THE SOURCES OF TRACE ELEMENTS AND ACID RAIN WHICH ARE COLLECTED BY SEQUENTIAL RAIN SAMPLER IN ISTANBUL

by

Nihan UYGUR

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

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

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October 2008

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M. S. Thesis - Environmental Engineering
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ABSTRACT

In this study, rain water chemical parameters including, pH, conductivity, heavy metals (Pb, Cu, Co, V Ni, Fe) of 60 wet and dry rain samples were measured in rain samples collected at Fatih University campus which is located between 41.04° longitude and 28.59° latitude in Istanbul Büyükçekmece watershed area between October 2007 and May 2008. Descriptive statistics; weighted averages, arithmetic means, standard deviations, medians and minimum-maximum values were calculated and discussed.

Wet and dry deposition samples were collected using home made wet only rain sampler that collect separately rain or snow events and dry deposition. Major heavy metals in rainwater and dry deposition were measured using Graphite Furnace Atomic Absorption Spectrometer (GFAAS) and Flame Atomic Absorbtion Spectrometer (FAAS). Ammonia (NH_4^+) concentrations in wet and dry deposition samples were measured using Nessler Colorimetric Method by spectrophotometer.

The rainwater average pH was found 6.79 which is not considered acidic. Obtained data were compared with similar other studies. The natural sources and crustal elements are locally produced around the study area, whereas the anthropogenic components are transported from remote sources. It was observed that human originated long range transports were effective in the formation of acid rain. Long range transport and its effects were investigated by HYSPLIT back trajectory model that was implemented on Google Earth.

The back trajectory analysis showed that some of the anthropogenic components were transported from various source regions from Europe and some near industrial cities which are located west of Turkey.

Keywords: Acid rain, pH, volume weighted average, H^+ ion concentration, back trajectory, heavy metal, Atomic Absorption Spectrophotometer

İSTANBUL'DA ARDIŞIK YAĞMUR ÖRNEKLEYİCİ İLE TOPLANAN YAĞMUR SUYUNDAKİ ESER ELEMENTLERİN VE ASİT YAĞMURUNUN KAYNAKLARI

Nihan UYGUR

Yüksek Lisans Tezi – Çevre Mühendisliği
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ÖZ

Bu çalışmada 01.10.2007-01.05.2008 sezonunda 41.04° boylam, 28.59° enlem koordinatları arasında yer alan Fatih Üniversitesi Kampus sınırları içinde toplanan 60 adet yaş ve kuru çökelme örneğinin pH, iletkenlik, ağır metal (Pb, Cu, Co, V Ni, Fe), katyon, ölçümleri yapılmıştır. Elde edilen bu değerlerin ağırlıklı ortalama, aritmetik ortalama, standart sapma, medyan, minimum ve maksimum değerleri elde edilmiştir.

Yaş ve kuru çökelme örnekleri, bu örneklerin ayrı ayrı toplandığı el yapımı otomatik ardışık yağmur örnekleyici ile toplanmıştır. Örneklerdeki ağır metaller Grafit Fırınlı Atomik Absorpsiyon (GFAAS) ve Alevli Atomik Absorbsiyon (FAAS) ile analiz edilmiş, NH_4^+ ise Nessler kolorimetre yöntemi ile analiz edilmiştir. Fatih Üniversitesi kampusünün de içinde bulunduğu Büyükçekmece İçme suyu havza alanında yapılan bu çalışmada yağmur suyunun ortalama pH değeri 6.79 olup, bu değer asidik değildir.

Bizim çalışmamızda elde ettiğimiz değerler yapılan diğer benzer çalışmalarla karşılaştırılmıştır. Doğal kaynaklı (toprak kaynaklı) elementler çalışma bölgesine yakın noktalarda üretilirken, antropojenik kirleticilerin uzak noktalardan taşındığı gözlemlenmiştir. Asit yağmuru oluşumunda özellikle insan kaynaklı uzun mesafeli taşınımların etkili olduğu saptanmıştır. Uzun mesafeli taşınımlar ve etkileri Google Earth desteği ile çalışan HYSPLIT geri yürünge modeli ile belirlenmiştir.

Geri yörünge analizleri antropojenik bileşenlerin bazılarının uzun mesafeli taşınımlarla Avrupa'nın değişik bölgelerinden taşındığını, bazılarının ise özellikle Türkiye'nin batısında yer alan endüstriyel şehirlerden geldiğini göstermiştir.

Anahtar Kelimeler: Asit yağmuru, pH, hacimsel ağırlıklı ortalama, H^+ iyon konsantrasyonu, geri yörünge, ağır metaller, Atomik Absorpsiyon Spektrofotometresi

DEDICATION

To my lovely family

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SYMBOL/ABBREVIATION

Pollution Standards Index (PSI)
Air Quality Index (AQI)
Ozone-Depleting Substances (ODS)
Chloroflorohydrocarbon Gases (CFC)
National Atmospheric Deposition Program (NADP)
Particulate Matter (PM)
Japan Environment Agency (JEA)
Soluble Fraction/Particulate Fraction (SF/PF)
Clean Air Act Amendments (CAAA)
National Acid Precipitation Assessment Program (NAPAP)
European Monitoring and Evaluation Programme (EMEP)
Programmable Logic Control (PLC)

CHAPTER 1

INTRODUCTION

1.1 AIR QUALITY AND AIR POLLUTION

Air pollution is a result of harmful chemicals, particulates or biological materials that effect human health and environmental system's balance. Recently there is an increasing interest about air pollution and its effect on the environmental systems and human health. CO, NO_x, SO_x, $PM_{10-2.5}$, O_3, Pb, and CFC (Chlorofluorohydrocarbons gases) are considered the most important air pollutants in urban atmosphere (Galloway et al., 1987).

Air pollution (natural or anthropogenic) is briefly defined as any gaseous or solid form of harmful substances which have effects on all life systems from the smallest to the biggest. On the other hand; they can danger our buildings especially its corrosion effects. Atmosphere and environment inter-related to each other. One of them can affect other one.

Harmful substances can be grouped in two parts namely, natural and anthropogenic sources. Natural sources contain volcanic emissions, forest fire, wind, erosion. On the other hand, anthropogenic sources are stack gases (house hold heating), industrial activities, traffic emission etc. Anthropogenic sources can be divided into two main parts; mobile sources and stationary sources (Krupa et al., 2002).

Natural sources can release into the atmosphere CO_2, CO, PM. CO_2 ratio in atmosphere is very sensible. A little of CO_2 can result in climate changes. Other important effects are concerning with green house gas effect.

Global warming is expected to occur as a result of increase of carbon dioxide and other greenhouse gases. When sunlight reach to the earth, great amount of the solar energy is absorbed by the earth surface, but some is reflected back to atmosphere.A natural layer of atmospheric gases absorb a portion of this reflected solar radiation, causing the earth's surface layer to be heated.

The greenhouse effect is a phenomenon whereby greenhouse gases, create a condition in the upper atmosphere causing a trapping of heat and leading to increased surface and lower troposphere temperatures. It shares this property with many other gases, the largest overall forcing on Earth coming from water vapor. Methane, (HFC) hydro fluorocarbons, (PFC) per fluorocarbons, (CFC) chlorofluorocarbons, NO_x, and ozone are effective other greenhouse gases (Lohse et al., 2008).

This effect has been agreed upon by scientists for about a century, and technological progress during this term have helped rise the breadth and depth of information relating to the phenomenon. A number of projects have also investigated the potential for long-term rising levels of atmospheric carbon dioxide to cause slight raises in the acidity of ocean waters and the possible effects of this on marine ecosystems.

There are very important environment and health effects of air pollutants in big cities particularly metropolitans likely Istanbul, Ankara, İzmir, Konya, Gaziantep in Turkey; New York, Hong Kong etc. in the world. Because of these cities are industrially developed, they are heavily populated and receive high rate of migration. High concentration levels can be observed for principal air pollutants (criteria pollutants) in the big cities. As a primary air pollution control strategy in metropolitan cities, fuel consumption should be decreased and shifted to prevalent use of natural gases or renewable sources. As a result of this action considerable reduction in SO_2 concentrations in Istanbul had been achieved during last decade (Karaca et al. 2005).

Regulations of air pollution and control are made by arrangement via the governments. Generally, there are accepted two types of regulations in the world. One of them is the National Ambient Air Quality Standards of that country and the International Ambient air Quality Standards to address whole world (Raddum and Skjelkvale, 2001).

In the 1960s, 70s, and 90s, the United States Congress enacted a series of Clean Air Acts which significantly strengthened regulation of air pollution. Each state of U.S.A, some European nations and finally the European Union followed these enterprises. The Clean Air Act places numerical limits on the concentrations of a basic group of air pollutants and provide reporting and enforcement mechanism (Avila, 1996).

Acidic precipitation is primarily caused by incorporation of anthropogenic SO_x, NO_x and other acid precursors. Neutralizing ingredients like carbonates, bicarbonates and ammonia, also influence the last acidity of deposition (Das et al., 2005).

Generally, rainwater is often more acidic due to the natural emissions of SO_2, NO_x, or organics. The typical pH values of acid rain comes from anthropogenic emissions are in the range of 3.5–5.0 (Menz and Seip, 2004).

When gaseous acid precursors NO_x and SO_x or their oxidation products of HNO_3 and H_2SO_4 dissolve in atmospheric water, they supply H^+ ions to the medium, consequently acidity increases and acid precursors turn into, NO_3^- and SO_4^{2-} anions (Alagha, 2000). If there isn't any pollution in the atmosphere, clean atmosphere pH is 5.6. Organic acids can also contribute to the acidity of rainwater, but this type of benefit was found to be insignificant in the Western Mediterranean (Ozsoy and Saydam, 2000).

Acid rain and atmospheric aerosols are considered to be typical environmental pollution affecting human health, resulting in the deterioration of monuments, and the acidification of lakes and soil and natural equilibrium (Spanos et al., 2002).

Also, there is a contribution of organic acid in acidity of rainwater. Generally these contributions have been ignored especially in urban atmosphere, where its contribution compared to strong acids is insignificant. On the other hand, as Keene et. al. (1983) indicated, week organic acids contributed 64% of free acidity and 63% of total acidity to precipitation in rural forest area during part of the 1981-1982 wet seasons at Katherine, Australia.

1.2 WET AND DRY DEPOSITION

Particulate Matter PM has a potential contrary health impact, making it necessary to control (Wu, et al., 2006). It can be divide into two part as a fine and course particles properties and potential health impacts of the particles sized between the dimension of 2.5 µm and 10 µm diameters are coarse and smaller particles 2.5 µm are fine.

Deposition is the process by which aerosol particles are collected or deposited themselves on surfaces, decreasing the concentration of the particles in the air. Deposition can be divided into two processes: dry and wet deposition process. The rate of deposition, or the deposition velocity, is related to particle size and type. Mechanisms for deposition can be effective for either very small or very large particles. This is because very small particles coagulate in few hours until they achieve larger diameter. Reaching a certain dimension they dont coagulate any more. This has a great influence on the quantity of PM present in the atmosphere (Aas et al., 2007).

Wet and dry deposition has been monitored on large scale in Europe and North America over the last hundred years. It has been shown to be the most important processes by which the airborne pollutants impact terrestrial and aquatic ecosystem.

1.2.1 Wet deposition

Wet deposition flow is conventionally calculated using the concentration measured in precipitation samples and the amount of precipitation recorded for each accumulation period (Sakata et al., 2008).

Rainout and washout are the two major mechanisms that transfer contaminant into rainwater. Rainout contains processes that take place in clouds. Washout is the important and effective mechanism that cleans up air pollutants between the cloud and the Earth’s surface (Pena et al., 2002).

1.2.2 Dry deposition

Dry deposition is caused by:

- Gravitational sedimentation: In this process, atmospheric and settle on the surface particles fall down due to gravitation.
- Interception: This is when small particles follow the design of fluid, but if they flow too close to an obstruction, they may collide on that surface and settle.
- Impaction: This is the process that occurs when small particles, act as an interface a bigger obstacle, are not able to follow the curved streamlines of the flow due to their inertia, so they hit or impact the droplet or the surface. The larger the masses of the small particles facing the big one, the greater the move another place from the flow streamline.
- Diffusion or Brownian motion: This is the process by which submicron aerosol particles move randomly due to collisions between gas molecules. Such as collisions may lead to further collisions with either obstacles or surfaces area.

1.3 RELATED STUDIES IN TURKEY

Istanbul: Tayanç and co-workers (Tayanç et al., 2000) has investigated composition of wet deposition samples that collected at four different regions of Istanbul, Topkapi, Bagcilar, Maltepe and Göztepe, during the period January 2001–May 2001. Akkoyunlu and Tayanç (2003) has collected bulk deposition samples together with wet deposition samples at only one station, Göztepe, during the period of January 2001–December 2001. During this study fifty four wet deposition samples and 21 bulk samples were collected.

Izmir: Wet and dry deposition samples were collected in Izmir especially near an industrial area on the Aegean coast of Turkey. Concentrations of major ions (Cl^-, SO_4^{2-}, H^+, Na^+, K^+, Ca^{2+} Mg^{2+} and NH_4^+ were determined. The pH of the precipitation, calculated from the volume weighted H^+ concentration as to be 5.6, indicating extensive neutralization of the acidity in the rain. Neutralization was found to be a regional process. The main base responsible for the neutralization of acidity was NH_3 come from fertilizers used in rural areas. The $CaCO_3$ from re-suspended soil accounts for 16% of the neutralized acidity. The annual wet deposition of ions was determined by two parameters, namely the precipitation amount and concentrations of ions in the precipitation. Precipitation amount accounted for approximately 70% of the annual wet deposition of ions in the Menemen region, whereas concentrations of ions in precipitation have only a minor influence (Odabasi et al., 2002; Muezzinoglu and Cizmecioglu, 1998).

In another study, the particulate sulfate dry deposition was measured using a smooth surrogate surface between September 2000 and June 2001 in Izmir, Turkey. Concurrently, ambient air samples were collected. Average particulate sulfate fluxes and ambient concentrations were 49.3±24.3 mg m^{-2} d^{-1} and 11.2±6.6 µg m^{-3}, respectively (Muezzinoglu and Cizmecioglu, 2006).

Mediterranean Region: Elemental and ionic composition of the eastern Mediterranean precipitation were in this study by Al-Momani et al., (1997) on the Mediterranean coast of Turkey between January 1992 and January 1994. Measured concentrations were comparable with the concentrations reported from other rural stations. Concentrations of elements and ions show strong short-term and well-defined long-term variations. Short-term variations are due to transport from different source areas whereas long-term (seasonal) variations are governed by the seasonal changes in the wet removal of particles during their transport from source areas to the eastern Mediterranean region

Samples from precipitation events collected at Erdemli during February 1996 to June 1997 were analyzed to determine their particulate aluminum content, in addition to pH and conductivity measurements. Backward air mass trajectories corresponding to the rainy days were analyzed to determine potential source regions of acidic and alkaline constituents transported to the Cilician Basin. Approximately 28% of the rain samples were found to be acidic and the trajectories associated with half of the acid precipitation events were from the Mediterranean Basin and the Balkan Peninsula, while the other half were from the Anatolian mainland and local sources. Rain samples were found to be alkaline 58%, with their trajectories originating from North Africa and the Middle East. As a result of its $CaCO_3$ content, mineral dust from these arid regions significantly increased the pH of rainwater (Gullu et al., 2000).

Major ions were analyzed in wet and dry deposition samples collected for 1992 whole year using daily and weekly sampling periods at the Eastern Mediterranean coast of Turkey. The dry deposition fluxes of marine and crustal ions were found to be higher than their corresponding wet deposition. However, wet deposition fluxes of ions with anthropogenic sources, such as SO_4^{2-} and NO_3^- were found to be higher than their dry deposition rates. The annual average pH of the precipitation was 5.17, with high variability in the observed values due to different source regions. High concentrations of SO_4^{2-} and NO_3^- measured in samples with high pH indicated extensive neutralization of acidity by alkaline species. Results suggest that more than 70% of the acidity has been neutralized by $CaCO_3$ which originate both from airborne local soil and dust transported from North Africa.

In another study, (Demirak et. al, 2006) chemical composition of the rainwater was investigated in Muğla from February to April 2002. The Yatağan Power Plant is located 30 km northwest of Muğla city. The values of pH and the concentrations of major ions (Ca^{2+}, Na^+, K^+, $SO^{2-}{}_4$, $NO^-{}_3$, $NH^+{}_4$) in the rainwater samples were analyzed. The pH varied from 4.5 to 7.7 with an average of 6.9 which was in alkaline range considering 5.6 as the neutral pH of cloud water with atmospheric CO_2 equilibrium. In the total 30 rain events, only two events were observed in acidic range (<5.6) which occurred after continuous rains. The equivalent concentration of components followed the order: $Ca^{2+} > SO^{2-}{}_4 > NH^+{}_4 > NO_3 > Na^+ > K^+ > H^+$. The volume-weighted mean (VWM) of the measured ionic sum was 371.62µeq/l. The ratio of between sum cat ions and sum anions (Σ cations /Σ anions) was 1.52 μeq/l. The alkaline components (Ca^{2+}, Na^+, K^+) contribute 52%, NH^+_4 8%, whereas, the contribution from the acidic components was relatively small (40%). The low concentrations of H^+ found in rainwater samples from Muğla suggest that an important portion of H_2SO_4 and HNO_3 have been neutralized by alkaline particles in the atmosphere. The dust-rich local and surrounding limestone environment might have caused the high concentration of Ca^{2+} in Muğla area. The relatively high concentration of NH^+_4 observed in Muğla was suspected to be related to agricultural activities in the region.

Ankara:

1-) Tuncel and Kaya, 1997 studied daily where wet only precipitation samples were collected over a two year period and were analyzed for SO_4^{2-} , NO_3^-, CI^-, NH_4, H^+, Ca, Mg, K, Na, AI, Cu, Cd, Cr, Zn, V and Ni. The wet deposition fluxes are the lowest among literature values, owing to small annual precipitation in the region. Although, annual average pH in precipitation is 4.7, episodic rain events with fairly low pH's were observed. Approximately half of the acidity in Ankara precipitation is neutralized in the winter season, while the acidity is completely neutralized by airborne soil particles that are rich in $CaCO_3$ in the summer precipitation. Crustal elements and ions have higher concentrations during summer season, while anthropogenic ions and elements did not show well-defined seasonal cycles.

2-) Topçu et al., 2002 studied chemical composition of rain during September 1994 and December 1996 that the chemical characteristics of rainfall and its seasonal variation at the EMEP (The Cooperative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe) station located in Cubuk, Ankara. The wet deposition samples collected were analyzed for pH, major ions concentrations and conductivity. Some major ions have seasonal behavior generally, maximum concentrations appeared in winter season or autumn, and minimum concentrations of wet deposition in spring or summer seasons. The average pH of rainwater samples was almost 6.3 due to neutralization. For 4% of the rain samples had a pH below 5.0 and about 15% of the total rainwater samples had a pH below 5.6 normally pH 5.6 though. This reflects strong inputs of alkaline species to rainwater samples in this location. There is a strong relationship between pH and other ions in summer time. But in winter, a weak relationship is found between SO_4^{2-}, NO_3^- , Na^+ and Mg^{2+} though. On the other hand, relationships between the conductivity and SO_4^{2-} concentration are stronger in summer than in winter.

Antalya: Concentrations of elements and ions measured in aerosol samples collected between March, 1992 and December, 1993 were investigated to understand temporal variability of elemental concentrations. Collected samples were analyzed by atomic absorption spectrometry, instrumental neutron activation analysis, ion chromatography and colorimetry for approximately 40 elements and major ionic species. Concentrations of elements were found to vary greatly on time scales ranging from days to seasons. Short-term variations in the concentrations of pollution-derived elements are explained by transport from source regions. Short-term variations in the concentrations of sea-salt and crustal elements, on the other hand, are due to the episodic nature of wind-induced particle generation mechanisms (Güllü et al,. 2000).

Erzurum: Seasonal variations in the chemical characteristics of wet and bulk deposition samples collected in Erzurum (Bayraktar and Turalioglu, 2005) were investigated for the period March 2002–January 2003. Major cations (Ca^{2+}, K^{+}, Mg^{2+}) and major anions (SO_4^{2-}; NO_3^-) were determined in bulk and wet deposition samples; pH was also measured in wet deposition. The average pH of the wet deposition at Erzurum was 6.6 due to extensive neutralization of the acidity. A strong relationship between pH and SO_4^{2-}concentrations was observed in all seasons; however, only a weak relationship was found between pH and NO_3^- on a seasonal basis, the correlation between Ca^{2+} and SO_4^{2-} concentrations was stronger in winter than in summer

Composition of wet deposition in Kaynarca, Turkey is studied by collecting precipitation samples during more than a 2-year period, August 1993–November 1995. Concentrations of the main cations Na^+, Mg^{2+}, Ca^{2+}, K^+, NH_4^+ and the main anions Cl^-, NO_3^- and SO_4^{2-} together with pH were studied. The average pH value at Kaynarca was near neutral, 5.59. Results indicated that SO_4^{2-} concentration in precipitation was very high, as was Ca^{2+}, neutralizing the acidity. Acidic wet deposition samples were generally obtained in winter. Enrichment factors for sea and soil indicate the strong effects of sea and soil, specifically limestone on the composition of precipitation. Non-sea salt fractions of SO_4^{2-} were found to range from 0.955 to 0.980, showing the effect of non-sea sources, especially emissions from fossil-fuel combustion, on the pH of samples. Trajectory analysis showed that cyclones originating from northwestern, central and eastern parts of Europe have generally high sulfate and nitrate concentrations and low pH (Okay et al., 2002).

1.4 ACID RAIN

Acid rain can be explained as: rainwater snow, fog, and other forms of precipitation containing those mild acidic solutions fall to the earth as "acid rain''.

Other important topic is the acidity of rain, which is important property of rainwater. Especially, the last pH values after a rain event is of particular important neutralization study which mainly indicate rainout. Precipitation chemistry is indicative of the changes in chemical composition of the atmosphere over time.

Acid precipitation does not responsible for all of the acidity that falls back to earth from pollutants. About half the acidity in the atmosphere falls back to the earth through dry deposition as gases and dry particles. The wind blows these acidic particles and gases which can adverse effect onto buildings, cars, homes, and trees. In some occurrence, acidic gases and particles can corrode the surfaces on which they settle. Dry deposited particles are once in a while washed from trees and other surfaces by storm events. When that happens, the acidified water runoff combined with the precipitation can create a mix that is more acidic than the precipitation alone.

Acid precipitation the smoke and fumes from burning fossil fuels rise into the atmosphere and combine with the moisture in the air to form. The important chemicals in air pollution that create acid deposition are sulfur dioxide and nitrogen oxides. Acid deposition usually forms high in the clouds where sulfur dioxide and nitrogen oxides respond with water, oxygen, and other oxidants.

Two decades ago it was there was acid deposition most of around the world. This is a very important topic worldwide because of its significant damage to terrestrial and aquatic systems and potential impacts (Galloway et al., 1987).

Rain events play an important role in scavenging soluble compounds from the atmosphere. A useful index, therefore, for the pollution level of a site and the cycling of material through the atmosphere would be the chemical composition of its rainwater (Morales et al., 1998). The composition of the rainwater depends on the local emissions, transportation of pollutants , pollution degree and drop size, which in turn influence the rainout (in-cloud scavenging) and the washout (below-cloud scavenging) (Migliavacca et al., 2005).

Acidic pollutants come from especially anthropogenic and human source. Namely major sources of acid rain are sulfur dioxide SO_2 and nitrogen oxides NO_x in the atmosphere. Power plants are the primary sources for SO_2 and NO_x gases. Because of the difficulty and costly in disposing these gases, they are often emitted into the atmosphere with little or no treatment. Suburban and urban environments and air quality can be effect Automobiles, trucks and buses are another sources of NO_x in (Zhang et al. 2007).

Great amount of SO_2 released from coal burning and NO_x from traffic emission (Ye et al., 2000).

In the US, electric power generation is by far the largest single source of SO_2 emissions accounting for approximately 67 percent of total SO_2 emissions and 22 percent of total annual NO_x emissions nationwide in 2002 (EPA, 2004).

The result of the fossil fuel's burning is significant amount of SO_2 mainly from coal combustion and NO_x gases give into atmosphere. The transport of gases is provided mainly by winds. The average local wind direction is a good indicator of the source regions of air, which contribute to pollutant loading. For the most part, differences in ion inputs between periods can be explained by rainfall input and the prevailing meteorological factors.

Significant part of these gases caught up by the clouds. When sulfur dioxide and nitrogen oxides gases and particles come in contact with water droplets in clouds, chemical reactions can occur, resulting in acid rain. This process called rainout and additional process is washout mix these acidic gases, liquids, and particles mix into rain drops and snowflakes and they are carried them to the ground (Alagha, 2000).

In recent years, acid rain has received global interest, especially in East Asia and European countries where a rapid industrialization and an economic growth have been observed.

Nowadays, in Europe has reduced deposition of air pollutants. Through the 1970s the emission of SO_2 and heavy metals increased, but during the last decade the emission of SO_2 has decreased by 30-70% in most of Western Europe (Avilla, 1996).

As a Japan heavy acidification of precipitation has been observed in winter at areas close to west coasts of the Japan Islands and is related to the long distance transportation of the acidic pollutants across the Sea of Japan (Hara et al., 1990).

Acid rain is important problem for East Asia, as a result of fast growing economy and increased fossil fuel emissions. Emission of acidic gases in this region is higher than that for Europe and North America. East Asia is the third largest in the world for the emission of SO_2 and NO_x. This situation was evaluated by the Japan Environment Agency (JEA).

1.4.1 Environmental Effect of Acid Rain

Acid rain is a serious environmental problem allover the world. It has adverse effects on different areas. These areas are aquatic ecosystem, terrestrial ecosystem, materials and human health.

A study of precipitation chemistry was initially developed in response to the adverse effects of acidic rain phenomenon on vegetation, human beings, animals, soil, water, fish and buildings (Raddum and Skjelkvale, 2001). They proved the possible adverse effects.

In addition to that, acid rain is also responsible for reduction of visibility and deterioration of historical structures especially by damaging the details on historic places or sculptures (Elsom, 1987; Bierwagen et al., 2003).

Acid rain changes in the leaching rates of nutrients from plant foliage and soil nutrients, acidification of lakes and rivers, effects on metabolism of organisms and corrosion of structures (Kelly et al., 1989).

In the atmosphere, SO_2, NO_x, and NH_3 may form secondary pollutants such as particles and nitrogen species that could react with organic compounds and contribute to ozone O_3 formation. The gases, particularly SO_2 and O_3, may cause vegetation damage. Corrosion of many materials increases with the SO_2 concentration in the atmosphere (Menz and Seip, 2004).

In the aquatic media it causes fish deaths and plant deaths in waters. It would be harmful to human beings if we eat these fish, drink these waters, and consume foods from these plants (Menz and Seip, 2004).

As (Elsom, 1987) indicates ,the impact of acid precipitation on aquatic terrestrial ecosystem depends not simply on the pH value of the precipitation, but also on the capability of lakes and soils to neutralize or buffer the acidic inputs of the precipitation. This ability to tie up the excess hydrogen ions introduced by acid precipitation is largely determined by the composition of the bedrock on which the lakes and soil form, with hard, impervious igneous or metamorphic bedrock giving rise to low calcium and magnesium content producing the most susceptible situation.

1.4.2 Adverse Effect of Acid Rain on Human Health

Current studies of atmospheric pollutants mainly in urban areas have been considered of greater importance due to their harmful effects on human health (Hontoria et al., 2003).

Experimental studies of acid rain have shown adverse effect on human health. Especially acid rain has mixed with surface water which are lake, river etc.

1.5 AIM OF THE STUDY

The aims of this study can be summarized as;

i) To determine chemical (ions and heavy metals) composition of wet dry deposition around the Büyükçekmece watershed area,

ii) Investigate heavy metals characteristic variations in terms of sources of atmospheric heavy metals.

iii) To investigate the acid rain’s acidity and it’s source.

iv) Determine the long-range transport of the pollutant via back trajectory.

CHAPTER 2

MATERIAL AND METHODS

2.1 SAMPLING LOCATION

Selection of the sampling site is an important and difficult step in determining the ambient air quality. The sampling location can be influenced by air mass originated from different regions with different degrees of pollutants. They can be separated into two parts then into, remote (long range transport) and local sources. One should keep in mind some important criteria that assist in judging about the selection of sampling location a long with influencing air masses. The sampling site should not be influenced directly by any anthropogenic pollution sources such as industrial facility, power plants, highways, near by organized industrial region etc. Sampling site location must be settled to 10 km from the nearest pollution sources.

On the other hand, sampling site must be representative for the sampling period which includes wet and dry samples. Sampling site must be suitable for periodically (weekly or every rain events) visit.

Another important point is security for sampling site. This site should be protected from thirdly parts and animals. Availability of electricity is another important criterion for choosing the sampling site.

Under these considerations, one precipitation station was established in November 2007 at suburban area of İstanbul, Turkey. It was located in the Büyükçekmece Lake Watershed Area, particularly at Fatih University Campus (41.0916º N, 28.6185º E). The sampling location is given in Figure 2.1.

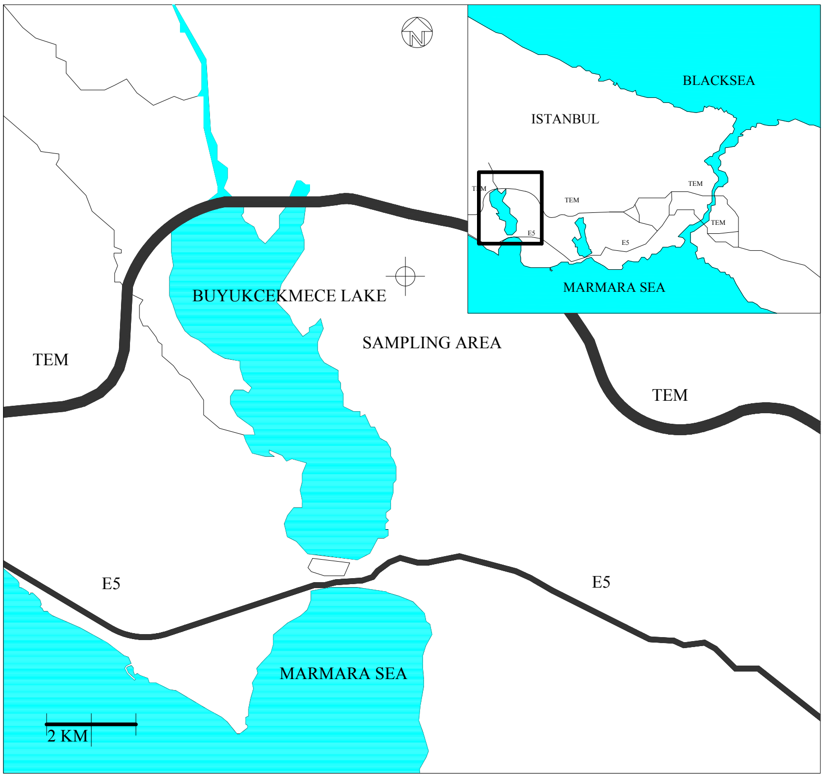

Figure 2.1 Sampling site location at the Fatih University Campus.

The Büyükçekmece Lake is a lagoon formed at a point where Karasu Stream descends from the north. Other streams that feed the lake include the Sarısu and Çakıl. The lake is separated from the sea by a coastal strip, over which the E-5 highway connecting Europe and Asia passes. The lake waters, whose link with the sea has been cut and which have therefore become fresh, are used to supply the city of İstanbul with water for drinking and other purposes. The lake’s shores are shallow and covered on the north and west by reeds and cattails. The lakes maximum depth does not exceed 4 m. Fish such as grey mullet, carp and bream are found in the lake (Başak, 2004).

2.2 COLLECTION OF WET AND DRY DEPOSITION SAMPLES

Atmospheric deposition occurs through both wet and dry processes. Wet deposition flux is conventionally calculated using the concentration measured in precipitation samples and the amount of precipitation recorded for each collection period. However, there are many uncertainties in the methods of quantifying dry deposition (Yi et al., 1997; Shah et al., 2007).

2.2.1. Sampling Device

Wet and dry deposition samples were collected via home made Wet Only Rain Sampler. Rain sampler's design and operating system allow separating of each sample which are dry and wet precipitation sample.

For the purpose of rainwater and dry deposition samples collection, Home made wet only rain samplers was designed and manufactured totally at Fatih University Air Pollution Laboratory and used at the sampling (Figure.2.2). This device is in agreement with device used for National Atmospheric Deposition Program (NADP) used in the USA. Sampler consist of rugged body, wet and dry buckets, electronic sensor, digital controlling panel and screen which shows rain events as wet and dry events. In addition to that, system contains Programmable Logic Control (PLC) which controls the sensors and motor of the cover.

All system's parts consist of aluminum and stainless steel. The two sampler buckets (13 L volume and 28 cm diameter) are made from HDPE (high density polyethylene). The samplers have a mobile cover which initiated by rain sensor which send a signal to the PLC which gives a signal to the motor to open the rain bucket. When rain stops the PLC unit sends a signal to the motor to close the rain collection bucket.

In order to collect wet rain samples, we followed the procedure described by Alagha (2000). The procedure is as follows: the collected rain samples measured for rain volume is being measured by means of deionized water prewashed graduated cylinder. A portion of the sample is used to measure pH and conductivity. The rest of the sample is being filtered through 0.45 µm Millipore Sartorious cellulose acetate filter and stored in a refrigerator at 4 °C prior to chemical analysis. Field blanks were prepared by washing its bucket will 100 ml of de-ionized water while the cover is opened. Every collected sample, a record sheet is filled out to record any activity during sampling (e.g. rain period, electric cut off, sample volume, pH).

Figure 2.2 a) Our homemade type Wet/Dry Rain sampler, b) PLC digital information part c) Rain sensor.

Dry deposition samples were collected by the same sampler which consists of HDPE dry bucket during the dry period. If there isn’t rainfall for one week period and the sampler’s dry bucket is always opened and the dry samplers obtained in certain periods by adding 100 ml water to the dry bucket.

2.2.2 pH and Conductivity Measurement

After rainfall event, the samples were immediately transported to the laboratory. Snow samples were collected in the sampling bucket and allowed to melt at the room temperature in the laboratory.

pH, volume and specific conductivity of the samples were determined immediately after collection of the samples. For pH measurement pH meter equipped with a combination glass electrode was used (sper scientific ®) Calibration was always carried out before measurement using standards buffer solutions of pH 4.00 and 7.00 (Al-Khashman, 2005). The samples was filtered using 0.45 µm cellulose acetate filter and then they were stored in Nalgene bottles at 4 °C Nalgene bottles and funnels were properly washed with deionized water and HNO_3, and then rinsed with deionized water and dried before use. Then the samples were given an ID number and stored 4 °C. Each sample was kept in the refrigerator at 4ºC until analysis.

2.3. INSTRUMENTATION AND ANALYSIS TECHNIQUES

Rainwater composition was elucidated by the determination of major and trace ions using different instruments including, Atomic Absorption Spectrometer (AAS), Ion Chromatography (IC) and VIS-Spectrometer. For the determinations of major anions like chloride, sulfate and nitrate IC is used, for the determination of ammonium ion a visible spectrometer was used and for major and trace metals AAS was used. The analytical techniques used are given in Table 2.1.

Table 2.1 Analytical Techniques Used in Elucidating Rain Composition.

Parameter measured	**Analytical technique**
H^+	Sper Scientific® pH meter
NH_4^+	Spectrophotometer (Nessler’s)
Conductivity	Conductivity meter WTW
Ca, Na ,K , Mg and Al	Varian FS 240 FAAS
Pb, Ni, Cr, Cu, Co, Fe, and V	Varian GTA 120 GFAAS

2.3.1 Major and Trace Metal Analysis Methods

Graphite Furnace Atomic Absorption Spectrometer (GF-AAS) and Flame Atomic Absorption Spectrometer (FAAS) techniques were used for trace and major element analysis. Almost fifteen element’s concentrations were measurement via these techniques.

Graphite Furnace Atomic Absorption Spectrometry (GFAAS) method has long been the preferred analytical method. These techniques are used for the routine determination of trace metals in environmental and biological samples owing to it’s reliability, sensitivity, low detection limits and relatively low cost (Udas et al., 2000, Bettinelli et al., 2000).

GFAAS is very sensitive technique and trace elements with concentrations at ppb levels can be determined accurately (Alagha, 2000).

In this study, Varian GTA 120 Model along with GTA 120 unit, graphite furnace atomic absorption spectrometer was used to determine the concentrations of trace elements. The recommended parameters that used in this study are given in the below table.

Table 2.2 Recommended and Optimized Parameters for GFAAS Technique

	Co	**Pb**	**Ni**	**Cr**	**Cu**	**Fe**	**V**
λ, nm	240.7	217.	232	357.9	324.8	248.3	318.5
Slit width	0.2	1	0.2	0.2	0.5	0.2	0.2
Inject Vol. (ul)	20	40	40	20	12	40	20
Lamp Curr.	7	5	4	7	10	15	20

The concentration of NH_4^+ was determined spectrophotometrically using Nessler methods (Al-Momani, 2003). Ammonium ion was determined with Jasco V-530 UV-Vis Spectrophotometer.

Firstly was added Nessler Reagent which is alkaline mixture of mercuric and potassium iodide (K_2HgI_4) that produces yellow to brown color with ammonia. The ammonia amount depends on samples color after the Nessler reagent is added.

Quartz cells were used for measurement with path length was 1 cm. Each measurement was made at 425 nm wavelength.

2.4 FIELD AND LABORATORY BLANK

To be sure that there is not any significant contamination during the sampling procedure or treatment of the samples blanks were collected. Four field blanks and one laboratory blank were used for this goal.

2.4.1 Detection Limits

The detection limit (DL) for the rain is calculated to be three times the standard deviation of the blank results, as given in Equation 2.1.

$$DL=3,0xS_b \qquad (2.1)$$

S_b = Standard deviation

Descriptive statistics were calculated using SPSS software. Some basic statistical methods were used to evaluate the relationships of the elements and to define their possible sources.

CHAPTER 3

RESULT AND DISCUSSION

3.1. BASIC STATISTIC

Seasonal variations in the chemical characteristics of wet and dry deposition samples collected at Fatih University Campus were investigated for the period October 2007–June 2008. During this study, 60 precipitation samples were collected by home made automatic wet only rain sampler.

In order to understand the seasonal variability in chemical composition of wet atmospheric precipitation, the precipitation samples were collected for the period of autumn, winter and spring from 2007 to 2008 in Büyükçekmece watershed area, Istanbul. All the rainwater samples were analyzed for pH, conductivity, NH_4^+, Na, K, Ca, Mg, Cr, Co, Cu, Al, Ba, Mn, Pb, Ni and V concentration.

3.2. SOLUBLE FRACTION SUMMARY STATISTICS

During 07.11.2007-05.05.2008 autumn-spring, this study 60 wet and dry precipitation samples were collected at Fatih University Campus where located in Büyükçekmece Watershed Area. The calculated statistical parameters are average, minimum, maximum concentrations, standard deviation, coefficient of variation (COV) and median values of the samples. Summary Statistics were shown in Table 3.1.

Al and Fe follow Normal Distribution with low Skewness and Kurtosis values. The other elements have high Skewness and Kurtosis values, which indicate other distribution patterns than normal. The highest concentration is observed for Al and Fe, which are mainly lithophilic elements. Whereas, the lowest concentration was for cobalt.

Hydrogen ion concentration has an average concentration of 8.85 mg/L (average pH = 6.8) with lowest and highest values of 4.3 and 9.2 respectively. This indicates that the rainwater is not acidic with some possible acidic events. For ammonia ion, except 2 extremely low values, the values measured in this area are lower than 1 mg/L and possibly indicating that no nearby sources.

Average volume weighted pH value is 6.8. For each season, the averaged pH values in time scale are 6.25, 6.03, and 7.8. According to these values, the highest pH value was observed during the later part of the study (summer) and the minimum acidic rain events were observed during the middle part of the study (from end of the 2007 winter to 2008 spring).

Table 3.1 Summary Statistic of Total Composition.

	Al	**Ca**	**Co**	**Cond.**	**Cr**	**Cu**	**Fe**	**H**	**K**	**Mg**	**Na**	**NH_4**	**Ni**	**Pb**	**pH**	**V**
Count	59	59	59	59	59	59	59	59	59	59	59	59	59	59	59	59
Average	7,66	0,66	0,32	24,2	0,58	1,45	2,75	3,68	0,15	0,11	1,42	0,20	0,77	1,47	6,96	6,63
Std. Dev.	4,75	0,84	0,67	21,5	0,74	2,10	3,31	9,73	0,33	0,19	2,55	0,140	1,01	2,68	1,25	5,84
COV	62,0%	128%	211%	88,7%	127%	145%	120%	264 %	222%	179 %	179%	69,5%	130%	183%	18,2%	88,1%
Minimum	0,78	0,03	0,01	1,00	0,04	0,03	0,06	0,001	0,003	0,004	0,011	0,0	0,05	0,01	4,3	0,01
Maximum	16,1	3,58	4,26	109,	4,05	13,3	15,4	50,1	1,61	1,34	16,4	0,68	6,5	11,1	9,26	28,7
Range	15,3	3,55	4,25	108	4,01	13,3	15,3	50,1	1,61	1,34	16,34	0,68	6,45	11,1	4,96	28,7
Skewness	0,117	5,82	13,3	6,68	8,61	11,9	5,79	10,7	10,4	16,9	12,6	3,56	11,6	7,84	-1,36	6,94
Kurtosis	-2,50	4,51	33,6	7,44	14,3	27,7	4,99	18,9	17,2	51,8	31,8	2,27	28,2	8,60	-0,97	9,00

3.3. SEASONAL VARIATION IN RAINWATER

In order to observation seasonal differences in wet and dry deposition samples, time series of the measured elements can be investigated. The period of the sampling campaign is not a complete 1-year study, only three seasons were observed, while four seasons are available in Turkey during one year. We did not extend our study in to the last autumn season, due to some technical problems. Some values like pH has sharp fluctuations during three seasons. Similarly, some other parameters also fluctuated during the study period. These fluctuations need a special attention, because they indicate a significant seasonality in data set. We simply created time-plot series to evaluate seasonal behaviors.

The time series plots of measured parameters are shown in Figure 3.1, Figure 3.2, Figure 3.3, Figure 3.4, Figure 3.5, and Figure 3.6. In these figures, parameters which have similar trends and magnitudes were grouped and illustrated in the same graphs.

In Figure 3.1, the seasonal variations of ammonia were given. It can be clearly seen that there is not a typical seasonality in this parameter. On the other hand, some sharp decreases were observed at the latter part (during summer 2008 period) of the study.

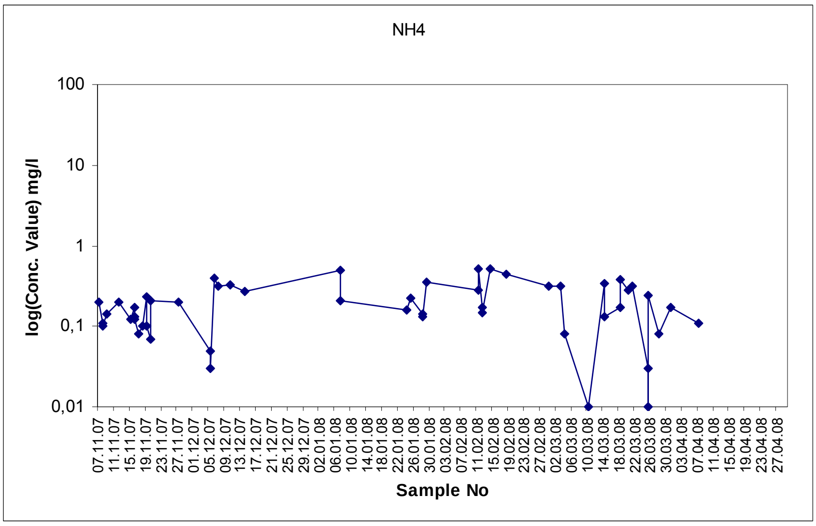

Figure 3.1 Seasonal variation of NH_4^+

In Figure 3.2, lead and nickel show have a similar pattern, which indicates that they are probably produced or carried to the sampling site by the same mechanism during study period. The seasonality of both elements can not be clearly seen in this figure.

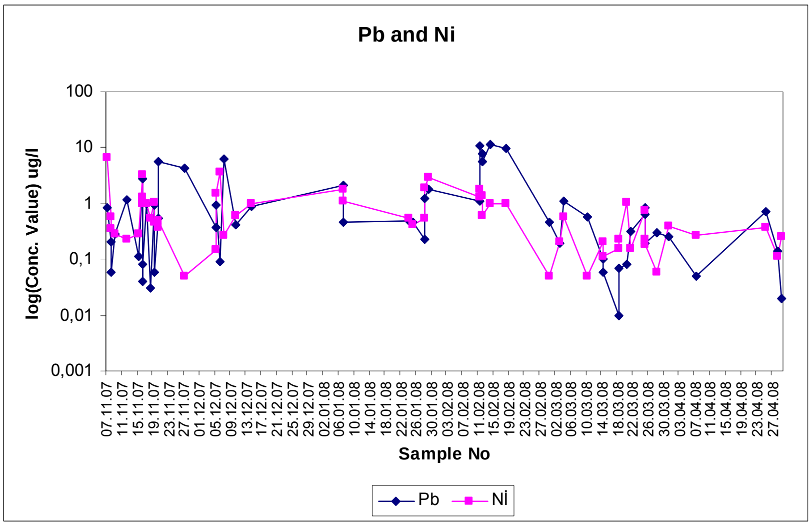

Figure 3.2 Seasonal variation of Pb and Ni concentrations.

In Figure 3.3, time series of the Na and K were given. Sodium and potassium have not similar trends but we gave them in same chart because, their magnitudes are in the same level. Both of these elements have also not any seasonality. The different behavior of Na and K in rainwater samples may indicate different generation mechanism that affects their concentrations.

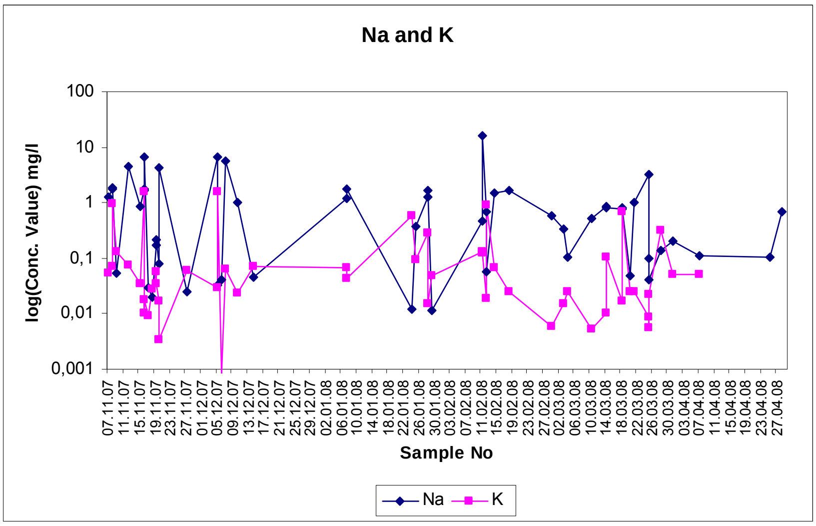

Figure 3.3 Seasonal variation of K and Na concentrations.

Calcium and magnesium were groped and their time series were given in Figure 3.4. These elements have very similar trends. They are known as typical crustal elements and their neutralizing effects on rain samples are well known (Alagha and Tuncel, 2003). Figure 3.4 clearly show us that, both of the elements are generated from common sources and they are mixed into rainwater under similar conditions showing similar behaviors.

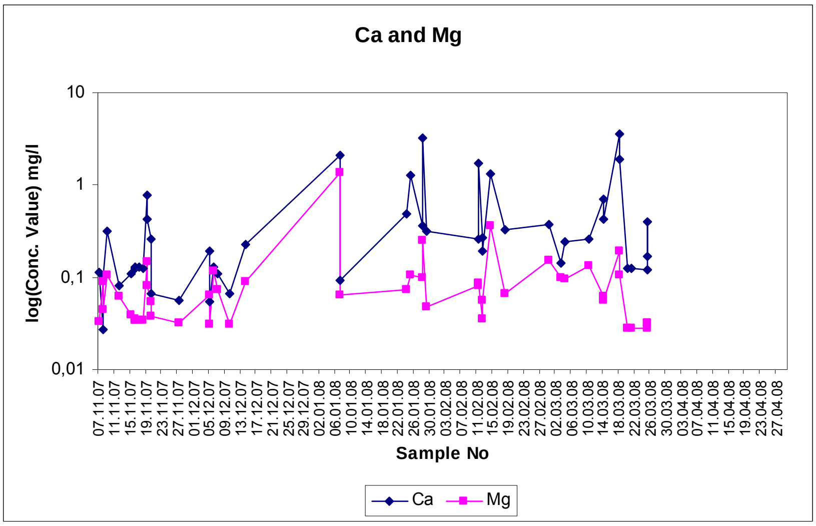

Figure 3.4 Seasonal variation of Ca and Mg concentrations.

The acidity of the samples are characterized by the pH parameter. The time series of the measured pH values during study period was given in Figure 3.5. Visually, it is seen that it is not easy to talk about a seasonal trend in the graph. It should be not that in the middle part of the study (from end of the 2007 winter to 2008 spring) the pH trend is nearly steady. At the latter part of study, the acidity of the samples were increased and became steady with little fluctuations. This indicates that pH is increased by some summer time activities. Some very low pH values indicating serious acidity (lower than < 5) were observed during 2007 winter. On the other hand, very high pH values (tree episodes) were also measured in the rain samples higher than 8.5.

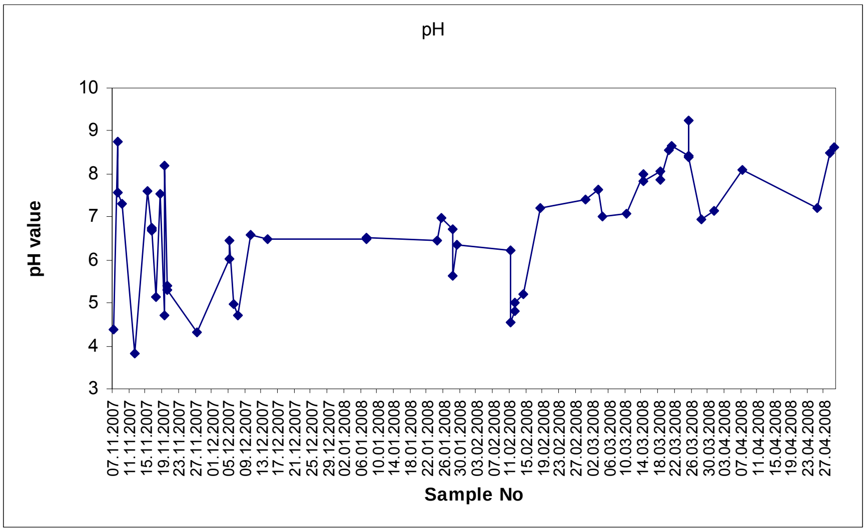

Figure 3.5 Seasonal variation of pH.

On the discussion of acidity of the rain samples, it can be better to extend the discussion on hydrogen ion concentrations. We simply calculated H^+ concentrations by using measured pH values and their monthly averages were given on Figure 3.6. On February 2007, the maximum average H^+ concentration were observed, while the concentrations of March, April and may (2008) were minimum. It can be clearly said that during the latte part of this study, the rain acidity was neutralized very effectively by crustal originated Ca and Mg cautions.

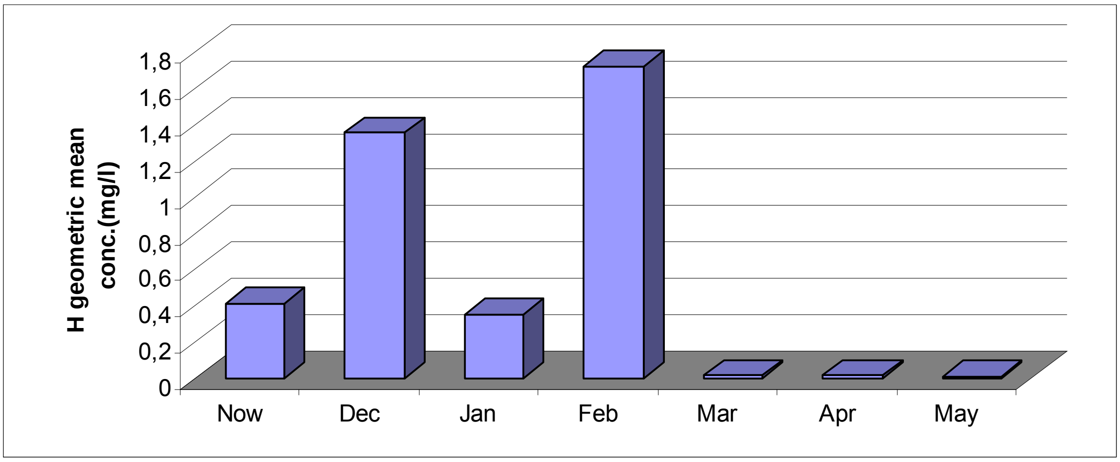

Figure 3.6 Monthly Change of Hydrogen Ion Concentration in Rainwater.

Lastly, the conductivity data was illustrated in the Figure 3.7. the data has very sharp fluctuations but the general trend is not follow a seasonal behavior.

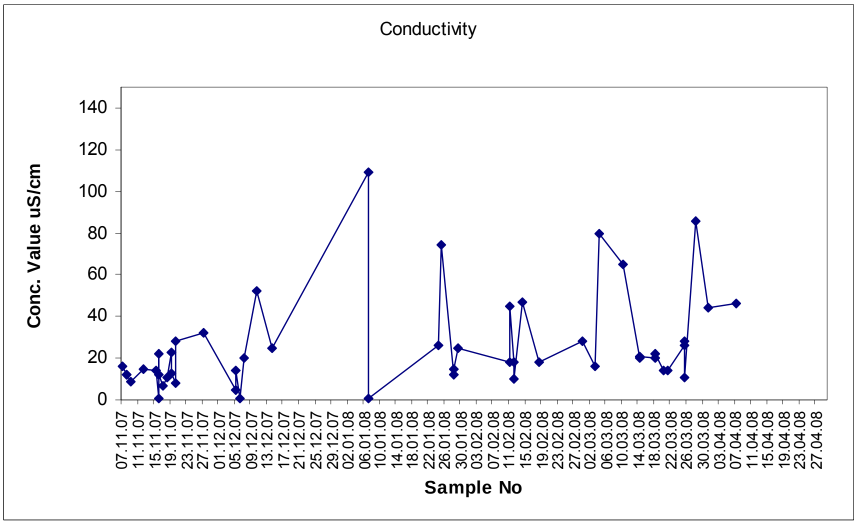

Figure 3.7 Time series plot of Conductivity.

In order to clarify the season behaviors of the measured parameters there is need for additional research efforts. Seasonal average values of each measured parameters are calculated and illustrated on Figure 3.8.

Figure 3.8 Seasonal average values of measured parameters.

In Figure 3.8, Seasonal differences can be seen. Conductivity, ammonia, K, Fe, Cu, Na, Al, Mg, Ni, Cr and Pb had highest seasonal average concentrations during winter time. Their increased wintertime concentrations can be related to anthropogenic emissions and other wintertime related meteorological conditions. However, some crustal elements, Al, Ca, Mg and Fe, were characterized by higher wintertime averaged values. This is inserting, because it is well known that the concentrations of crustal originated elements might having be decreased atmospheric concentrations during winter season due to surface wetness. In this point, the value of seasonal averages is under question, because there is not an equal distribution within the seasonal groups. Most of the samples were collected during winter (20) and autumn (16) samples while spring (7) samples are significantly lower than this period. Limited number of samples can be representative of seasonal behaviors. This may be one of the logical but not an emission related explanation of the situation. This point needs further investigations.

Calcium is the only element having higher springtime average concentration. This is a typical crustal element, and the possible sources of this element are some natural activities. On this point, it should be noted that, approximately 10 km far from the sampling site, there are some calcite mines, which are providing raw materials for the cement factory that is located about 7 km far from the sampling site. Currently, we don’t have detailed information about the seasonal activities of the mines, but the cement factory is working continuously during all the seasons. Springtime meteorological factors, especially wind direction, and the local and regional back trajectories of the rain clouds, can be the most important factors which is responsible of the calcium enriched precipitation events. Some detailed investigation focusing on the back trajectory analysis is given in the following parts.

Lastly, during autumn period, average value of the received amount of rainwater and is hydrogen ion concentrations are higher than the other parameters. The study region was received longer and some times heavy rain events during autumn season (2007) than the following seasons. A clearly, the acidity of the rain events are higher during that season.

3.4 WET DEPOSITIONS

Especially in arid regions or arid seasons like summer time, the water resources can be shortened. Under such conditions, the rain chemistry will became very important for surface water reservoirs. Büyükçekmece Lake is one of the must important water resources in Istanbul. During last two years, we had a very limited amount of precipitation events in Istanbul. Because of the lack of rain, Büyükçekmece Lake water level decreased to 10 %. After an arid period, when a plenty amount of water received, the chemical characteristics of a lake completely governed by the rain chemistry.

In this part, the wet deposition amounts per square meter for the measured elements are calculated and given in Figure 3.9.

Aluminum and iron are the most enriched elements and they were deposited over than 100 mg and 40 mg per meter square area, respectively. Calcium and cupper are the following elements. They were deposited on the surfaces aver than 20 mg per meter square.

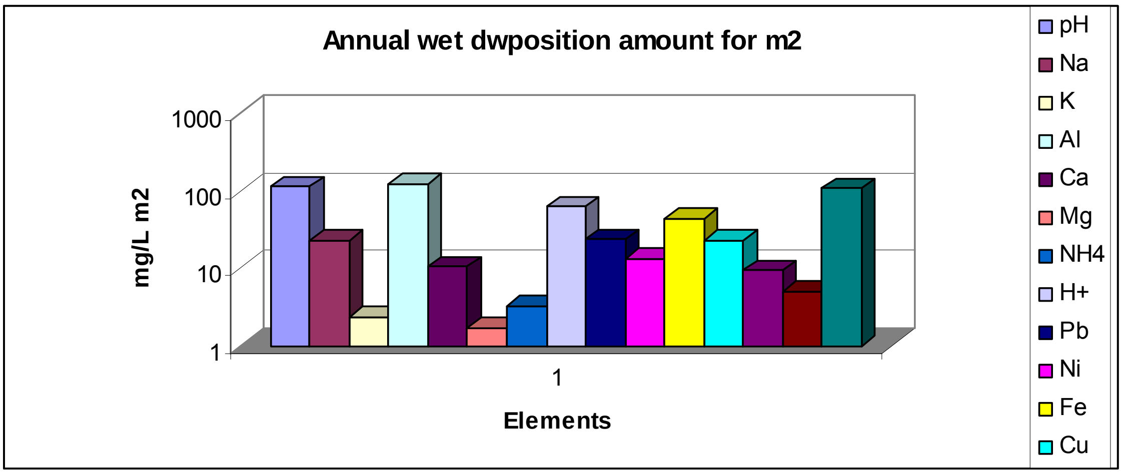

Figure 3.9 Wet deposition amounts during study per meter square.

3.5 CORRELATION ANALYSIS

In a correlation analysis, generally, P value is used as an indicator, which is the statistical importance of the estimate of correlation. If a P value is below 0.05 that indicate a statistical importance non-zero and its correlation confidence level is 95%. In statistical hypothesis testing, the **p-value** is the probability of obtaining a result at least as extreme as the one that was actually observed, given that the null hypothesis is true. The fact that p-values are based on this assumption is crucial to their correct interpretation. More technically, a p-value of an experiment is a random variable defined over the sample space of the experiment distribution under the null hypothesis [0,1].

In this part we performed a correlation analysis to evaluate the parametric relationships between the measured elements. All the measured parameters were statistically treated to evaluate their source region or their variations and similarity between them. The correlation matrix contains all the measured elements for wet or dry deposition samples. Correlation coefficients between all the measured parameters are given in Table 3.2.

Table3.2 Correlation matrix and p values for all data.

	Al	Ca	Co	cond	Cr	Cu	Fe	H	K	Mg	Na	NH4	Ni	Pb	pH	V
Al		0,0278	-0,1563	-0,0749	-0,0692	-0,0336	-0,0936	-0,1619	-0,0464	-0,1222	-0,1526	-0,1466	-0,1085	-0,1634	0,0547	0,0574
		0,8343	0,2372	0,5728	0,6027	0,8006	0,4807	0,2204	0,7272	0,3565	0,2487	0,2680	0,4135	0,2161	0,6810	0,6661
Ca	0,0278		0,1525	0,2979	0,0530	-0,0711	-0,0936	-0,0839	-0,0887	0,4170	0,0628	0,0643	-0,0446	-0,0012	0,0979	0,2268
	0,8343		0,2489	0,0219	0,6904	0,5926	0,4809	0,5274	0,5040	0,0010	0,6368	0,6287	0,7371	0,9926	0,4606	0,0841
Co	-0,1563	0,1525		0,5899	0,3263	0,0587	-0,0338	-0,1052	0,1392	0,6746	-0,0856	0,3313	0,2612	0,0852	-0,0535	0,1289
	0,2372	0,2489		0,0000	0,0117	0,6588	0,7996	0,4280	0,2929	0,0000	0,5194	0,0104	0,0457	0,5213	0,6873	0,3304
cond	-0,0749	0,2979	0,5899		0,4878	0,0955	0,0291	0,0220	-0,1342	0,5732	-0,0042	0,1627	-0,0428	0,1357	-0,0910	0,1791
	0,5728	0,0219	0,0000		0,0001	0,4719	0,8270	0,8684	0,3109	0,0000	0,9748	0,2181	0,7476	0,3054	0,4932	0,1747
Cr	-0,0692	0,0530	0,3263	0,4878		-0,0319	0,1367	-0,0958	-0,1435	0,2203	-0,1010	0,2138	-0,0283	0,0107	-0,0221	0,2151
	0,6027	0,6904	0,0117	0,0001		0,8106	0,3018	0,4705	0,2783	0,0936	0,4466	0,1040	0,8312	0,9358	0,8679	0,1019
Cu	-0,0336	-0,0711	0,0587	0,0955	-0,0319		0,3557	0,3465	-0,0224	0,0870	-0,0540	0,0915	0,0112	0,4078	-0,3036	0,0138
	0,8006	0,5926	0,6588	0,4719	0,8106		0,0057	0,0072	0,8665	0,5121	0,6846	0,4909	0,9329	0,0013	0,0194	0,9173
Fe	-0,0936	-0,0936	-0,0338	0,0291	0,1367	0,3557		0,3448	-0,0182	-0,0843	0,0702	0,3304	0,0836	0,5675	-0,3365	0,0281
	0,4807	0,4809	0,7996	0,8270	0,3018	0,0057		0,0075	0,8912	0,5256	0,5974	0,0106	0,5289	0,0000	0,0092	0,8325
H	-0,1619	-0,0839	-0,1052	0,0220	-0,0958	0,3465	0,3448		-0,0503	-0,0715	0,2831	0,1379	0,4087	0,4482	-0,6836	-0,0256
	0,2204	0,5274	0,4280	0,8684	0,4705	0,0072	0,0075		0,7053	0,5905	0,0298	0,2978	0,0013	0,0004	0,0000	0,8474
K	-0,0464	-0,0887	0,1392	-0,1342	-0,1435	-0,0224	-0,0182	-0,0503		-0,0821	-0,0582	-0,1299	0,2161	0,0535	-0,0954	-0,0449
	0,7272	0,5040	0,2929	0,3109	0,2783	0,8665	0,8912	0,7053		0,5364	0,6616	0,3269	0,1002	0,6874	0,4721	0,7355
Mg	-0,1222	0,4170	0,6746	0,5732	0,2203	0,0870	-0,0843	-0,0715	-0,0821		-0,0282	0,2799	0,0712	0,0849	-0,0386	-0,0633
	0,3565	0,0010	0,0000	0,0000	0,0936	0,5121	0,5256	0,5905	0,5364		0,8323	0,0318	0,5918	0,5225	0,7719	0,6339
Na	-0,1526	0,0628	-0,0856	-0,0042	-0,1010	-0,0540	0,0702	0,2831	-0,0582	-0,0282		0,2010	0,0976	0,4395	-0,3156	-0,0225
	0,2487	0,6368	0,5194	0,9748	0,4466	0,6846	0,5974	0,0298	0,6616	0,8323		0,1269	0,4619	0,0005	0,0149	0,8655
NH4	-0,1466	0,0643	0,3313	0,1627	0,2138	0,0915	0,3304	0,1379	-0,1299	0,2799	0,2010		0,1042	0,4281	-0,1113	0,3495
	0,2680	0,6287	0,0104	0,2181	0,1040	0,4909	0,0106	0,2978	0,3269	0,0318	0,1269		0,4323	0,0007	0,4012	0,0067
Ni	-0,1085	-0,0446	0,2612	-0,0428	-0,0283	0,0112	0,0836	0,4087	0,2161	0,0712	0,0976	0,1042		0,1794	-0,4141	-0,0402
	0,4135	0,7371	0,0457	0,7476	0,8312	0,9329	0,5289	0,0013	0,1002	0,5918	0,4619	0,4323		0,1739	0,0011	0,7625
Pb	-0,1634	-0,0012	0,0852	0,1357	0,0107	0,4078	0,5675	0,4482	0,0535	0,0849	0,4395	0,4281	0,1794		-0,5627	0,0158
	0,2161	0,9926	0,5213	0,3054	0,9358	0,0013	0,0000	0,0004	0,6874	0,5225	0,0005	0,0007	0,1739		0,0000	0,9057
pH	0,0547	0,0979	-0,0535	-0,0910	-0,0221	-0,3036	-0,3365	-0,6836	-0,0954	-0,0386	-0,3156	-0,1113	-0,4141	-0,5627		0,0350
	0,6810	0,4606	0,6873	0,4932	0,8679	0,0194	0,0092	0,0000	0,4721	0,7719	0,0149	0,4012	0,0011	0,0000		0,7925
V	0,0574	0,2268	0,1289	0,1791	0,2151	0,0138	0,0281	-0,0256	-0,0449	-0,0633	-0,0225	0,3495	-0,0402	0,0158	0,0350	
	0,6661	0,0841	0,3304	0,1747	0,1019	0,9173	0,8325	0,8474	0,7355	0,6339	0,8655	0,0067	0,7625	0,9057	0,7925	

Calcium has a good and significant correlation with Mg. Both elements are typically generated from soil related sources, which may account for their high concentration. In addition to that, Ca has weak but significant negative correlation with H^+. The negative correlation clearly indicates that hydrogen ions were most probably neutralized by Ca and Mg salts.

Magnesium also has a very significant correlation with Co. This may indicate some anthropogenic sources that add to the observed concentrations.

Ammonia and lead shows a good significant correlation. This could be an indication of fertilizer application around the study area surrounded by agricultural areas. Ammonia has also significant correlation (0.38-0.43) with Co and V respectively. These elements may indicate anthropogenic sources like oil burning or incineration (cement factory).

Lead correlated is significant with Fe and Cu. This may indicate that the correlated pairs were emitted to atmosphere from common sources like electroplating industry, cement industry and/or coal combustion.

3.6 BACK TRAJECTORY ANALYSIS

Back trajectory analysis is a useful technique used to indicate source regions of measured pollution parameters. All rain sample back trajectories are calculated by HYSPLIT model and shown in Figure 3.10.

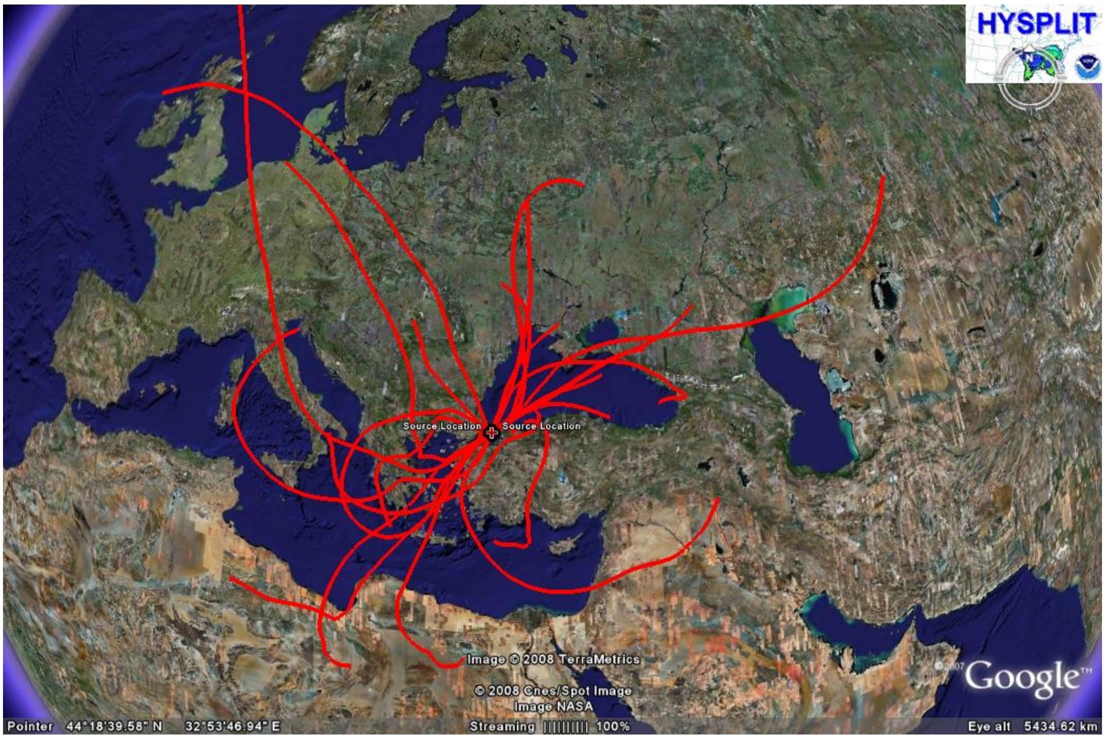

Figure 3.10 All rain sample back trajectory plots during study period (Source for the map: Google^{TM})

All the back trajectories were be separated four sub group up to their direction according to their four main air mass trajectory systems (Figure 3.11). Thirty five percent of pollution source came over the Black Sea, 10 % of pollution came over Italy Greece. Other twenty five percent came over the coastal region of Mediterranean (Africa). The rest thirty percent was originated from East Europe.

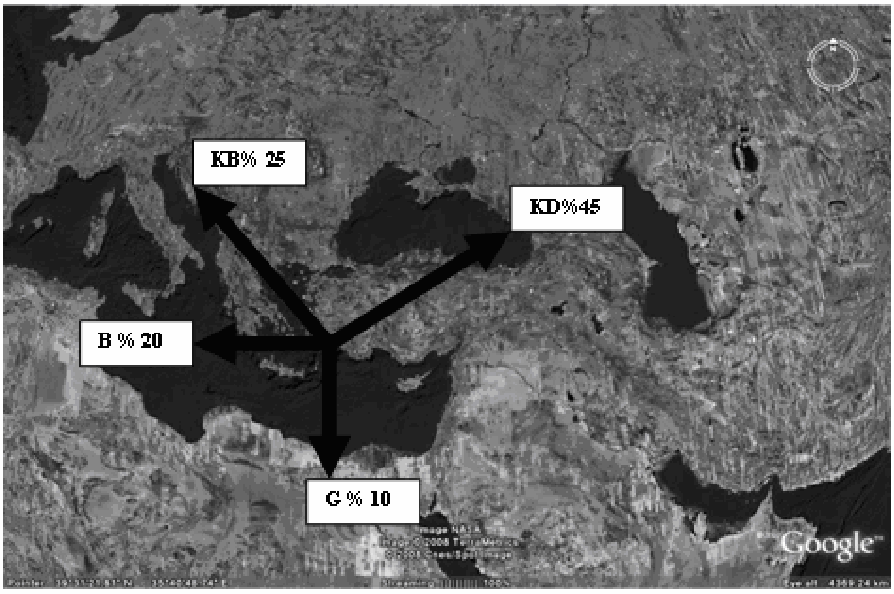

Figure 3.11 Back trajectory percentage shares of the main directions during studied period (Source for the map: Google^{TM}).

3.7 EPISODE ANALYSIS

In the literature, generally episode values are determined based on percentages. Commonly used percentage value is the highest 30%. Since we have 60 samples, 30% corresponds to 17-18 samples approximately. However, selection of the episodes can be determined with respect to average pH value also. In our studies, average pH value was calculated to be 6.86. The number of samples that are greater than this value is 27. In this study the values of 8 samples, which have pH level less than 5.0, are considered to be episode values. Episode lower bounds are determined respectively to be 5.0 and 10 meq/l for pH and H^+.

In addition to pH based back trajectory analysis, the datasets are classified according to episodic values of the elements. By this way, it will be possible to figure out the possible anthropogenic or natural long-range sources of these enriched systems.

Back trajectory plots of Ca, Mg, Na, Al and NH_4 episodes were shown in Figure 3.12, Figure 3.13, Figure 3.14, Figure 3.15, and Figure 3.16 respectively.

According to the episode back trajectories of the pollutants generally came from west countries and the western party of Turkey, industrial developed regions. Other important region is Mediterranean countries. Generally Saharan dust carried over Mediterranean. The trajectories belong to highest NH_4 episodes are attributed to Saharan dust. There are similar discussions in the literature (Al-Momani et al., 2000;

Jaradat et al., 1999). Precipitation chemistry in Northern Jordan is similar to that of other areas of the Mediterranean basin. Although, concentrations of NO_3^- and SO_4^{2-} were high neutralization by the alkaline soil dust allows the precipitation to be neutral (Al-Momani et al., 2003). In the same manner, Al-Momani et al. (2000) and Jaradat et al. (1999) indicated that the neutralization mainly occurs by the dissolution of Saharan dust containing large fractions of calcite ($CaCO_3$), dolomite ($CaCO_3.MgCO_3$) and gypsum ($CaSO_4.2H_2O$) into rain water, because Saharan dust important sources of the base caution.

Previously, higher springtime Ca concentrations were attributed to local stone mines. Contrary the fact that, another possibility of these higher springtime Ca concentrations became being a possible source under the light of the discussions in this part. That is long range transportation from Saharan Desert.

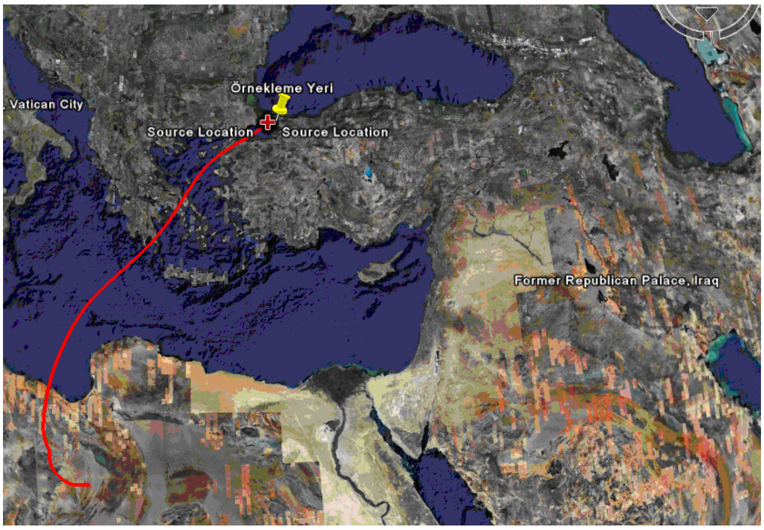

Figure 3.12 Back trajectory Plot Correspond to Highest Ca Concentrations (Source for the map: Google^{TM}).

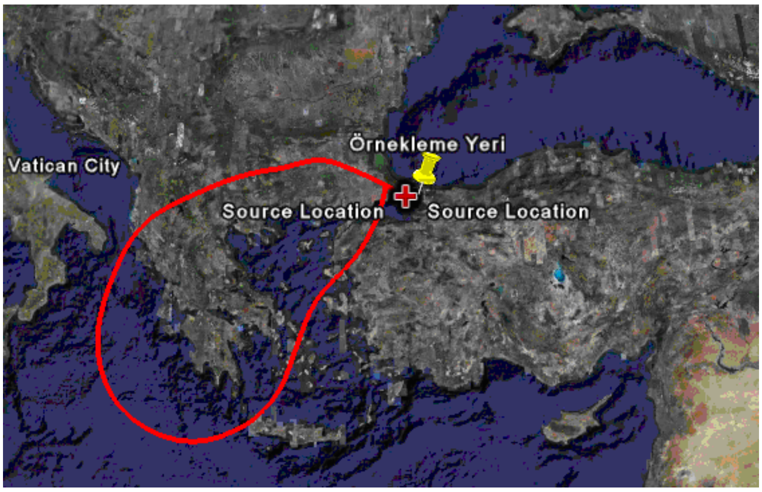

Figure 3.13 Back trajectory Plots of Mg episode concentrations (Source for the map: Google^{TM}).

Figure 3.14 Back trajectory Plots of Na episode concentrations (Source for the map: Google^{TM}).

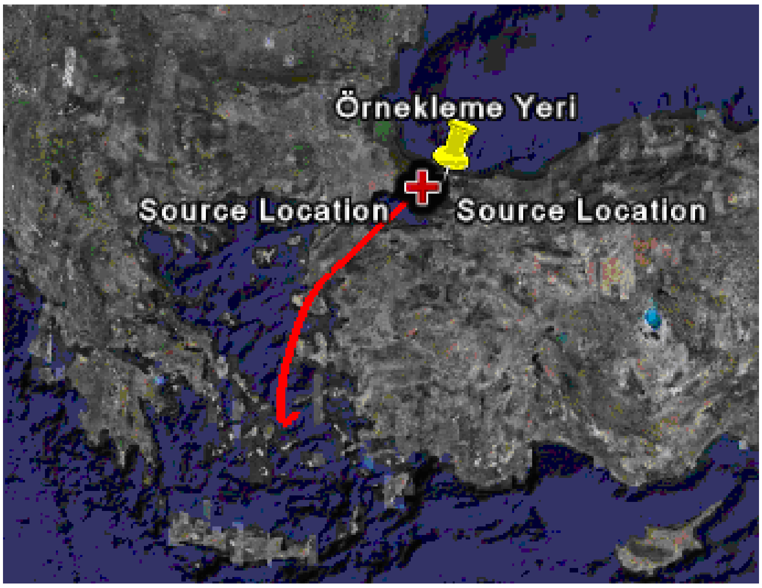

Figure 3.15 Back trajectory Plots of Al episode concentrations (Source for the map: Google^{TM}).

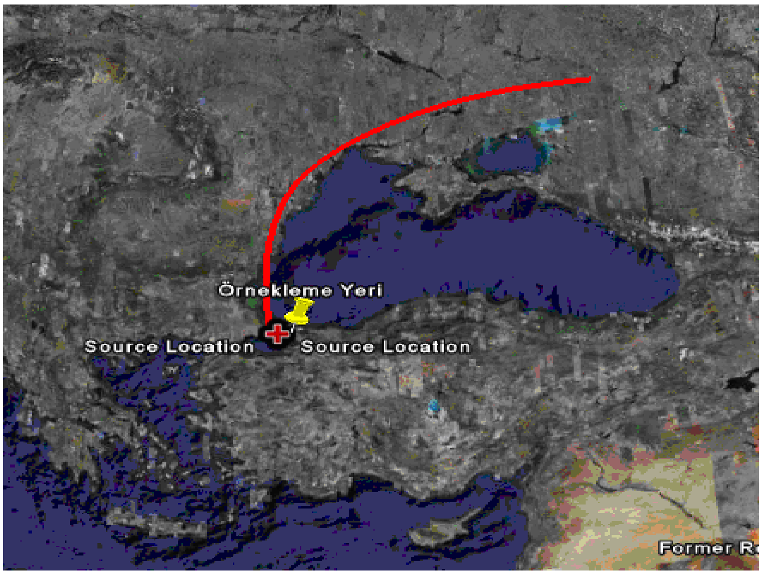

Figure 3.16 Back trajectory Plots of NH_4 episode concentrations (Source for the map: Google^{TM}).

CHAPTER 4

CONCLUSION

Wet and dry precipitation samples collected at the Fatih University Campus located in the Büyükçekmece Watershed Area (41.04° longitude, 28.59° latitude) between October 2007-June 2008. Total 60 samples were collected using home made wet and dry Rain Sampler.

All the collected samples were analyzed by means of pH, conductivity, volume, ions (H^+ , NH_4^+) metals (Ca ,Mg ,K , Na ,Pb, AI, Cu, Cr, Zn, V and Ni). Average of pH measurement is 6.79 during the study period. The pH value measured is higher than unpolluted rainwater pH, 5.6. Some episodic pH values were observed as 4.83, 9.26. Finally, the seasonal changes of neutralization factors in the measured cat ions, Na, Mg, Ca, NH_4^+ were investigated.

Wet and dry precipitation samples collection period was extended for three seasons, namely 2007-Autumn, 2007-Winter and 2008-Spring.

One of the most significant contributions of this study is that we developed our own sampling system in Fatih University workshop. All wet and dry precipitation samples were collected successfully by that handmade wet-dry rain sampler.

During the study period average H^+ ion concentration and pH were found to be 8.85 mg/L and 6.79, respectively. According to those results, it can be simply said that the rain throughout the study period was not acidic.

Furthermore, seasonal pH averages were calculated to be 6.25, 6.03, and 7.08 during 2007-Fall, 2007-Winter and 2008-Spring, respectively. Monthly average of H^+ concentration rates has shown that the highest H^+ concentration rate was in February. Especially in March, April and May H^+ ion concentration average found to be very low, since in these periods rain water was neutralized with the crustal elements such as Ca and Mg.

During our study period, although pH changes showed a stable trend without a sharp increase, at the later part of our study (2008-Spring) very high pH levels (higher than 8.5) were measured. This may be a result of the increase in some summer activities in that period. Minimum pH level is also considered as an episodic event, which was measured to be 4.83 in the winter period. The lower pH rates in the winter period may be attributed to the coal combustion and traffic originated emissions during the cold weather.

During the study period, a typical trend or behavior for NH_4^+ could not be found. In addition to that ammonia concentrations were lower than 1 mg/L except two very low events. The reason of this may be the lack of a stationary ammonia source influencing this area. The sources of atmospheric NH_4^+ can be attributed to the area source such as fields used in the local agricultural activities.

According to summary statistic results, Fe and Al, which are among crustal elements, has shown normal distribution and lower level Skewness and Kurtosis rates have been found. During the study period these two elements had very close fluctuations. This situation confirmed that the emissions and transports of these two elements come from common sources.

Anthropogenic originated elements Pb and Ni have also shown similar behaviors in data set which indicate that they are coming from the same source. On the other hand, Na and K have shown different and nonparallel results. As a result, we may mention the presence of different mechanisms, which are affecting the concentrations of these two elements.

Crustal elements, Ca and Mg have similar trends during our study period. Here, we will give a same conclusion to common sources. Especially in March, April and May, most probably these two elements were the most effective parameters on the decrease of H^+ ion average concentration.

When averages of all measured parameters regarding three seasons are focused, generally 2007-Winter period was found to have high rates. Winter season average concentrations of the parameters; conductivity, NH_4^+, K, Fe, Cu, Na, Al, Mg, Ni, Cr and Pb were very high. Actually, among these parameters Mg, Fe, Cu, Ca are crustal elements. Although the concentrations of these elements during the winter season are expected to decrease due to surface humidity and wetness, the concentrations of elements except Ca have been observed to increase. Calcium concentration in rain samples was mainly contributed from local and regional Ca sources. Turkey is a calcium-enriched country, and neutralization of rainwater over Turkey is a well-known phenomena mentioned in the previous literature (Başak and Alagha, 2004). Also, collecting different amounts of samples in each season may be a reason of this. Namely, autumn (16 samples), winter (20 samples), spring (7 samples) have been collected.

Sometimes, different pH rates have been obtained in different rain samples collected at the same day. It is because air parcels carrying rain come from different systems. In addition, the change in the intensities of industrial and traffic-originated pollutants at different hours on the same day can be another factor. All the collected rain samples were transported from our country by systems coming from East Europe and southeastern direction. When back trajectory of air parcels belonging to the sampling day was evaluated, some systems were observed to have similar behaviors. In this way, it is seen that air parcels arriving Istanbul is being transported mainly by four air corridors. Thirty-five percent of the sources defined by the back trajectory system come from the northeast direction to the sampling area above The Black sea, ten percent came over Italy and Greece, and twenty-five percent came from south, especially from African countries, which are located in the Mediterranean Coast. The last 25% came from the northeast direction above Europe passing Poland, Ukraine, Germany and England.

According to result of the correlation analysis; ammonia and lead showed a good significant correlation. This could be an indication of fertilizer application around the study area surrounded by agricultural areas. Ammonia has also significant correlation (0.38-0.43) with Co and V respectively. These elements may indicate anthropogenic sources like oil burning or incineration (cement factory). In addition, Calcium has a good and significant correlation with Mg. Both elements are typically generated from soil related sources, which may account for their high concentration.

Opposite Ca has weak but significant negative correlation with H^+. The negative correlation clearly indicates that hydrogen ions were most probably neutralized by Ca and Mg salts. Magnesium also has a very significant correlation with Co. This may indicate some anthropogenic sources that add to the observed concentrations.

As a conclusion, this study has some significant contributions in the existing literature adding some data related to rain chemistry over Istanbul, Büyükçekmece Area. Such studies should be extended for upcoming years to differentiate the basic factors, which define the characteristics of rain acidity over the region. In the area, a very good contribution can be made by making continuous works to investigate the effects of local, regional and remote region sources on the rain chemistry.

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