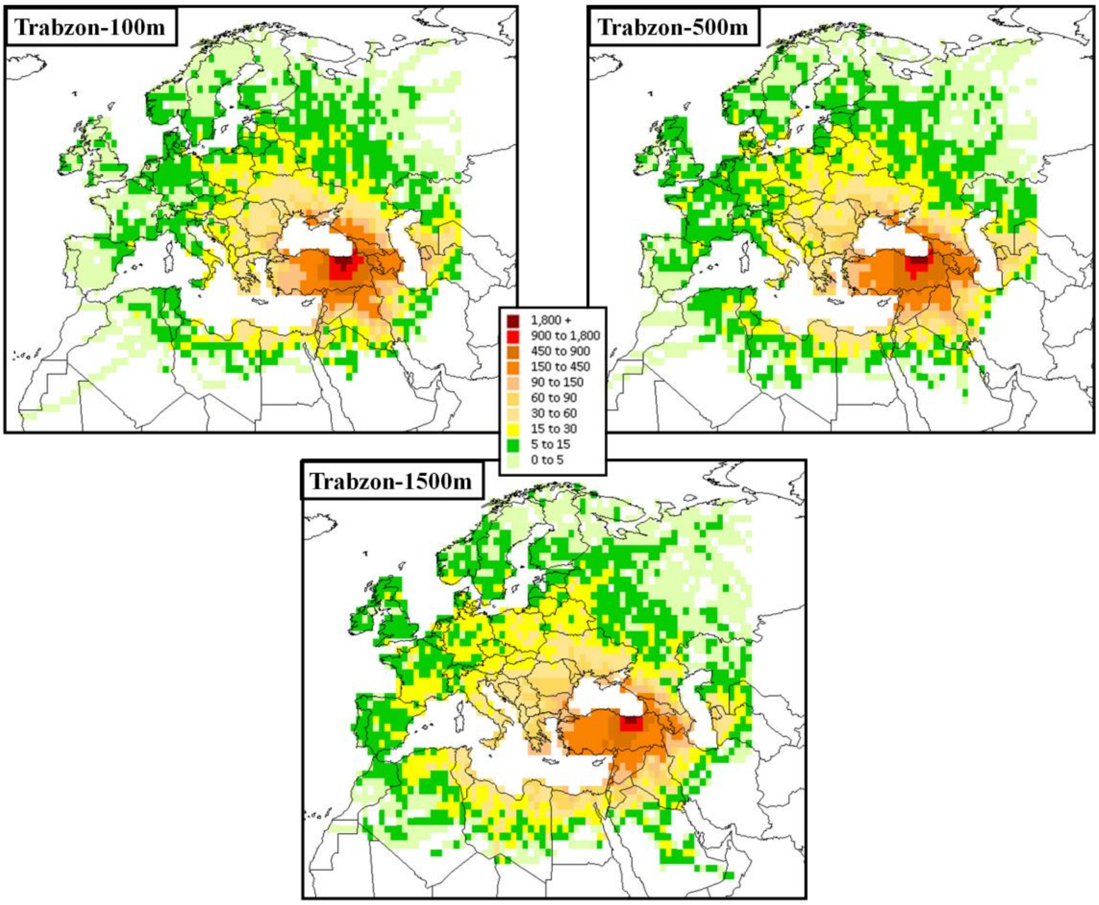


Figure 4. 7 Distributions of residence times of 100 m, 500 m and 1500 m trajectories for Trabzon Station

With these graphs, it is supported that higher starting point trajectories are longer. However, the more important part of this study is that the flow climatology gives an idea about where the pollutants come from to sampling stations. Therefore, it can be understood that the difference on starting altitude does not play an important role on pollutant transportation pathways. That's why in source apportionment studies, rather than 100m, 500m and 1500m separated trajectories, the combined altitude trajectories were used.

In literature studies, it was seen that flow pattern differs seasonally and this difference causes important results of air mass transportation. For this reason, flow patterns of all stations were analyzed for both summer and winter seasons separately.

And the results were compared with each other. Difference graphics were calculated by (summer-winter) divided by (summer+winter) trajectory data (see Figure 4.8).

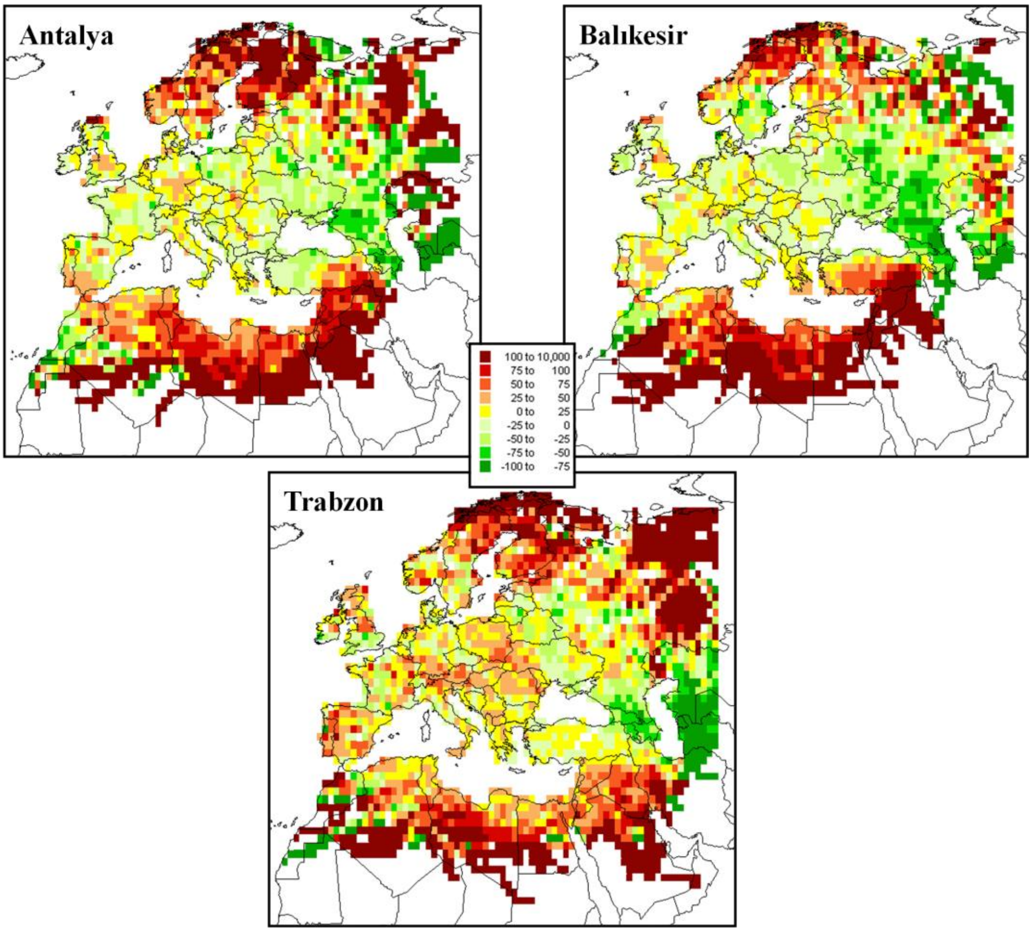


Figure 4. 8 Distribution of Difference of Summer to Winter Trajectories at Antalya, Balıkesir and Trabzon Stations

In figure 4.9 combined trajectory distributions for three stations are given. These graphs were prepared by counting segments at each wind sector; they are not based on grids. According to the figure, the most frequent flows at Antalya and Balıkesir stations are observed in N, NE, SW, W and NW sectors. At Trabzon station, on the other hand, flows from N and NE sectors are not as dominant as others. The most frequent wind sector for Trabzon station comes from sector W.

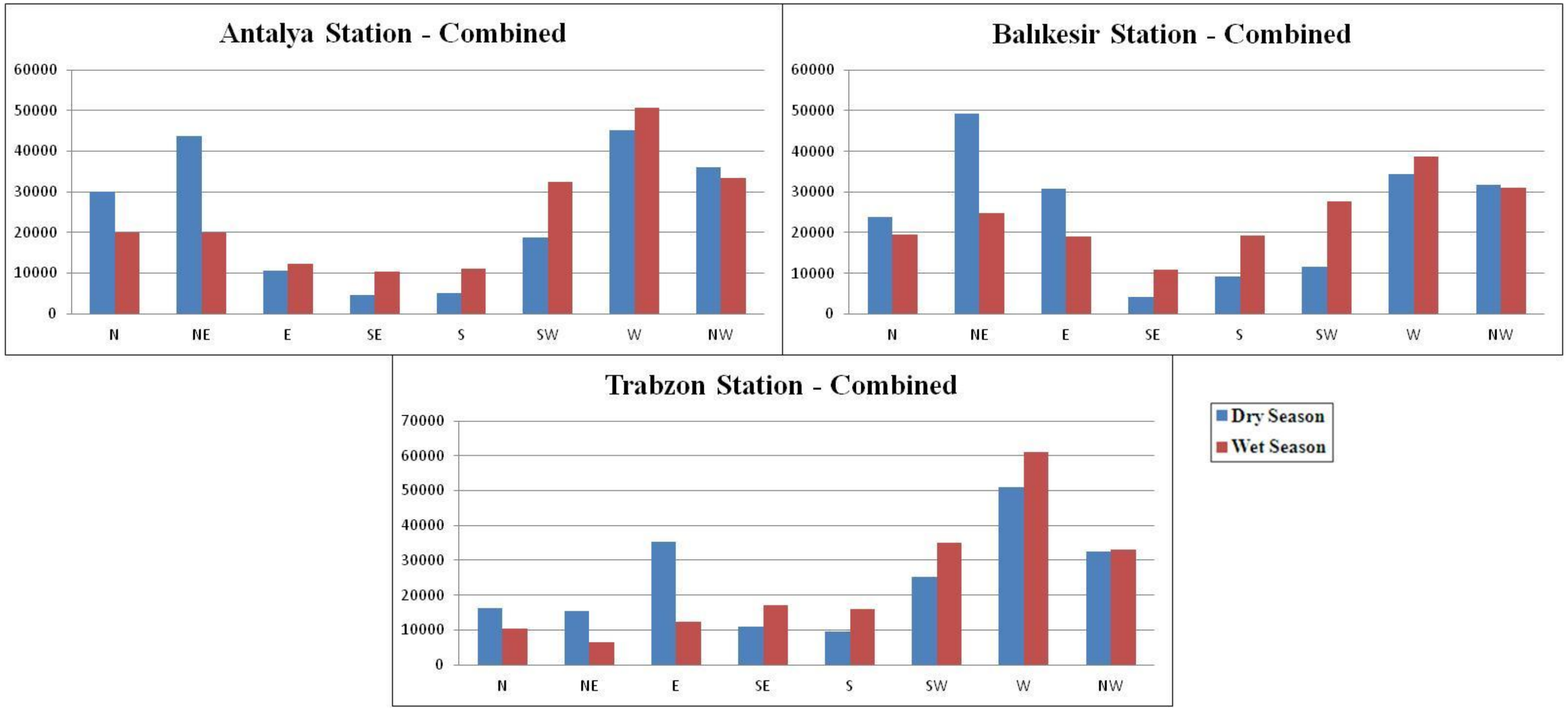


Figure 4. 9 Combined trajectory distributions of Antalya, Balıkesir and Trabzon Stations

The more sparse air flows are, as clearly seen from previous studies, the ones coming from sectors E, SE, S and SW. This pattern means a lot of important information for pollutant transportation to Turkey. It is not possible that pollutants come to Turkey from southern sector because of two reasons; there is no pollution source in the south part of Turkey and air motion is limited from south wind sector. On the other hand, W and N sectors both pollutant emissions are high and air movement is frequently coming through them. Therefore it can be deduced that these sectors are important with regards to the pollution transport.

Another important point is that, as a consequence of the stations location, each sector refers to different regions for different stations. For example, while for Trabzon station W sector refers to Black Sea region of Turkey, for Antalya station it refers Greece and Italy.

Most of the wind sectors there is a difference between summer and winter retention times of air mass. In N, NE and E sectors summer retention times are higher than winter; other sectors are the opposite. Therefore, while in summer season transportation is denser on N, NE and E sectors, in winter season transportation gets denser on SW, W and NW sectors.

4.2. Ionic Composition of Wet Deposition

4.2.1. Ion Balance

Ion balance represents the ratio of total anions to total cations (∑anions/∑cations). This ratio can be used as a criterion of evaluating the accuracy of chemical analysis. If the ratio is not equal to unity, it means in measurement some ions are excluded.

The plots of the sum of the anions (SO_4^{2-}, NO_3^-, Cl^-) against the sum of cations (NH_4^+, Mg^{2+}, H^+, Na^+, Ca^{2+}, K^+) of rainwater samples for three stations are given in Figure 4.10.

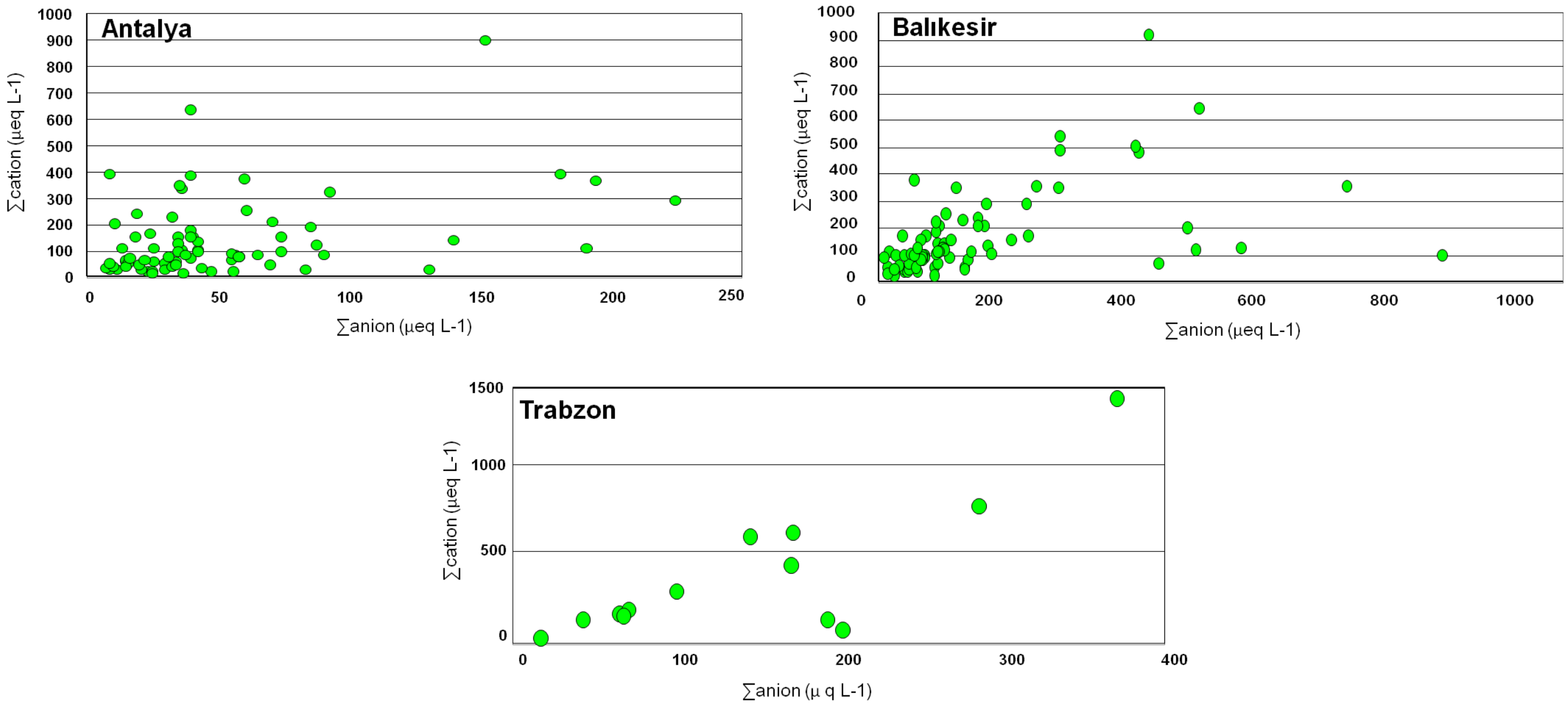


Figure 4. 10 The Plot of the Equivalent sum of cations to equivalent sum of anions

According to the figure above, there is an anion deficiency observed for all stations. In theory, the regression line of ∑anion vs. ∑cation plot should pass through (0, 0) point with a slope 1.0.

For this study, there is a statistical significance between total anion mass and total cation mass. Unfortunately slopes are not equal to 1. The anion to cation ratios are lower than 1 for all stations. The largest deficiency is observed at Antalya station and the smallest deficiency is observed at Balıkesir station. Anion deficiency percentages of Balıkesir and Trabzon stations are 15 % and 18 %, respectively. These values are in a reasonable level that can be seen in literature. However, the average anion deficiency value of Antalya station is 58%, which is quite high.

The reason for the anion deficiency is generally due to the non measured anions in the study. One of the common non measured anion is the anions produced from organic acids. However, organic acids originated from biogenic sources and mostly faced in studies carried out around the equator region. Turkey is in mid latitude region and does not have too much forested land. Therefore it can be wrong to say that organic acids don’t have an important role on the observed anion deficiency.

The main reason for the anion deficiency observed in this study is the HCO_3^- ion. HCO_3^- ion is a part of carbonate buffer system and produced from the dissolution of atmospheric CO_2 in rain droplets. It does not have an anthropogenic source and measured by ion chromatography device and an additional analysis. Therefore in such studies it cannot be measured. However concentration of HCO_3^- ion in a rain droplet depends on the rainwater pH. If the pH is less than 5.0, the bicarbonate concentration is considerably smaller than other ion concentrations.

$pH = 5.0 \rightarrow HCO_3^- = 0.89\ \mu eq\ L^{-1}$

$pH = 5.5 \rightarrow HCO_3^- = 2.8\ \mu eq\ L^{-1}$

$pH = 6.0 \rightarrow HCO_3^- = 9.0\ \mu eq\ L^{-1}$

$pH = 6.5 \rightarrow HCO_3^- = 28\ \mu eq\ L^{-1}$

pH = 7.0 → HCO_3^- = 89 μeq L^{-1}

Total anion level at Antalya station is 87μeq L^{-1}, at Balıkesir station is 117 μeq L^{-1} and at Trabzon station is 170 μeq L^{-1}. The pH of rainwater should be higher than 6.0 if it is assumed that HCO_3^- ion affects the anion-cation balance. The average pH values of Antalya, Balıkesir and Trabzon station are 5.9, 5.4 and 7.0 respectively. This values show that HCO_3^- ion may affect the anion-cation balance.

Expected HCO_3^- concentrations were calculated by using following equation:

$(HCO_3^-) = 10^{(pH - 5.05)}$ (Tiwari et al., 2000) (4.2)

Variations of anion deficiency with respect to H^+ ion concentration for three stations are given in figure 4.10. If the anion deficiency is associated to HCO_3^- ion, with the increase of H^+ ion concentration or decrease of pH, anion deficiency is supposed to decrease. None of the stations show a notable alteration on anion deficiency depending H^+ ion. In Balıkesir station, anion deficiency decreases as H^+ ion concentration increases but this decrease is not statistically significant.

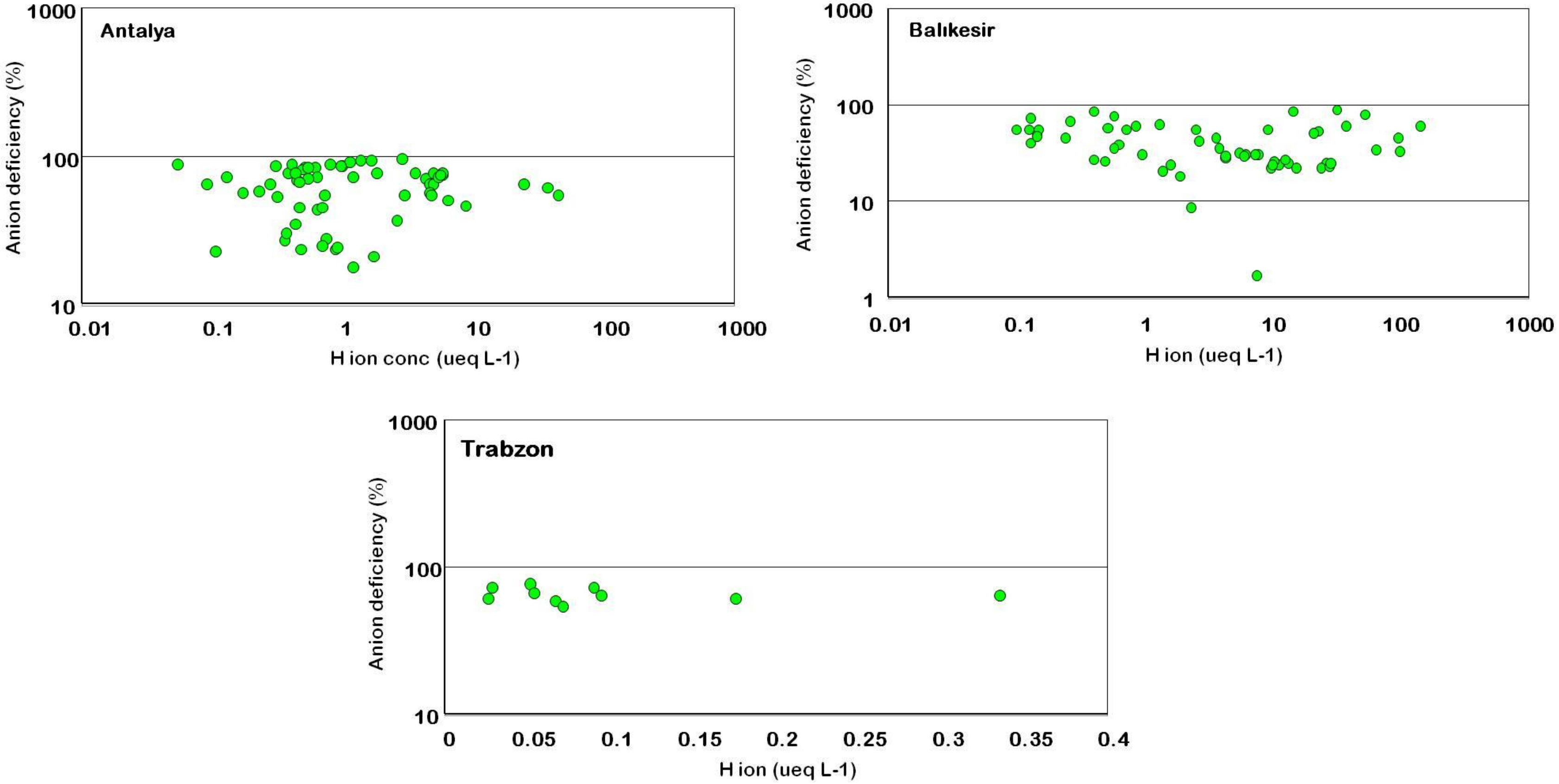


Figure 4. 11 Plot of anion deficiency to H^+ ion concentration for Antalya, Balıkesir and Trabzon Stations

In Figure 4.11 variation of cation to anion ratio with respect to time is given. In order to show how much the ratio depends on HCO_3^- ion, figure was prepared twice; HCO_3^- ion counts in and out. According to the figure, HCO_3^- ion pulls the ratio to 1.0 only at Trabzon station. At Antalya and Balıkesir stations, whenever the ratio is close to 1.0, the difference can be explained by HCO_3^- ion. Otherwise, it is hard to explain the difference by HCO_3^-.

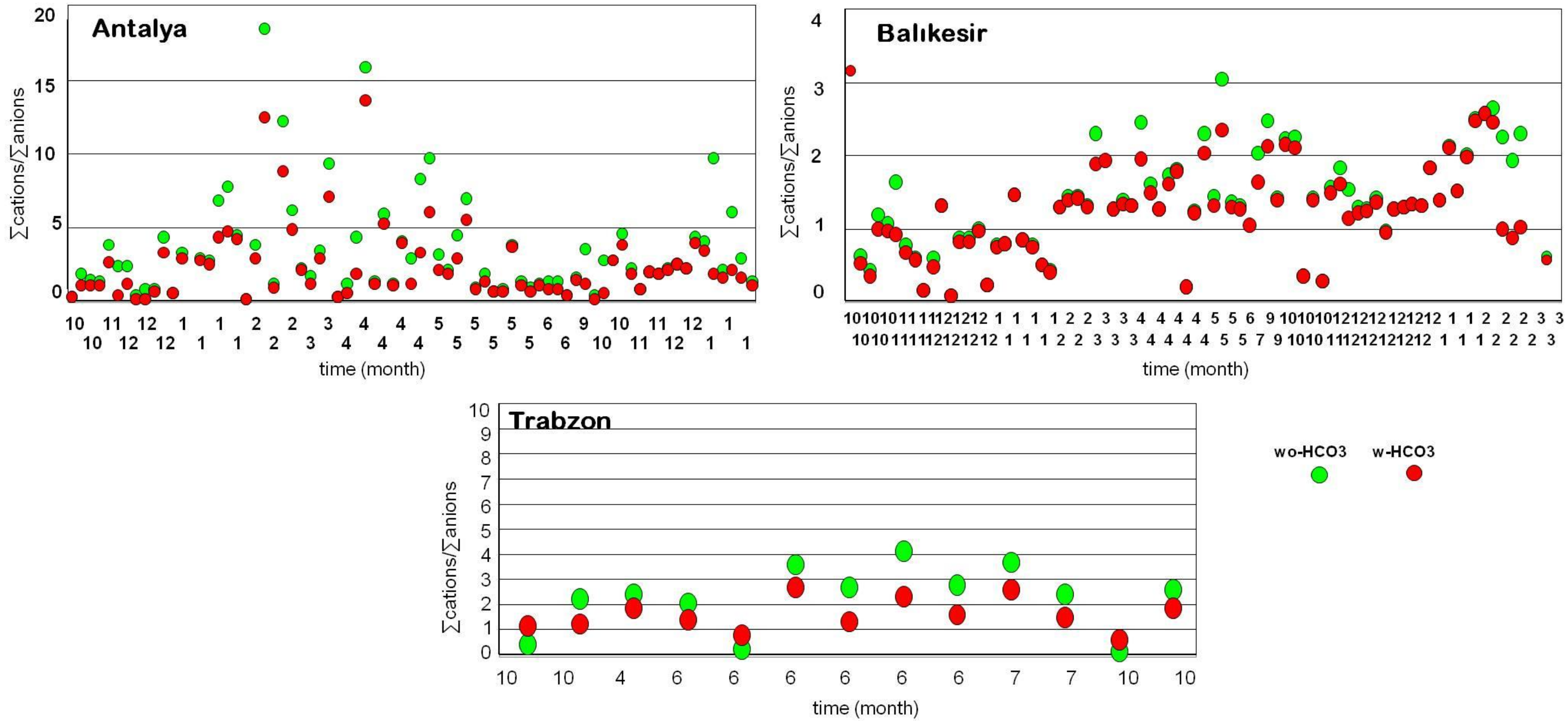


Figure 4. 12 Monthly variation of cation to anion ratio with and without HCO3- ion for Antalya, Balıkesir and Trabzon Stations

Anion deficiency is 15 % at Balıkesir station. If the calculated HCO_3^- concentration is added, the deficiency decreases to 8 %. Therefore it can be supported that the anion deficiency at Balıkesir station is because of ignoring the HCO_3^- ion during measurement. Similarly at Trabzon station, the average anion deficiency is around 18 %, and decreases 10 % when HCO_3^- ion is included to the calculation. Therefore the anion deficiency can be linked to the ignoring HCO_3^- ion during measurement. At Antalya, the situation is different, average anion deficiency is 58 %.

4.2.2. Contributions of Ions to Total Ion Mass

Contributions of ions to total ion mass for Antalya, Balıkesir and Trabzon stations are given in Table 4.5. There is a general similarity between the stations. SO_4^{2-}, NO_3^- and Ca^{2+} are the ions having biggest portion among total ion mass. Contributions of these ions are varying between 54 % and 77 %, mostly higher than 60 %.

Table 4. 5 Contributions of ions to total ion mass for Antalya, Balıkesir and Trazbson Stations

	Cations (µg/l)						**Anions (µg/l)**		
	H^+	$(NH_4)^+$	Na^+	Mg^{2+}	Ca^{2+}	K^+	$(SO_4)^{2-}$	$(NO_3)^-$	Cl^-
ANTALYA									
% Total	0.076	8.525	7.646	2.153	27.072	5.805	20.702	16.534	11.489
BALIKESİR									
% Total	0.152	6.309	6.808	1.493	15.313	1.170	33.630	19.334	15.792
TRABZON									
% Total	0.001	0.550	3.538	2.606	39.687	1.642	30.872	14.190	6.914

Ca^{2+} is a naturally originated ion and comes from soil. Contribution of Ca^{2+} ion is high in samples because the soil is calcareous, which means rich in $CaCO_3$ in

Turkey. High Ca^{2+} content represents the rain water has a high acid neutralization capacity.
SO_4^{2-} and NO_3^- are anthropogenic originated ions and represent the acidity of rain. Summation of these two ions contribution varies between 40 % and 55 %, which is quite high. In the light of these percentages, rain water should be very acidic. However SO_4^{2-} and NO_3^- are not the only indicative ions for the acidity of rainwater. Other neutralizing parameters are discussed in the following chapters.

Another anthropogenic ion is NH_4^+ and its contribution is around %10. Other measured ions, Mg^{2+}, K^+, Na^+ and H^+, have totally between 9 % to 18 % contributions to total ion mass. The least contribution belongs to H^+ ion with 0.001 %to 0.1 %.

One surprising point is that contribution of Ca^{2+} to total ion mass at Trabzon station is higher than at Antalya and Balıkesir stations. Ca^{2+} is a soil originated ion therefore its concentration should be higher at the Antalya station where lower rain events are observed. However Ca^{2+} ion percentage at Antalya station is not as high as Trabzon station. This result may occur due to the minority of rainwater samples collected at Trabzon station.

General form of the atmospheric Na and Cl ions is NaCl salt. Especially the regions under the sea effect, Cl/Na ratio is expected to be 1.0 (1.8 in mass). However, it was observed from several studies conducted at different regions that the Cl/Na ratio in aerosol samples is under 1.8 due to the reaction below.

$NaCl\ (s) + H_2SO_4\ (l) \rightarrow Na_2SO_4(s) + HCl\ (g)$

The Cl deficiency in aerosols results in a lower value than 1.8 of Cl/Na ratio on rainwater samples. Na vs. Cl concentration plots for three stations and Cl to Na ratio for each sample are given in Figure 4.12.

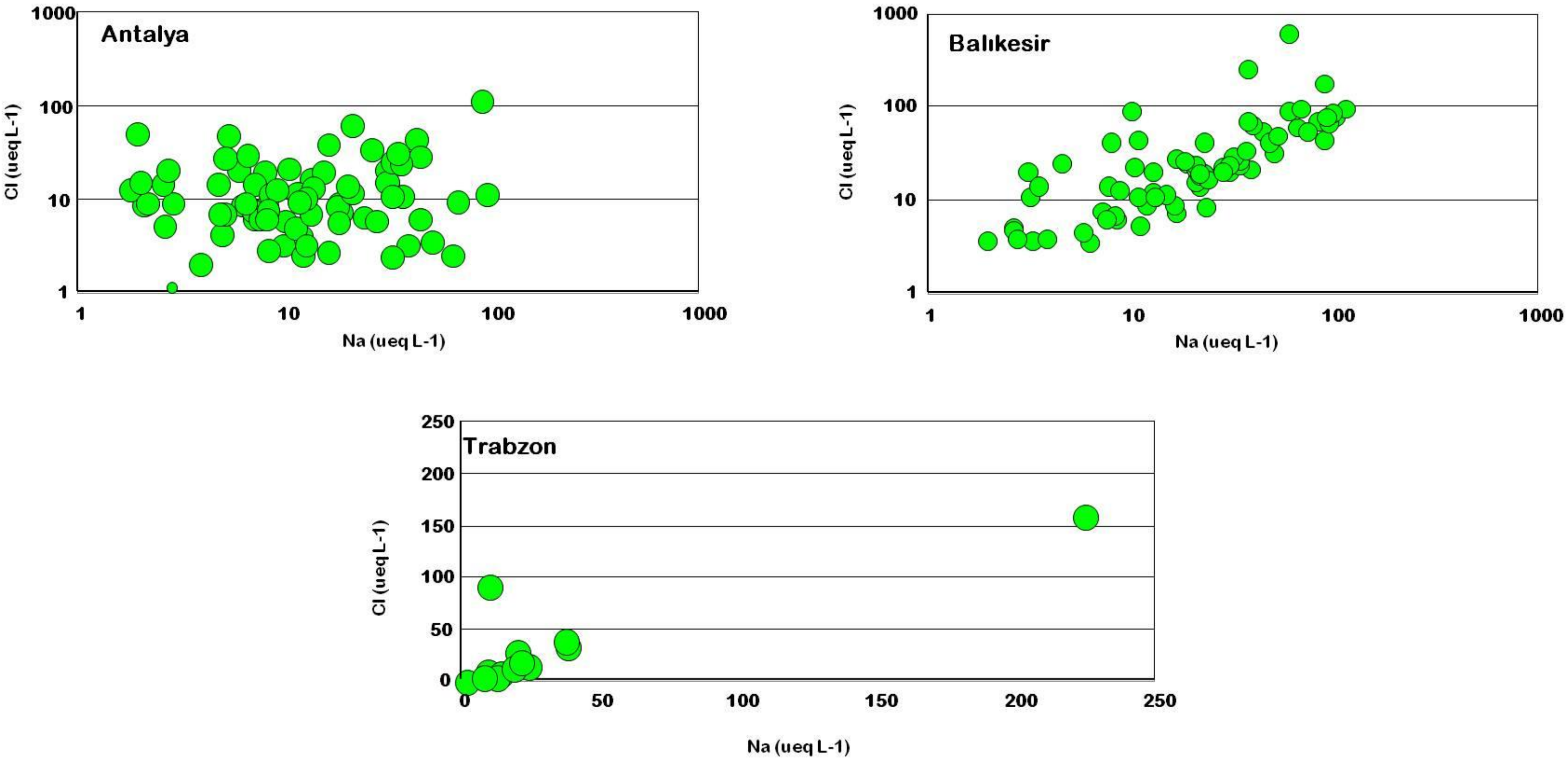


Figure 4. 13Plot of equivalent Na concentration to equivalent Cl concentration for Antalya, Balıkesir and Trabzon Stations

Na and Cl relationships at Balıkesir and Trabzon stations are as expected and supports that ions are coming from NaCl salt. For each station, Na and Cl ions are correlated with each other with 99 %statistical significance. Moreover, for both stations Cl to Na ratio varies around 1.0. At Balıkesir station, the ratio is little smaller than 1.0, which indicates that Cl ion was removed as gaseous form of HCl as stated at the previous reaction.

At Antalya station, on the other hand, no relationship was observed between Na and Cl ions. Antalya station is the nearest station to the sea coast; therefore, it is expected to be affect from the sea salt much more than other stations.

Variation of Cl to Na ratio with respect to time explains reason of the bad correlation. Cl to Na ratio of Balıkesir station does not show an important fluctuation. Although the ratio is around 1.0 at Antalya station, due to the big fluctuations, ions do not correlate with each other.

In order to identify the variation, it was realized that there is a relationship between Cl to Na ratio and H^+ ion. In figure 4.13 for Antalya station both variation of Cl to Na ratio and H^+ ion concentration were represented. The relationship was showed with arrow marks. It can be seen that samples at which H^+ ion concentration is high, Cl to Na ratio is low.

In order to expand the relationship, the variations of Cl to Na ratio with respect to H^+ concentration were checked for all stations. Therefore Cl to Na ratio vs. H^+ concentration plot was sketched. The results are given in figure 4.14. As a result of the figure, neither at Balıkesir station nor at Trabzon station there is a systematic variation of Cl to Na ratio with H^+ concentration. The ratio is always around 1.0.

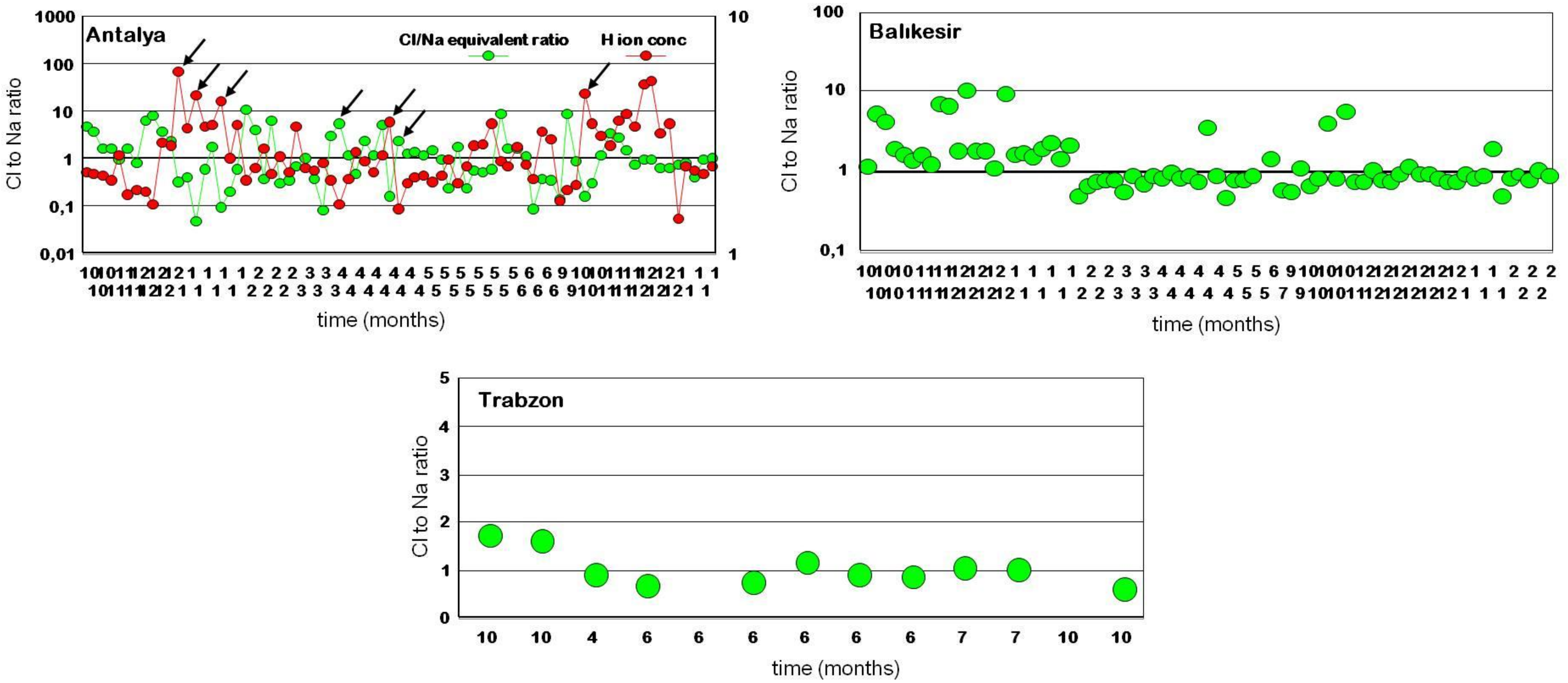


Figure 4. 14 Monthly variation of Cl to Na ratio for Antalya, Balıkesir and Trabzon Station

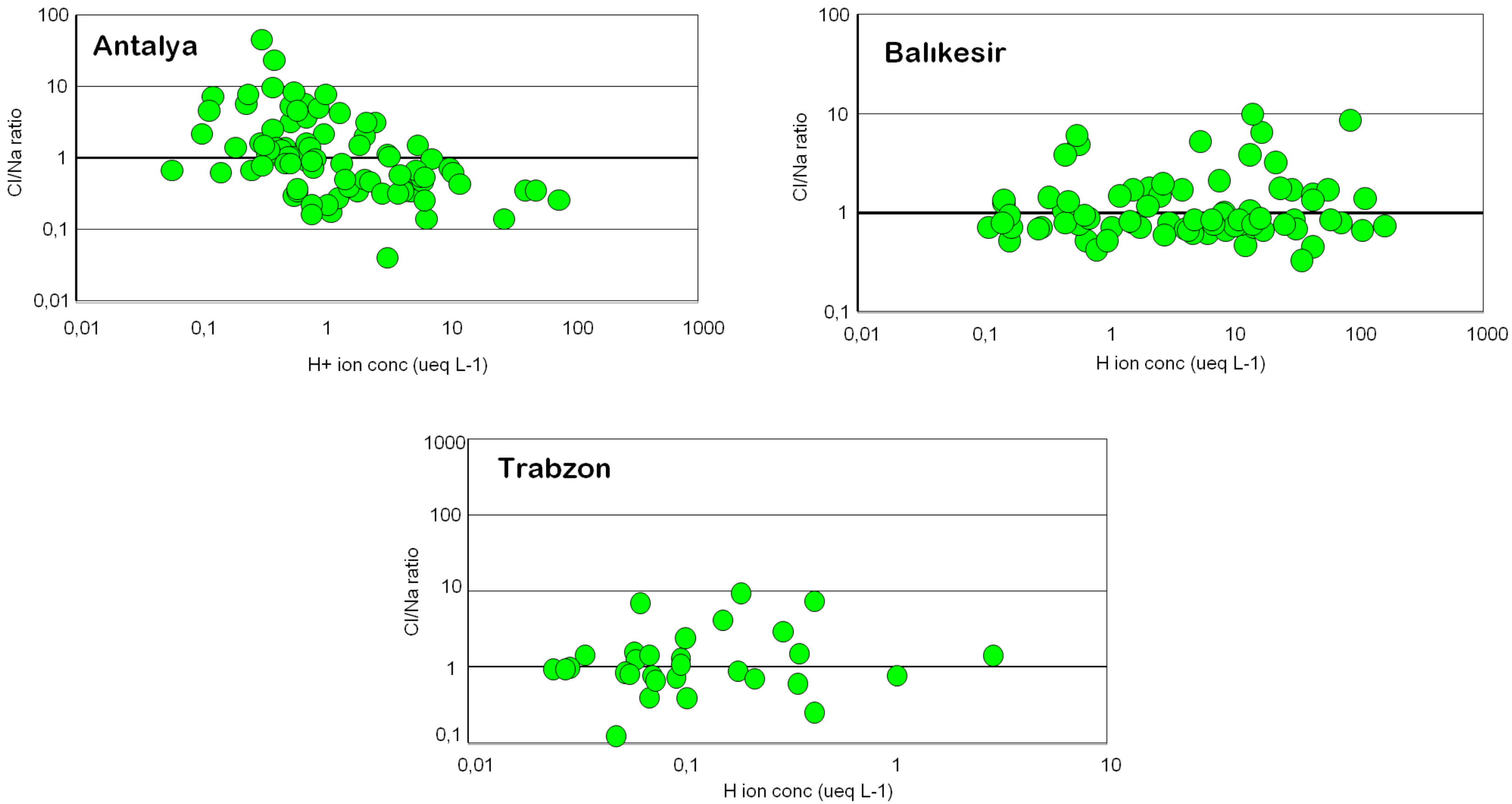


Figure 4. 15 Plot of Cl to Na ratio to H$^+$ ion concentration for Antalya, Balıkesir and Trabzon Stations

On the other hand, Antalya station has a different pattern. Cl to Na ratio is obviously decreases with H^+ ion concentration. The relationship between these two parameter has a statistically significance of 95 %.

4.2.3. Concentration of Ions in Different Wind Sectors

Wind sector analysis is an important method to identify the source regions of measured ions. For local studies, this approach that pollutant concentration identified with surface wind is called “pollution rose”. However this study is regional scaled, therefore pollutant level is not related with surface winds. The indicative transportation occurs on the upper atmosphere; therefore ion concentrations are related with upper atmosphere air motion. In Figure 4.15 upper atmospheric wind roses for summer and winter seasons are represented for sampling stations.

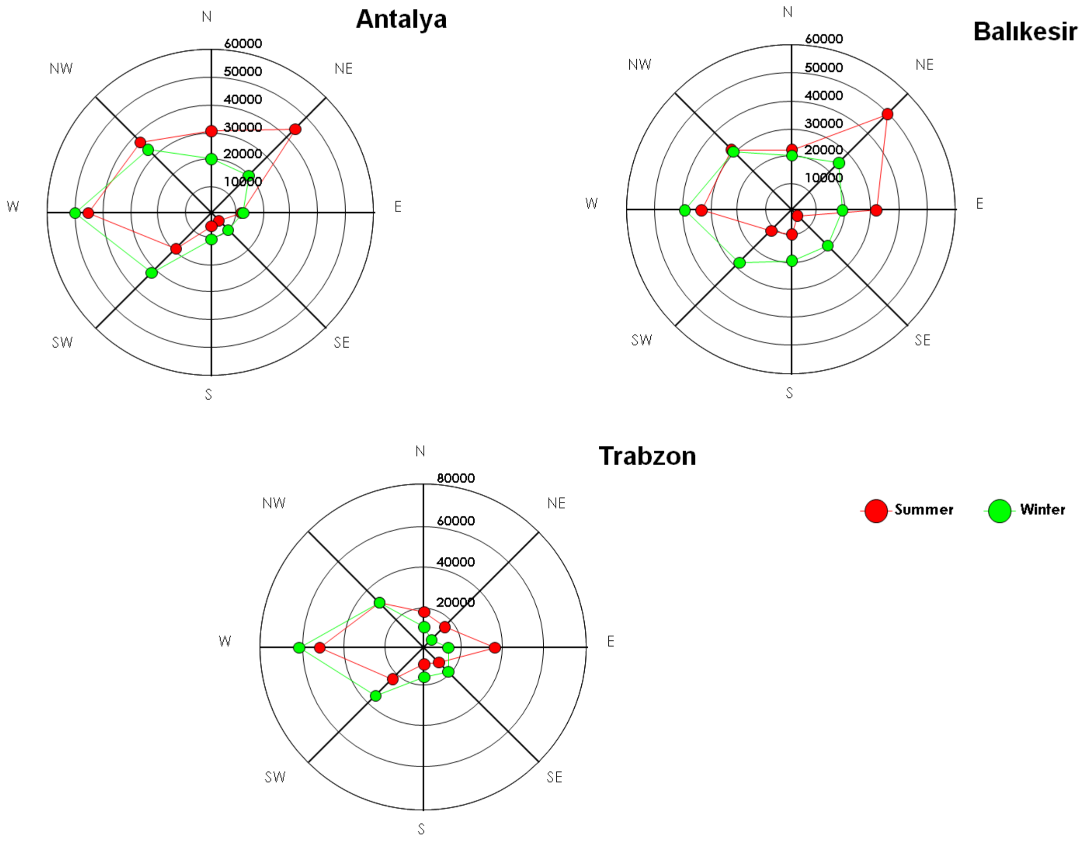


Figure 4. 16 Upper Atmospheric wind roses for Antalya, Balıkesir and Trabzon Stations

Back trajectories corresponding to each sample were calculated. Afterwards, each trajectory was assigned to a wind sector on which it spent its majority of time by counting segments. As a result each sample was associated with one sector, and concentrations of each ion on each sector were determined. Concentrations of ions in different wind sectors at Antalya station and Balıkesir station are given in figure 4.16.

By the reason of having few numbers of samples at Trabzon station, some sectors were left only one or two samples; even some sectors have any samples. Therefore Trabzon station is not included in wind sector analysis.

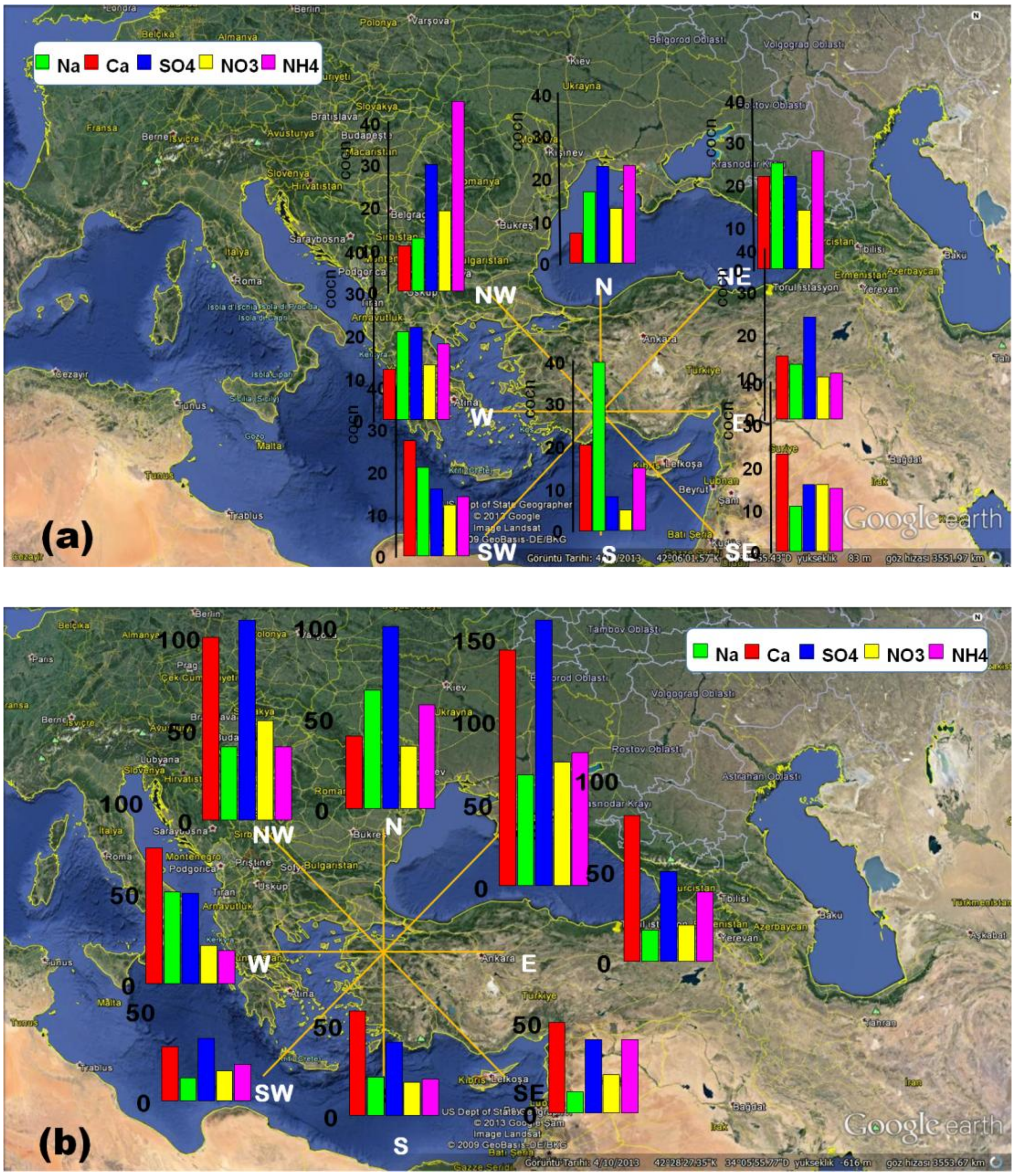


Figure 4. 17 Average concentratons of ions in each wind sector at Antalya station (a) and at Balıkesir station (b)

Distributions of ions on wind sectors of Antalya and Balıkesir stations are similar. Ca^{2+} represents soil originated elements and at Antalya station it is high in S, SE and SW sectors. It is an expected result because those sectors are exposed to dust transportation. In other words, dust transport originated from Africa and Arabian Peninsula, is indicator for the concentration of soil originated ions. Ca^{2+} concentration distribution is little different at Balıkesir station. Concentration is low in S, SE and SW sectors, high in E, NE, N, NW and W sectors. Balıkesir is twice as much far away North Africa than Antalya station. Local emissions are important and Saharan dust is dominant through episodes but it is not stable all the year round. Therefore Balıkesir station represents the regional soil minerals rather than dust transportation from North Africa. High Ca^{2+} concentrations in E, N and W sectors indicate the regions where soil is calcareous, not about transportation.

Na^+ is a marine element coming from sea salt. As expected, its concentration is high in S, SW and W sectors. Na concentration is higher in NE sector than others at Balıkesir station. Balıkesir station is located 100 km far away Marmara and Aegean Sea which is long enough distance for the coarse sea salt particles to scavenge out by dry deposition. Therefore this observation cannot link to sea salt. A considerable part of the measured Na^+ ion concentration can be stated as soil originated. Still, higher Na^+ ion concentration in W, N and NE sectors than other sectors proves that even if the distance is too much, sea salt is transported to the station.

Anthropogenic ions SO_4^{2-}, NO_3^- and NH_4^+ are the most important ones over the measured anions and cations for environment. Distributions of the anthropogenic ions over wind sectors are similar for both stations. They are high in NW, N and NE sectors and low in Southern sectors. Aerosol studies conducted in literature for a long time and those studies shows that locations sources are different for each sector.

In this study it can also be seen that pollutants measured in Mediterranean region are mostly coming from Europe and Russia. These regions represent N and NW sectors for the study stations. The Soviet Union, which is on the NE sector, also has source regions because of the uncontrolled pollutant emissions. Moreover Ukraine and Georgia have such kind of source regions (Stevens et al., 1984). Therefore high concentrations of SO_4^{2-}, NO_3^- and NH_4^+ ions are not surprising. On the other hand, sectors E, S, SE and SW do not have important pollutant sources. For this reason SO_4^{2-}, NO_3^- and NH_4^+ concentrations are low in those sectors at both stations.

4.3. Acidity of Wet Deposition

4.3.1. Rainwater Ph

The pH is the term that represents the acidity level. The pH value of rainwater is determined dynamically by the result of the acid-base reactions occur between alkaline and acidic compounds in cloud droplets and in rain droplets (Losno et al., 1991).

Natural, unpolluted rainwater has a pH of about 5.6, which is due to the global atmospheric concentration of CO_2 (330 ppm) (Gülsoy et al., 1999). The rainwater with a pH of less than 5.6 is considered as acid rain and compounds as sulfur and nitrogen oxides emitted from both anthropogenic sources and/or organic acids are in abundance (Tang et al., 2005).

However, acidic species are not the only decision making mechanism for rainwater pH. Chemical form of the measured acidic species and absence of the alkaline species as NH_3 and $CaCO_3$ also plays an important role on pH of the rainwater.

If hundred percent of the measured SO_4^{2-} and NO_3^- ions are in H_2SO_4 and HNO_3 form, average pH of rain water have to be 4.5 at Antalya station, 3.9 at Balıkesir station and 3.7 at Trabzon station. And if the majority of the rainwater composed of alkaline ions the pH will be higher than 5.6.

$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$

$HNO_3 \rightarrow H^+ + NO_3^-$

Both the frequency distributions and annual average pH values show that the rain water in different parts of Turkey is not acidic (see figure 4.17). For example at Antalya station, most frequent pH value is around 6.0, at Trabzon station between 7.0 to 7.5 and Balıkesir station which is fairly acidic than others but still higher than 5.0.

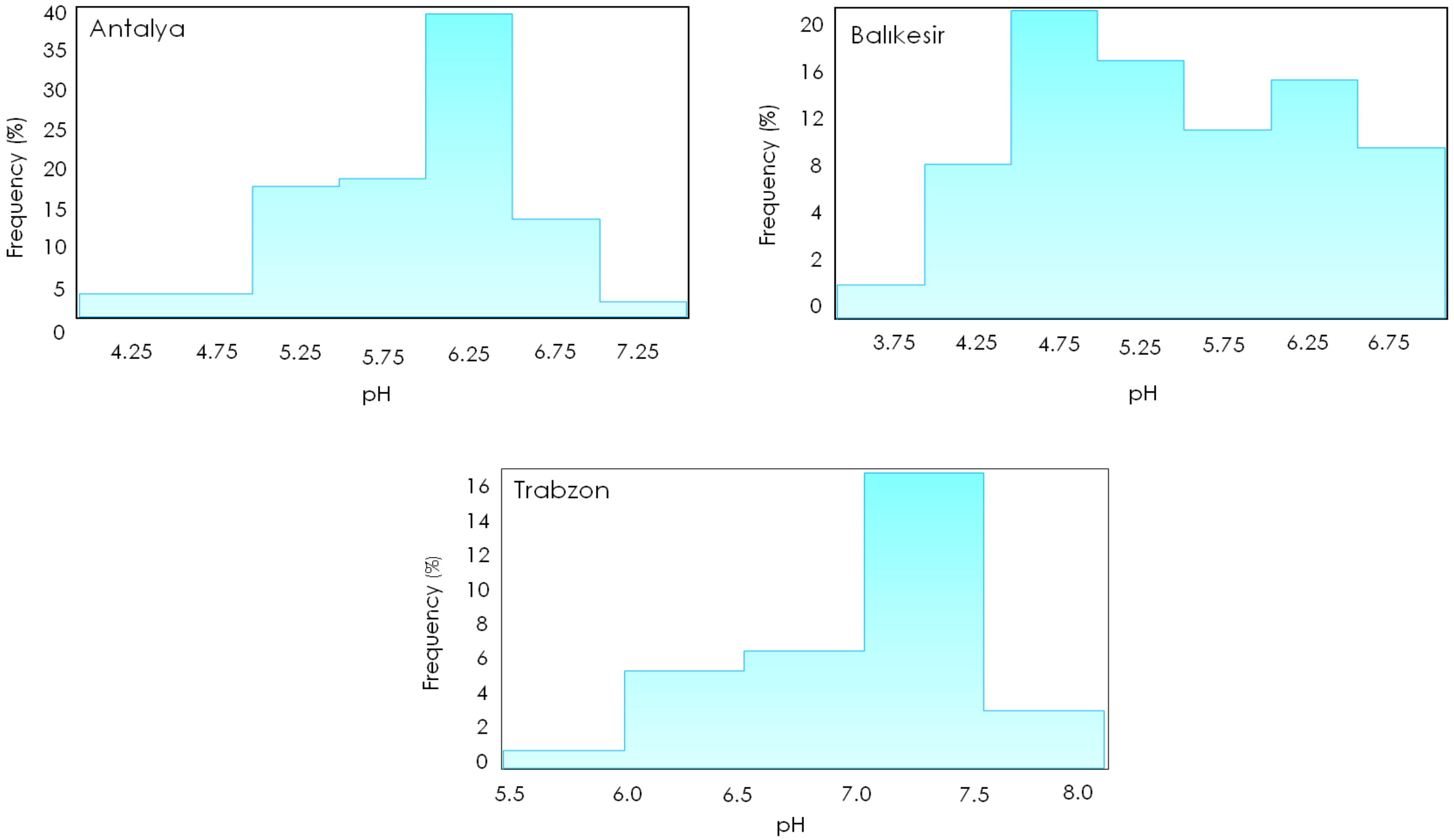


Figure 4. 18 Frequency Distributions of pH for Antalya, Balıkesir and Trabzon Stations

In each station, some portion of the rain events are included in acid rain category which represents the rainwater has pH lower than 5.0. This ratio for Antalya station is 25 % and Balıkesir station is 37 %. Balıkesir station faces with the acid rain more than Antalya station. Position of the Balıkesir city may be the reason for that, because Balıkesir is close to Istanbul. Istanbul contains lots of industrial facilities that emits SO_4^{2-} ion to the atmosphere. That's why SO_4^{2-} ion concentration is also higher at Balıkesir station than Antalya station.

Back trajectories corresponding pH values lower than 5.0 are plotted for Antalya and Balıkesir stations are given in figure 4.18. As it can be seen from the figure, trajectories with pH less than 5.0 mainly are coming from North and North West directions.

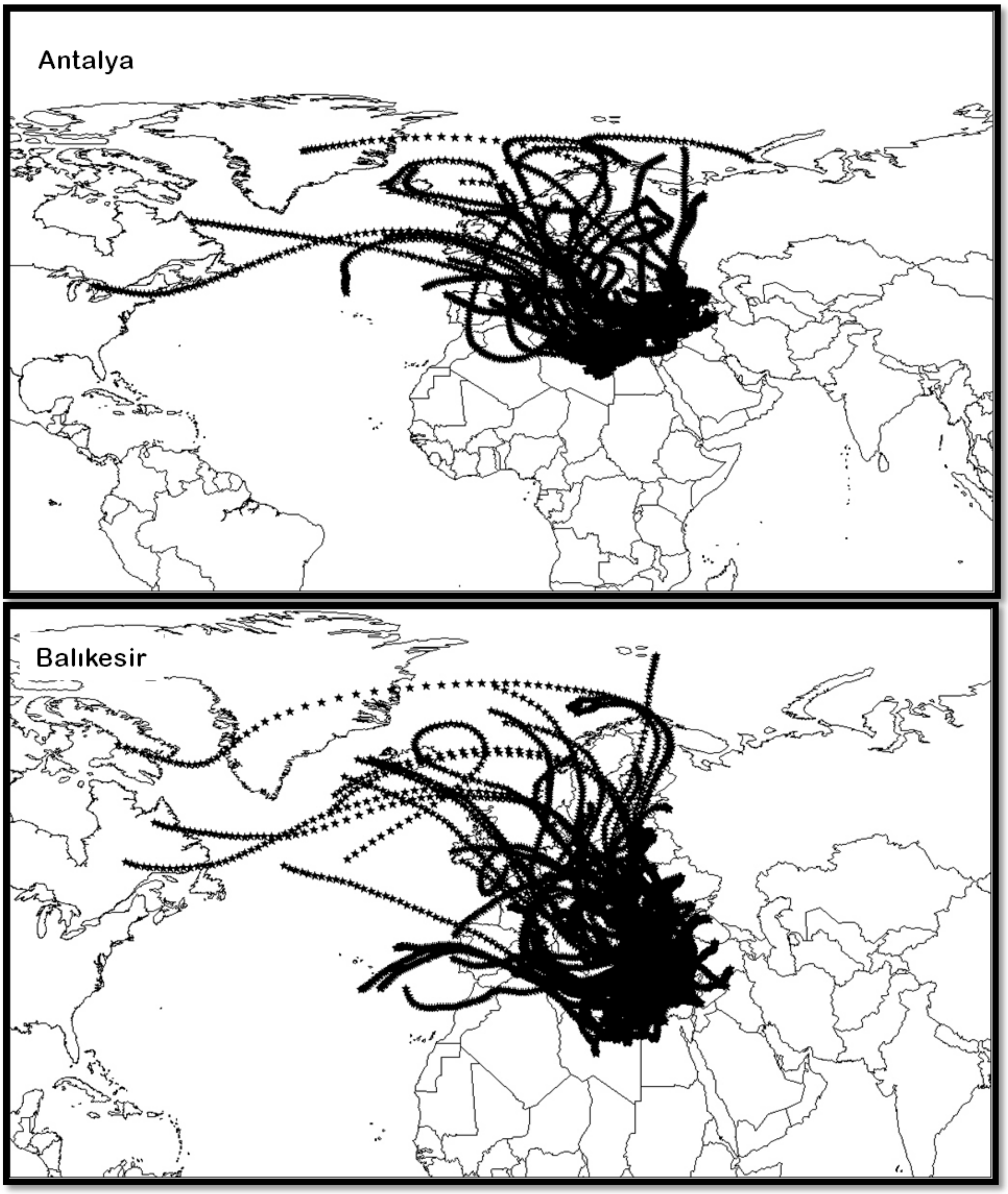


Figure 4. 19 Trajectory plots of pH lower than 5.0 for Antalya and Balıkesir Stations

This is an expected result. For the sampling stations in this study, anthropogenic emission sources are in North and North West sector for both inside and outside of Turkey. These trajectory pathways represent that when air mass is coming from North and North West directions, its pH is lower than 5.0.

4.3.2. Neutralization of Acidity

In addition to the acidic products, alkaline products also present in the atmosphere. There are mainly aerosol of calcite ($CaCO_3$) and gaseous ammonia (NH_3). At the pH found in rains, they react as strong neutralization species with the hydronium ions to give, respectively, HCO_3^- and NH_4^+.

SO_4^{2-} and NO_3^- are the main ions that increase H+ ion concentration and decrease the pH in rainwater, whereas NH_3, Ca^{2+}, Mg^{2+},K^+ ions are the common neutralizing species. The relative amounts of these ions determine the final pH of the rain. Although an areas exposed to high SO_4^{2-} and NO_3^- emissions, by alkaline species the rain water can be neutralized and high pH values can be obtained.

Before identifying the neutralization process and neutralizing ions, the dominating specie that causes rainwater acidity should be clarified. The rainwater acidity is originated from H_2SO_4 and HNO_3 with respect to the emission sources. The ratio of SO_4^{2-}/NO_3^- indicates the relative contributions of H_2SO_4 and HNO_3 to rainwater acidity.

Studies conducted on Europe and North America on 1980s represented that % 70 of rainwater acidity is originated from H_2SO_4 and % 30 is originated from HNO_3. However SO_2 emission controls are easier than NO_X. Therefore, SO_2 and SO_4^{2-} levels in Europe and North America are decreased before NO_2 and NO_3^- levels (Tuncel, 2004). As a result, according to today's EMEP stations measurements' SO_4^{2-} to NO_3^- ratio, contribution of H_2SO_4 and HNO_3 are equal to % 50 and % 50.

Monthly average SO_4^{2-} to NO_3^- concentration ratios are given in figure 4.20.

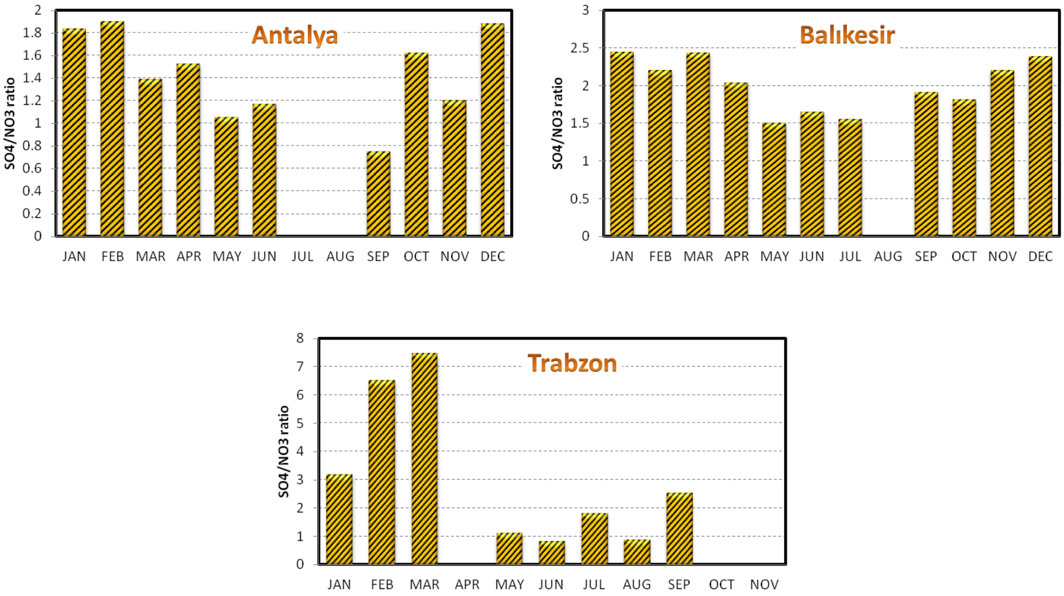


Figure 4. 20 Monthly variations for the equivalent ratio of SO_4/NO_3 in rainwater for Antalya, Balıkesir and Trabzon stations.

In Figure 4.19 it was represented that the ratio does not show an important seasonal variation. Studies conducted in our departmental air pollution group in 1990s show that SO_4^{2-}/ NO_3^- ratio is high in winter and low in summer season (Tuncer et al., 2001). While SO_2 emission control was applied commonly in Western Europe before 2000s, in Eastern Europe countries that exist after destruction of Union of Soviet Socialist Republics, due to economic reasons. Therefore when air masses are coming from Eastern Europe, its SO_4^{2-}/NO_3^- ratio is around 2.5, when air masses coming from Western Europe, the ratio is less than 2.0.

At Antalya station the ratio is around 2.0 during whole year. At Balıkesir station, the situation is different. During winter season $SO_4^{2-}$to NO_3^- ratio is fairly high, while summer season the ratio is less than 2.0. This result is observed probably due to the close location of Balıkesir to Istanbul.

In recent years, SO_2 emission control also becomes widespread over Eastern Europe, therefore SO_4^{2-} to NO_3^-ratio of rain water is less than 2.0 no matter from which direction the air masses coming from.

In this study, average pH values are high for all stations. This result was handled out in terms of two questions; “Does neutralization rate stay constant during whole year?” and “What was the main element that neutralizes acidity?”

In order to evaluate the variation of neutralization rate with time, $(H^+) / [(SO_4^{2-}) + (NO_3^-)]$ equivalent ratio versus months graphs were plotted for three stations. If all of the SO_4^{2-} and NO_3^- ions are in the H_2SO_4 and HNO_3 forms, this ratio should be equal to 1.0. As the neutralization increases, so ratio decreases less than 1.0.

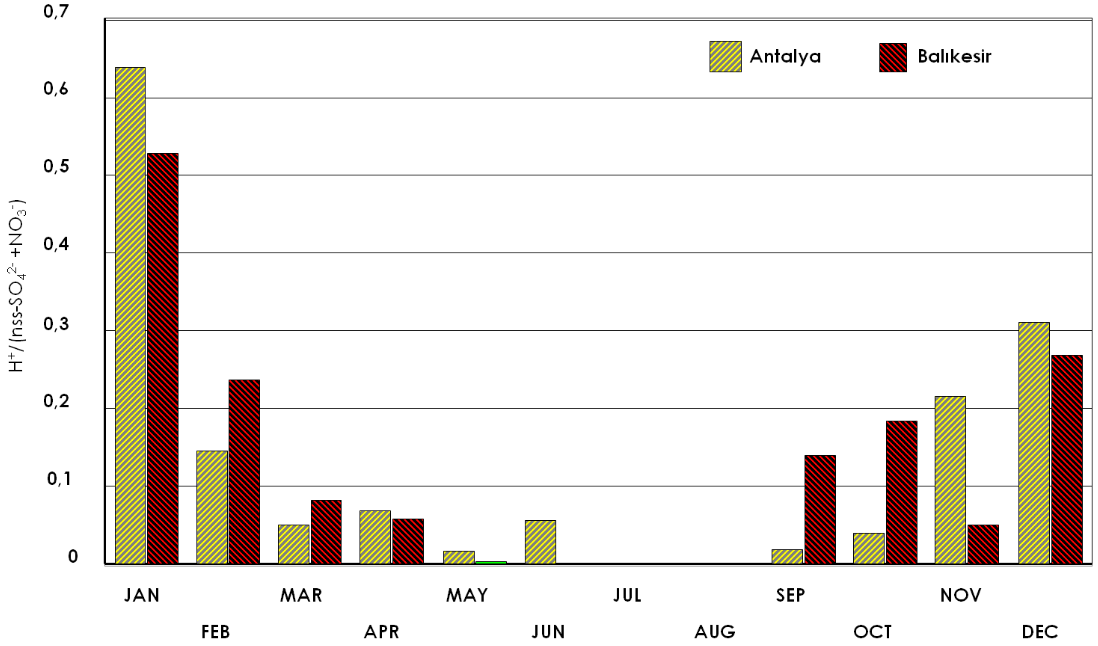


Figure 4. 21Monthly variations for the equivalent ratio of H/ nss-SO4 + NO3 in rain water for Antalya and Balıkesir stations.

Monthly average (H^+) to $[(SO_4^{2-}) + (NO_3^-)]$ ratios for Antalya and Balıkesir stations are given in figure 4.20. As it can be seen from the figure, neutralization is changing seasonally. It is high during summer months and low during winter months. At Antalya station for example, on January 35 % to 40 % of the acidity of rainwater is neutralized. This ratio is increased to 85 % on February and 95 % on March. During summer, approximately whole acidity is neutralized. Free acidity was increased to 5 % on October, 20 % on November and it reaches 30 % on December.

Seasonal variation on (H^+) / [(SO_4^{2-}) + (NO_3^-)] at Balıkesir station is also approximately similar with Antalya. Free acidity level dramatically decreases during spring and summer months. However, neutralization of acidity of Balıkesir rain water is little less than Antalya.

The second important point is the determination of the dominating ion of neutralization process. Acidity of the atmosphere can be neutralized by two important alkaline species: $CaCO_3$ released from soil and NH_3 released from agricultural, industrial and natural activities.

The $CaCO_3$ is particularly important for this study, because soil along Turkey is calcareous and contains high concentrations of $CaCO_3$. Therefore, it is possible that the rainwater acidity is neutralized by aerosols produced from soil (Erdoğan, 1999).

The second base that can neutralize the rain water acidity is NH_3. Fertilizer applications and livestock farming are the dominant sources of the NH_3 in the precipitation. Studies conducted on Antalya and Black sea region, seasonal variation of NH_4^+ ion was linked with fertilizer applications (Alagha et al., 2003; Al-Momani et al., 1995).

In order to compare the contribution of Ca^{2+} and NH_3 ions to neutralization process, for each station H^+ versus Ca^{2+} and H^+ versus NH_4^+ plots are scattered (see Figure 4.21 and 4.22). According to the figures, it can be clearly seen that the acidity of rainwater is mainly neutralized by $CaCO_3$. Moreover, for three stations Ca^{2+} is strongly correlated with H^+. For all stations samples, as Ca^{2+} ion concentration increases, H^+ ion concentration decreases.

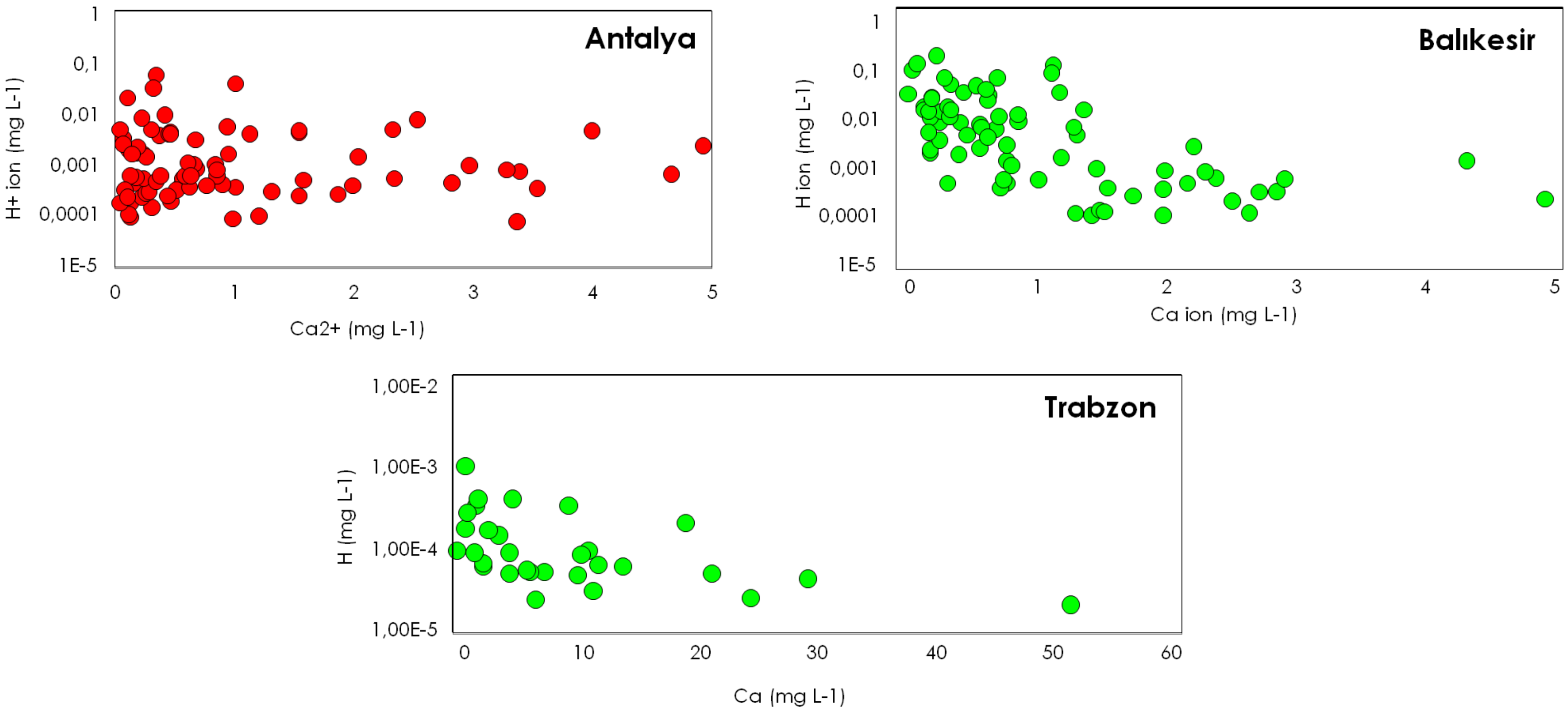


Figure 4. 22 The plot of Ca^{2+} versus H^+ ion concentrations for Antalya, Balıkesir and Trabzon stations

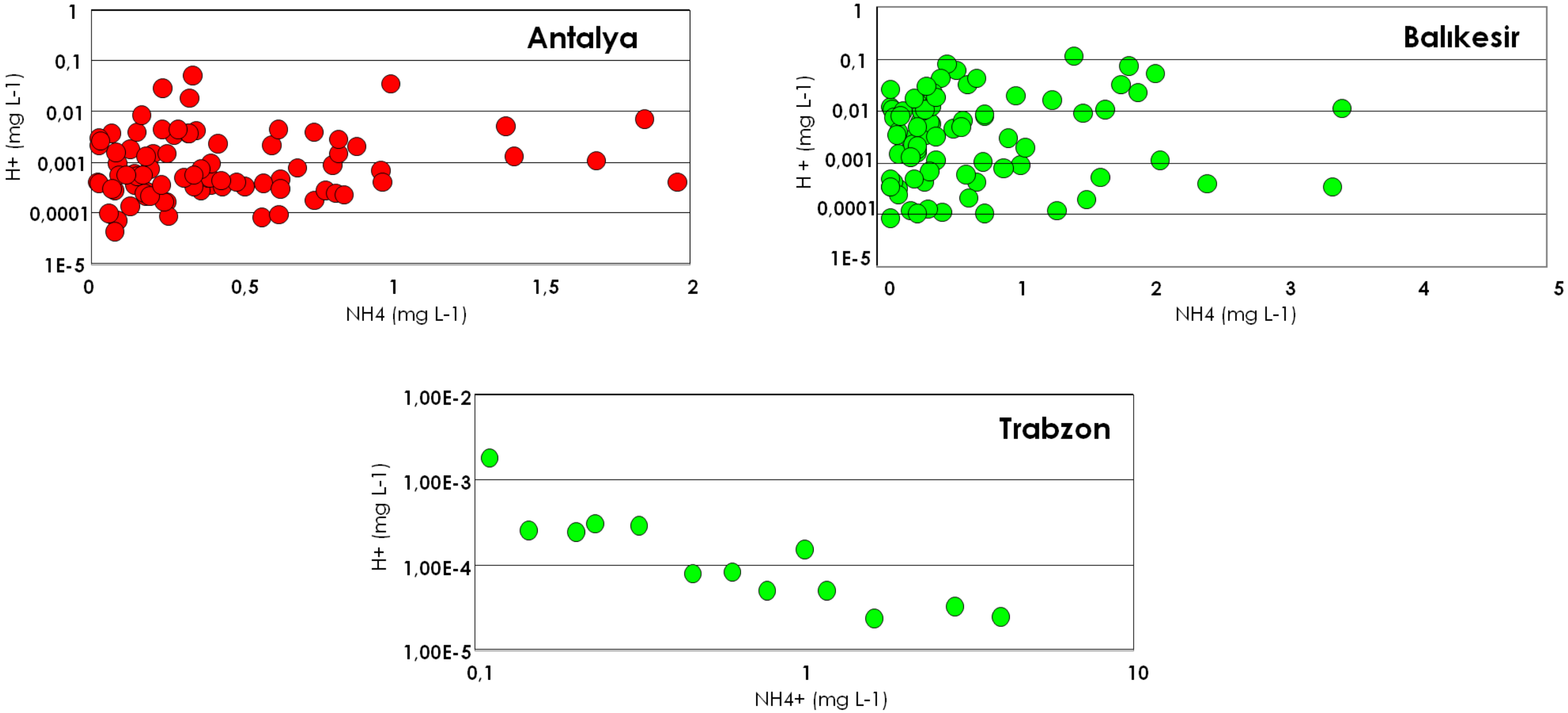


Figure 4. 23 The plot of NH4$^+$ versus H$^+$ ion concentrations for Antalya, Balıkesir and Trabzon stations

In addition to that, seasonal variation of the neutralization of acidity, which was mentioned at previous sections, also shows that $CaCO_3$ is the dominating ion of acidity neutralization. During summer, when neutralization increases, the soil is dry. Therefore soil particles can be easily resuspended and then scavenged by rain droplets. During winter, on the other hand, soil is in sludge form or covered by snow or ice, soil particles that contain $CaCO_3$ cannot easily resuspended to the atmosphere and the neutralization decreases.

4.4. Seasonal Variability of Wet Deposition

In order to investigate the seasonal variations of ion concentrations, the rain water data were separated into two groups; wet season samples and dry season samples. Wet season was assumed as the period between the beginning of October and the end of March; dry season was between the beginning of April and the end of September. Seasonal variations in the contributions of each ion to total ion mass for Antalya, Balıkesir and Trabzon stations were given Figures 4.23.

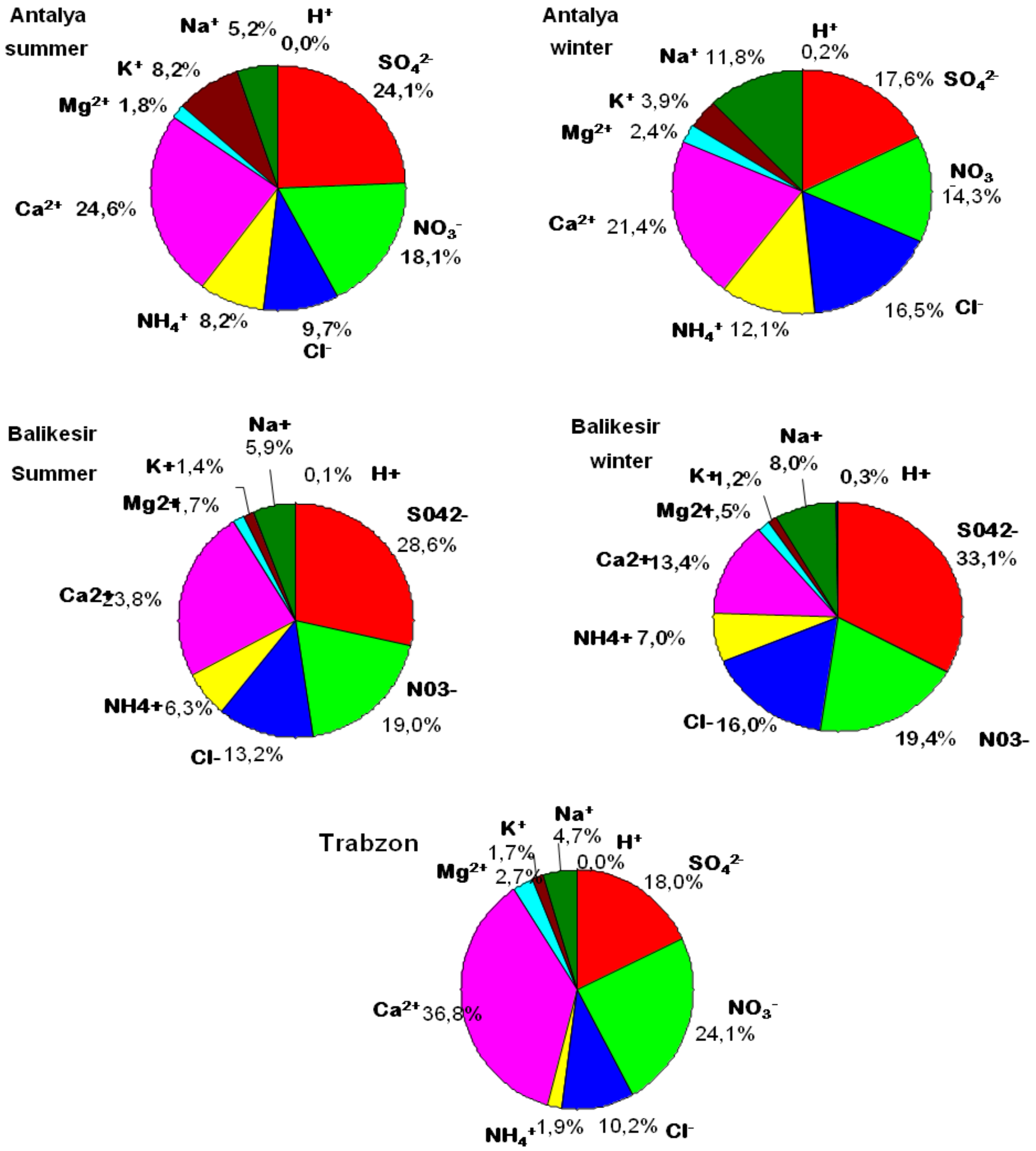


Figure 4. 24 Seasonal variations in the contributions of ions to total ion mass for Antalya, Balıkesir and Trabzon stations

Atmospheric pollutants generally show seasonally variations. Meteorological factors, for example variation of mixing height systematically between summer and winter, result in variations of ion concentrations seasonally. Moreover, in winter season frequent and intense precipitation events restrict the long range transport of pollutants and reach the sampling stations. Another reason of seasonal variations of ion concentrations is the seasonal variations of emission sources.

In this section seasonal variations of ion concentrations are discussed. In figures, on behalf of crustal ions Ca^{2+} and sea salt ions Na^{+} was chosen. Other crustal ions, K^{+} and Mg^{2+} and other sea salt ion Cl^{-} are not represented in figures because their variations are similar with Ca^{2+} and Na^{+} respectively.

Concentrations of ions changes on timescales. Monthly median concentrations of SO_4^{2-} , NO_3^{-}, NH_4^{+}, Na^{+} and Ca^{2+} at Antalya, Balıkesir and Trabzon stations are given in Figures 4.24, 4.25, 4.26, 4.27 and 4.28.

Antalya station is closer to the sea coast than other stations. Therefore, sea salt affect found to be denser in ion concentrations than other stations. According to the Figure 4.24, Na^{+} ion concentration is higher during wet season at all stations. These ions are mainly released during a mechanism called bubble bursting. Bubble bursting process is the wave motion over sea traps air into water. Later it forms bubbles at the interiors of the sea. Next, bubbles burst over sea surface. After evaporation of surrounding water, sea salt ions remain in the air. Since winds are stronger in winter, during wet season the bubble bursting is enhanced by strong winds.

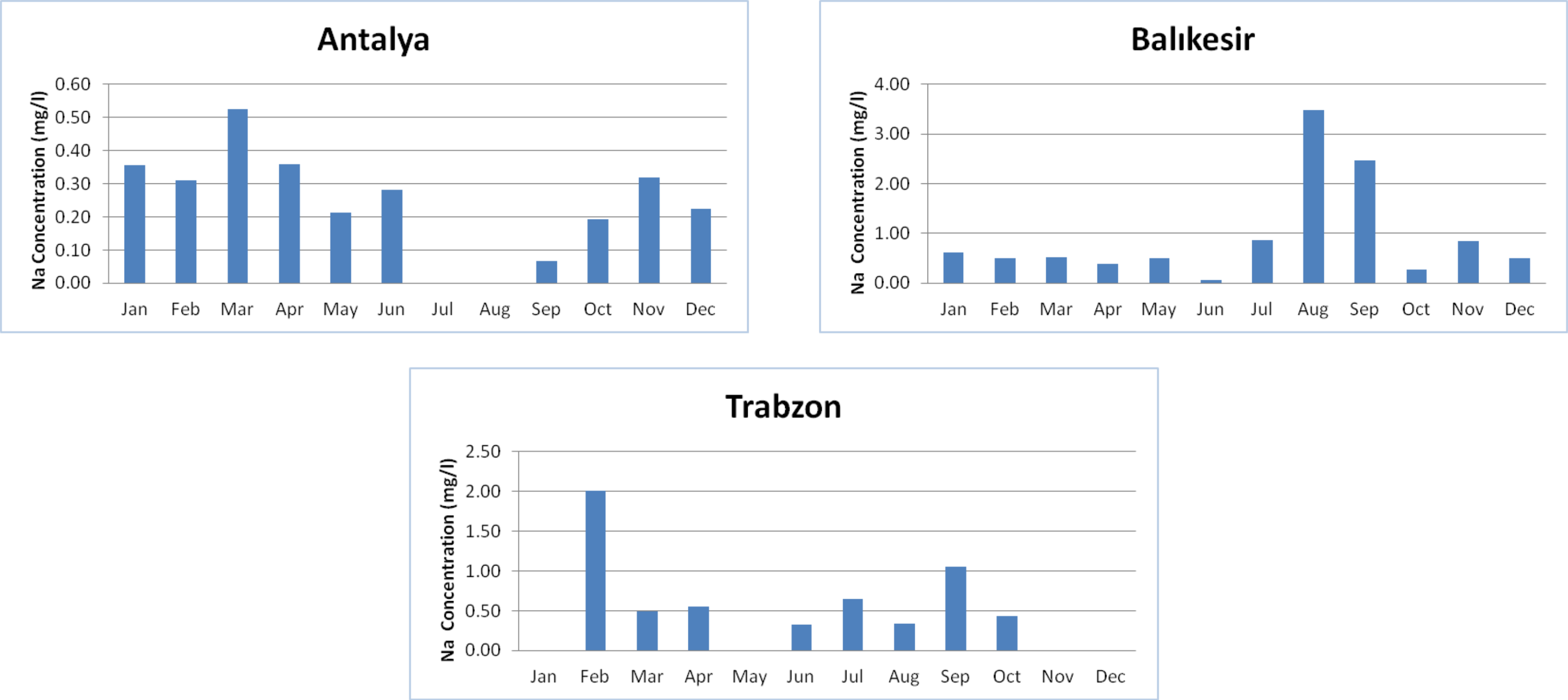


Figure 4. 25 Monthly median concentrations of Na+ for Antalya, Balıkesir and Trabzon stations

Ca^{2+} is chosen as the representative soil originated ion. According to the Figure 4.25, Ca^{2+} ion concentrations are higher during dry season. This trend has two reasons. The dust episodes which originate from the North Africa occur in May and April and to a lesser extent in September and October (Ganor et al., 1991). These periods belong to the dry season; therefore Saharan dust transport contributes to the observed crustal element concentrations in dry season. Moreover, another source of crustal elements is local soil. Soil particles that are suspended from sampling region by wind blows also reached the receptor. Therefore even during the wet season its concentration may not be very low.

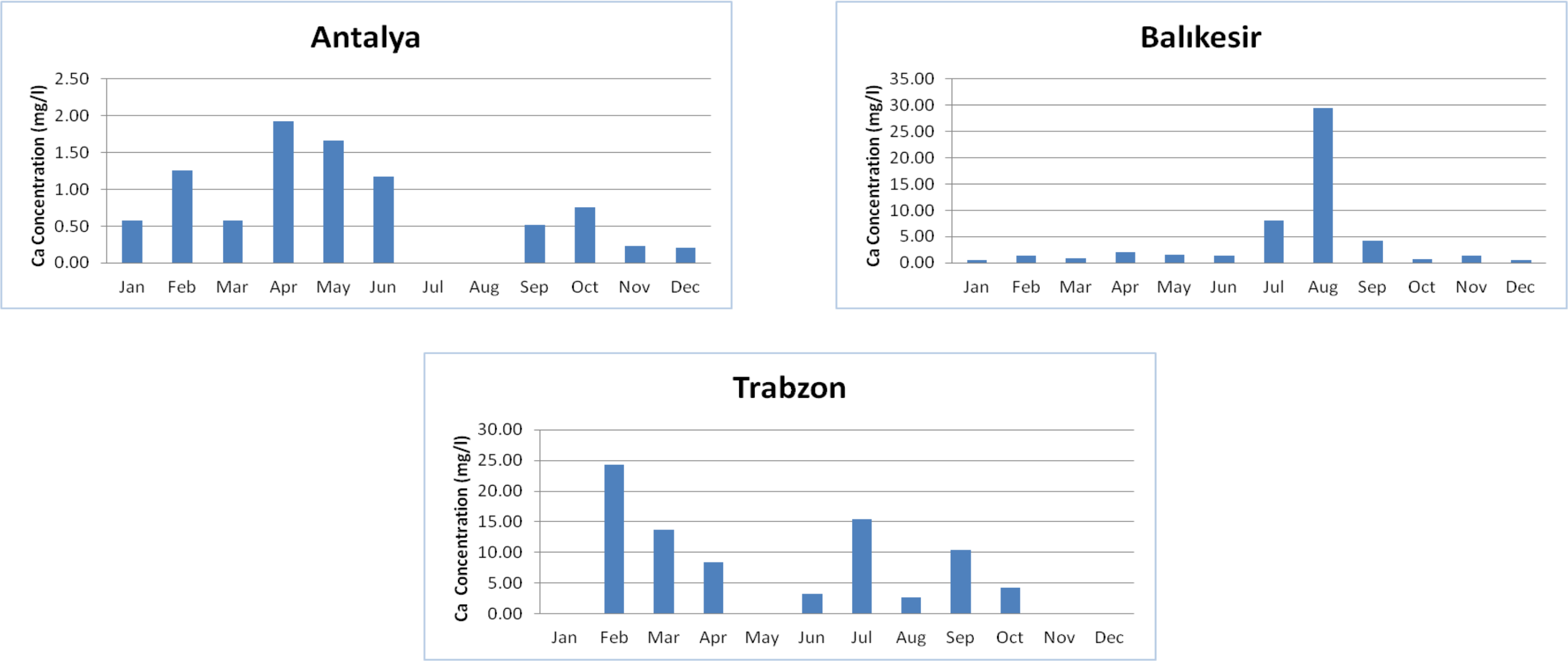


Figure 4. 26 Monthly median concentrations of Ca^{2+} for Antalya, Balıkesir and Trabzon stations

SO_4^{2-}, NO_3^- and NH_4^+ concentrations are higher during dry season and lower during wet season. It has two reasons. First reason is the photochemical reactions. These ions are secondary pollutants and are not directly emitted to the atmosphere. They were produced with photochemical reactions of primary pollutants. The photochemical reactions are effected directly from sunshine intensity and temperature. Since hours of sunshine are longer and temperature is higher, the photochemical reactions are dominant in summer. Therefore concentrations of those ions are higher during dry season than wet season (URL 10).

NH_4^+ ion concentration generally shows an increase during dry season and decrease during wet season. This alteration can be explained by the agricultural activities. NH_3 is included in fertilizers in agriculture. During summer months both agricultural activities and with the high temperatures, volatility of NH_4^+ are increased. During winter season, on the other hand, soil is in sludge form, which obstructs particle emission to the atmosphere.

Furthermore, these anthropogenic originated ions also come from long range transport such as Europe, Ukraine, Russia and western parts of Turkey where the industry is more developed. During wet season rain events are more frequent. Therefore, transportation of these ions from long distances are not possible, they are scavenged immediately by the rain near the emission regions. Concentration of these ions measured at wet season is mainly due to regional sources, such as industrial facilities, traffic emissions or residential heating processes.

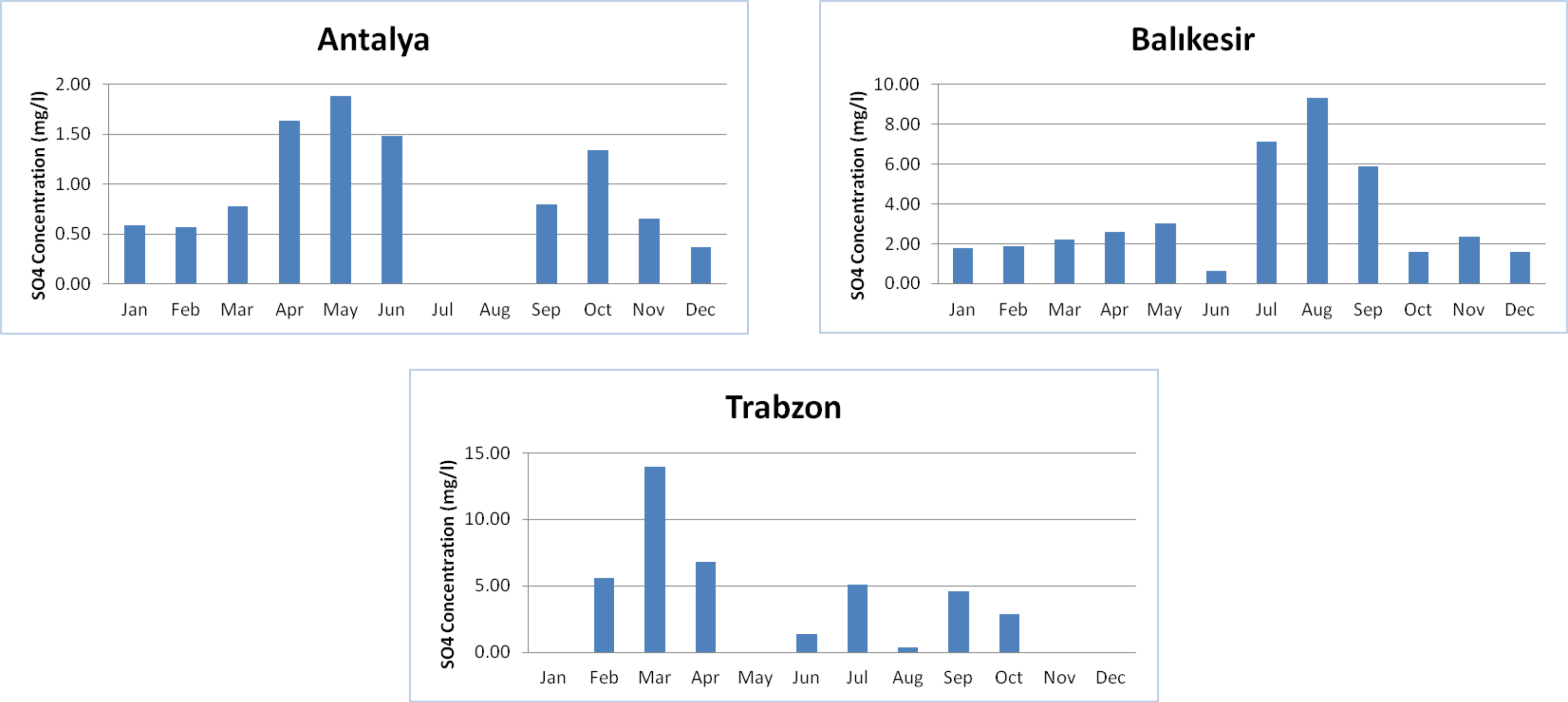


Figure 4. 27 Monthly median concentrations of SO_4^{2-} for Antalya, Balıkesir and Trabzon stations

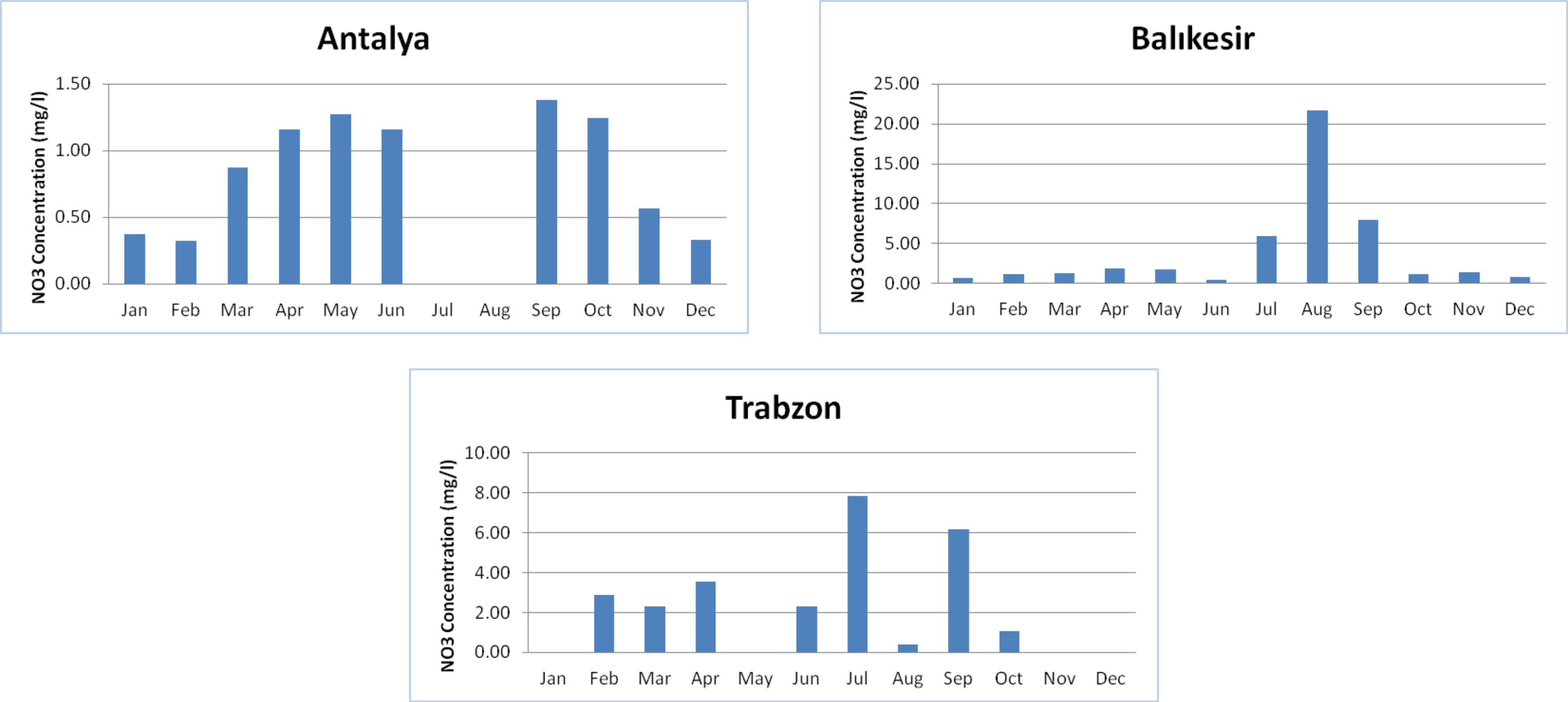


Figure 4. 28 Monthly median concentrations of NO_3^- for Antalya, Balıkesir and Trabzon stations

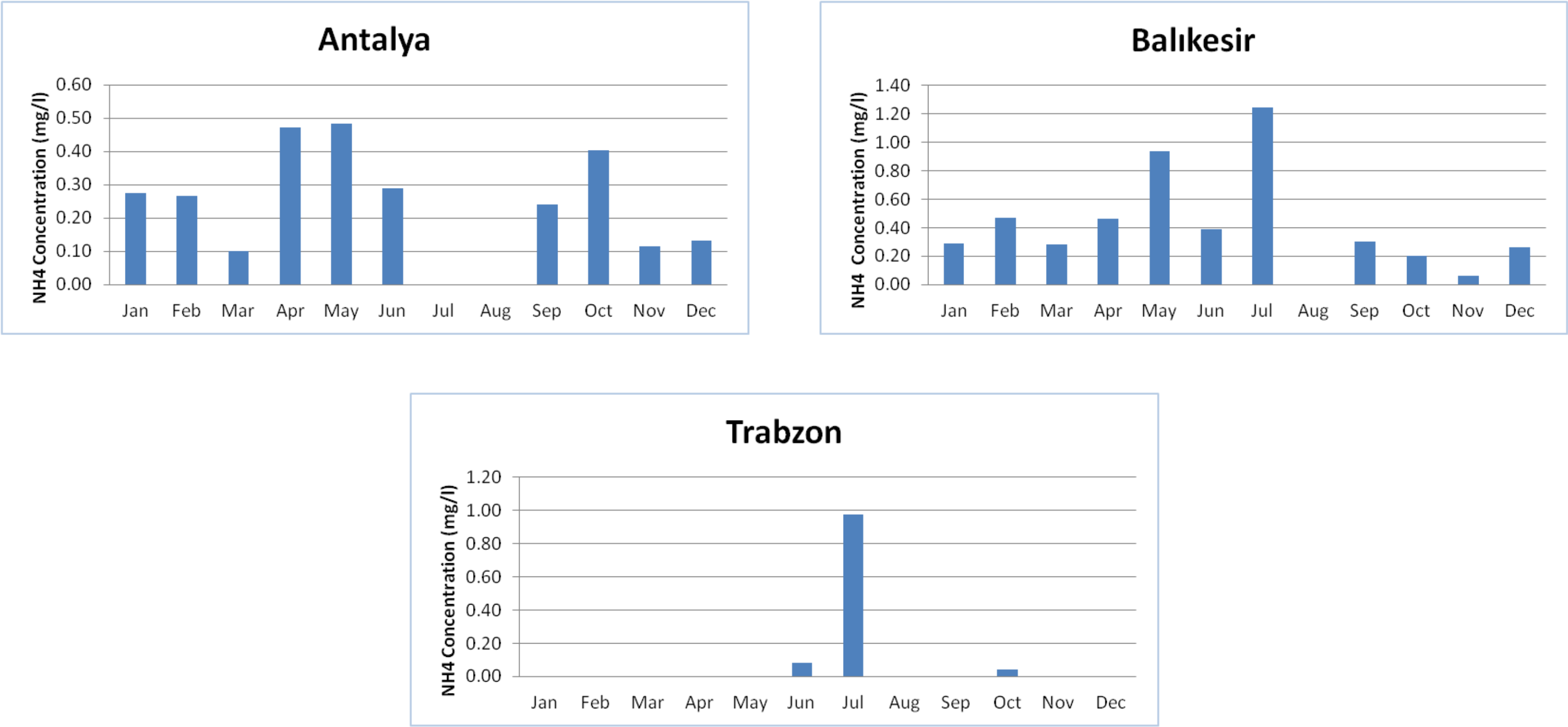


Figure 4. 29 Monthly median concentrations of NH_4^+ for Antalya, Balıkesir and Trabzon stations

According to the figures, variations of anthropogenic ions SO_4^{2-}, NO_3^- and NH_4^+ at Balıkesir station are similar with those observed at Antalya station. All three ions are high in summer due to similar reasons with Antalya station.

Moreover, seasonal variation of Ca^{2+} ion is similar with Antalya station. Ca^{2+} ion concentration is high in summer due to similar reasons with Antalya station.

The only different variation is observed on Na^+ ion. At Antalya station, Na^+ ion concentration is high in winter season. However at Balıkesir station Na^+ ion concentration is high in summer season. The reason for the difference is, while Na^+ ion emission source is sea salt at Antalya station, it is emitted from soil at Balıkesir station because Balıkesir is far away from the sea coast. Therefore, likewise other soil originated ions; Na^+ ion concentration is high in summer at Balıkesir station.

Monthly distributions of ion concentrations of Trabzon station are statistically insignificant because collected sample number is few and while they are grouped into months, numbers are getting fewer. Therefore, Trabzon station is omitted from seasonal variation analysis. Summer and winter median concentrations and summer to winter ratios are given in Table 4.6.

Table 4. 6 Summer and winter concentrations of major ions at Antalya, Balıkesir and Trabzon stations. (Volume weighted average concentrations are in mg L^{-1})

	Antalya			Balıkesir			Trabzon		
	Winter	Summer	Sum/Wint	Winter	Summer	Sum/Wint	Winter	Summer	Sum/Wint
SO_4^{2-}	0.63	1.64	2.6	1.77	3.2	1.8	3.37	2.4	0.7
NO_3^-	0.42	1.3	3.2	1.08	1.7	1.5	2.11	2.7	1.2
Cl^-	0.42	0.42	1.0	0.91	0.53	0.6	1.49	0.77	0.5
NH_4^+	0.23	0.4	2.0	0.28	0.9	3.2	0.00	0.3	
Ca^{2+}	0.45	1.5	3.3	0.72	2.3	3.2	6.63	5.2	0.7
Mg^{2+}	0.06	0.08	1.3	0.09	0.17	1.8	0.40	0.5	1.2
K^+	0.08	0.3	3.8	0.06	0.12	2.0	0.23	0.18	0.8
Na^+	0.32	0.25	0.8	0.49	0.47	0.9	0.50	0.39	0.8

Table 4.6 makes the qualitative representation of figures into quantitative form with the numeric values.

Summer to winter ratios of anthropogenic ions, SO_4^{2-}, NO_3^- and NH_4^+, ranges between 2.0 and 3.2 at Antalya station. The ratio for Balıkesir station is lower than Antalya, and ranges between 1.5 and 3.2.

Both summer and winter concentrations of SO_4^{2-} , NO_3^- and NH_4^+ at Balıkesir are higher than Antalya. This result is caused by the close distance from Istanbul.

Another point is that Na^+ ion summer to winter ratio at Balıkesir station, although to a lesser extent than Antalya, is lower than crustal and anthropogenic ions. This result represents that some amount of Na^+ ion are coming from sea salt.

Summer to winter ratio of Trabzon station is different than Antalya and Balıkesir stations. At Trabzon station, concentrations of all ions are higher in winter than summer. It is not possible to make judgment whether it is caused by the few number of samples or it is a regional property.

4.5. Wet Deposition Fluxes of ions in The Stations

One of rationales of measuring pollutant concentrations in different forms of precipitation is to determine wet deposition fluxes of pollutants from atmosphere to earth’s surface. Such scavenging of particles and gases is generally considered to be as cleansing mechanism for the atmosphere. However, the same mechanism may be dangerous for living species on the surface, because pollutants are transferred from cloud level to the surface. Since wet deposition enhances solubility of otherwise insoluble species, it increases the bioavailability of pollutants to living organisms, particularly in the marine environment.

For example solubility of trace elements in the atmosphere increases significantly if particles bearing these elements are processed in cloud droplets where pH is fairly low (pH 3.0 can be considered as typical for cloud droplets). When they deposit with in rain droplets they are > 50% soluble. However if they deposit to sea water or lake water with particles, without cloud processing their solubility is much lower due to higher pH of sea or lake water.

Wet deposition fluxes of pollutants at a particular airshed strongly depend on rainfall at that area. In the regions where rainfall >1000 mm (as in most of the Northern Europe), wet deposition of major ions dominates over their dry deposition (Matejko et al., 2009; Pan et al., 2012; 2013). However in the Mediterranean area where rainfall is <1000 mm, dry deposition fluxes of elements and ions are comparable to their wet fluxes (Al-Momani et al., 1998; Im et al., 2013).

Data generated in this study should be viewed with these considerations. Annual, Seasonal and Monthly rainfall at three stations are given in Table 4.7. Rainfall and all other meteorological data are obtained from Automated Meteorological stations that are closest to our sampling stations. At Antalya and at Balıkesir meteorological stations are collocated with rain samplers, but at Trabzon station is at the city of Trabzon, which is located approximately 30 km from the sampling point. Values shown in the table are 50-years-long averages, between 1960 and 2012.

Table 4. 7 Monthly, seasonal and annual rainfall fluxes at three stations (URL 3)

	Trabzon	Antalya	Balıkesir
	kg/m^2	kg/m^2	kg/m^2
JAN	74.3	214.4	77.5
FEB	60.3	155.8	67.4
MAR	58.8	98	58.1
APR	60.3	54.1	52.3
MAY	51.5	30.5	41.9
JUN	51.4	7.3	22.2
JUL	35.5	2.7	7.7
AUG	44.5	1.8	6.1
SEP	75	12.5	23.8
OCT	117.1	70.8	43.5
NOV	94.2	144.1	74.7
DEC	82.4	251.2	100.8
Annual	805,3	1043,2	576
Winter	487,1	934,3	422
Summer	318,2	108,9	154

The highest annual average rainfall is recorded at Antalya station (1043 mm), then at Trabzon (805 mm) and the least at Balıkesir (576 mm). Since these averages cover a 50 year period, uncertainties are expected to be minimum. We expected to see the highest rainfall at Trabzon station, but it turns out that Antalya receives more rain that cities on the Black Sea cost.

Annual rainfall on the Black Sea coast varies between 706 kg m^{-2} at Samsun and 2236 kg m^{-2} at Rize. Trabzon with 805 kg m^{-2} annual rainfall is ninth in line among fifteen Black Sea cities. On the Mediterranean cost there are five coastal cities, namely Hatay, Adana, Mersin, Antalya and Muğla. With the exception of Adana and Mersin, which have 663 and 595 mm annual rainfall, respectively, the three remaining cities have rainfall that is higher than 1000 mm. The annual rainfall recorded at Balıkesir (576 mm) is typical for the interior of the country.

Effect of these differences in rainfall amount on average concentrations of Ions measured in this study is overcome by using volume weighted averages in our discussions. However, same differences have fairly strong influence on calculated fluxes.

In most of the country winter-to-summer ratio in rainfall depicts fairly large variations. This can be clearly seen in the table. Winter-to-summer rainfall ratios are 1.5 at Trabzon, 2.7 at Balıkesir and 8.7 at Antalya. Obviously summer and winter rainfall is comparable at Trabzon and dramatically different on the Mediterranean coast.

These differences in annual and seasonal rainfall at three stations are expected to have significant contribution on wet deposition fluxes of major ions in these locations. Annual wet deposition fluxes of ions at Antalya, Balıkesir and Trabzon stations are given in Figure 4.29.

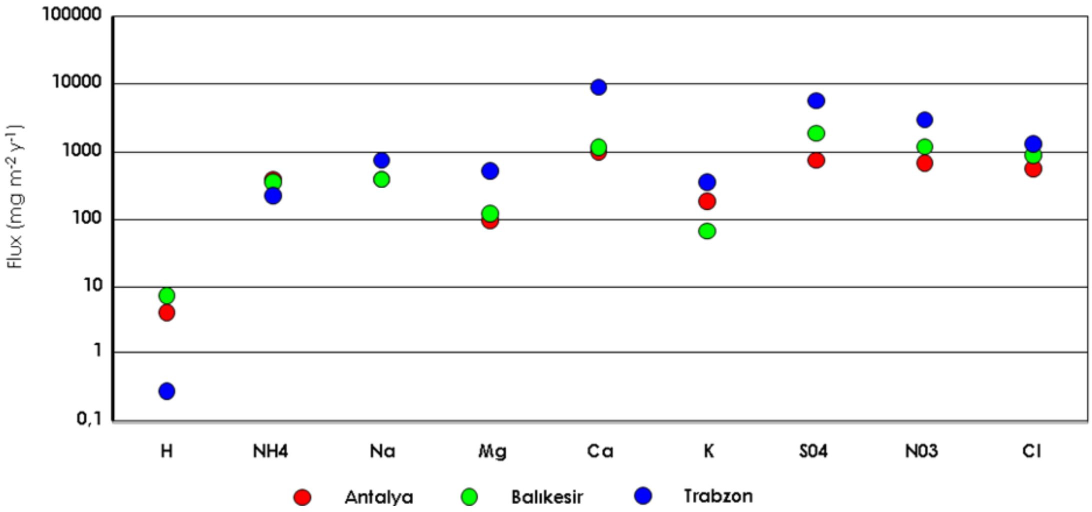


Figure 4. 30 Comparison of wet deposition fluxes of Antalya, Balıkesir and Trabzon stations

Wet deposition fluxes of ions and other parameters should be calculated by multiplying measured concentration with rainfall for each event and then summing the calculated event-based fluxes over the desired time interval (month, season, year etc.). This is the ideal approach if most of all rain events in a year were consistently collected. However, in this study, number of missed rain events (rain events which were not sampled) was too high to adopt this approach. A different approach was adopted to avoid underestimation of deposition fluxes due to missed rain events. Wet deposition fluxes of ions were calculated by multiplying average concentrations of ions in each month with long-term average monthly rainfall obtained from the nearest meteorological station. Monthly fluxes were then summed up to obtain seasonal and annual fluxes.

Wet deposition flux of H^+ ion is the highest at Balıkesir, which is followed by Antalya. The lowest free acidity in rain water is measured at the Trabzon station. This contradicts with deposition fluxes of SO_4^{2-} and NO_3^-, because the highest SO_4^{2-} flux is measured at the Trabzon station. Observed pattern indicates more extensive neutralization of acidity on the Eastern Black Sea. Higher Ca^{2+} ion concentrations measured at Trabzon station supports this hypothesis. High rain water Ca^{2+} concentrations on the Black Sea coast compared to Mediterranean is observed not only in this study, but also in rain water samples collected at Amasra in an earlier study in our group (El-Agha et al., 2003; El-Agha and Tuncel, 2003). Wet deposition fluxes of ions with anthropogenic origin, namely SO_4^{2-} and NO_3^- are the highest at Trabzon and lowest at Antalya stations. Higher concentrations of these ions at Balıkesir may reflect the influence of emissions at Istanbul and Kocaeli industrial zone to the chemical composition of rainwater at Balıkesir. Similarly high wet fluxes of SO_4^{2-} and NO_3^- at Trabzon may indicate transport of pollution from North and northeast. Contribution of N and NE wind sectors to the regional air quality at the Eastern Black Sea coast of Turkey is also reported in previous studies, both by measurements (Balcılar etal., 2013) and by modeling.

Wet deposition flux of NH_4^+ ion is comparable at the three stations. Main source of NH_4^+ in Turkey is the use of synthetic fertilizers, which is comparable around three stations. Calcium flux, which is a typical crustal element, is the highest at Trabzon station, which explains extensive neutralization of acidity on the Black Sea region.

Seasonal variations in wet deposition fluxes of major ions are given in Table 4.8 and Figures 4.30 and 4.31, where monthly deposition fluxes are plotted for Antalya and Balıkesir stations. Small number of rain events were collected at Trabzon station was not suitable to calculate monthly fluxes in this station.

Table 4. 8 Annual and seasonal fluxes of ions at three stations (mg/m^2)

	Antalya				Balikesir				Trabzon			
	Annual	Winter	Summer	W/S	Annual	Winter	Summer	W/S	Annual	Winter	Summer	W/S
H^+	4.20	4.07	0.13	31	7.68	7.20	0.48	15	0.29	0.20	0.08	2.5
NH_4^+	408	350	58	6.0	362	213	149	1.4	228	129	99	1.3
Na^+	420	387	33	11	390	303	87	3.5	750	535	215	2.4
Mg^{2+}	99	80	19	4.2	89	59	30	1.9	555	373	182	2.0
Ca^{2+}	1062	747	315	2.3	916	500	416	1.2	9028	6273	2755	2.3
K^+	189	126	63	2.0	71	44	28	1.6	383	271	112	2.4
$S0_4^{2-}$	791	607	184	3.2	2014	1293	721	1.7	6100	3849	2251	1.7
$N0_3^-$	671	530	141	3.7	1172	757	415	1.8	2978	1674	1305	1.3
Cl^-	589	524	65	8.1	933	815	118	6.9	1318	853	465	1.8

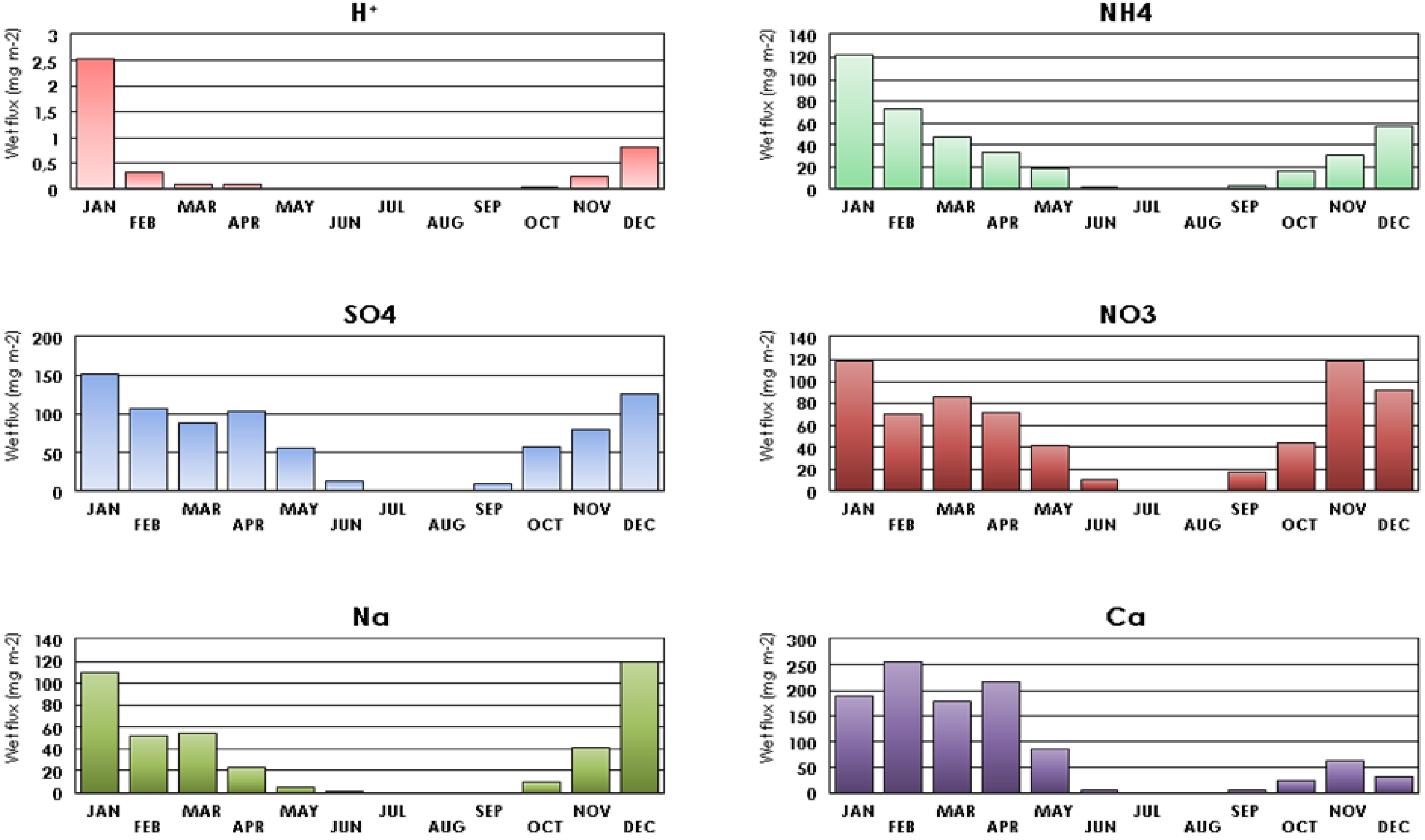


Figure 4. 31 Monthly fluxes of ions at Antalya station

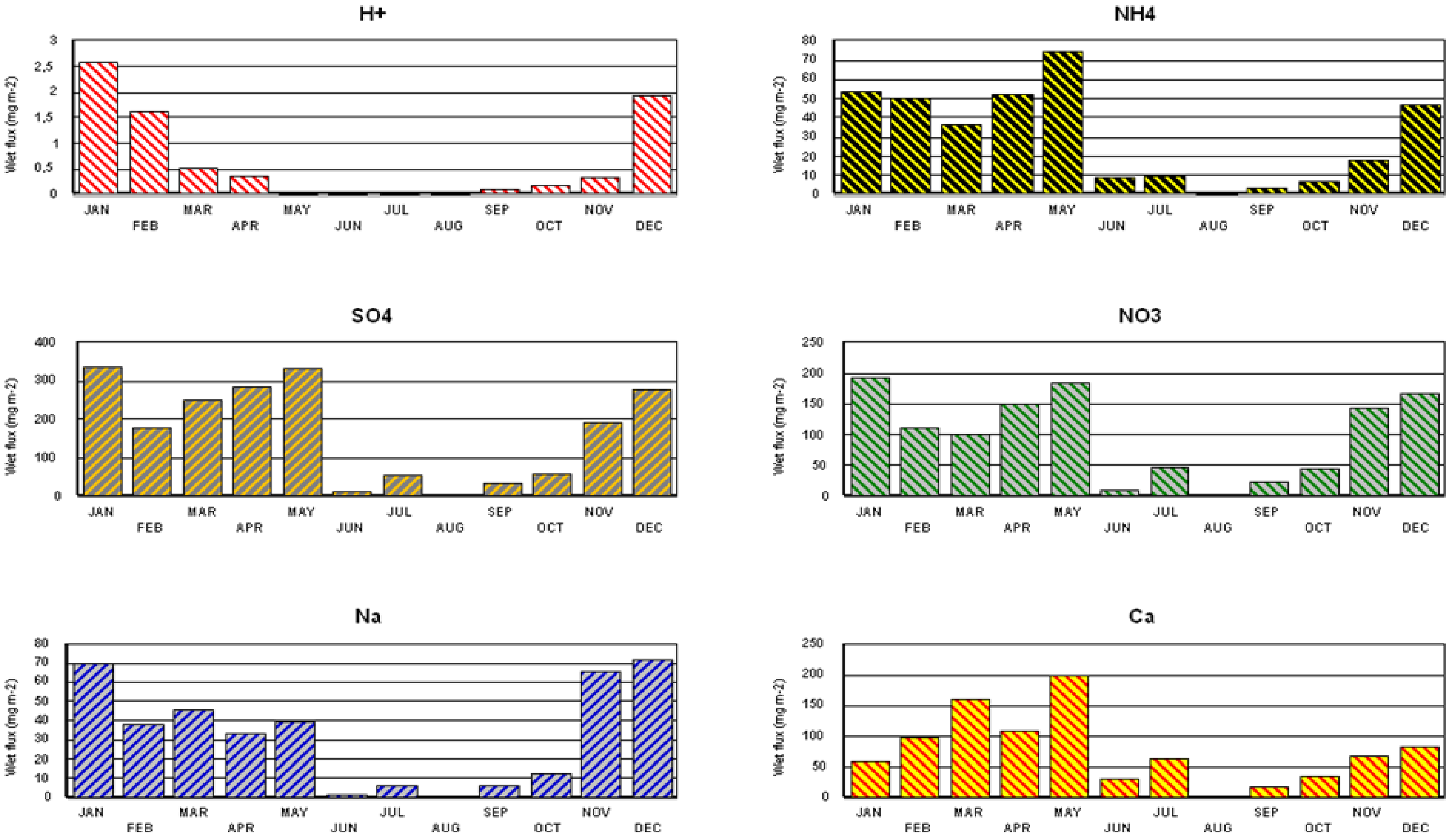


Figure 4. 32 Monthly fluxes of ions at Balıkesir station

Wet deposition fluxes of ions in summer season are higher than corresponding fluxes in winter. Although this statement is true for all three stations, the magnitude of difference changes from one station to another. Winter-to-summer flux ratio changes between 2 and 11 at Antalya, between 1.2 and 6.9 at Balıkesir and between 1.3 and 2.4 at Trabzon. Larger seasonal variations in wet deposition fluxes of ions at Antalya station is probably due to larger difference between winter and summer rainfall at this station (winter to summer rainfall ratios were 8 at Antalya, 2.7 at Balıkesir and 1.5 at Trabzon, as discussed previously.

Stronger polarity of deposition fluxes of ions can also be seen by comparing Figure 4.30 where monthly average fluxes are plotted for Antalya station with Figure 4.31 where monthly fluxes are plotted for the Balıkesir station. Although wet deposition fluxes of ions are lower during summer months, magnitude of decrease is not the same. At Antalya, fluxes decrease consistently between from January and June. They then increase between September and December. However, at Balıkesir, wet deposition fluxes of ions do not decrease systematically starting from January. Flux values remain firstly high between January and May, and then they sharply decrease in June and remain low until October. These different patterns in deposition fluxes of ions at Antalya and Balıkesir stations is due to differences in seasonal variations in concentrations of ions and rainfall in these two stations.

Seasonal variation in H^+ flux is significantly higher than seasonal variations in fluxes of other ions. At Balıkesir station summer-to-winter fluxes of ions vary between 1.2 and 6.9 with most of the values centering around 1.5 – 2.0. Summer-to-winter flux ratio for H^+ at Balıkesir station is 15. Similarly, summer to winter flux ratios for ions at Antalya station vary between 2 and 11, but corresponding ratio for H^+ is 31.

Larger seasonal variation in wet H^+ deposition fluxes at Antalya and Balıkesir is due to higher seasonal variation in concentration of H^+ ion, which in turn is due to dependence of H^+ ion concentration on concentrations of NH_3 and particularly $CaCO_3$ in the atmosphere.

Another interesting feature observed in wet fluxes of all ions in all stations is the episodic nature of wet deposition. Fractions of rain events, which accounted for 80 and 90 % of annual wet deposition fluxes of ions at Antalya and Balıkesir stations, are given in Table 4 9. At Antalya station, 16 % - 42 % of the rain events accounted for the 80 % of the annual wet deposition fluxes of ions. At the same station 31% - 57 % of rain events accounted for 90 % of annual deposition of ions. Fractions are very similar in the Balıkesir station as well. These figures clearly demonstrate that wet deposition fluxes of ions measured in this study occurs with few intense rain events and wet fluxes of ions are strongly related with intensity and duration of rain event.

Table 4. 9 Percentage of rain events that account for 80 % and 90 % of wet deposition of major ions at Antalya and Balıkesir stations

	Antalya		Balıkesir	
	% events accounting 80% of annual deposition	% events accounting 90% of annual deposition	% events accounting 80% of annual deposition	% events accounting 90% of annual deposition
Rainfall	42	58	76	87
H^+	16	27	19	30
NH_4^+	30	44	39	54
Na^+	30	46	41	56
Mg^{2+}	27	40	38	52
Ca^{2+}	19	31	33	48
K^+	18	33	44	59
SO_4^{2-}	40	54	43	58
nss-SO_4^{2-}	38	52	43	57
NO_3^-	42	57	43	58
Cl^-	31	48	38	53

4.6. Sources of Measured Species

4.6.1. Components of precipitation at Balıkesir and Antalya: Source apportionment using PMF

One of the key objectives in most of the environmental pollution studies is to identify, both types and locations of sources that are contributing to deprivation of environment. This very same objective also applies to studies related with air quality management, both in local and regional scale.

Attempt to identify sources contributing to measured concentrations of pollutants at an airshed is known as “source apportionment”. Source apportionment can be performed either using source-oriented approach, namely numerical modeling, or by using receptor oriented approaches.

In source oriented approach, data about emissions and parameters affecting dispersion and transport of pollutants are main inputs. Models, using this information, simulate dispersion and transport of pollutants and calculate ground level pollutant concentrations at a given receptor.

Models provide numerous advantages for source apportionment. They are relatively cheap, they do not require highly trained people and they can be run for future scenarios. The only disadvantage of numerical models in source apportionment is relatively high uncertainty in results.

Receptor oriented approach on the other hand uses concentrations of a pollutant or pollutants measured at the receptor and resolve these concentrations into their components. These techniques are collectively called “receptor models”. Receptor models are more expensive and require fairly trained people. However, since they are based on measurement results and do not involve assumptions, uncertainties of results are significantly lower than uncertainties in results of numerical models.

There is a variety of statistical tools that are used in receptor modeling. In this study ionic composition of precipitation collected at Antalya and Balıkesir stations, resolved into their components using a relatively new statistical tool, namely positive "matrix factorization".

Positive Matrix Factorization is the method which results give an idea about the possible pollution sources through separately grouped species at where they show similar increase and decrease rates at the same time.

Uncertainty values of each ion were inserted to the model with the concentration values because it is an important parameter of factor determination. The mathematical expression of the model was explained in Section 3.7.3, therefore it will not be repeated here.

Composition of factors in Antalya and Balıkesir PMF exercise are given in Tables 4.10 and 4.11, respectively. These so called "F-loading" values and other diagnostic parameters for Antalya and Balıkesir stations are depicted in Figure 4.32.

Table 4. 10 Ionic compositions calculated for Antalya data set (F-loadings are in mg L^{-1})

	Factor 1	Factor 2	Factor 3	Factor 4
SO_4^{2-}	0.03	0.09	0.98	0.17
NO_3^-	0.01	0.12	0.76	0.09
NH_4^+	0.00	0.41	0.00	0.04
Ca^{2+}	1.19	0.21	0.13	0.00
Na^+	0.06	0.02	0.01	0.30
Cl^-	0.005	0.009	0.12	0.39
Mg^{2+}	0.07	0.005	0.01	0.03
K^+	0.05	0.04	0.01	0.02

Table 4. 11 Ionic compositions calculated for Balıkesir data set (F-loadings are in mg L^{-1})

	Factor 1	Factor 2	Factor 3	Factor 4
SO_4^{2-}	0.70	0.28	0.25	2.71
NO_3^-	0.27	0.22	0.01	1.78
NH_4^+	0.00	0.66	0.05	0.00
Ca^{2+}	0.19	0.00	1.97	0.12
Na^+	0.61	0.05	0.15	0.01
Cl^-	0.93	0.00	0.00	0.17
Mg^{2+}	0.07	0,01	0.09	0.00
K^+	0.02	0.05	0.06	0.01

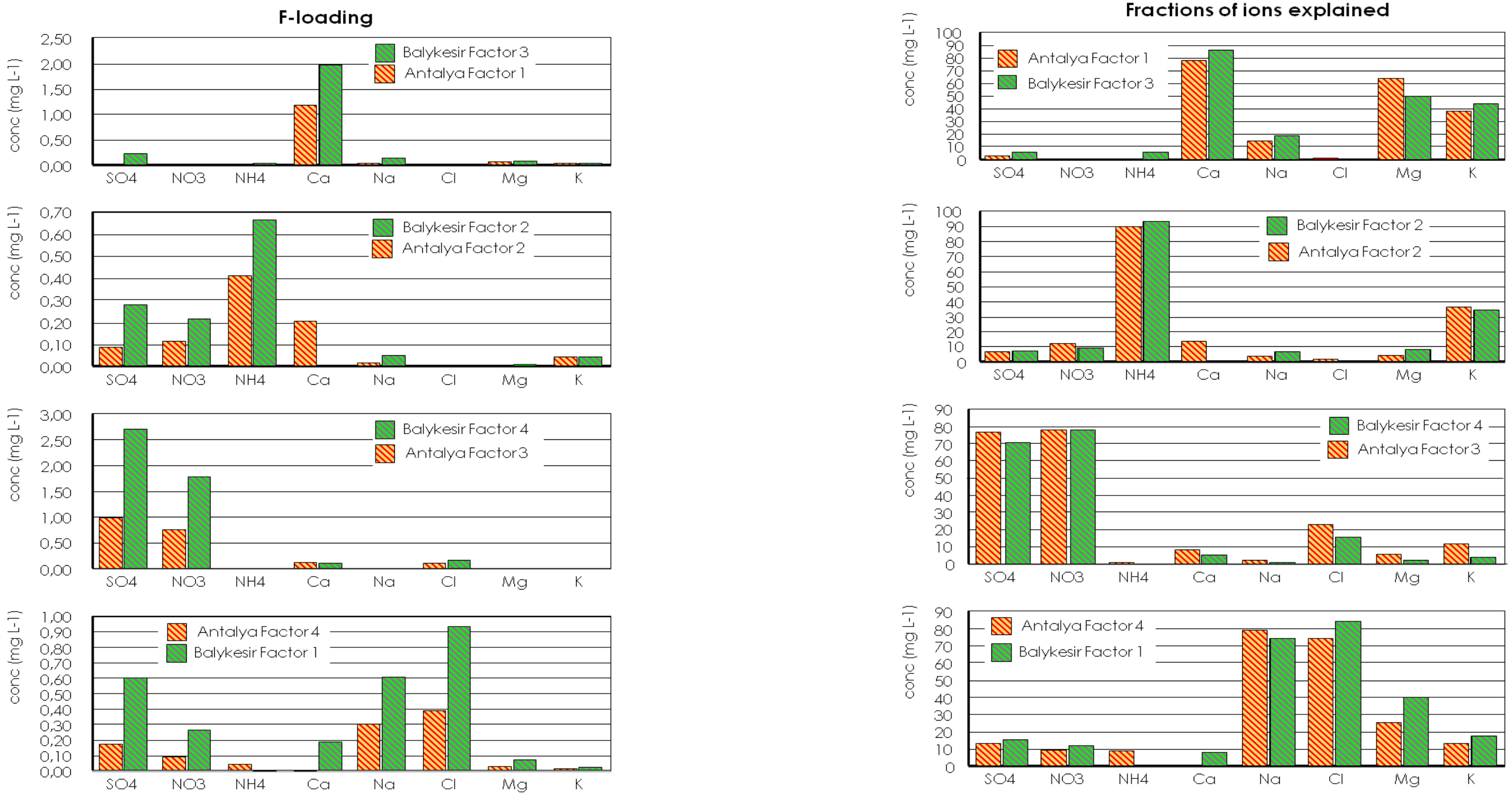


Figure 4. 33 F Loadings and Fractions of ions explained by each factor

Parameters plotted in these figures include F-loadings, fractional contributions of factors to each ion and monthly averages of G-scores. F-loadings are the concentrations of ions in each factor. Its unit is mg L^{-1}. Fractional contributions indicate percent contribution of each factor on ions. This parameter corresponds to "explained variance" in factor analysis. In our opinion fractional contribution plots are more informative than F-loading values in identifying types of sources making up each of the factors.

G-score is an output of the PMF code. It indicates the weight of each factor in each sample. It is a unitless parameter and when it is multiplied with an F-loading value, it gives concentration of the corresponding specie in that factor in that particular sample. Since seasonal variations of particles emitted from different sources are not the same, as discussed previously in manuscript, monthly average g-score values can be informative on the type source types affecting rain ionic-composition at Antalya or Balıkesir.

Positive matrix factorization exercise resulted in very similar four factors in Antalya and Balıkesir stations. However, although composition of factors was similar, their ordering was different. Factor 1 in Antalya PMF has high loading (F-loading) of Ca. However, it accounted for 80 % of the total concentration of Ca, and more than 60 % of the total concentration of Mg and approximately 30 % and 15 % of the total concentrations of K and Na, respectively. Since these are all crustal elements, Factor 1 in Antalya PMF was identified as "CRUSTAL" factor representing soil particles in atmosphere that are captured either by falling rain droplets or by cloud droplets through in-cloud processes. Earlier rain studies in our group reveled that crustal particles are scavenged mostly by below-cloud processes during rain events (Almomani et al., 1998; Kaya and Tuncel, 1997). Factor 1 has higher g-scores in summer season due to more extensive soil resuspension in summer months when the soil is dry.

Crustal factor in Antalya, in terms of composition, is identical with Factor 3 produced by Balıkesir PMF run. Although percent contribution of factor 3 on ions measured at Balıkesir station are slightly different from contributions found in Antalya PMF, elements contributed by this factor are identical. Consequently, Factor 3 in Balıkesir PMF study is also a crustal factor.

Factor 2 in Antalya PMF study has high loadings of NH_4^+ and Ca, and to a lesser extent SO_4^{2-} and NO_3^-. However, investigation of % of these ions accounted by Factor 2, shows that Factor 2 accounts for almost all of the measured NH_4^+ concentration. Concentrations of other ions, which also have high F-loading values in Factor 2, are accounted for by other factors, but not by factor 2. Consequently factor 2 in Antalya PMF study is identified as NH_4^+ factor. A factor consisted of NH_4^+ only was encountered in almost all factor analysis and PMF studies in Turkey and attributed to fertilizer use (Güllü et al., 2005; Doğan et al, 2010; 2008; Alagha et al., 2003). Synthetic fertilizers containing NH_4NO_3 and $(NH_4)_2SO_4$ are generally applied in late spring after spring rains ended to avoid washing out of fertilizers applied to the field. Some of these fertilizers are directly resuspended with soil and become NH_4NO_3 and $(NH_4)_2SO_4$ particles, which can be captured by clouds and rain droplets. Most of the fertilizer reduces and evaporate as NH_3. In the atmosphere NH_3 gradually converts to NH_4NO_3 and $(NH_4)_2SO_4$ through reactions with H_2SO_4 and HNO_3. These particles are again captured by cloud droplets and/or falling hydrometeors. This scenario explains higher g-scores found in summer months as shown in Figure 4.32.

This fertilizer factor found in Antalya PMF study corresponds to Factor 2 in Balıkesir PMF exercise. Composition of Factor 2 at Balıkesir is very similar to the composition of Factor 2 at Antalya. Hence, Factor 2 found at Balıkesir PMF study was also identified as “Fertilizer” factor.

Factor 3 at Antalya data set high F-loadings of SO_4^{2-} and NO_3^- ions. Approximately 90% of the measured concentrations of these two ions are also accounted for by factor 3. G-scores of factor 3 are higher in summer months. This seasonal pattern is similar to the monthly average concentrations of SO_4^{2-} and NO_3^- ions. Factor 3 at Antalya PMF study represent anthropogenic component in rain and it is named as "Long-range transport" factor. Similar long range transport factor was also identified in previous rain water studies in this group, where only ions were measured (as in this study) (Tuncer et al., 2001). When trace elements are also measured and included in the PMF study, anthropogenic factor is generally separated into more than one anthropogenic factor (Almomani et al., 1998; Alagha et al., 2003).

Long range transport factor in Antalya PMF study corresponds to Factor 4 at Balıkesir data set. Composition of the factor (F-loading values), fractions of ions accounted by the factor and monthly averages of g-scores are very similar. Thus Factor 4 in Balıkesir PMF studs is also named as long-range transport factor (or anthropogenic factor).

Factor 4 in Antalya PMF is a typical sea salt factor. This factor accounts for approximately 80% - 90% of the concentrations of Na and Cl. Concentrations of SO_4^{2-} ion is also relatively high in Factor 4, as sea salt accounts for 10% - 30% of SO_4^{2-} concentration in the eastern Mediterranean aerosol (Uzun et al., 1999). Monthly averages of g-scores of Factor 4 are high in winter months and low in summer. This seasonal pattern is due to more frequent storm activity which generates sea salt particles in winter. Factor 1 in Balıkesir PMF study is very similar to Factor 4 in Antalya and named also as "sea salt" factor.

Although factors found in Antalya and Balıkesir PMF studies are similar to each other, there may still be some differences between the two. Factors found in both studies are compared in Figure 4.32, to see if their compositions are truly identical.

It is clear from the figure that fractions of ions explained by factors are very similar in both Antalya and Balıkesir PMF results. However, there are some differences in factor compositions (F-loadings). Calcium concentration in Antalya crustal factor is a factor of 2 smaller than the Ca concentration in Balıkesir crustal factor. However, percentage of Ca^{2+} accounted for crustal factor is comparable in both locations. Percentages are approximately 80% in Antalya and 85% in Balıkesir. The same pattern is also observed in fertilizer and, long-range transport and sea salt factors. In all of these cases, concentrations of major contributors to factors are higher at Balıkesir PMF results, but fractions accounted by factors are comparable in both PMF studies.

Accuracy of PMF results were tested by comparing calculated concentrations of ions with their measured concentrations. Scatter plots of measured versus calculated concentrations of ions prepared for total ionic mass, SO_4^{2-}, NO_3^- and NH_4^+ concentrations are depicted in Figures 4.33 and 4.34 for Antalya and Balıkesir PMF studies, respectively.

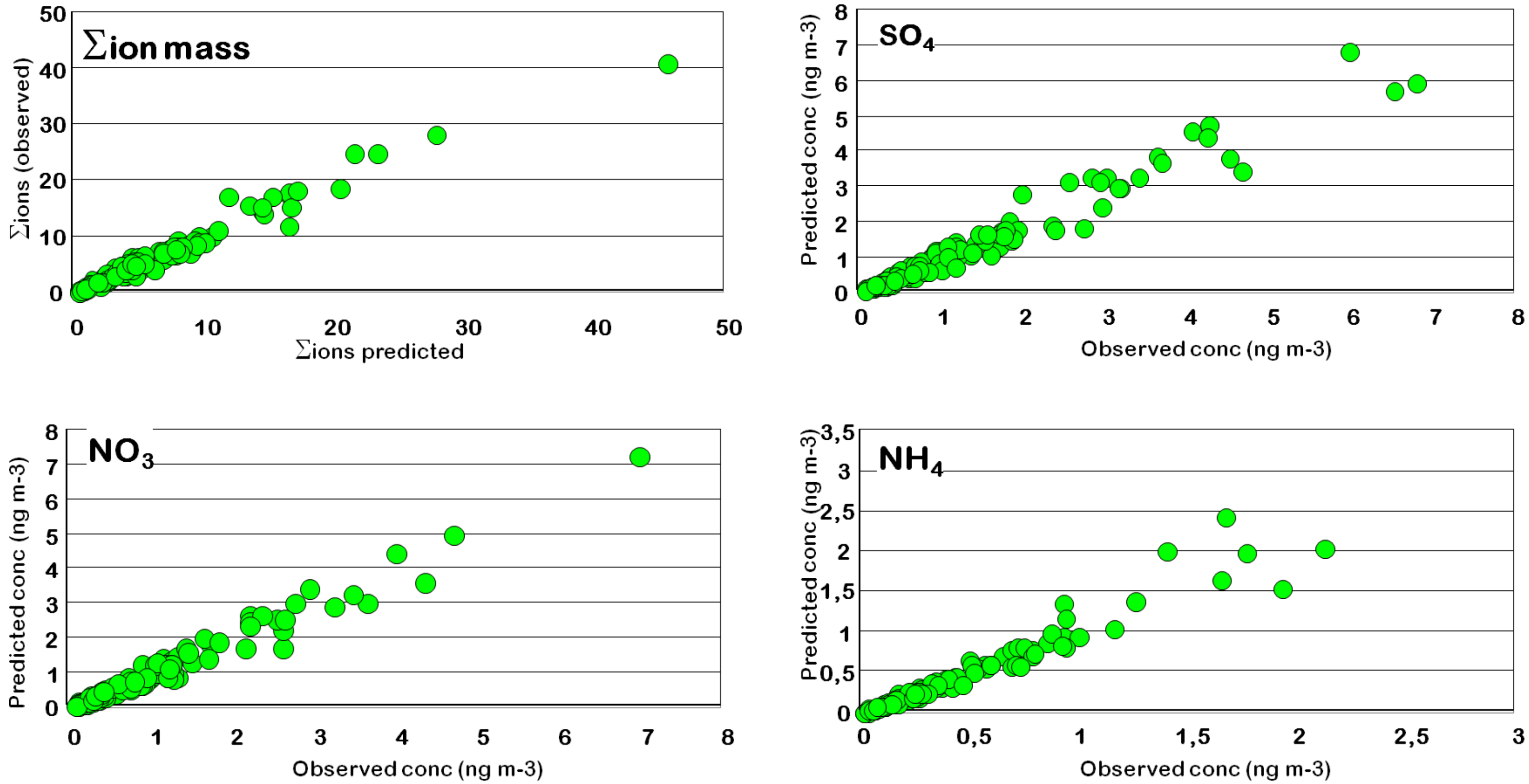


Figure 4. 34 Observed versus Predicted concentrations of ions for Antalya station

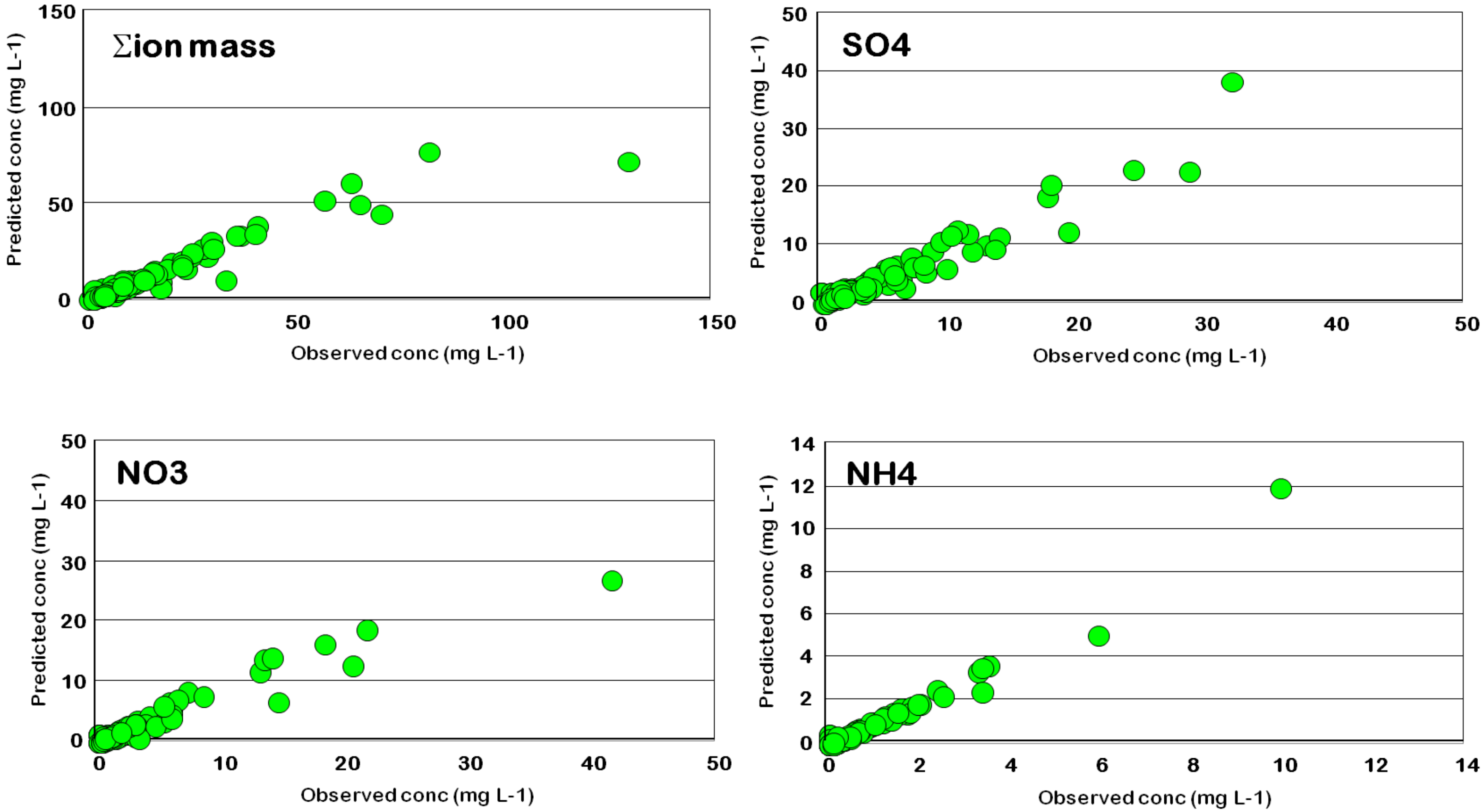


Figure 4. 35 Observed versus Predicted concentrations of ions for Balıkesir station

Concentrations of ions predicted by PMF model were calculated by multiplying factor loading of ions in each factor with corresponding g-score of that factor for a particular day. In this way, calculated concentrations in each sample are assigned in individual factors by summing concentrations of that ion.

The agreements between observed and predicted concentrations of ions are remarkable, not only for anthropogenic ions shown in the figure, but also for remaining ions as well. R^2 values for all ions in both stations are > 0.90 which corresponds to $p < 0.001$. Such high correlations between observed and predicted concentrations of ions indicate that PMF identified sources affecting composition of rain water fairly reliably in this study. However, it should also be noted that, one important reason for very good agreement between observed and calculated concentrations is the lack of trace elements that would increase resolution of the PMF study in the expense of degraded uncertainty. If other trace elements which are good markers for different sources were included in PMF exercise, then anthropogenic factor (LRT factor), which now includes all anthropogenic sources would split into several anthropogenic factors, increasing uncertainty in source estimates.

Table 4. 12 Contributions of factors to measured ion concentrations at Antalya Station

	Factor 1	Factor 2	Factor 3	Factor 4
SO_4^{2-}	2.56	6.88	77.32	13.24
NO_3^-	0.60	12.08	78.13	9.19
NH_4^+	0.00	89.99	0.96	9.05
Ca^{2+}	77.68	13.72	8.59	0.00
Na^+	14.51	4.14	2.12	79.23
Cl^-	0.89	1.65	23.11	74.35
Mg^{2+}	63.91	4.70	5.67	25.73
K^+	37.80	36.78	12.13	13.28

Table 4. 13 Contributions of factors to measured ion concentrations at Balıkesir Station

	Factor 1	Factor 2	Factor 3	Factor 4
SO_4^{2-}	15.7	7.2	6.4	70.6
NO_3^-	11.6	9.6	0.6	78.2
NH_4^+		93.61	6.39	
Ca^{2+}	8		87	5
Na^+	74	6,3	19.0	0.7
Cl^-	84.3			15.7
Mg^{2+}	40	7.8	50	2.0
K^+	17.3	35	44	4.1

Contributions of factors to ions are presented in Tables 4.12 and 4.13 for Antalya and Balıkesir stations, respectively. These tables are prepared by rearranging data and used to generate figures 4.35 and 4.36.

Approximately 80% of measured concentrations of SO_4^{2-} and NO_3^- ions are accounted for Long-range transport factor (which is factor 3 in Antalya and Factor 4 in Balıkesir PMF studies) in both stations. Most of the remaining SO_4^{2-} comes from sea salt in both stations. Approximately 10% of NO_3^- concentration comes from fertilizer factor, which is not surprising, because approximately 30% (by mass) of the fertilizer is NH_4NO_3, some of which can directly resuspend to atmosphere. Approximately 90% of the measured NH_4^+ concentration originates from fertilizer factor. 87% and 78% of Ca, 50% and 64% of Mg, 40% and 38% of K concentration are accounted for by crustal factor in Balıkesir and Antalya PMF studies, respectively. Sea salt factor contributed to 75% - 85% of measured Na and Cl concentrations in both stations. Most of the remaining Na and Cl are accounted for by crustal and long-range transport factors, respectively.

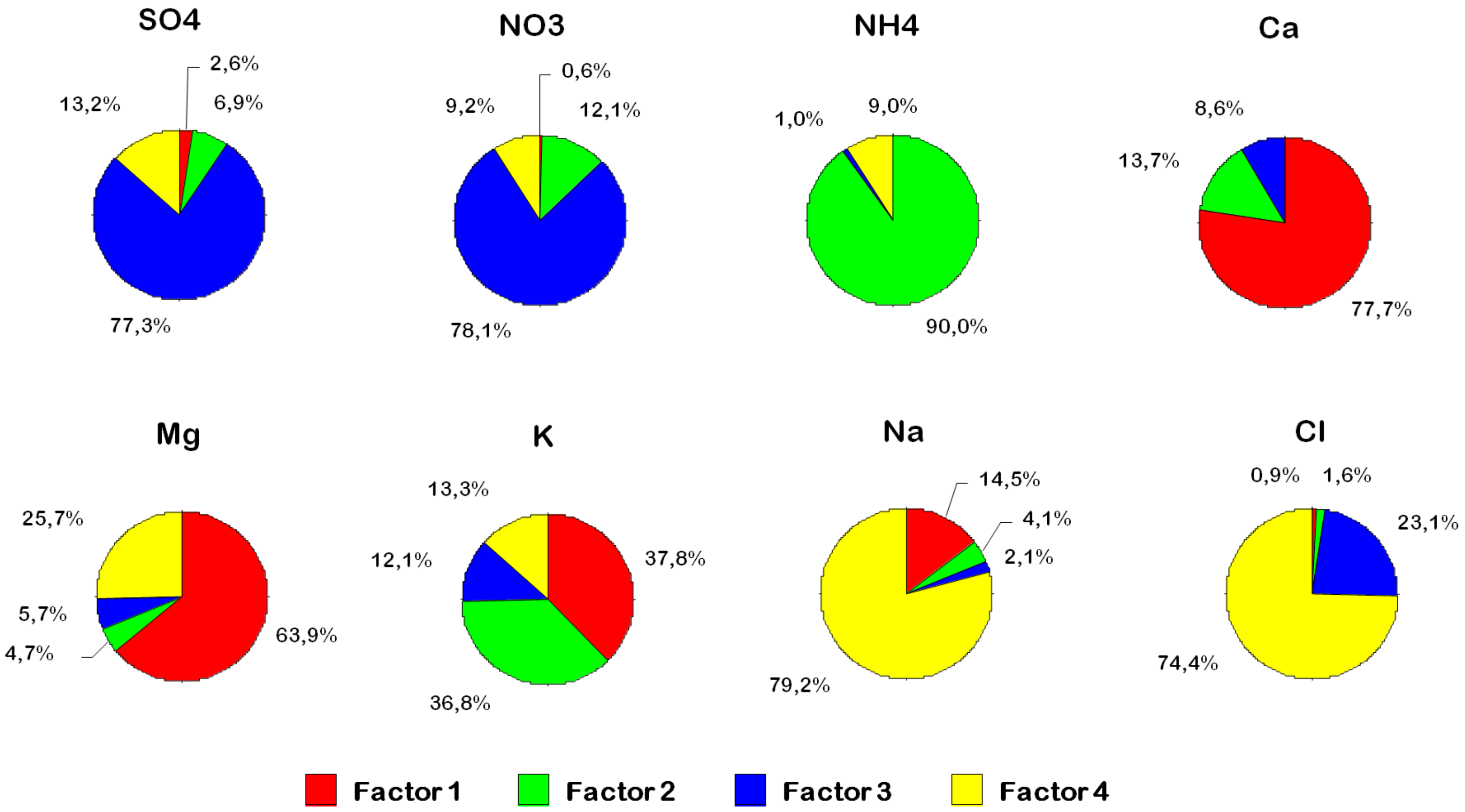


Figure 4. 36 Contributions of ions to each factor for Antalya station

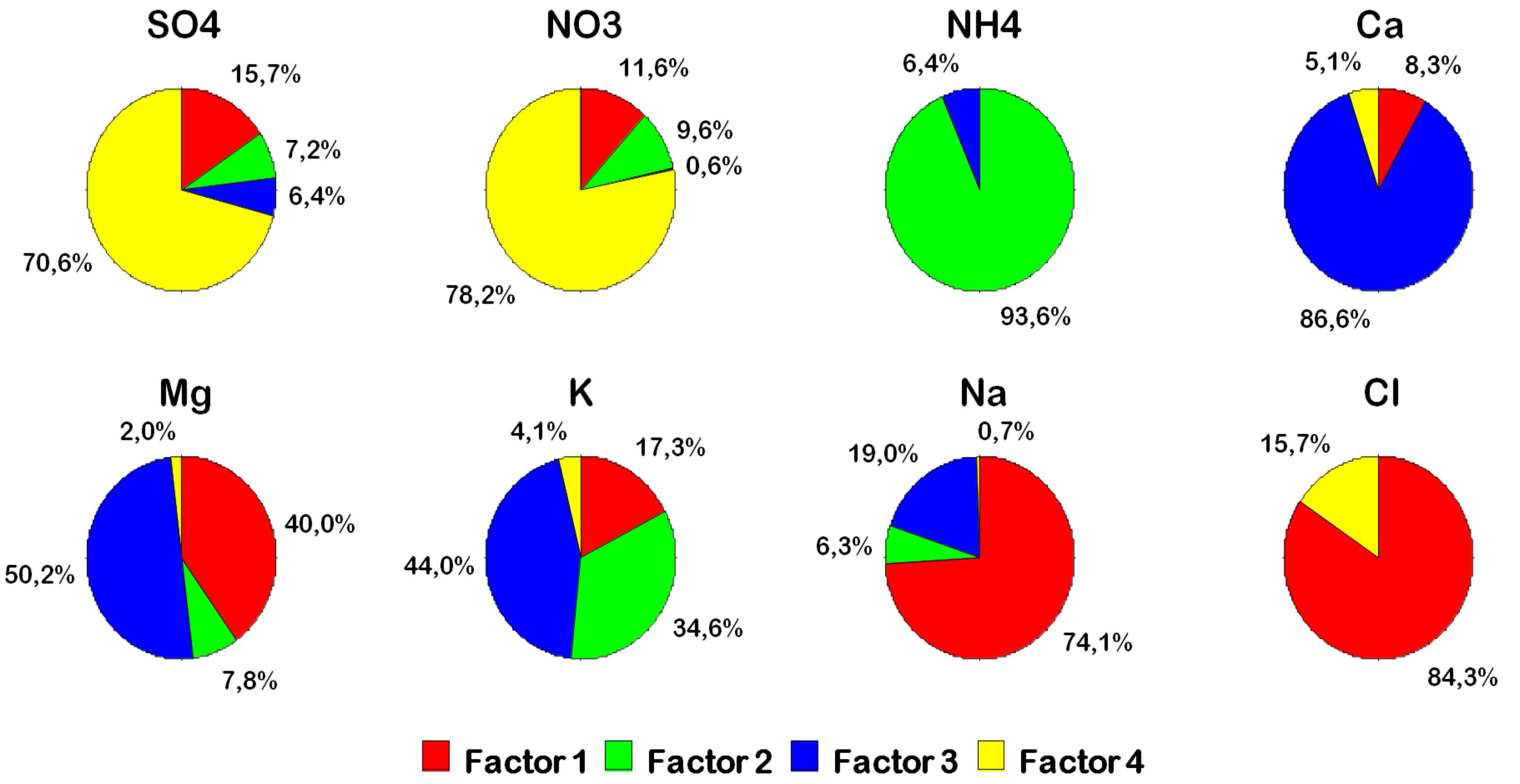


Figure 4. 37 Contributions of ions to each factor for Balıkesir station

One interesting result in both Antalya and Balıkesir PMF studies is high contribution of fertilizer source on measured K^+ concentrations. Approximately 40% of K^+ concentration comes from crustal factor in both stations, but more or less same percentage of K^+ concentration is accounted for by fertilizer factor. Since this is observed in both stations association of K^+ with fertilizer factor should be real. However, nature of such association is not clear.

CHAPTER 5

CONCLUSION

In this study, chemical composition of rainwater at three stations of General Directorate of Meteorology, located in Antalya, Balıkesir and Trabzon, was investigated. Rainwater samples were collected during different periods between years 2010 and 2013, and then analyzed for pH, and concentrations of Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, and SO_4^{2-} ions at the laboratory of General Directorate of Meteorology.

Volume weighted arithmetic mean values represent that anthropogenic ions, SO_4^{2-}, NO_3^-, and marine originated ions, Cl^- and Na^+ are highest in Trabzon and lowest in Antalya station. Crustal ions Ca^{2+} and Mg^{2+} are highest in Trabzon station and lowest in Balıkesir station. NH_4^+ concentration, on the other hand, is highest in Antalya station and lowest in Trabzon station.

In order to identify the ionic balance of samples, the ratio of sum of anions to sum of cations was calculated and the results were presented on a scatter graph. Sum of anion to sum of cation ratios were lower than 1.0 for all stations, which links to anion deficiency. This deficiency was attributed to unmeasured HCO_3^- concentration of the samples due to applied measurement techniques.

Contributions of individual ion masses to total ion mass were also calculated. The biggest portion belongs to SO_4^{2-}, NO_3^- and Ca^{2+} ions accounting around 60 % of the total measured ion mass. Contribution of other measured ions, Mg^{2+}, K^+, Na^+ and H^+, ranges between 9 % to 18 % percentages to total ion mass. At Antalya station, dominating ion is Ca^{2+} and followed by SO_4^{2-} and NO_3^- ions. At Balıkesir station, SO_4^{2-} ion is the dominating ion, and followed by NO_3^-, Cl^- and Ca^{2+} ions. Trabzon station's highest portion belongs to Ca^{2+} ion, and followed by SO_4^{2-}, NO_3^- ions.

Results showed that rainwater pH varies between 4.15 and 7.26 with average value of 5.96 at Antalya station, between 3.83 and 6.99 with average value of 5.43 at Balıkesir station, and between 5.55 and 7.62 with average value of 6.94 at Trabzon station. These results are very close to the widely accepted background pH of precipitation, 5.6. That means the sampling stations are under strong influence of alkaline particles. The main acidity causing ion is SO_4^{2-} ion produced from the SO_2 emissions, and the main neutralizing ion is Ca^{2+} coming from $CaCO_3$ emissions.

In order to monitor affects of meteorological factors to ion concentration, seasonal variations of SO_4^{2-}, NO_3^-, NH_4^+, Na^+ and Ca^{2+} ions were investigated. SO_4^{2-}, NO3-, NH_4^+ and Ca^{2+} ions show similar trend; their concentrations increase during dry season and decrease during wet season. Seasonal alteration of SO_4^{2-} and NO_3^- ions are parallel because their emission sources are similar. NH_4+ ion is both emitted from anthropogenic activities like SO_4^{2-} and NO_3^-, and agricultural activities. Agricultural activities also increase during dry season, which together explain its seasonal variation. Soil dust released from both regional geography and transported from Saharan desert are the main factors of the higher Ca^{2+} level during dry season.
Na+ ion concentration, on the contrary, is higher during wet season at all stations. Its major source is sea salt. Due to bubble bursting mechanism defined in section 4.4, its concentration is higher during wet season than dry season.

Annual and seasonal wet deposition fluxes were also calculated for measured data. Wet deposition flux of ion depends on the precipitation amount at the sampling area. Descending order of the annual average rainfall amounts of the sampling stations is Antalya-Trabzon-Balıkesir. Highest wet deposition flux of H^+ ion belongs to Balıkesir station. The lowest wet deposition flux of H^+ ion belongs to Trabzon station. Although wet deposition flux of SO_4^{2-} and NO_3^- ions are highest in Trabzon station, with high Ca^{2+} flux, most of the acidity is neutralized and that result was obtained.

Wet deposition flux for all stations in winter is higher than the values in summer. Although concentrations of SO_4^{2-}, NO_3^-, NH_4^+, and Ca^{2+} ions are high in dry season and low in wet season; due to high rain events that occur in winter, wet deposition fluxes are higher in winter than summer. Winter to summer flux ratios differ from station to station as the rainfall amount varies from winter to summer.

Flow climatology and subsequently wind sector analysis are the trajectory calculating methods applied in this study by using MapInfo software. With flow climatology analysis residence times of air mass on segments were calculated and distributed on a map. During three years between 2010-2012, grits that air mass spent its majority of time was calculated for Antalya, Balıkesir and Trabzon stations and those grits were represented different colors. The flow climatology analysis gives an idea about the regions from where pollutants can be transported. As a result, for Antalya station, Western part of Turkey, Greece, Bulgaria and some parts of Romania and Ukraine; for Balıkesir station, up to Southern part of Poland, Western part of Turkey, Greece and Ukraine; and for Trabzon station, Western parts of Turkey were the regions that air masses spent majority of their time.

Afterwards, by using wind sector analysis, each ion was individually assigned to one of the eight wind sectors; N, NE, E, SE, S, SW, W, NW. All three stations are generally surrounded by industrial countries in the west, northwest and north wind directions, and Saharan desert in the east and southeast wind directions.

Major findings of those trajectory statistical analyses are as follows: N, NE and NW are the sectors that have high concentrations of SO_4^{2-}, $NO_3^-$and NH_4^+, ions for both Antalya and Balıkesir stations. Moreover, while S, SE and SW sectors have high Ca^{2+} concentration for Antalya station, for Balıkesir station E, NE, N, NW and W sectors have the higher Ca^{2+} concentration. Na^{+} is a marine element coming from sea salt; therefore it is coming from S, SW and W sectors to Antalya station and NE sector to Balıkesir station.

The chemical composition of rain water in Antalya, Balıkesir and Trabzon were compared with similar previous studies in Turkey and other countries. Moreover, ion concentrations and wet deposition fluxes were compared with the European Monitoring and Evaluation Program (EMEP) database for same years with this study. As a result of the comparison, anthropogenic ions, SO_4^{2-}, NO_3^{-}, and soil originated ion Ca^{2+} concentrations are higher than Europe. Wet deposition fluxes, on the other hand, are not that high, because annual rainfall amounts in European countries are higher than Turkey.

The rain water samples collected at all stations were exposed to both anthropogenic and natural emissions. Those emission sources were classified into four factors by using Positive Matrix Factorization model. Antalya and Balıkesir stations both result in four same factors, but the orders are different than each other. Factor 1 for Antalya station represents the crustal factor caused by African desert dust and local soil. Crustal factor was defined with Factor 3 for Balıkesir station. Factor 2 both in Antalya Balıkesir stations represent agricultural factor emitted from fertilizer usage. Factor 3 for Antalya station and Factor 4 for Balıkesir station represent anthropogenic factor which is mainly caused by long range transport. Factor 4 for Antalya station and Factor 1 for Balıkesir station represent sea salt factor.

CHAPTER 6

RECOMMENDATIONS FOR FUTURE RESEARCH

Major ion composition, acidity of rain water was evaluated and potential source regions of measured ions were found. However trace elements were excluded to the study. In further stage, composition of trace elements should be investigated for the samples.

The PMF exercise provided useful information about type of sources affecting ionic composition of rainwater intercepted at Antalya and Balıkesir stations. Since more specific source markers, such as trace elements or organic compounds were not included in the PMF, all anthropogenic sources are compiled into one factor. Later this anthropogenic factor, which is referred to as “long-range transport” factor in the manuscript can be resolved into more than one source groups if more specific marker species can be measured in later studies.

As it was stated in previous sections, not enough samples can be collected from Trabzon station. Because of that reason, some statistical analyses cannot be applied to Trabzon station. Therefore the missing analyses should be applied to Trabzon station after collecting enough data.

The study duration is approximately 3 year for Antalya and Balıkesir stations. This duration is also not long enough to investigate the sampling sites and reach a decision for the emission sources.

Potential Source Contribution Function (PSCF), which is a method to identify the source regions of the emissions, cannot be performed to any station. Therefore, in order to identify the source regions clearly, sampling should be continued and more data should be collected.

In addition to that, more sampling stations can be helpful to make reasonable comparison.

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