DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

DETERMINATION OF CHEMICAL COMPOSITION OF PRECIPITATION IN İZMİR

by
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İZMİR

DETERMINATION OF CHEMICAL COMPOSITION OF PRECIPITATION IN İZMİR

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We certify that we have read this thesis and "**DETERMINATION OF CHEMICAL COMPOSITION OF PRECIPITATION IN İZMİR**" completed by Mutlu ADALI under supervision of Assoc. Prof. Dr. Abdurrahman BAYRAM and that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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DETERMINATION OF CHEMICAL COMPOSITION OF PRECIPITATION IN İZMİR

ABSTRACT

The major aim of this thesis is to determine the chemical nature of rainwater in İzmir atmosphere. To achieve determining chemical character of rainwater samples are collected at five stations in İzmir, and these studies are conducted by the collaboration between İzmir Regional Meteorological Office and Department of Environmental Engineering of Dokuz Eylül University. Sample collections are done by personnel of meteorological offices and analyses are done in Environmental Engineering Department laboratories of Dokuz Eylül University. The chemical properties of the rainwater are determined as pH, elemental and anionic concentrations of the samples. The selected anions are SO_4^{2-}, NO_3^-, Cl^-, F^-, Br^-, NO_2^{2-}, PO_4^{3-}, and the elements are Al, Ba, Ca, Cd, Zn, Cr, Pb, Sr, V, K, Mn, Mg, Na, Ni, Cu, Co, Fe. Measurement results are exposed to some statistical methods in order to obtain significant relations between acid causing ions and other chemical parameters. The results of these statistical analyses are used for the explanation of possible contributing pollutant sources in İzmir atmosphere. By the highlights of these studies, mean pH value of wet deposition for İzmir atmosphere was determined as 6.1. It is found that 94 % of the pH values are above 5 that are measured in the sampling period, and neutralising process of the acidity of precipitation is achieved by high alkali ion concentrations with respect to local geographical properties. Trace element concentrations are similar to previous studies in the literature. The increase in the concentrations of trace metals in the atmosphere of the region is related to the consumption of fuels in urban areas, industrial activities, and long range transport of chemical components especially with air masses from Europe. As İzmir is located in the Aegean shoreline, marine originated chemical components have important effect on the composition of precipitation as expected.

Keywords: acid rains, rainwater, chemical composition, wet deposition, atmospheric pollutants, ion chromatography, ICP-OES, heavy metals.

İZMİR' DEKİ YAĞIŞLARIN KİMYASAL KOMPOZİSYONUNUN SAPTANMASI

ÖZ

Bu çalışmanın ana hedefini İzmir şehri atmosferine ait yağmurların kimyasal doğasının saptanması oluşturur. Çalışmada İzmir atmosferine ait yağmursuyu örneklerinin kimyasal karakterlerini saptamak için şehir içinde 5 adet örnekleme noktası seçilmiştir. Araştırma, İzmir Meteoroloji Bölge Müdürlüğü ile Dokuz Eylül Üniversitesi'nin işbirliğiyle gerçekleştirilmiştir. Örneklerin toplanması meteoroloji ofislerindeki personel tarafından yapılmış, analizler ise Dokuz Eylül Üniversitesi Çevre Mühendisliği laboratuvarlarında gerçekleştirilmiştir. Yağmurların kimyasal özellikleri pH, elemental ve anyonik konsantrasyonlar olarak saptanmıştır. Çalışmada tespit edilen anyonlar SO_4^{2-}, NO_3^-, Cl^-, F^-, Br^-, NO_2^{2-}, PO_4^{3-}; elementler ise Al, Ba, Ca, Cd, Zn, Cr, Pb, Sr, V, K, Mn, Mg, Na, Ni, Cu, Co, Fe'dir. Elde edilen verilere, pH değerleri ve diğer kimyasal parametreler arasında anlamlı ilişkiler olup olmadığını tespit etmek amacıyla bir takım istatistik analiz yöntemleri uygulanmıştır. İstatistik analizlerinin sonucuna göre kirletici kaynaklarının tespitine çalışılmıştır. Çalışmalar sonucunda, İzmir için yaş çökelmenin sahip olduğu ortalama pH değeri 6.1 olarak saptanmıştır. Ayrıca ölçülen pH değerlerinin % 94'ünün 5'in üzerinde olduğu ve nötralizasyonun bölge çoğrafyasına bağlı olarak yüksek miktarlardaki alkali iyonlar ile sağlandığı tespit edilmiştir. Saptanan eser metal konsantrasyonları literatür verileriyle benzer değerlere sahiptir. Bölgedeki yağışların eser metal konsantrasyonlarının şehir alanlarındaki çeşitli yakıt tüketimlerinden ve çevredeki sanayi faaliyetleri ile bölgenin maruz kaldığı, özellikle Avrupa kökenli hava kütlelerinin hareketleri doğrultusunda uzun mesafeli taşınımından etkilendiği düşünülmektedir. İzmir kentinin deniz kıyısında bulunması nedeniyle, beklendiği gibi deniz kökenli mineraller de yağmur sularının kimyasal kompozisyonunda önemli bir yer tutmaktadır.

Anahtar sözcükler: asit yağmurları, yağmur suyu, kimyasal kompozisyon, yaş çökelme, atmosferik kirleticiler, ağır metaller, iyon kromatografisi, ICP-OES.

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CHAPTER ONE
INTRODUCTION

1.1 Importance of the Study

The studies abut chemical compositions of rainwater are especially significant, because of immediate influence on human health and ecosystems in general. Chemical components in the rainwater (acidic components, anions, cations, and trace metals) damage the environment significantly (surface waters, plants, animals, and human beings).

Acid precipitation has been a growing problem in the world; especially in the cities that are located near the industrial regions and affected from long range transportation of atmospheric aerosols. The pH of rainwater, as a result of atmospheric carbon dioxide, is moderately acidic with a pH of 5.6. Precipitation with a pH lower than this regarded as acidic. However, due to the presence of other naturally generated gases, such as nitrogen oxides and sulphur dioxides, the pH value of precipitation in un-polluted areas might be expected to be about pH 5.0. In Turkey, some of researches showed that the contamination from agricultural implementations (due to local effects) (Al-Momani et al., 1995; Akkoyunlu & Tayanc, 2003) and natural alkaline dust neutralizes much of the acidity periodically (due to atmospheric properties of seasons) (Al-Momani et al., 1995). Although many of researches designate that the acidity of precipitation is neutralized by local formations or atmospheric seasonal variations, following the variations of the chemical composition of rainwater is very important for having a database to obtain effects of erratic anthropological and natural contaminations to the atmosphere.

Trace metals, particularly heavy metals, are increasingly released into the environment as contaminants and pollutants, by-products of industry and human civilization. An important environmental compartment in the biogeochemical cycles of trace metals is the atmosphere. There is considerable research interest in the atmospheric trace metals because of a number of reasons. First, atmospheric

deposition is considered to be a major source of toxic metals such as Hg, Cd, and Pb and other trace metals to ecosystems (Veron et al., 1992). Second, in atmospheric droplets, trace metals such as Fe, Mn, and Cu have been implicated in the catalysis of SO_2 oxidation, leading to enhanced acidity of hydrometeors (Brandt & van Eldik, 1995). Third, certain trace metals, emitted from particular source types, can be used to help identify the origin of the precipitating air masses (Heaton et al., 1990) and the sources from which the acid precipitation is derived. Furthermore, the contribution of wet deposition to the mass balance of some elements in surface water run-off has been recognized as an important aspect of water quality (U.S. EPA, 1993).

Huge percentage of metals fall through the rain at the place of their production. However, the aerosols, which have a very small falling velocity, are easily transferred by the wind and it is possible to be deposited through the rain at long distances from the point of their emission (Smirnioudi et al., 1998). The chemistry of trace elements in the atmosphere is influenced by different sources of gases and aerosols, they can have various origins such as natural emissions (marine, biogenic, crustal) or anthropogenic emissions. During a rain event, these gases and aerosols are incorporated into raindrops; by using the analysis of rain waters, we can identify and quantify the chemical species present in the atmosphere and obtain information about the atmospheric constituent reservoirs.

1.2 Aim of the Study

Five sampling sites were selected for having geological homogeneous results in Izmir. Sampling points are selected meteorological offices because of manual sampling procedures. Bornova, Çiğli, Güzelyalı, Adnan Menderes Meteorological Offices and Dokuz Eylül University Kaynaklar Campus were selected as sampling points. Grab sampling method based on rain event sampling were used to collect rainwater samples.

The first aim of the study covers the determination of chemical properties of rainwater in three steps when the mentioned factors above were considered. These

are the finding acidity degree, anionic and cationic constituents concentrations, and trace metal concentrations of rainwater. The second aim comprises to find out the relations between chemical parameters. The third aim of our study is to discover the origin of the mentioned pollutants by using statistical methods.

CHAPTER TWO
LITERATURE REVIEW

This chapter presents background information on atmospheric removal mechanisms, acid rains, dry and wet deposition, ionic and metallic compositions of rainwater and other some related studies reported previously.

2.1 Removal Processes of Atmospheric Pollutants

Natural as well as man-made sources of particles and gases considered as air pollutants. Natural pollution includes plant and animal respiration, the decay of living matters, volcanic emissions, forest fires and ocean spray. On the other hand, anthropogenic pollution is derived commonly from the combustion of fossil fuels, roasting of ores for refining metals, processing of crustal materials for manufacturing cements and burning of waste materials.

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

Wet and Dry Deposition: Atmospheric deposition is the process whereby airborne particles and gases are deposited on the earth's surface. These pollutants

come either from natural sources, such as forest fires, volcanoes, and oceanic salt, or from power plants, newly plowed fields, motor vehicles, and other human activities. Wet deposition is the fraction of atmospheric deposition contained in precipitation, predominantly rain and snow. Dry deposition (the remainder) is the fraction deposited in dry weather through such processes as settling, impaction, and adsorption. Acidic atmospheric precipitation is called acid deposition and acidic wet deposition is called acid precipitation or, more commonly, acid rain.

The deposition of acidic pollutants can occur via one of these three pathways:

- Wet deposition – The deposition of pollutants in rain and snow, commonly termed "acid rain". This is the main pathway for most upland areas.
- Cloud deposition – The capture of cloud droplets by terrestrial surfaces. Pollutants are generally more concentrated in cloud than in rain; therefore, over high ground this pathway can provide a significant input of acidic pollutants.
- Dry deposition – The deposition of gases and particles directly onto terrestrial surfaces. In many parts of the Europe, dry deposition is larger than wet deposition.

2.2 Background of Acid Deposition

2.2.1 Chemical acidification properties of rainwater

Acid deposition is a combination of wet and dry deposition, while wet acid deposition is commonly referred to as acid rain. The acidification of precipitation results from the accumulation of hydrogen ion, $[H^+]$ in water.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$
$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$
$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \qquad K_1 = 4.45\times10^{-7} \text{ at } 25^{o}\text{C.} \qquad (2.1)$$

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \qquad K_2 = 4.7\times10^{-11} \text{ at } 25^{o}\text{C.} \qquad (2.2)$$

Typical unpolluted precipitation, at a temperature of 20°C has a pH of 5.6 owing to the presence of dissolved CO_2 or sea salts (Heinsohn & Kabel, 1999). CO_2 dissolves in raindrops forming carbonic acid, which acts as a buffer system as seen in the following reactions.

However, pH of the rainwater differs from one region to another due to the presence of acidic precursors or neutralizing species.

2.2.2 Effective Factors on Rainwater "pH"

The driving force behind much of the research in the atmospheric sciences today is the recognition that anthropogenic activity may be altering (perturbation) Earth's climate.

About half of the acidity in the atmosphere falls back to earth through dry deposition as gases and dry particles. Winds transport these acidic particles and gases onto buildings, cars, homes, and trees. In some instances, these gases and particles can eat away the things on which they settle. Dry deposited gases and particles are sometimes washed from trees and other surfaces by rainstorms. When that happens, the runoff water adds those acids to the acid rain, making the combination more acidic than the falling rain alone. The combination of acid rain plus dry deposited acid is called acid deposition. Prevailing winds transport the compounds, sometimes hundreds of miles, across state and national borders.

Scientists have discovered that air pollution from the burning of fossil fuels is the major cause of acid rain. Acid rain occurs when emissions of sulphur dioxide (SO_2) and oxides of nitrogen (NO_x) react in the atmosphere with water, oxygen, and

oxidants to form various acidic compounds. This mixture forms a mild solution of sulphuric acid and nitric acid. Sunlight increases the rate of most of these reactions (USEPA, Mid Atlantic Integrated Assesment).

The main cause of acid rain is sulphur dioxide. Natural sources which emit this gas are volcanoes, sea spray, rotting vegetation and planktons. However, the burning of fossil fuels, such as coal and oil, are largely to be blamed for approximately half of the emissions of this gas in the world. When sulphur dioxide reaches into the atmosphere, it is oxidized to form a sulphate ion. It then becomes sulphuric acid as it joins with hydrogen atoms in the air and falls back down to earth. Oxidation occurs mostly in clouds and especially in heavily polluted air where other compounds such as ammonia and ozone help to catalyze the reaction, converting more sulphur dioxide to sulphuric acid. However, not the entire sulphur dioxide is converted to sulphuric acid. In fact, a substantial amount can float up into the atmosphere, move over to another area and return to earth unconverted. The following are the stoichiometric equations for the formation of sulphuric acid:

$$S \text{ (in coal)} + 0_2 \longrightarrow SO_2$$
$$2\ SO_2 + 0_2 \longrightarrow SO_3^{2-}$$
$$SO_3^{2-} + H_20 \longrightarrow H_2SO_4$$

Nitrogen oxide and nitrogen dioxide are other components of acid rain. Their sources are mainly from power stations and exhaust fumes. Like sulphur dioxide, these nitrogen oxides rise into the atmosphere and are oxidized in clouds to form nitric acid. These reactions are also catalysed in heavily polluted clouds where iron, manganese, ammonia and hydrogen peroxide are present.

Mentioned before, there are also natural sources of acids such as volcanoes, natural geysers and hot springs. But, nature has developed ways of recycling these acids by absorbing and breaking them down. These natural acids contribute to only a small portion of the acidic rainfall in the world today. In small amounts, these acids actually help dissolve nutrients and minerals from the soil so that trees and other plants can use

them for food. The large amounts of acids produced by human activities overload this natural acidity.

2.2.3 Principal Agents of Neutralization

Sulphuric acid (H_2SO_4) and nitric acid (HNO_3) are subjected to neutralization to some extent before being deposited on the ground surface.

Certain compounds such as Ca^{2+}, Mg^{2+}, Na^{+} and NH_3 can neutralize the H_2SO_4 and HNO_3 in the rain droplets and increase pH of the rainwater (Elsom, D., 1982).

Although the major source of Ca^{2+} in the atmosphere is the soil, Ca^{2+} is also emitted from combustion processes. For example, atmospheric concentration of Ca^{2+} in Europe decreases from south to north. High Ca^{2+} concentrations are attributed to calcareous soil in the Mediterranean region and in North Africa, whereas the excess Ca^{2+} in the Northern Europe is attributed to industrial emissions (Hedin et al., 1994). The major emission source of atmospheric NH_3 is agricultural activities whereupon NH_4^{+} is formed.

2.3 Major and Trace Elements in Environment and Pollution Terms

There are 90 naturally occurring elements on the earth, the magnitude and chemical form of which can widely vary either between or within environmental geological, biological, or marine systems. The elemental composition of the earth's crust is predominantly O, Si, Al, Fe, Ca, Na, K and Mg. An example of an element that varies widely in magnitude between the various systems is aluminium. As one of the main constituents of the earth's crust, Al in rocks commonly ranges from 0.45% to 10%. However, the content of this element in plants is generally lower than 200 mg/kg (dry weight), and in seawater it is 2μg/dm^3. Similarly, the relative amounts of the major elemental constituents in seawater follow the order Na^{+}> Mg^{2+}> Ca^{2+}> K^{+}. In biological systems elements can be basically grouped into three categories: major elements consisting of C, H, N, and O; minor elements comprising Ca, CI, Mg, P, K,

and Na; and the remainder are referred to as trace elements. The term 'trace elements' relates to the time when minute amounts of a number of elements were found in biological systems but they could not be precisely quantified using classical methods of analysis. Although more sensitive and specific analytical techniques have been developed this terminology has remained in popular usage (Fifield & Haines, 1995).

In human and animal systems, trace elements are denned as being essential if depletion consistently results in a deficiency syndrome and repletion specifically reverses the abnormalities. The trace elements fulfilling these requirements are As, Co, Cr, Cu, F, Fe, I, Mn, Mo. Ni, Se, Si, Sn, V, and Zn. Some elements, Cd, Hg, and Pb are prominently classified as toxic. This is because of their detrimental effects even at low levels. All trace elements are prominently toxic when their levels exceed the limits of safe exposure. These limits vary widely from one element to another.

All trace elements occur to a varying extent within all components of the environment. The term pollution of the environment refers to an increase of a trace element relative to the natural occurrence of that element. This increase may relate to natural events, but in general is associated with human activities. In particular, industrial and agricultural practices result in a more widespread trace element contamination of the environment than natural occurrence. Air pollution is generally related to gaseous emissions into the atmosphere (carbon monoxide, carbon dioxide, hydrocarbons, halocarbons, sulphur dioxide, hydrogen sulphide, nitrogen oxides and ammonia). Trace element or heavy metal contamination can result primarily through atmospheric particles or particulates. The main sources are coal and fuel power generation plants, metal processing and smelting, transportational combustion, waste incineration, and aerosol sprays (Fifield & Haines, 1995).

Metal air pollution is of major concern in that it is global and contributes to contamination of all the components of the environment. In most cases the maximum pollution levels are within a few kilometres of the emission sources, but small particulate and aerosol pollutants can contaminate all areas of the Earth. A recent problem of metal particulate air pollution is their role in the oxidation of sulphur

dioxide and the formation of acidic aerosols involved in global acid rain (Gregory et al., 1996). Trace elements (Fe, V, Ca, Pb, Br, and CI) also contribute to the formation of photochemical smog. As a result of increased industrial and transportational emissions the release of metal particulates into the environment is now under strict control in air quality regulations.

2.4 Previous Studies

Measurements of the chemical composition of precipitation have been made for many years in various regions around the world with varying degrees of success. In general, more measurement sites and more sophisticated research programs have been implemented in regions where acid deposition has been identified as a major environmental concern. In other regions, the number of measurement sites has been low and the measurement quality very often uneven. Inconsistencies in instrumentation and sampling protocols around the world continue and have made international data comparisons and atmospheric modeling efforts difficult. In June 1989, the World Meteorological Organization (WMO) established the Global Atmospheric Watch (GAW) Programs to address the lack of coordination among the research and monitoring networks. The goal of the GAW Programs was, and continues to be, to monitor the long-term evolution of the atmospheric composition and properties on global and regional scales in order to assess this contribution to climate change and other environmental issues. Several programs, including the former Background Air Pollution Monitoring Network (BAPMoN) were combined to form the GAW. The GAW Programs coordinates global monitoring of aerosols, ozone, greenhouse gases, ultraviolet radiation, selected reactive gases and precipitation chemistry.

The “Cooperative Programs for Monitoring and Evaluation of Long-range Transmission of Air Pollutants in Europe” (EMEP) was launched in 1977 as a response to the growing concern over the effects on the environment caused by acid deposition. EMEP was organized under the auspices of the United Nations Economic Commission for Europe (ECE). Today EMEP is an integral component of the

cooperation under the Convention on Long-range Transboundary Air Pollution. The main objective of EMEP is to provide governments with information on deposition and concentration of air pollutants, as well as on the quantity and significance of long-range transmission of pollutants and transboundary fluxes. The program includes three main elements: emission data, measurements of air and precipitation quality, and atmospheric dispersion models. The work is coordinated by three international centers: two centers for modeling activities and one Chemical Co-ordinating Centre (CCC) for coordination of the chemical measurements.

Most of the current acid deposition researches originate from wet deposition maps based on the results of both long-range transport models and actual measurements which demonstrated high levels of acid precursors in the certain parts of Central Europe, which is attributed to the intense industrial activity. Very high SO_4^{2-} levels and fluxes were found in the so called Black Triangle (the border area between Germany, Czech Republic and Poland), Ukraine and former Yugoslavia. Similarly, nitrate NH_3 fluxes were large in the region extending from Southern Scandinavia to Northern Italy and Former Yugoslavia (Van Leeuwen et al., 1996).

Additionally, wet deposition of alkaline particles was studied in relation to the issue of acidification through their ability to neutralize acidity **(**Raper & Lee, 1996.**;** Hedin et al., 1994**;** Gorham, 1994.**)**. In large parts of the Southern Europe more than 50% of the potential acid deposition was found counteracted by deposition of non-sea magnesium, calcium and potassium ions, which were largely caused by anthropogenic emissions. In Central and North-Western Europe, base cation deposition usually amounted to less than 25% of the acid input. **(**Draaijers et al., 1997). Transport of dust from Sahara is a major source of base cations in precipitation around the Mediterranean Sea, but the influence diminishes further to the north (Semb et al., 1995). Smallest base cation deposition relative to potential acid deposition was found in Southern Scandinavia, Denmark, Northern Germany and the Netherlands.

The Mediterranean region is extensively studied by research groups from France, Spain, Italy, Greece, Turkey and Israel for wet deposition. In Western

Mediterranean, it has been documented that wet deposition accounts for almost 75 % of the total deposition (Guerzoni et al., 1995). The multivariate analysis supported classification of rains into four principle groups: marine, local, European and African. It was found out that acid rain was associated to rains of Atlantic and European origin and alkaline rain was associated to African dust, so called "red rains" (Avila & Alarco, 1999; Hernandez et al., 1996; Alastuey et al., 1999; Guerzoni et al., 1995).

Besides the Saharan influence, high calcium levels of the soils in the region also contribute to neutralization of the acidity transported to the Mediterranean region (Avila & Alarco, 1999; Alastuey et al., 1999; Guerzoni et al., 1995; Plaisance & Guillermo, 1997; Plaisance et al., 1996). By analyzing rainwater samples collected at nine stations in Eastern France, (Sanusi et al., 1995) have shown that the major ion concentrations were higher in urban areas and the precipitation acidity was surprisingly lower in rural areas due to the presence of calcium carbonate in the upper Rhine Valley, which is an urban area.

In another study carried out at the southern coast of France (Chester et al., 1997) interpreted the distribution of trace metals in a series of rain samples in relation to aerosols. They showed that pH values of the rain waters reflect the type of aerosol scavenged from the air. Another conclusion they have reached was that urban dominated aerosol, which originates from Western Europe gives rise to acidic rains and crust dominated aerosol from North Africa results in neutral to basic rains.

Similar results were reported for the Eastern Mediterranean region (Glavas, 1988; Singer et al., 1993; Mamane & Gottlieb, 1995). At the Eastern Mediterranean coast of Turkey, it was found that 70 % of the acidity has been neutralized by $CaCO_3$, which originates from airborne local soil and dust transported from North Africa. Additionally, dry deposition of marine and crustal ions was higher than their corresponding wet deposition due to their large masses and proximity of the station to the coastline. Whereas, wet deposition fluxes of ions with anthropogenic sources such

as SO_4^{2-} and NO_3^- were found to be comparable with their dry deposition rates (Al-Momani et al., 1995).

Contrary to the Mediterranean sites, in Northern Central Europe, NH_3 is the dominating neutralizing agent (Glavas, S., 1988; Fuhrer, J., 1986; Mamane, Y., & Gottlieb, J., 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 (Borbely-Kiss et al., 1999). According to the 1989 EMEP database, NH_3 fluxes were largest in Central Europe and large calcium fluxes were observed in the Black Triangle and Ukraine, which could be attributed to the intensive industrial activity (Van Leeuwen et al., 1996).

Another study carried out in 1981 in the Northern UK, presented distribution maps of HNO_3, and non-sea SO_4^{2-} concentrations showing gradients increasing from the northwest to the south and east (Cape et al., 1984). In the UK and Wales, it was estimated that nitrogen deposition contributed 60% of the total acid deposition in 1995 (Reynolds et al., 1999).

Concentrations and wet deposition fluxes of 12 trace metals (Al, Cd, Cr, Cu, Co, Fe, Mn, Ni, Pb, Zn, V, and Ti) were measured in Singapore for one year by Balasubramanian & Hu (2000). The order of volume-weighted concentrations of the trace metals in this study were detected as Fe > Al > Zn > Cu > Ni > V > Pb > Mn > Cr > Ti > Co > Cd. The calculation of enrichment factors provided important information about the origin of these metals. The calculation of crustal enrichment factors with Al as the reference element indicated that while Ti, Fe and Mn originated from crustal sources, the remaining trace metals (Cd, Cr, Co, Cu, Ni, Pb, Zn and V) were mainly derived from anthropogenic sources. With the exception of Al and Fe, the wet deposition fluxes were derived predominantly from non-crustal sources. The concentrations of trace metals measured in the Singapore rainwater were influenced by a number of factors including precipitation volume, the acidity of rainwater, the particle size, and the solubility. There was no clear seasonal variation in the monthly wet deposition of the trace metals. The wet deposition of crustal and

some non-crustal elements reached peak values in October, mainly due to the advection of contaminated air masses from the heavily industrialized area in Singapore. The measured average annual deposition fluxes of Al, Fe, and some combustion-generated elements were considerably higher in literature data for other sites outside Singapore, which were mainly attributed to the heavy rainfall throughout the year. Atmospheric deposition in Singapore appeared to provide significant fluxes of many trace metals of environmental concern (Balasubramanian & Hu, 2003).

As a part of the program of the German Environmental Specimen Bank (ESB), precipitation was sampled on a weekly basis from eight sites in different ecosystems throughout Germany by Grömping, A. H. J., Ostapczuk, P., & Emons, H.. Sampling and analysis of precipitation from different sites throughout Germany resulted in several observations (Grömping et al., 1997):

- The lead deposition showed a strong decline during the last decade due to the use of unleaded gasoline as well as more efficient filter systems in industry.
- The deposition of Na and Cl was higher at only one of the marine sites, List, than at the others sites.
- Heavy metal deposition was higher in urban-industrial regions than at the more rural sites.
- An influence of agricultural activities was observed for instance by comparing the ammonium deposits.
- The average pH of 4.2 was relatively low with respect to other literature data.

Rainwater samples were collected in a rural region in Northern Jordan using 24-h sampling periods from December 1998 to April 2000 by Al-Momani. All samples were analyzed for major ions and trace metals. Precipitation chemistry in Northern Jordan was similar to that of other areas of the Mediterranean basin. Even though concentrations of SO_4^{2-} and NO_3^- were high, precipitation was neutral. The average pH value of rainwater was 6.36. High values of pH were attributed to the neutralization by natural alkaline local dusts which contain large fractions of calcite, while ammonium played a minor role in the neutralization process. The annual

average SO_4^{2-} to NO_3^- ratio was obtained as 1.8, which is close to that observed in more polluted regions. Some elements in the rain such as Zn, Cd, Se and As were potentially soluble, while the soluble and insoluble concentrations were comparable for Cu, Ni, Cr, V, Mn and Co. Enrichment factor calculations indicated that V, Ni and Cu were moderately enriched compared to mean crustal composition while Zn, Pb, As, Sb, Ag and Cd were highly enriched indicating the influence of anthropogenic input for these metals. Factor analysis had reasonably separated the major sources into four sources: Crustal, marine, road traffic emission, and finally combustion products and secondary aerosol formation (Al-Momani, 2003).

Similar studies were also present in Turkey but the number of the acid deposition or wet deposition monitoring station in Turkey is not enough to evaluate continuously the variation of atmospheric pollutants as dry or wet depositions. Some studies are applying independently by some universities, research institutions, and government establishments. Recently, Turkish State Meteorological Service has begun to monitoring long range transportation of air pollutants continuously for three points in Turkey.

The chemical characteristics of rainfall and its seasonal variation at the EMEP station located in Çubuk, Ankara were studied for the period between September 1994 and December 1996 (Topcu et al., 2002). The station is located in a rural area about 50 km north of Ankara and is considered as a background station for air pollution. The rainwater samples collected were analyzed for pH, major ions concentrations and conductivity. Seasonal variations for some major ions are pronounced. Generally, maximum concentrations appeared in winter or autumn, and minimum concentrations in spring or summer seasons. The average pH of rainwater samples is around 6.3 due to neutralization. Only about 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. This reflects strong inputs of alkaline species to rainwater samples in this location. The average pH of the samples higher than 5.6 observed in rural area of Ankara is due to a high loading of calcium ions in the form of $CaCO_3$ because of the alkaline nature of the soil. There is a strong relationship between pHs and other ions in summer. However, in winter, a weak relationship is found between SO_4^{2-}, NO_3^-, Na^+

and Mg^{2+}. On the other hand, relationships between the conductivity and SO_4^{2-} concentration are stronger in summer than in winter. The low concentrations of H^+ found in rainwater samples from Çubuk suggests that an important portion of H_2SO_4 and HNO_3 have been neutralized by alkaline particles in the atmosphere. Weak correlations are found between the hydrogen ions and SO_4^{2-} or NO_3^- ions for all seasons because of neutralization of these ions with alkaline particles. The dust-rich local and surrounding limestone environment might have caused the high concentration of Ca^{2+} in Çubuk area. The relatively high concentration of NH_4^+ observed at Çubuk is suspected to be due to surrounding agricultural activity. This agricultural activity has been found to be effective not only in spring, but also in autumn and winter to cause neutralization of the rainwater.

In another study, wet and dry deposition samples were collected near an industrial area on the Aegean coast of Turkey (Al-Momani et al., 1994). Concentrations of major ions (Cl^-, SO_4^{2-}, NO_3^-, H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, and NH_4^+) were determined. The pH of the precipitation, calculated from the volume weighted H^+ concentration, was found to be 5.6, indicating extensive neutralization of the acidity in the rain. Neutralization was found to be a local process. The main base responsible for the neutralization of acidity was NH_3 from fertilizer used in the region. 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 had only a minor influence. Although concentrations decrease with precipitation amount due to dilution in heavy rain, precipitation amount is not the only factor affecting concentrations of ions in precipitation. The main source of ions in wet deposition is the emissions from nearby industries. However, airborne NH_4NO_3 and $(NH_4)_2SO_4$ fertilizer particles may also contribute to observed concentrations of SO_4^{2-} and NO_3^- in rainwater. Dry deposition of most of the ions was higher than their annual wet deposition.

A study, was realized by Akkoyunlu & Tayanc (2003), presents the chemical composition of wet deposition that was collected at four different regions of İstanbul; Topkapı, Bağcılar, Maltepe and Göztepe, during the period January 2001–May 2001. Bulk deposition was collected together with the wet deposition at only one station, Göztepe, during the period of January 2001–December 2001. Fifty four wet deposition samples and 21 bulk samples were collected during the study period. The mean value of pH of wet deposition samples for all regions was found to be 5.26. Results indicate that Ca^{2+} concentration in precipitation was high, as was SO_4^{2-}, neutralizing the acidity. The mean value of the non-sea-salt fraction in the wet deposition for Ca^{2+} and SO_4^{2-} were 98 %, 91 % indicating that Ca^{2+} and SO_4^{2-} were mainly coming from sources other than sea. Difference between bulk and wet deposition of Ca^{2+} and SO_4^{2-} was found to be highest. Those differences between bulk and wet samples with respect to the overall concentration (wet + bulk) were lower than 30 % for ammonium and nitrate, while the differences of SO_4^{2-}, Ca^{2+}, Mg^{2+}, Cl^-, Na^+ vary between 62 % and 36 %. Higher enrichment factors were found for most ions and higher correlation coefficients were obtained among most of the ions in dry and bulk deposition, in comparison with wet deposition.

In another work, daily aerosol and wet-only precipitation samples were collected, between January 1992 and January 1994 at a permanent station established on the Mediterranean coast of Turkey (Al-Momani et al., 1997). Collected aerosol and rain samples were analyzed for major ions and a host of trace elements using a combination of analytical techniques, including ion chromatography, atomic absorption spectrometry and instrumental neutron activation analysis. The results have demonstrated that concentrations of parameters studied are higher than corresponding concentrations measured in the Western Mediterranean and western parts of the Black Sea due to longer transport distances to source regions of particles and precipitation scavenging from atmosphere. Elemental composition of aerosols and rain differ due to different scavenging efficiencies of elements associated with coarse and fine particles. Temporal behavior of elements was explained by variations in source strengths and variations in scavenging efficiency in this study.

In another work studied by Marmara University, composition of wet deposition in Kaynarca, Turkey is studied by collecting precipitation samples during more than a 2-year period, August 1993–November 1995 (Okay et al., 2001). 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, especially 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.

Concentrations of major ions, SO_4^{2-}, NO_3^-, Cl^-, H^+, Ca^{2+}, K^+, Mg^{2+}, Ca^{2+} and conductivity were measured in approximately 300 daily, wet-only rain samples collected at a permanent rural station between 1993 and 1998 at Ankara (Tuncer et al., 2001). Concentrations of anthropogenic ions NH_4^+, SO_4^{2-} and NO_3^- were among the highest values reported in whole EMEP network, suggesting that the Anatolian plateau is under strong influence of distant emission sources. Although transport of pollutants has significant influence on the chemical composition of precipitation, average pH of the rainwater is 6.2 due to extensive neutralization of acidity. Approximately 95 % of the acidity in collected samples is neutralized, particularly in summer season. The neutralizing agents are primarily $CaCO_3$ and NH_3. Concentrations of crustal ions are higher in summer season due to enhanced re-suspension of soil particles from dry surface soil. Concentrations of anthropogenic ions SO_4^{2-} and NO_3^- do not change significantly between summer and winter due to higher intensity of rains in summer season. Although concentrations of ions measured in this study is among the highest reported in EMEP network, wet deposition fluxes are low compared to flux values reported for similar sites in Europe, due to low annual precipitation in the Anatolia. Wet deposition fluxes of all

measured parameters are highly episodic. Source regions affecting chemical composition precipitation in the Central Anatolia is investigated using trajectory statistics.

Another study presents the chemical composition of bulk deposition during the period of February 1996–May 1997 and the chemical composition of sub-event wet deposition on 13 August 1997 in Gebze (Akkoyunlu et al., 2003). Samples were analyzed for SO_4^{2-}, NO_3^-, Cl^-, Ca^{2+}, K^+, Mg^{2+}, Na^+, and NH_4^+ in addition to pH. The source of some ionic components in the bulk deposition such as K^+ and Ca^{2+} were found to be the terrestrial regions, as expected. The [non-sea Cl^-]/[Cl^-] ratio of 0.05 suggests that the very large portion of Cl^- in the bulk deposition was of marine origin. The ratio of [non-sea SO_4^{2-}]/[SO_4^{2-}] varied between 0.86 and 0.99, indicating that the main source of sulfate was not the sea. It is found that the sulfate and calcium concentrations were highest in summer and lowest in fall. The analysis of bulk deposition also indicated that nearly 24 % of the events were acidic (pH < 5.6). During sub-event wet deposition collected on the same site pH decreased continually, and during the passage of cold front concentrations of Cl^-, SO_4^{2-} and NO_3^- increased.

In another study on precipitation chemistry, the precipitation near Buyukcekmece Lake, which is one of the important drinking water sources of Istanbul city, was studied during October 2001–July 2002 (Basak & Alagha, 2004). Seventy-nine bulk precipitation samples were collected at two sampling stations near the lake. The study comprised the determination of H^+, SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na, K, Mg, Ca, Al, Ba, Fe, Cu and Mn concentrations in bulk deposition rain event samples. The average volume-weighted pH value was found to be 4.81, which points out that the rain is slightly acidic. High sulfate concentrations were observed together with high H^+ ion values. Sulfur emissions were the major cause for the observed high hydrogen ion levels. On the basis of factor analysis and correlation matrix analysis, it has been found that in this region, acid neutralization is brought about by calcium rather than the ammonium ion. The varimax rotated factor analysis grouped the variables into four factors, which are crustal, marine and two anthropogenic sources.

In a study applied in Ankara metropolitan city in Turkey; daily, wet-only precipitation samples collected over a two year period were analyzed for SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, H^+, Ca, Mg, K, Na, AI, Cu, Cd, Cr, Zn, V and Ni. Weekly dry-deposition samples collected on petri-dishes over the same period were analyzed only for major ions (Kaya & Tuncel, 1997). Concentrations of ions and elements in Ankara precipitation were comparable with concentrations reported in literature for other urban areas. However, the wet deposition fluxes were the lowest among literature values, owing to small annual precipitation in the region. Although, annual average pH in precipitation was detected 4.7, episodic rain events with fairly low pH's were observed. Approximately half of the acidity in Ankara precipitation was neutralized in the winter season, while the acidity was completely neutralized by airborne soil particles that are rich in $CaCO_3$ in the summer precipitation. The SO_4^{2-} and, NO_3^- contributed approximately equally on the free acidity in winter. Main forms of SO_4^{2-} and, NO_3^- in precipitation were $CaSO_4$ and $Ca(NO_3)_2$, respectively. Crustal elements and ions had higher concentrations during summer season, while anthropogenic ions and elements did not show well-defined seasonal cycles. The lack of industrial activity in Ankara had profound influence on the temporal behavior of elements and ions.

General Review on Similar Studies

Local conditions such as geological, meteorological and anthropogenic conditions are important factors affecting to the results of these studies. Sea sprays are the main responsible for the majority of sea salts, such as Na, Cl, and Mg according to literatures. Another geological factor is geomorphology of the region soils because of regional impacts of earth's crust. Many of studies showed that the acidity of rains is neutralized thanks to calcareous structure of region soils by local process. Meteorological conditions are affecting the transportation of atmospheric pollutants to urban or rural areas. Industrial activities in the study areas are the main responsible for the majority of trace metals and acidification types in rain waters by the lights of these studies. A summary of literature data were given in Table 2.1.

Table 2.1.a Comparisons of volume weighted mean concentrations or arithmetic mean concentrations of pH, main and trace elements as reported in the literatures (ppb).

Parameter & Stations	Suburban						Urban		Worldwide Review[9]
	Antalya[1,i]	Ankara[2,i]	Eastern Mediterranean Basin[3]	Athens[4,i]	Ajlune[5]	Western Massach.[6]	Al-Hashimya[7,i]	Singapore[8]	
pH	5.2	4.7		6.5	6.4		7.5		
Al	580.0	980.0	73.0	5.9	382.0	53.0	386.0	18.4	
Ca		2640.0					12900.0		
Na	10000.0	530.0					3717.0		
Cd	4.5	9.5	4.3	0.2	0.4	0.31	11.8	0.3	0.5
Co								0.6	
Cr	9.0	3.0	3.7	1.3	0.8	0.14	6.2	1.6	0.44
Cu		6.1	3.1	15.4	3.1	0.95	9.9	5.6	5.4
Fe	530.0	750.0		4.4	92.0	65.0	363.0	23.9	
K	710.0	139.0					896.0		
Mg		240.0					820.0		
Mn			3.6	3.6	2.1	1.3	48.6	2.8	5.7
Ni		4.1	11.0	4.1	2.6	0.75		3.9	2.4
Pb		19.1	6.4	0.9	2.6	4.5	27.0	3.4	12
V	0.7	2.2			4.2	1.1		3.5	9
Zn	140.0	0.03	124.0	33.5	6.5	3.7	1230.0	7.2	36
Cl	18000.0	1460.0					7410.0		
NO_3	4900.0	2200.0					6020.0		
SO_4	6200.0	2500.0					20630.0		
NH_4	1300.0	1200.0					110.0		
Br	9.0								

Table 2.1.b Comparisons of volume weighted mean concentrations and arithmetic mean concentrations of pH, main cations and anions as reported in the literatures (µeq/L).

Parameter & Stations	Menemen[10] (Suburban)	Cubuk[11] (Suburban)	Ankara[12] (Suburban)	Kaynarca[13,i] (Suburban)	Patras[14] (Suburban)	Ajlune[5] (Suburban)	Galilee[15] (Suburban)	Albany[16,i] (Suburban)	Germany[17,i] (average values of 8 sites in different	Netherlands[18,i] (Suburban)	Colmar[19,i] (Suburban)	Pyrenees[20] (Suburban)
pH	5.6	6.3	6.1	5.6		6.4	4.2	4.1	4.2	4.1	5.7	
Na^+	117.0	15.6	21.0	69.4	90.2	50.0	60.9	5.0	60.9	290.0	70.0	23.0
K^+	17.0	9.8	19.0	40.7	6.6	11.1	3.8	6.0	3.8	28.0	83.0	9.0
Mg^{2+}	101.0	9.3		23.1	30.4	30.7	13.2	3.0	13.2	90.0	16.0	8.0
Ca^{2+}	81.0	71.4	210.0	290.0	98.5	108.1	15.0	10.0	15.0	60.0	166.0	94.0
NH_4^+	43.0	86.4	12.0	40.7	16.3	14.8	27.8	17.0	27.8	78.0	140.0	22.0
Cl^-	117.0	20.4		91.0	114.3	37.0	38.4	8.0	38.4	313.0	167.0	20.0
NO_3^-	23.0	29.2	62.0	31.6	19.4	75.5	42.3	45.0	42.3	47.0	78.0	18.0
SO_4^{2-}	66.0	48.0	150.0	305.9	46.1	62.1	75.2	68.0	75.2	140.0	147.0	51.0
F^-				30.3								

Notes: i. Values in these columns were given as arithmetic mean concentrations; others were given as volume weighted mean concentrations.

[1.] Al-Momani et al., 1997. [2.] Kaya & Tuncel, 1997. [3.] Al-Momani et al., 1998. [4.] Kanellopoulou, 2001. [5.] Al-Momani, 2003. [6.] Dasch & Wolff, 1989. [7.] Al-Momani et al., 2002. [8.] Balasubramanian & Hu, 2003. [9.] Galloway et al., 1982. [10.] Al-Momani et al., 1995. [11.] Topcu et al., 2002. [12.] Tuncel & Ungor, 1996. [13.] Khwaja & Husain, 1990. [14.] Glavas, 1988. [15.] Herut et al., 2000. [16.] Okay et al., 2001. [17.] Grömping et al., 1997. [18.] Schuurkes et al., 1988. [19.] Sanusi et al., 1995. [20.] Camarrero & Catalian, 1993.

Trace metals and major ions in rain waters have been investigated frequently in the world for the last one fourth century. Long Range Transportation of atmospheric pollutants and its impacts on the urban areas organize generally the main aims of studies. Moreover regional applications and middle range transportation are also other goals of many of these studies carried out on rainwater. There is no detailed investigation on rain waters in our region for these purposes. By the lights of mentioned studies before, we programmed a study on rainwater chemistry in İzmir to obtain chemical composition of precipitations, and to evaluate of data in a regional perspective. We aimed at least to take the first step to be able to carry out a useful investigation in our region, in İzmir.

CHAPTER THREE
MATERIALS AND METHODS

3.1 Sampling Sites

This study was carried out in city of İzmir, located at the east coast of Aegean Sea and surrounded by relatively high mountains (~500-1000 m). There are many industrial activities located in industrial zones such as Çiğli Industrial Zone (located on northwest of the city), Bornova (east), and Gaziemir Free Zone (south). İzmir is also surrounded by several industrial counties like Kemalpaşa (east, ~20 km), Torbalı (south, ~30 km), Menemen (north, ~30 km), and Aliağa (north, ~40 km). There are many heavy industries in Aliağa like a petroleum refinery, a petrochemical complex and electric arc furnaces etc.

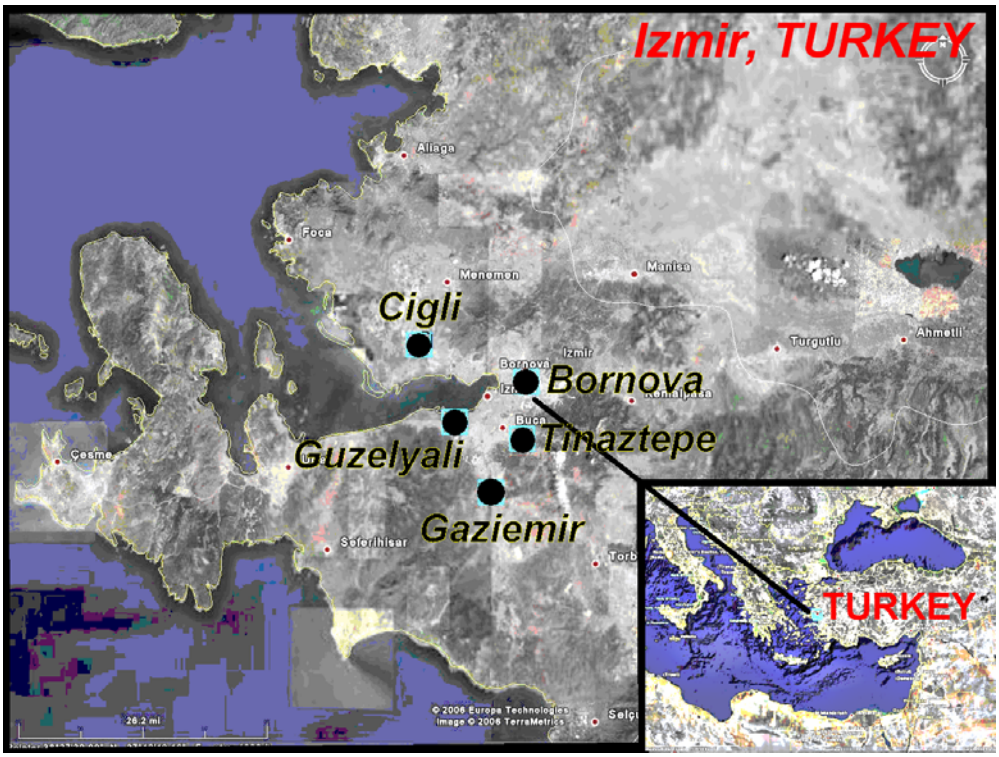


Figure 3.1 Geological perspective of sampling stations.

Rain samples were collected from five sampling stations located in Buca (Tınaztepe), Güzelyalı, Bornova, Gaziemir and Çiğli (Figure 3.1). These sampling

stations are characterized in Table 3.1 and 3.2, together with some micro-climatic conditions, respectively.

Tınaztepe sampling station is located at Tınaztepe Campus of Dokuz Eylül University, 10 km far from city center and has suburban characteristics. The campus is relatively far from any settlement zones or industrial facilities. There are residential areas located ~2km southwest and a highway 0.5 km south of the sampling site. Land cover in the immediate area is a young coniferous forest.

Güzelyalı sampling station takes place in a settling point near the Aegean Sea shoreline in İzmir at 38^{o} 23' N, 27^{o} 05' E and 29 m height from sea level. The sampling equipments are located in meteorological observation area located at 5 km southwest of İzmir centre. Composition of rainwater in this station is affected from local micro-meteorological conditions and local sources together with transported pollutants. Local pollutant sources in this site are residential heating and motor vehicle emissions.

Table 3.1.a Monthly average meteorological properties of Güzelyalı and Bornova sampling stations.

Meteorological Conditions / Months / Stations	**GÜZELYALI**			**BORNOVA**		
	Monthly Average Precipitation Amount	**Average Wind Speed**	**Prevailing Wind Direction**	**Monthly Average Precipitation Amount**	**Average Wind Speed**	**Prevailing Wind Direction**
January	130.1	3.5	SE	105.2	2.0	NE
February	101.3	3.7	SE	88.4	2.0	NE
March	74.7	3.5	SE	68.2	1.9	NE
April	44.8	3.3	SE	48.9	1.4	NE
May	30.7	3.1	WNW	31.3	1.6	W
June	7.9	3.2	WNW	8.4	1.9	NE
July	2	3.4	W	2.7	2.5	NE
August	2.6	3.3	W	2.3	2.4	NE
September	11.4	2.9	WNW	13.5	2.0	WSW
October	37.8	2.8	SSE	36.3	1.8	WSW
November	95.4	3.0	SE	87.5	1.6	ENE
December	149.7	3.5	SE	122.4	1.9	ENE
Annual Average or Totals	688.4	3.3	SE	615.1	1.9	NE

Table 3.1..b Annual average meteorological properties of Güzelyalı and Bornova sampling stations.

Meteorological parameters	**Unit**	**Güzelyalı**	**Bornova**
Annual Average Pressure	mb	1011.1	1011.7
Annual Average Temperature	° C	17.7	17.3
Annual Average Max. Temp.	° C	22.5	23.1
Annual Average Min. Temp.	° C	13.3	11.7
Annual Total Precipitation	mm	686	613
Average Wind Speed at 10 m upper	m/s	3.3	1.9
Prevailing Wind Direction	-	SE	NE
Average Humidity	%	62.1	58.8
Average Cloudiness	10/10	3.4	6.1
Number of Rainy Days (amount ≥0.1 mm)	Day	78	77
Number of Stormy Days (Wind Speed≥17.2 m/s)	Day	18	-
Number of Cloudiness Days (Cloudness≤1.9)	Day	152	171
Number of Cloudy Days (Cloudness, 2.0 - 8.0)	Day	176	156
Number of Most Cloudy Days (cloudness≥8.1)	Day	36	38

Bornova sampling station was meteorological observation area of Bornova Meteorological Station takes part in a settling point located from 10 km east way from the city center at 38^{o} 28’ N, 27^{o} 13’ E and 27 m height from sea level. There are two cement plants and many stone quarries in eastern part of the station. This station is about 10 km far from Tınaztepe and 15 km from Güzelyalı sampling station

Gaziemir sampling station located in an airport (Adnan Menderes Airport Area) area 5 km far from nearest sampling site and 14 km far from the Aegean Sea shoreline in İzmir. The sampling equipments are located in meteorological observation area in airport area. This station satisfy the conditions requested for monitoring a long range atmospheric pollutant transportation except located in an airport. Composition of rainwater in this station is affected from local micro-meteorological conditions and local sources together with transported pollutants. The nearest local pollutant source in this site are residential heating with substantial contribution from aircraft vehicle emissions.

Gaziemir sampling station is located approximately 20 km south of İzmir's center. But the sampling point is relatively far from any industrial facilities. There are

approximately 10-15 km between this station and Tınaztepe sampling point and Güzelyalı sampling point, and approximately 20 km between this station and Bornova sampling point. Meteorological conditions belonged to this sampling point are listed in Table 3.2.

Table 3.2 Meteorological properties of Gaziemir and Çiğli sampling station.

Meteorlogical parameters	**Unit**	**Gaziemir**	**Çiğli**
Average Temperature	° C	16.3	16.9
Average Max. Temperature	° C	22.2	22.7
Average Min. Temperature	° C	10.8	11.4
Annual Total Precipitation	mm	690	484
Average Humidity	%	56.1	60.3
Number of Rainy Days (amount ≥0.1 mm)	Day	72	63
Prevailing Wind Direction	-	NW	N-NE

Çiğli sampling station is located at military aircraft area in the north of İzmir Bay. The sampling equipments are located in meteorological observation area. This station takes place between two industrial organised districts. There are power plant and many different industries in Menemen Leather Manufacturing Free Zone and Atatürk Organised Industrial Region. Çiğli sampling station is also the nearest sampling point to the Aliağa Industrial Region. The distance is approximately 35 km far on north direction from İzmir. The sampling site is located approximately 18 km northwest of İzmir's centre. Average meteorological conditions are given also in Table 3.2.

3.2 Sampling

3.2.1 Sampling Equipments

Rainwater samples were taken by automatic sampler in Tınaztepe station. Automatic Sampler was modified similar to EIGENBRODT NSA 181 wet only precipitation sampler, especially its working mechanism.

An impulse from the precipitation sensor at the start of precipitation causes the cover device to open up the collection funnel in the following way: the lid moves up,

swings to the side and sinks down to prevent introducing aerodynamic interference to the sampling process. The precipitation coming from the funnel flows over a pipe into the bottle. When precipitation has ceased, a signal from the Precipitation Sensor, causes a motor to close the collection funnel.

In other four stations, samplings of rainwater succeeded manually by meteorological personnel at the meteorological stations. The sampling equipments is very similar to a bulk precipitation sampler. Working as a grab sampling mechanism is the only difference between them. Equipments consist of a polycarbonate plastic funnel, plastic sampling line, a HDPE sampling bottle and a steel frame.

Rainwater samples were taken manually as wet deposition type. When precipitation started or before approximately 1-2 hour, the portative equipments were immediately located to the frame in the observation park by cleaning with distilled deionise water. After the precipitation ended, the precipitation samples were taken to the HDPE sampling bottle from HDPE field sampling box. Gloves were used to prevent the contamination from the environment by personnel. Then the portative apparatus was dislocated, cleaned with 3 % HNO_3 solution and distilled deionise water, and saved safely to prevent the contamination from the environment at the meteorological station. Samples were saved in the refrigerator at 3-5^{o}C until they were brought to the laboratory. Also, to prevent contamination portative sampling apparatus were dislocated every month the new clean ones. Samples taken by this way were accepted as daily samples, and registered methodically. A detailed form was used regularly to register sampling observations and some meteorological parameters at sampling periods. (Appendix – Form 1).

The automated wet only sampler was located on the roof of a platform at Tınaztepe sampling point (on Kaynaklar Campus of the Dokuz Eylül University) and was illustrated in Figure 3.2.

Figure 3.1 (a) General view of Tınaztepe sampling platform, (b) and (c) general perspectives of automated sampler, (d) plastic collection funnel of sampler, (e) rain sensor of sampler.

Other manual sampling apparatus were located in meteorological observation parks at the station. The top level of the sampling equipment was high approximately 1.80-2.00 m from ground and the opening area is 700 cm^2. Steel frame was immobilized in the park, other apparatus were portative and they were saved in the station safely except rainy days. The general view of equipments of portative sampler was illustrated in Figure 3.3.

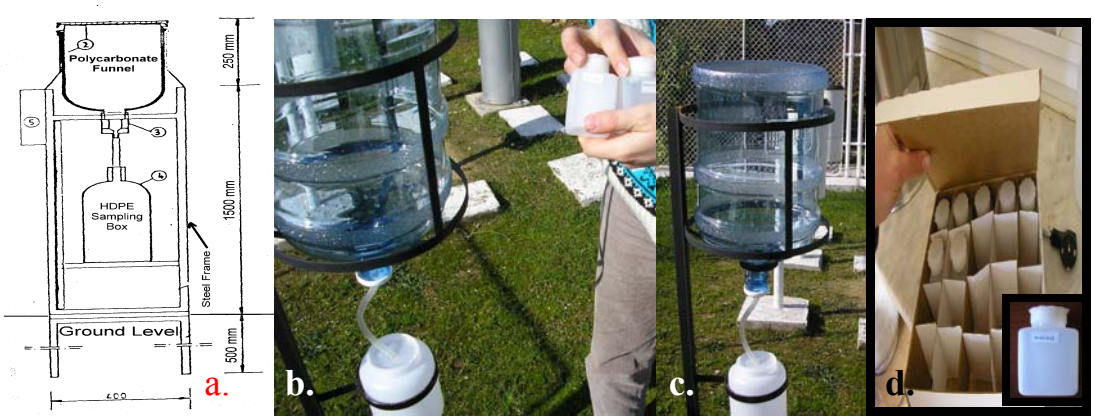


Figure 3.2 (a) Schematic view of manual sampling equipments, (b) and (c) general views of manual sampling equipments located in meteorological observation parks, (d) storing of sampling bottles.

3.2.2 Sampling Procedure

Polyethylene bottles used for sampling were firstly soaked in 20% HNO_3 for two days. Then, they were kept in a more diluted HNO_3 solution for two more days. Following that, they were washed with distilled deionize water three times. After drying them, if the value of electrical conductivity belong to bottles' washing water is smaller than 1 $\mu S\ cm^{-1}$, it was concluded that the bottles were clean enough to be used for sample collection. Only non-acidified bottles for rainwater collection in the instrument was used because of preventing the contamination of the sample with nitrate from the acid added to achieve solubility of metals. They only be washed by de-ionized water and stored in Class-100 clean laboratory, Environmental Engineering Department, DEU. Finally, their taps were closed; they were given an identification number, and sealed in a big plastic bag before they are shipped to the field. Then the bottles were sent with sampling information sheet to the sampling stations.

Daily wet deposition sampling was the main procedure. By using manual system or automated system all samples were taken daily and registered systematically. Rain samples were collected in 2 L HDPE box for manual sampling units and 5 L HDPE box for automated sampling units. The sampling bottles prepared at the laboratory as mentioned above were transferred to the site in plastic bags. Rainwater collection bottles used in this work was non-acidified portion collection bottles. The boxes were removed from the sampler every month, and changed the new ones. At each visit to the

site, in this regard, the cleanness of the sampler, organic materials (flies, insects, etc.), fertilizer activities and coal burning activities around the region were checked and recorded. In addition to the above listed points, field blank was sampled by washing the sampler by 100 ml. of deionised water. However, in cases of no rain, no field blank was taken. Then the samples were transported to the laboratory every Monday in a collection vessel. Before they were transported to the laboratory, and stored in a dark place in a refrigerator at the stations. The samples had ambient temperature during their transport, which lasts about 1-2 hour.

The rainwater samples and field blanks were sent to the laboratory at approximately a month prior to the analysis. The samples were kept in the refrigerator at 4°C until analysis. During sample handling processes, all sample manipulations were done using Teflon coated tweezers and polyethylene gloves.

The sample handling and preparation manipulations were carried out in a clean area in the Environmental Engineering Department. The clean room consisted of two parts. The big part of the rooms was used as a laboratory for storage of samples in the refrigerator and there were pH meters and de-ionized water preparation units in this room. The other one contains Ion Chromatography and ICP-OES instruments.

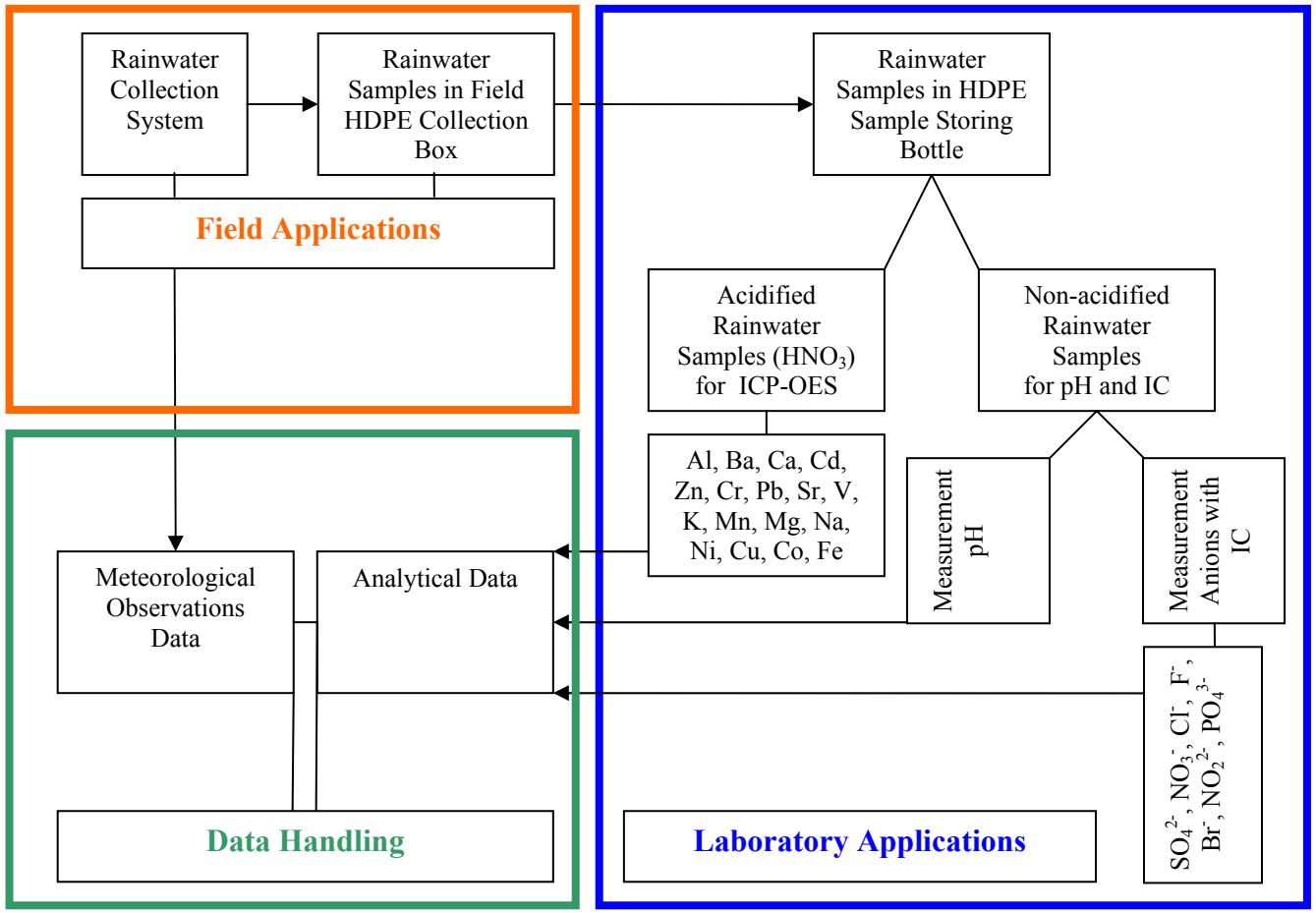


Figure 3.3 Flow diagram used in our studies for rain samples treatment.

At the laboratory, the taps of the sampling bottles were opened and the bottles with the collected precipitation are weighted. Then the difference between the pre-sampling and after-sampling weights was accepted as the sample precipitation volume. Determinations of volume were not necessary for samples collected from Meteorological Office. The precipitation heights in those samples were taken from meteorological observations.

The majority of concentrations, type of the pollution sources, and satisfactoriness of the chemical applications and instruments are effective in selecting the type of the chemical parameter. According to our working procedure in this study pH, anionic concentrations and elemental concentrations were measured. To measure pH and anionic concentration the samples were not acidified. The non-acidified portion of rainwater was used for analysis of major anions, SO_4^{2-}, NO_3^-, Cl^-, F^-, Br^-, NO_2^{2-}, PO_4^{3-} by using the ion chromatograpy. Acidified portion of samples were used for the determination of the concentrations of major or trace metals, Al, Ba, Ca, Cd, Zn, Cr, Pb, Sr, V, K, Mn, Mg, Na, Ni, Cu, Co, Fe, by using inductive coupled plasma optic emission spectroscopy (ICP-OES).

3.3 Analysis

EPA Methods, WMO and EMEP Guidelines related to this work on chemistry of wet deposition were evaluated, sampling and analytical procedures contained in those methods were tried to apply adequately in every steps of this study.

Related analytical methods, instrumentations, chemicals and standard solutions applied in these studies are listed below in Table 3.3, and Table 3.4. Analysis techniques and the devices used to measure the anions, cations, and pH were also given in Table 3.5. The measurement procedures for the corresponding ions were explained in the subsequent sub-sections.

Table 3.1 Standard solutions used in this study, and their specifications.

Analyse	**Type of Standard**	**Manufacture**
pH (0-14)	WTW D 82362 Certificated NIST/PTB	WTW
IC	Seven Anion Standard Na_2CO_3 as eluent	Dionex
ICP-OES	ICP-SS (ICP Stock Solution) ICP-CCV-1 (ICP Continuing Check Verification Standard	High Purity Standards
Conductance	KCl, Analytical Grade	Merck

Table 3.2 Chemicals used in this study, and their specifications.

Chemicals	**Instrumentation or manufacture**	**Specifications**
Deionise water	Millipore	Conductance<18μΩ
Analytical grade HNO_3	Merc	
Ultrapure HNO_3	Merc	Density, 65.5 %
KCl	Merc	
Na_2CO_3	Dionex	

Table 3.3 Detailed lists of measured parameters, related analytical techniques and instruments.

Parameters	**Analytical Techniques**	**Instrumentation**
Volume, Liter	Volumetric	GEC Avery
pH	Electrometric	WTW pH 720 Model Sentix 81 pH Electrode
SO_4^{2-}, NO_3^-, Cl^-, F^-, Br^-, NO_2^{2-}, PO_4^{3-}	Ion Chromatography	Dionex ICS-3000 Series IonPac AS9-HC Analytical Column (4 x 250 mm). IonPac AG9-HC Guard Column(4x50mm) Suppressed Conductivity ASRS-ULTRA II AutoSuppression Recycle Mode
Al, Ba, Ca, Cd, Zn, Cr, Pb, Sr, V, K, Mn, Mg, Na, Ni, Cu, Co, Fe	Optic Emission Spectroscopy	Perkin Elmer OPTIMA 2100 DV ICP/OES AS-93plus Autosampler

All reusable laboratory ware (Glass, Teflon, Polyethylene etc) were carefully rinsed prior to use to avoid contamination of the samples. Sampling boxes and bottles were rinsed with de-ionized water and soaked in 20 % HNO_3 for 24 hours. After the acid bath the bottles for storing of precipitation samples were rinsed 3 times. The sampling boxes were rinsed 3 times with de-ionized water, dried, stopped and packed in clean plastic bags with locks.

Disposable pipette tips were placed in a plastic can filled with 3 % HNO_3. The bottle was turned upside down a few times to assure that the tips were filled with the

acid solution. The tips were left in the acid solution for minimum 12 hours. The acid solution was poured out and rinsed the tips by filling the bottle with de-ionized water 3 times. Bottle was shook as much as possible of the water out of the bottle and tips, and they were kept in the stopped bottle until use.

Auto sampler tubes and cups (polystyrene or polyethylene) using for ICP analyses were rinsed with de-ionized water, soaked in 20 % HNO_3 for minimum 24 hours and rinsed 3 times with de-ionized water before use. Vials used for IC analyses were only one usage.

3.3.1 Determination of pH

In our study, the pH of the collected samples was measured using a WTW 720 pH meter, equipped with a Sentix 81 glass electrode. The pH meter is calibrated before each measurement using standard buffer solutions (manufactured by WTW) at pH 4.00, 7.00 and 10.00. The samples were placed in a 20°C water bath, then, pH was measured.

3.3.2 Determination of Anions by Ion Chromatography

The ion chromatograph was calibrated with standard solutions containing known concentrations of the ions of interest. Calibration curves were constructed from which the concentration of each ion in the unknown sample is determined (EMEP Manual for Sampling and Chemical Analysis, Revision May 2002).

The samples measured pHs were filtered through 0.2 μm Teflon filter into polypropylene container (vials for IC) at the clean air bench.

Since major ions were water soluble, they could be analyzed without significant sample preparation. However, fine particulate matter could clog the ion chromatographic column that they should be removed by the filtration procedure before Ion Chromatography (IC) analysis.

Precipitation samples were analyzed for the ions SO_4^{2-}, NO_3^-, Cl^-, F^-, Br^-, NO_2^{2-}, and PO_4^{3-} by using a Dionex DC-3000 model coupled with an AG9-HC guard column, an AS9-HC separation column, and an AMMS-II suppressor column with a flow rate of 200 ml min^{-1}. 10 mM Na_2C0_3 was used as eluent in the analysis. Operating parameters of IC were given in Table 3.6.

Table 3.6 Operating parameters of IC.

Instrument	Dionex ICS-3000 Series
Eluent (mobile phase)	10.0 mM Na_2CO_3
Anion guard column	Ionpac AG9-HC Guard Column (4x50 mm)
Anion exchange column	IonpacAS9-HC Analytical Column (4x250 mm)
Detection	Suppressed Conductivity ASRS®-ULTRA II AutoSuppression® Recycle Mode
Sample injection volume	200 – 400 µL
Standard Solution	Dionex Seven Anion Standard II (0.01, 0.02, 0.10, 0.20, 1.00, 2.00, 5.00 and 10.00 ppm as Floride concentrations).
Mobile phase flow rate	3.0 mL min^{-1}
Buffered pH (mobile phase)	11.0

Additionally, 1.00 g L^{-1} Dionex standard solutions were used in the analysis. Standard calibration solutions were prepared in the concentrations of 0.01, 0.02, 0.10, 0.20, 1.00, 2.00, 5.00 and 10.00 mg L^{-1} as Fluoride concentrations.

3.3.3 Determination of Major and Trace Metal by ICP-OES

Rainwater samples (total soluble fraction in the value pH<2) were analyzed for elemental concentrations of 17 elements (Al, Ba, Ca, Cd, Zn, Cr, Pb, Sr, V, K, Mn, Mg, Na, Ni, Cu, Co, and Fe) by using ICP-OES.

Samples, which were separated to determine elemental concentration by ICP-OES was stabilized and digested by adding ultra pure HNO_3 solution. The samples were prepared as 3 % HNO_3 solutions before minimal a week period prior to analyse. The blank samples and calibration samples were treated the same way to have same matrixes.

Table 3.1 Operating parameters for ICP-OES.

Power	1.50 kW
Plasma gas flow	15.0 L/min
Auxiliary gas flow	0.2 L/min
Nebuliser Gas Flow or pressure	0,7 L/min (45 psi)
Pump speed	1.5 rpm
Sample delay	15 second
Stabilization time	15 second
Rinse time	20 second
Replicate time	20 second
Replicates	2
Autosampler	AS-93plus Auto sampler
Instrumentation	Perkin Elmer OPTIMA 2100 DV ICP/OES

Perkin Elmer DV-2100 ICP-OES Spectrometer was used for determination of the chemical composition of rainwater samples. The operating parameters were given in Table 3.7. These parameters were found to be very crucial in determining elements with very low concentrations as it is the case in rainwater samples. Ca and Na were detected in radial mode while the rest were in axial mode.

At the beginning of analysis, all the instrumental parameters were optimized and the instrument was allowed to warm for about 20-30 minutes. The rainwater matrix was first scanned for the elements that could be measured under the optimized experimental conditions, then the sensitivity check where performed using at least 2 different High Purity Standards (CCV-1). The Standard Concentration has been certified by spectrometric analysis against an independent source which is directly traceable to National Institute of Standards and Technology (NIST), Standard Reference Material No. 3100 series (SRM 3100). Calibration curves were prepared by ICP-SS (ICP-Stock Solution) assured from High Purity Standards Company.

After all the sensitivity check tests were passed within ± 10 % error or better, the measurements were continued until all the assigned sets were analyzed. ICP-CCV-1 standard solutions assured from High Purity Standards Company were used as quality check standards. While analysing of samples was going on, QC (Quality Check Standard CCV-1) were analysed after every 10 analyte and the safety of the analysing examined between 90% and 110%.

3.4 Quality Assurance & Quality Control

3.4.1 Field Operations

In terms of field operations, as given in Section 3.2, field journals and records about precipitation samples, meteorological observations were kept at each visit to the site. Additionally, monthly journals are prepared regarding the state of the sampler and the collected samples. The field blanks were prepared at the sampling site by passing about 100 mL of deionized water through the rain samples.

Also, meteorological parameters were registered as an evenly file in journal folder in meteorological office by meteorological personnel. Ravinsonde files were also saved at sampling days. All of the meteorological observations were re-collocated along the sampling periods. Especially, wind directions were evaluated at surface and 850 hPa levels.

Furthermore, daily field blank samples were used in order to check the possible sample contamination errors. A field blank is a sample which has been prepared, handled and analyzed as a normal sample in every way, except that it has not intentionally been exposed and therefore should not contain the substance to be determined. The change in the field blank concentrations was monitored along the study. The collected field blanks were treated as a real sample and analyzed using ICP-OES and IC.

3.4.2 Laboratory Operations

Laboratory operations as data handling protocol consist of preparing of laboratory blanks, analysing of field and laboratory blanks to determine method detection limits and assurance of data quality of analytical results.

Laboratory blank samples were used in order to check the possible sample contamination errors. A laboratory blank was a sample which had been prepared,

handled and analyzed as a normal sample in every way, except that it had not intentionally been exposed and therefore should not contain the substance to be determined. The handled laboratory blanks were treated as a real sample and analyzed using ICP-OES and IC.

The change in the laboratory blank concentrations and field blanks concentrations was monitored along the studies and the related samples were not accepted reliable data when any contamination was experienced in blank samples.

pH - meter was calibrated at certificated reference solutions at the pH levels of 4, 7 and 10. For every ten samples, pH-meter was controlled by standard solutions and a reference rain sample. When some differences were obtained in reference sample or standard solutions' pH values, pH - meter was recalibrated and rain samples were re-measured.

The ICP-OES was calibrated daily using a certified standard solution. The analysis of samples was performed only if the *r* of calibration curve was greater than 0.99. A calibration check solution was prepared by another certificated solution and the calibration curves were checked just after the initial calibration and for every 15 samples. If the deviation was more than ± 10 %, the instrument was re-calibrated.

The repeatability of the ICP-OES was controlled many times in several days by analyzing some samples, recovery aliquots and calibration check solution. The deviation was lower than 10 %. The comparative test of The Scientific and Technical Research Council of Turkey-National Metrology Institute (TUBITAK-UME) was passed two times for 7 elements.

The IC was calibrated daily using certified standard solutions. The analysis of samples was performed only if the *r* of calibration curve was greater than 0.99. A calibration check solution was prepared by a certificated solution and the calibration curves were checked just after the initial calibration and for every 10 samples. If the deviation was more than ± 10 %, the instrument was re-calibrated.

The daily and periodic maintenance of the device was performed. The cleaning of sample conveying line, apparatus and optics of the device was performed periodically as explained in the user manual.

Calculation of Detection Limits: The detection limit was taken to be three times the standard deviation of the blank results. The probability for having of this size is less than 0.5 %. The detection limit was calculated by the following equations.

$$L_d = 3.0 \times S_b \tag{3.1}$$

$$S_b = \left(\left(\frac{1}{1-N} \right) \sum_{i=1}^{N} (C_i - \overline{C})^2 \right)^{1/2} \tag{3.2}$$

Where N is the number of field blanks, C_i is the concentration of the relevant substance in the i.*th* field blank and C is the field blank average after elimination of "extreme" blank values.

The detection limits for rainwater constituents were calculated from 10 replicates of the field blank samples. It was accepted that below this value data has significant limitations. Detection levels, sample average values, and ratios of sample average values to blank average values for ICP-OES analysis were listed in Table 3.8.

The detection limits of ion chromatography was defined also as three times the standard deviation of the blank as defined in Equation 3.2. The detection limits (ppb) of anions, which measured by IC analysis, were calculated with in these criteria and given in Table 3.8. All the detection limits calculated from these analytical techniques are much smaller than corresponding observed concentrations of the elements in the samples.

Table 3.8 Detection levels, sample average values, and S/B ratios for ICP-OES and IC analysis.

ICP-OES Analysis				IC Analysis		
Elements	**Dedection Limits (µg L^{-1})**	**Field Blank Levels (µg L^{-1})**	**Sample Average (µg L^{-1})**	**Ions**	**Dedection Limits (µg L^{-1})**	**Sample Average (µg L^{-1})**
Al	6.34	<DL	191.49	**F^-**	2	61.93
Ba	0.19	<DL	11.12	**Cl^-**	5	3631.75
Ca	57.9	<DL	4923.82	**NO_2^{2-}**	6	101.25
Cd	0.06	0.17	0.80	**Br^-**	6	14.00
Co	0.11	<DL	0.74	**NO_3^-**	8	1931.74
Cr	0.11	0.53	1.44	**PO_4^{3-}**	15	212.97
Cu	0.51	0.95	11.10	**SO_4^{2-}**	10	9115.28
Fe	3.47	5.88	140.40			
K	6.06	11.00	390.42			
Mg	9.02	<DL	490.09			
Mn	0.34	0.63	14.18			
Na	21.9	98.40	2280.92			
Ni	0.3	0.78	5.00			
Pb	0.82	0.58	7.71			
Sr	0.14	0.52	14.54			
V	0.66	<DL	6.18			
Zn	0.78	<DL	35.32			

Notes: Obtained values belong to field and laboratuary blank samples prepared for IC, and laboratuary blanks prepared for ICP-OES were obtained below the detection levels along the studies. The related samples were also not accepted reliable data when any contamination was experienced in blank samples.

3.5 Data Analysis

In this section, statistical methods used for data analysis were described with some experimental examples. These statistical methods consist of volume weighted mean value, basic and descriptive statistics, parametric or nonparametric statistics for independent groups, correlation matrixes and factor analysis as principal component analysis.

Since the concentrations of elements and ions in rain water were expected to be inversely related with the precipitation amount, variations in their measured concentrations were partly due to different precipitation volume in each sample. Volume weighted arithmetic averages were frequently used in the literature to avoid the contribution of precipitation amount on the annual average concentrations at the receptor (Kaya & Tuncel, 1997). In this way, large variations in the data set were smoothed out, presenting a better description.

Precipitation weighted arithmetic average is given by the following equation:

$$Cp = \frac{1}{\sum_x p_x} \times \sum_x (C_x \times p_x) \quad (3.3)$$

where C_p is the precipitation weighted concentration, p_x is the precipitation amount of day x and C_x is the concentration of an element or ion in that particular day.

Monthly wet deposition fluxes of trace metals were calculated as the product of the monthly volume-weighted precipitation concentrations and corresponding volume of the monthly precipitation depths:

$$F_{wd} = C_p . V_{mpd} \quad (3.4)$$

where F_{wd} is the calculated metal flux from precipitation (mg m^{-2} $month^{-1}$), C_p is the volume-weighted metal concentration measured in precipitation (μg L^{-1}), V_{mpd} is volume of the total precipitation depth during each month (m^3).

Enrichment factors (EFs) are good indicators for classifying sources of metals as either natural or anthropogenic (Mason, 1966). In this study, crustal enrichment factor (EF_c) and marine enrichment factor (EF_m) were calculated using the following equations:

$$EF_c(X) = (X/Al)_{rain} / (X/Al)_{crust}, \quad (3.5)$$

where (X/Al) rain and (X/Al) crust refer to the ratio of the concentration of metal X to that of Al in rainwater and to that in the Earth's crust, respectively.

The marine enrichment factors (EF_m) of different species with respect to Na were calculated using the equation:

$$EF_m(X) = ([X]/[Na])_{rain} / ([X]/[Na])_{seawater} \quad (3.6)$$

where; [X] = concentration of ion (x) of interest.

The sea salt fraction and non-sea salt fraction have also been calculated. The calculation of non-sea salt concentration using Na as a reference component can be expressed as in the equation:

$$NSS(X) = Total[X]_{rain} - f_x[Na]_{rain} \quad (3.7)$$

where; f_x = correction factor for (X) component.

Descriptive statistics of the elements, anions and pH measured at stations include arithmetic mean, associated standard deviation, geometric mean, median, minimum, maximum values and distribution properties. Descriptive statistics were calculated separately for each variable, and they provide such basic information as the mean, minimum and maximum values, different measures of variation, as well as data about the shape of the distribution of the variable. The measures of variation include the standard deviation, and the standard error. Numerous tests of whether the distribution of variables follows the normal distribution were also provided.

FA (Factor Analysis) was also commonly used a statistical method to determine the sources of environmental components all around the world. Statistica 6.0 software was used for FA. Principle component analysis with Varimax rotation was applied. The factors that eigenvalue was greater than 1 were taken into consideration.

The main applications of factor analytic techniques are: (1) to reduce the number of variables and (2) to detect structure in the relationships between variables, that is to classify variables. Therefore, *factor analysis* is applied as a data reduction or (exploratory) structure detection method.

Varimax normalized selection of the *Factor Rotation* performs a varimax rotation of the normalized factor loadings (raw factor loadings divided by the square roots of the respective communalities). This rotation is aimed at maximizing the variances of the squared normalized factor loadings across variables for each factor; this is

equivalent to maximizing the variances in the columns of the matrix of the squared normalized factor loadings. This is the method that is most commonly used and referred to as varimax rotation.

Parametric or nonparametric correlation represents the association between variables. Correlation coefficient (r) quantifies the amount and the way of this relation. Correlation coefficient is a familiar way to characterize the association between the variables. Statistica 6.0 was used to determine the correlation coefficients (r). This program gives the correlations (p=0.05) as a matrix named correlation matrix.

As mentioned in this section, all statistical tests and evaluating of results were performed and interpreted in the next chapter.

CHAPTER FOUR
RESULTS AND DISCUSSIONS

This chapter consists of measurement results together with statistical evaluations of results (especially distribution properties of data, parametric or nonparametric statistically evaluations, correlations and factor analysing), and the evaluation of results with respect to meteorological observations, and discussions on general evidence related with this research.

Five sampling points had been selected at the beginning of studies: Bornova, Çiğli, Güzelyalı, Adnan Menderes Meteorological Offices and Kaynaklar Campus. Some sampling stations were cancelled mandatory 2-4 months later because of difficulties in sampling and transportation steps and deficiencies of the number of meteorological personnel. Studies were carried on at Bornova, Güzelyalı and Tınaztepe sampling points at least 1 year. Detailed station properties such as sampling period, number of the samples, and sampling recoveries were listed in Table 4.1 for analysis of pH and element and Table 4.2 for analysis of anions, respectively.

Evaluation of data related with all of the studies on precipitations at İzmir firstly discussed individually for sampling points. Two sampling points Çiğli and Gaziemir sampling points have not enough data for meaningful evaluations because of difficulties in sample handling steps. Therefore, evaluation of data handled from these stations was considered superficially in this chapter. Detailed evaluations of datasets from other stations were conducted in sub-sections.

4.1 Experimental Results

There are several tools to infer about the distribution characteristics of the measured precipitation data. Arithmetic mean to geometric mean ratios and skewness coefficients are initial indicators of the type of distribution. Subsequently, statistical tests can be applied to verify the proposed distribution of data. Skewness is a value to measure the symmetry in the distribution of the data. If the mean is greater than the median, then the data is right skewed and the right end of the plot has a longer tail. If

the mean is less than the median, then the data is left skewed. Skewness coefficient is an indicator of the asymmetry in a distribution around its arithmetic mean. A positive index implies rightward skewness, whereas a negative index shows leftward skewness.

Table 4.1 Sampling period and number of the samples of sampling points for pH and elements.

Measured Parameter	***pH and Elements***										
Station	**2004-2005 Rainy Period (September-August)**					**2005-2006 Rainy Period (September-August)**					**Total number of the Samples**
	Starting Date for sampling	**Ending Date for sampling**	**Number of the Analysed Samples**	**Number of the rainy days (≥0.5 mm)**	**% Sampling Recovery**	**Starting Date for sampling**	**Ending Date for sampling**	**Number of the Analysed Samples**	**Number of the rainy days (≥0.5 mm)**	**% Sampling Recovery**	
Bornova	12/11/04	07/08/05	37	67	55	16/09/05	19/03/06	34	51	67	*71*
Güzelyalı	06/11/04	31/05/05	41	64	64	16/09/05	30/04/05	41	58	71	*82*
Tınaztepe	-	-	-	-	-	02/10/05	30/04/06	33	33	100	*33*
Çiğli	09/02/05	26/05/05	13	59	22	-	-	-	-	-	*13*
Gaziemir	21/01/05	27/05/05	26	65	40	-	-	-		-	*26*
Total	-	-	*117*	*255*	*46*	-	-	*108*	*142*	*76*	*225*

Table 4.2 Sampling period and number of the samples of sampling points for anions.

Measured Parameter	***Anions***				
Station	**2005-2006 Rainy Period (September-August)**				
	Starting Date for sampling	**Ending Date for sampling**	**Number of the Analysed Samples**	**Number of the rainy days (0.5 mm)**	**% Sampling Recovery**
Bornova	29/12/05	19/03/05	19	51	*37*
Güzelyalı	27/12/05	18/03/06	24	58	*41*
Tınaztepe	28/12/05	05/04/06	21	33	*63*
Total	-	-	*64*	*142*	*45*

Another indicator of skewed distribution is the ratio of arithmetic mean to geometric mean of the concentrations of ions. The more the ratio exceeds unity, the more the distribution deviates from normal distribution. In this regard, geometric mean or the median is a better parameter to describe the data population.

Although both skewness values and arithmetic-to-geometric mean ratios indicate that the data are not symmetric, they do not imply any type of distribution. The

Kolmogrov-Smirnov "goodness of the fit test" was applied to the concentrations of ions to test the assumption that the data for all measured parameters are log-normally distributed.

Additionally p-value of the performed test can be used as a quantitative proof for the assumed distribution. In this case, if the p-value of the Kolmogrov-Smirnov test is greater than 0.05, then the hypothesis that the variable comes from a log-normal distribution can not be rejected with 95 % confidence level.

All of the general descriptive statistics as mentioned above were discussed in the following sub-sections step by step for stations, sampling periods, and meteorological effects on chemical parameters.

A summary of the descriptive statistics of the measured chemical parameters at stations were presented in following sub-sections. The values given for pH, elements and anions include precipitation amount, volume weighted mean values, arithmetic means with standard deviations, geometric means, ± 95 % confidence levels, minimum and maximum values, skewness, kurtosis normality test results, and other parametric or non parametric test results. Numbers of the samples are also given in first column of the table as "Valid N".

Median values with 25-75 % percentiles, minimum and maximum values of all measured parameters at stations were also given as Box & Whisker plots. Also, all measured concentrations belong to some chemical parameters (Fe, Ni, Zn, V, SO_4, and NO_3) in the datasets were generally represented with confidence levels vs. precipitation amount related to the samples.

4.1.1 Tınaztepe

This sampling point was evaluated as a suburban sampling point. The campus was relatively far from any settlement zones or industrial facilities. There were residential areas located ~2km southwest and a highway 0.5 km south of the sampling site.

Thirty three wet deposition samples were collected between September 2005 and June 2006 on the roof of a four-story building located on the Kaynaklar Campus of the Dokuz Eylül University, İzmir, Turkey.

A summary of the descriptive statistics of the measured chemical parameters at Tınaztepe precipitation sampling station at 2005-2006 sampling period is presented in Table 4.3. Figure 4.1 and Figure 4.2 were also given to understand properties of datasets.

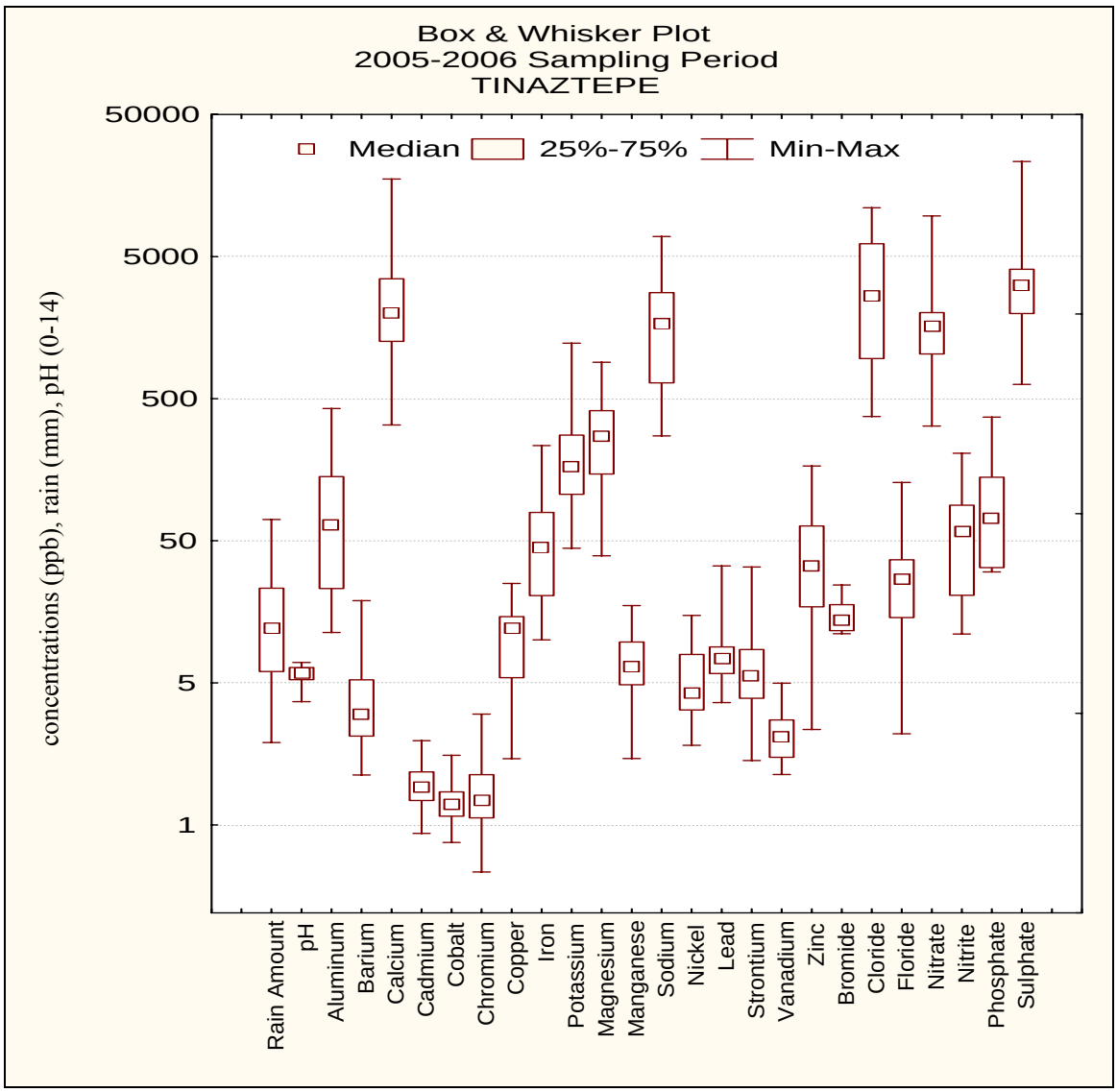


Figure 4.1 Box & Whisker plot for data handled from Tınaztepe sampling point

Table 4.3 Summary of data handled from Tınaztepe in 2005-2006 rainy periods.

Parameters	Sampling Periods	Valid N	VWMV[i]	Arithmetic Mean	Std.Dev.	Median	Min.	Max.	Confidence -%95	Confidence +%95	Geometric Mean
mm	02-10-05/ 30-04-06	33	-	17.56	16.20	12.10	1.90	70.40	11.81	23.30	12.08
pH		33	5.76	5.79	0.86	5.80	3.68	6.95	5.44	6.05	5.67
Al		31	84.48	95.48	103.04	65.04	11.29	426.60	57.68	133.27	58.39
Ba		33	3.32	4.48	3.90	3.00	1.12	18.91	3.10	5.86	3.44
Ca		33	2328.24	3018.52	3139.49	2018.00	326.20	17530.00	1905.30	4131.73	2088.63
Cd		32	0.95	0.97	0.36	0.93	0.44	1.96	0.84	1.10	0.90
Co		26	0.75	0.76	0.26	0.69	0.38	1.54	0.65	0.86	0.72
Cr		25	0.39	0.94	0.60	0.74	0.23	3.01	0.69	1.18	0.80
Cu		31	7.77	11.03	6.41	12.01	1.46	25.01	8.68	13.38	8.77
Fe		33	56.50	61.02	56.47	45.22	10.03	233.50	41.00	81.05	42.60
K		31	154.44	252.99	252.95	166.40	44.27	1228.00	160.21	345.78	180.57
Mg		33	275.50	327.23	238.78	273.80	39.13	901.00	242.57	411.90	249.68
Mn		33	6.57	7.49	4.22	6.46	1.47	17.48	5.99	8.98	6.37
Na		32	1551.02	1976.81	1611.77	1670.50	273.50	6924.00	1395.70	2557.92	1386.10
Ni		32	5.09	5.80	3.72	4.20	1.82	14.91	4.46	7.14	4.82
Pb		33	7.13	8.27	5.23	7.37	3.63	33.23	6.42	10.12	7.38
Sr		33	6.70	7.24	6.24	5.59	1.42	32.69	5.03	9.46	5.61
V		31	2.04	2.32	1.03	2.08	1.13	4.97	1.94	2.69	2.13
Zn		33	31.55	48.71	46.04	33.45	2.34	167.70	32.38	65.03	30.48
Br	28-12-05/ 05-04-06	11	8.91	15.40	4.44	13.73	11.09	24.36	12.42	18.38	14.87
Cl		20	3087.70	3787.87	3366.32	2620.01	374.45	11013.62	2212.39	5363.36	2261.86
Fl		20	26.61	30.13	27.18	26.66	2.19	128.34	17.41	42.85	20.90
NO_3		19	1551.30	2006.26	2011.47	1628.00	320.24	9666.00	1036.76	2975.75	1544.71
NO_2		20	62.52	65.54	53.89	58.34	11.02	206.45	40.32	90.77	46.89
PO_4		6	22.44	119.34	129.54	71.58	30.14	370.62	-	-	79.50
SO_4		20	3083.20	4358.59	4930.26	3115.50	630.33	23357.46	2051.16	6666.02	3068.19

Notes: i.Volume weighted mean values;
ii.Unit for rain amount was given as mm, and units of concentration of all chemical parameters were given as ppb.

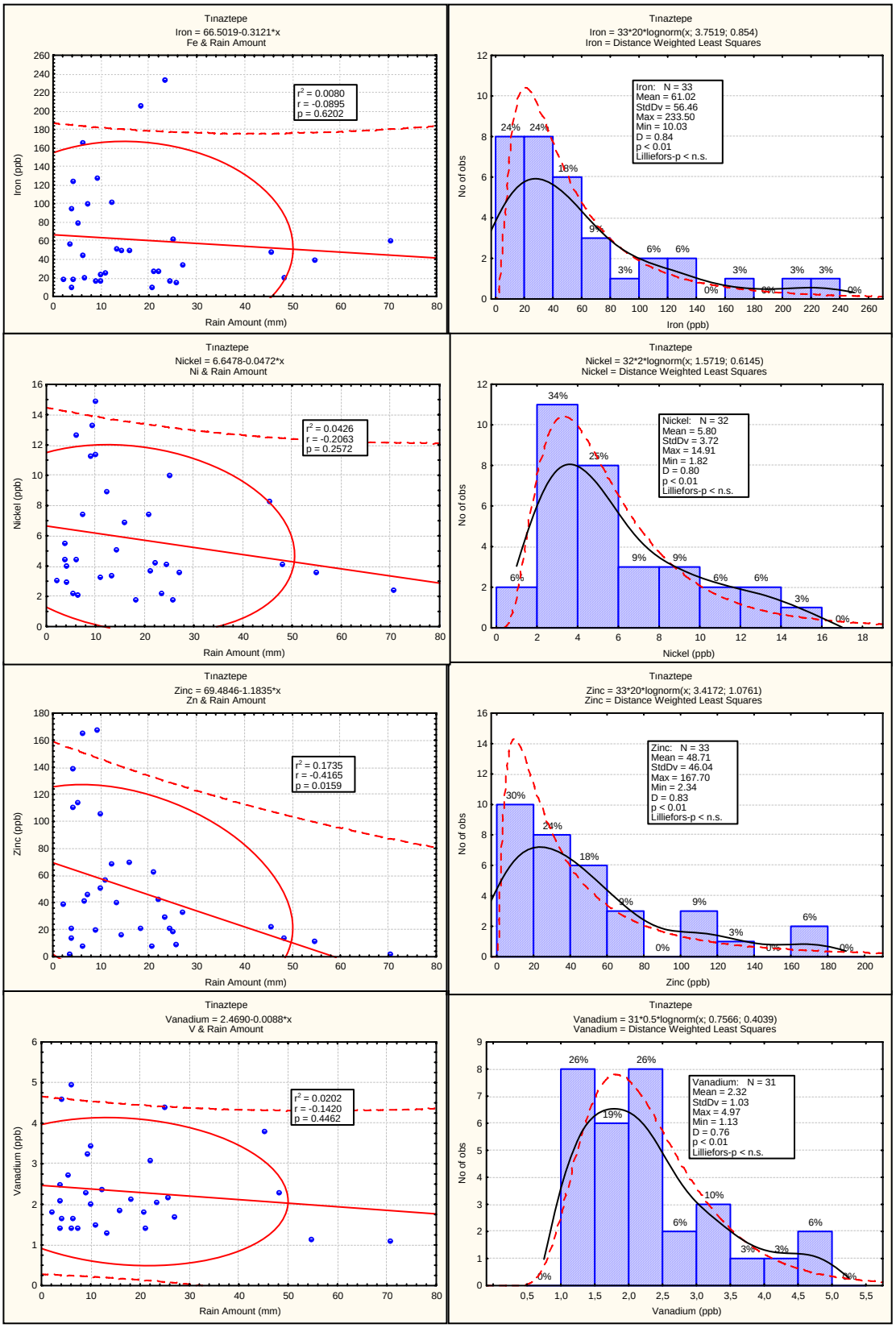


Figure 4.2 Distribution of all measured concentrations belongs to some chemical parameters versus rainwater amounts with also represented with frequency histograms (Tınaztepe). Concentrations for elements in every graphics were given as ppb, and rain amounts were given as kg/m^2). Eliptic ranges with coefficient ± 95 % and regression bands with prediction ± 95 % were also given as straight and truncated lines, respectively, to observe confidence ranges for visual inspections in figures located left part of the page. Truncated lines on histograms indicate the fitted normal or log-normal distribution curves, and black ones show the distance weighted least squared curves.

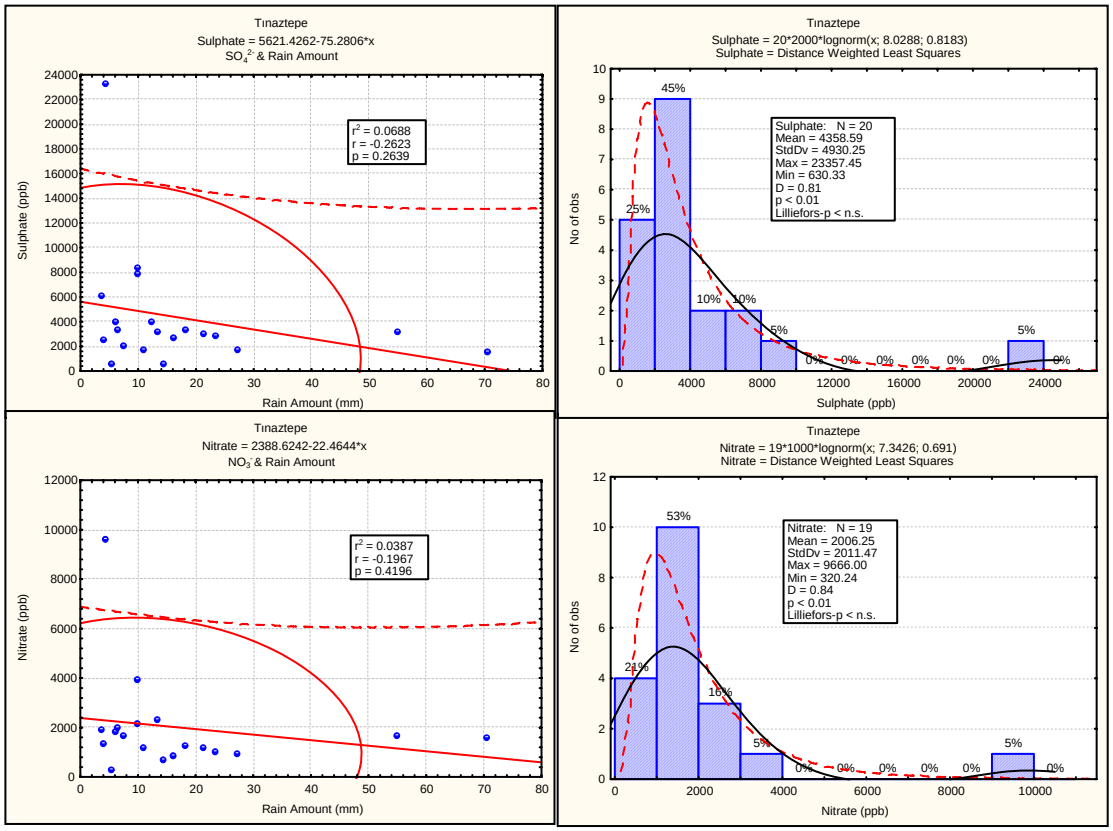


Figure 4.2 Continued.

Table 4.4 shows results of the other normality tests. According to statistical tests many of measured parameters in this study showed asymmetric distributions. Statistical tests to explain the distributions of data infer that many of data fits log normal distributions. This indicated that transportation from distant regions and mixing play a major role in the distribution of concentrations. Frequency histograms and the fitted log normal and normal distribution curves with distances weighted least square curves for some measured parameters were given exemplary Figure 4.2 for visual inspection.

Table 4.4 . Test for distribution properties of Tınaztepe in 2005-2006 sampling period (bolds italic values are significant).

Parameters	***Valid N****	***max D***	***K-S***	***Lilliefors***	***W***	***p***	***A/G*****	***Skewness***	***Kurtosis***
pH	33	0.16	p > .20	***p < .05***	***0.93***	***0.03***	1.01	-0.85	0.16
Al	31	0.21	p < .15	***p < .01***	***0.75***	***0.00***	1.64	2.04	4.27
Ba	33	0.23	***p < .05***	***p < .01***	***0.74***	***0.00***	1.30	2.29	5.80
Ca	33	0.22	p < .10	***p < .01***	***0.67***	***0.00***	1.45	3.31	14.24
Cd	32	0.09	p > .20	p > .20	0.96	0.29	1.07	***0.54***	0.53
Co	26	0.19	p < .20	***p < .01***	***0.91***	***0.03***	1.05	1.22	2.07
Cr	25	0.18	p > .20	***p < .05***	***0.82***	***0.00***	1.17	1.98	5.14
Cu	31	0.12	p > .20	p > .20	0.95	0.15	1.26	***0.32***	-0.54
Fe	33	0.21	p < .10	***p < .01***	***0.80***	***0.00***	1.43	1.68	2.47
K	31	0.26	***p < .05***	***p < .01***	***0.71***	***0.00***	1.40	2.44	6.79
Mg	33	0.18	p < .20	***p < .01***	***0.87***	***0.00***	1.31	1.17	0.78
Mn	33	0.16	p > .20	***p < .05***	***0.91***	***0.01***	1.18	0.97	0.59
Na	32	0.17	p > .20	***p < .05***	***0.88***	***0.00***	1.43	1.19	1.29
Ni	32	0.23	***p < .05***	***p < .01***	***0.86***	***0.00***	1.20	1.05	0.01
Pb	33	0.25	***p < .05***	***p < .01***	***0.63***	***0.00***	1.12	3.64	16.64
Sr	33	0.21	p < .10	***p < .01***	***0.72***	***0.00***	1.29	2.71	8.92
V	31	0.18	p > .20	***p < .05***	***0.87***	***0.00***	1.09	1.23	0.79
Zn	33	0.19	p < .20	***p < .01***	***0.82***	***0.00***	1.60	1.39	1.10
Br	11	0.20	p > .20	p > .20	0.88	0.10	1.04	0.95	-0.02
Cl	20	0.19	p > .20	***p < .05***	***0.88***	***0.02***	1.67	0.78	-0.48
F	20	0.22	p > .20	***p < .05***	***0.74***	***0.00***	1.44	2.59	9.07
NO_3	19	0.33	***p < .05***	***p < .01***	***0.58***	***0.00***	1.30	3.40	12.89
NO_2	20	0.16	p > .20	p > .20	***0.85***	***0.01***	1.40	1.31	1.56
PO_4	6	0.28	p > .20	p < .15	***0.75***	***0.02***	1.50	1.97	4.00
SO_4	20	0.32	***p < .05***	***p < .01***	***0.60***	***0.00***	1.42	3.31	12.52

*:Valid number of samples, **:Ratio of arithmetic mean to geomethric mean.

Notes: The magnitude of deviations from normality of data is related these criterias:

[i].The higher values as max D, the more deviation from normality and, the more similarity to log-normal distribution. (Kolmogorov-Smirnov test values must also be significant for log-normal distribution).

[ii].p values (of Lilliefors test and others) are significant if the values are smaller 0.05. This indicates that the deviations from the normality are expressiable.

[iii].The more clossness to the value 1 in Shapiro-Wilk's W tests, the more expressiable of the normal distributions of data.

[iv].If the arithmetic mean values is equal to geometric mean or skewness is equal to the value "0", the deaviation from normality is minimal.

[v].Kurtosis test is related to sharpness of the frequency distribution curves.

4.1.2 Bornova

This sampling point was evaluated as an urban sampling point. Seventy-one wet deposition samples were collected between November 2004 and March 2006 in this sampling site.

Summaries of the descriptive statistics of the measured chemical parameters at Bornova precipitation sampling station at 2004-2005 sampling period, 2005-2006 sampling period, and overall sampling periods were presented in Table 4.5. Median values with 25-75% percentiles, minimum and maximum values of all measured parameters at this station were also given Figure 4.3 as Box & Whisker plots. Also, all measured concentrations belong to some chemical parameters (Fe, Ni, Zn, V, SO_4, and NO_3) in the datasets were generally represented Figure 4.4 with confidence levels versus precipitation amount related to the samples.

Table 4.5.a. Summary of data handled from Bornova in 2004-2006 (overall sampling periods).

Parameters	Sampling Periods	Valid N	VWMV[i]	Arithmetic Mean	Std.Dev.	Median	Min.	Max.	Confidence -%95	Confidence +%95	Geometric Mean
mm	12-11-04/ 19-03-06	71	-	11.89	10.00	8.50	0.50	40.80	9.53	14.26	7.91
pH		70	6.46	6.66	0.72	6.70	4.58	8.43	6.49	6.83	6.62
Al		61	129.39	194.15	266.55	80.63	11.39	1139.81	125.89	262.42	92.83
Ba		70	8.80	13.26	14.57	9.63	0.95	76.77	9.78	16.73	8.31
Ca		68	4818.63	6841.24	6155.90	4278.00	112.89	26823.24	5351.20	8331.29	4487.13
Cd		62	0.67	0.83	0.40	0.85	0.11	1.87	0.73	0.93	0.71
Co		56	0.44	0.63	0.31	0.60	0.18	1.44	0.55	0.72	0.56
Cr		45	0.82	1.80	1.63	1.59	0.23	7.71	1.31	2.29	1.21
Cu		70	9.74	12.44	7.24	11.77	0.99	39.00	10.72	14.17	10.20
Fe		71	114.19	173.43	247.44	82.24	6.04	1147.50	114.87	232.00	76.26
K		71	259.14	422.99	472.70	252.80	18.83	2799.35	311.10	534.88	271.91
Mg		70	328.30	470.82	465.50	310.13	34.09	2457.23	359.83	581.82	315.70
Mn		70	9.51	14.04	15.30	7.76	1.48	75.35	10.40	17.69	8.64
Na		69	1435.14	1966.78	1537.73	1549.07	254.30	7034.87	1597.38	2336.18	1419.89
Ni		71	4.11	4.77	2.06	4.62	1.05	11.08	4.28	5.26	4.32
Pb		63	5.33	7.58	6.00	6.04	1.84	38.38	6.07	9.09	6.15
Sr		71	10.71	15.90	19.11	8.85	1.68	118.96	11.37	20.42	10.04
V		70	5.19	6.69	3.98	7.03	1.14	18.33	5.74	7.64	5.38
Zn		69	29.50	42.36	52.03	25.90	1.37	284.66	29.86	54.86	25.35

Notes i.Volume weighted mean values.
ii.Unit for rain amount was given as mm, and units of concentration of all chemical parameters were given as ppb.

Table 4.5.b. Summary of data handled from Bornova in 2004-2005 sampling period.

Parameters	Sampling Periods	Valid N	VWMV[i]	Arithmetic Mean	Std.Dev.	Median	Min.	Max.	Confidence -%95	Confidence +%95	Geometric Mean
mm	12-11-04/ 07-08-05	37	-	11.02	7.49	9.90	0.50	28.40	8.53	13.52	7.94
pH		36	6.45	6.72	0.83	6.70	4.80	8.43	6.44	7.00	6.67
Al		31	183.97	231.10	280.57	111.17	13.39	1139.81	128.18	334.01	123.44
Ba		36	10.82	14.67	14.63	10.08	2.05	65.01	9.72	19.62	10.30
Ca		35	5106.86	6053.67	5368.21	4142.24	112.89	26823.24	4209.62	7897.71	4258.75
Cd		28	0.52	0.70	0.36	0.74	0.19	1.24	0.56	0.85	0.60
Co		27	0.35	0.59	0.31	0.50	0.19	1.39	0.47	0.71	0.51
Cr		18	0.92	2.47	1.89	2.21	0.26	7.71	1.53	3.41	1.71
Cu		36	10.07	12.23	5.45	11.87	1.30	28.16	10.38	14.07	10.90
Fe		37	175.57	240.04	276.93	129.22	18.18	1147.50	147.70	332.37	132.72
K		37	269.06	404.46	509.07	246.11	18.83	2799.35	234.73	574.19	257.87
Mg		36	388.15	530.58	537.34	333.66	75.70	2457.23	348.77	712.40	350.79
Mn		37	12.67	16.59	17.32	9.50	1.78	75.35	10.81	22.36	10.61
Na		35	1531.62	1947.94	1460.00	1549.07	254.30	7034.87	1446.41	2449.47	1445.48
Ni		37	5.10	5.28	1.37	5.20	2.79	9.15	4.83	5.74	5.11
Pb		29	4.50	7.42	5.41	6.27	2.04	23.95	5.36	9.47	6.00
Sr		37	13.88	18.97	24.18	8.22	2.03	118.96	10.91	27.03	11.20
V		36	7.60	8.59	3.30	8.30	3.16	18.33	7.47	9.71	8.00
Zn		37	37.31	44.05	47.87	34.89	7.98	284.66	28.09	60.01	32.15

Notes i.Volume weighted mean values.
ii.Unit for rain amount was given as mm, and units of concentration of all chemical parameters were given as ppb.

Table 4.5.c. Summary of data handled from Bornova in 2005-2006 sampling period

Parameters	Sampling Periods	Valid N	VWMV[i]	Arithmetic Mean	Std.Dev.	Median	Min.	Max.	Confidence -%95	Confidence +%95	Geometric Mean
mm	16-09-05/ 19-05-06	34	-	12.84	12.22	7.60	1.00	40.80	8.58	17.11	7.88
pH		34	6.47	6.59	0.60	6.68	4.58	7.90	6.38	6.80	6.56
Al		30	78.42	155.98	250.18	71.18	11.39	1005.00	62.56	249.40	69.15
Ba		34	6.92	11.75	14.57	6.52	0.95	76.77	6.67	16.84	6.62
Ca		33	4549.50	7676.55	6879.40	4299.00	641.80	25030.00	5237.22	10115.88	4742.74
Cd		34	0.82	0.93	0.41	0.92	0.11	1.87	0.79	1.07	0.82
Co		29	0.53	0.68	0.30	0.68	0.18	1.44	0.56	0.79	0.61
Cr		27	0.74	1.35	1.28	0.82	0.23	6.14	0.85	1.86	0.96
Cu		34	9.43	12.67	8.83	11.67	0.99	39.00	9.59	15.75	9.50
Fe		34	56.86	100.96	189.27	42.96	6.04	967.00	34.92	166.99	41.72
K		34	249.87	443.15	436.43	259.15	30.19	1715.00	290.88	595.43	288.06
Mg		34	272.41	407.54	372.59	281.05	34.09	1761.00	277.54	537.55	282.36
Mn		33	6.56	11.19	12.30	5.73	1.48	52.31	6.83	15.56	6.86
Na		34	1345.00	1986.17	1635.72	1555.50	333.80	6108.00	1415.44	2556.90	1394.02
Ni		34	3.19	4.22	2.52	3.57	1.05	11.08	3.34	5.09	3.59
Pb		34	6.11	7.72	6.54	5.30	1.84	38.38	5.43	10.00	6.27
Sr		34	7.76	12.55	10.71	9.36	1.68	47.70	8.81	16.29	8.91
V		34	2.95	4.68	3.66	3.59	1.14	15.90	3.40	5.95	3.54
Zn		32	22.21	40.40	57.18	15.47	1.37	254.40	19.79	61.02	19.26
Br	27-12-05/ 19-03-06	10	3.58	14.68	4.36	14.39	7.75	22.99	11.56	17.79	14.07
Cl		18	2615.39	3612.39	3319.31	2550.98	561.76	10383.98	1961.73	5263.04	2309.04
Fl		18	51.29	65.37	50.54	43.90	6.35	196.53	40.24	90.50	49.42
NO_3		18	1454.18	2044.74	1393.12	1773.00	535.69	5034.08	1351.96	2737.52	1602.93
NO_2		18	115.81	144.44	98.91	113.50	22.73	342.15	95.26	193.63	114.32
PO_4		6	51.95	231.71	123.73	300.19	56.53	330.54	101.86	361.55	190.28
SO_4		18	5456.70	8070.05	6622.63	5811.67	2058.64	23511.55	4776.70	11363.41	5864.17

Notes i.Volume weighted mean values.
ii.Unit for rain amount was given as mm, and units of concentration of all chemical parameters were given as ppb.

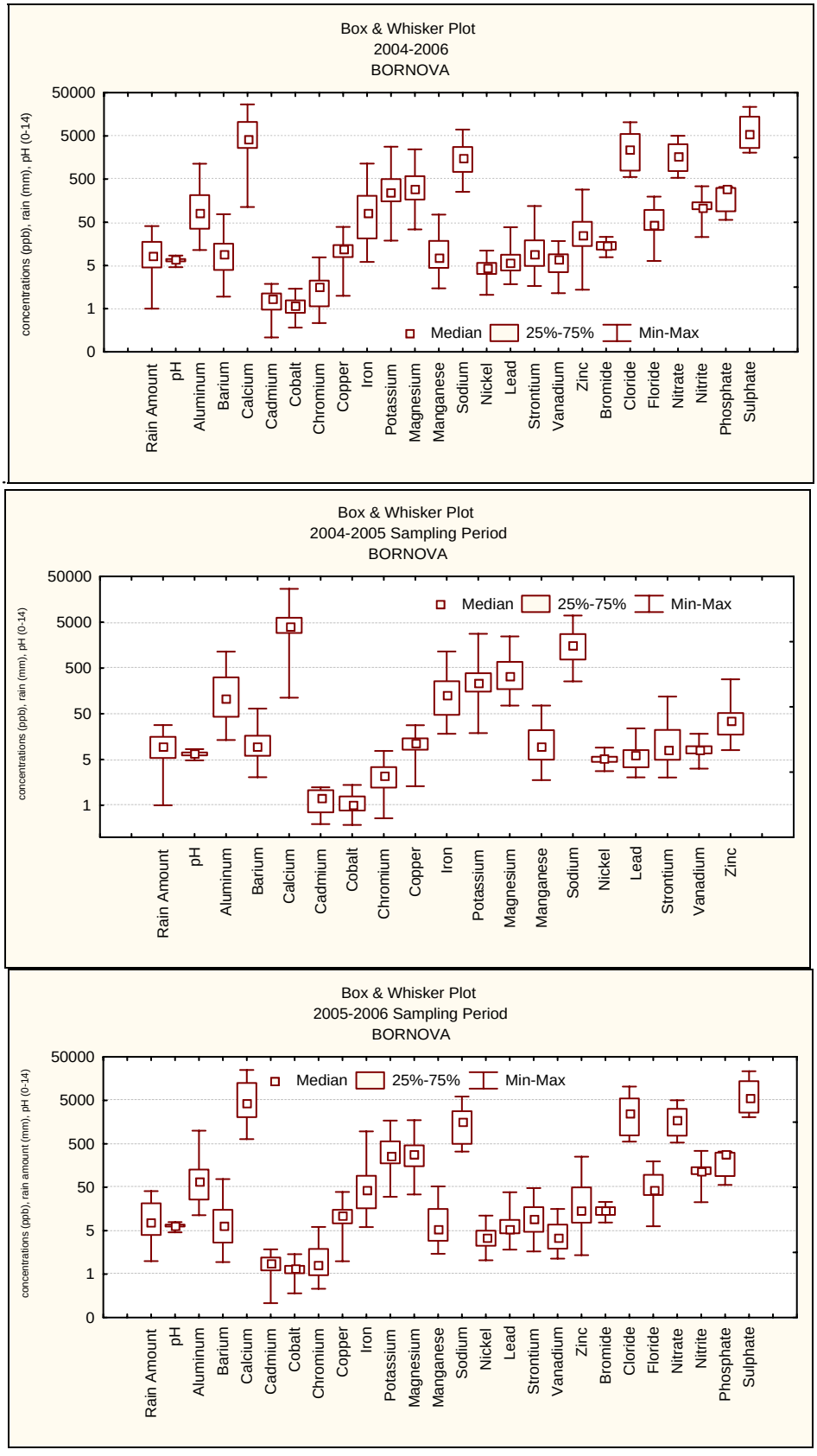


Figure 4.3 Box & Whisker plot for data handled from Bornova sampling point for two sampling periods and over all periods.

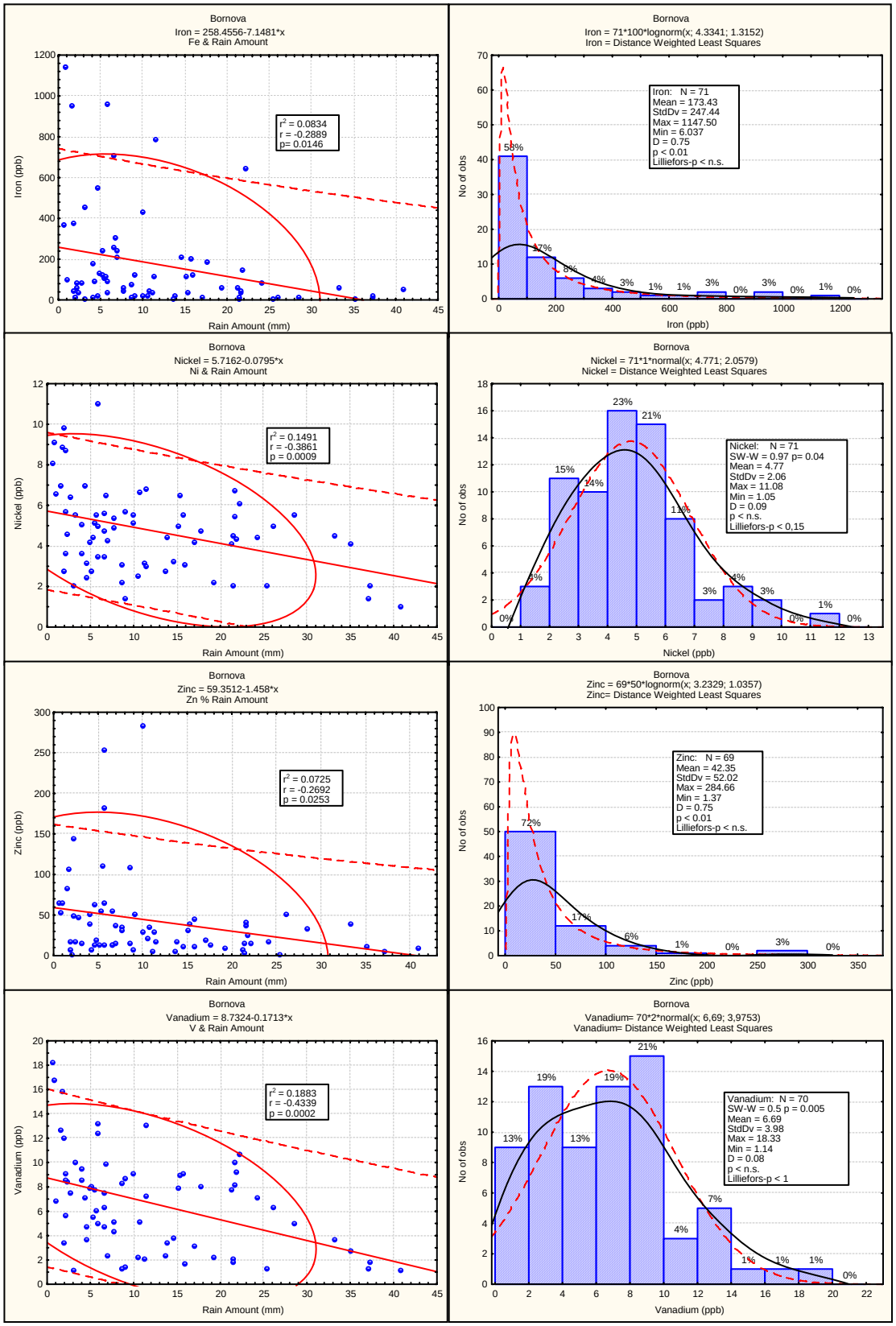


Figure 4.4 Distribution of all measured concentrations belongs to some chemical parameters versus rainwater amounts with also represented with frequency histograms (Bornova). Eliptic ranges with coefficient ±95 % and regression bans with prediction ± 95 % were also given as straight and truncated lines, respectively, to observe confidence ranges for visual inspections in figures located left part of the page. Truncated lines on histograms indicate the fitted normal or log-normal distribution curves, and black ones show the distance weighted least squared curves.

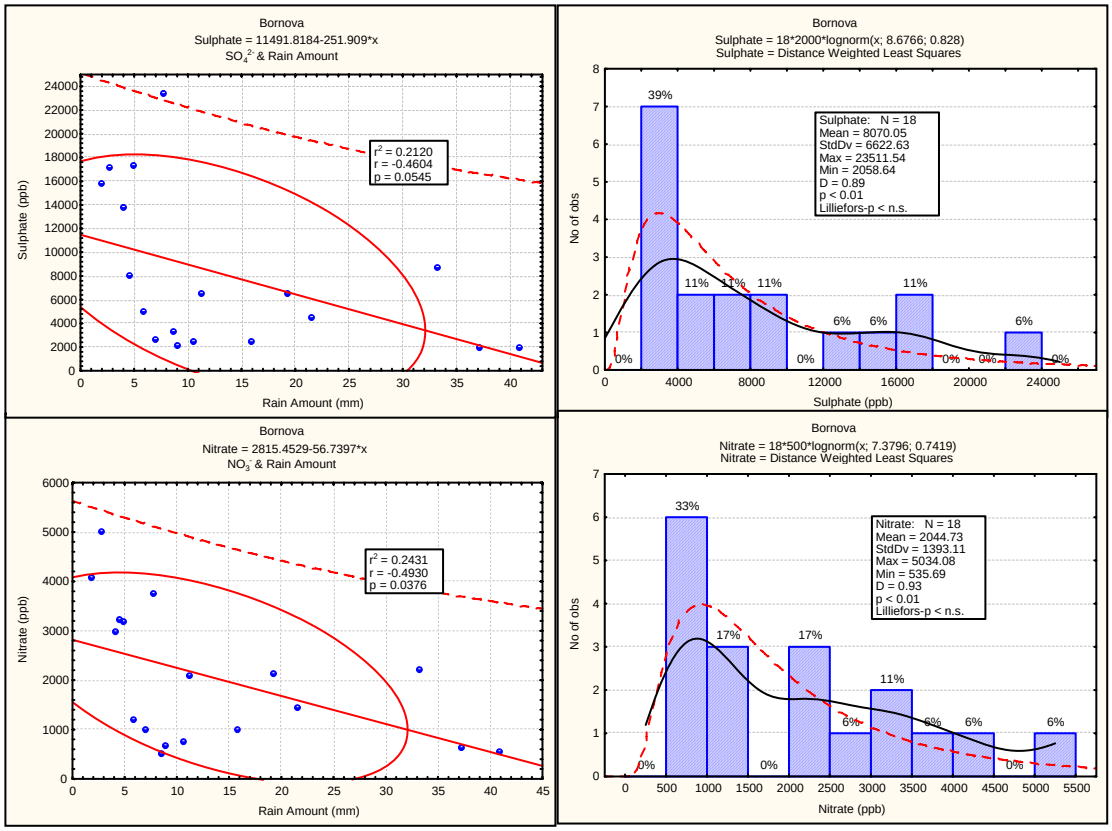


Figure 4.4 Continued.

Table 4.6 shows the result of other normality tests. According to statistical tests many of measured parameters in Bornova distributed asymmetrically similar to Tınaztepe site. Statistical tests to explain the distributions of data infer that many of data fits log normally distributions. Frequency histograms and the fitted log normal and normal distribution curves with distances weighted least square curves for some measured parameters were given exemplary Figure 4.4 for visual inspection.

Table 4.6.a. Test for distribution properties of Bornova in 2004-2006 sampling periods (overall sampling periods) (bold italic values are significant).

Parameters	***Valid N****	***max D***	***K-S***	***Lilliefors***	***W***	***p***	***A/G*****	***Skewness***	***Kurtosis***
rain	71	0.15	***p < .10***	***p < .01***	***0.88***	***0.00***	1.50	1.14	0.63
pH	70	0.10	p > .20	p < .10	0.97	0.06	1.01	***-0.22***	1.15
Al	61	0.25	***p < .01***	***p < .01***	***0.67***	***0.00***	2.09	2.21	4.34
Ba	70	0.21	***p < .01***	***p < .01***	***0.71***	***0.00***	1.60	2.60	7.69
Ca	68	0.21	***p < .01***	***p < .01***	***0.83***	***0.00***	1.52	1.41	1.50
Cd	62	0.07	p > .20	p > .20	0.98	0.31	1.16	***0.17***	-0.57
Co	56	0.08	p > .20	p > .20	***0.95***	***0.03***	1.13	0.70	0.25
Cr	45	0.18	p < .15	***p < .01***	***0.83***	***0.00***	1.49	1.67	3.32
Cu	70	0.14	p < .15	***p < .01***	***0.91***	***0.00***	1.22	1.23	2.42
Fe	71	0.26	***p < .01***	***p < .01***	***0.67***	***0.00***	2.27	2.32	5.15
K	71	0.24	***p < .01***	***p < .01***	***0.70***	***0.00***	1.56	2.68	9.05
Mg	70	0.18	***p < .05***	***p < .01***	***0.77***	***0.00***	1.49	2.16	5.37
Mn	70	0.22	***p < .01***	***p < .01***	***0.75***	***0.00***	1.63	1.95	3.77
Na	69	0.16	p < .10	***p < .01***	***0.89***	***0.00***	1.39	1.19	1.19
Ni	71	0.09	p > .20	p < .15	***0.97***	***0.05***	1.11	0.67	0.61
Pb	63	0.23	***p < .01***	***p < .01***	***0.73***	***0.00***	1.23	2.84	11.01
Sr	71	0.23	***p < .01***	***p < .01***	***0.65***	***0.00***	1.58	3.32	13.93
V	70	0.08	p > .20	p > .20	***0.95***	***0.00***	1.24	0.65	0.30
Zn	69	0.23	***p < .01***	***p < .01***	***0.65***	***0.00***	1.67	2.97	10.16

*:Valid number of samples, **:Ratio of arithmetic mean to geomethric mean.

Notes: The magnitude of deviations from normality of data is related these criterias:

[i].The higher values as max D, the more deviation from normality and, the more similarity to log-normal distribution. (Kolmogorov-Smirnov test values must also be significant for log-normal distribution).

[ii].p values (of Lilliefors test and others) are significant if the values are smaller 0.05. This indicates that the deviations from the normality are expressiable.

[iii].The more clossness to the value 1 in Shapiro-Wilk's W tests, the more expressiable of the normal distributions of data.

[iv].If the arithmetic mean values is equal to geometric mean or skewness is equal to the value "0", the deaviation from normality is minimal.

[v].Kurtosis test is related to sharpness of the frequency distribution curves.

Table 4.6.b. Test for distribution properties of Bornova in 2004-2005 sampling period (bold italic values are significant).

Parameters	***Valid N****	***max D***	***K-S***	***Lilliefors***	***W***	***p***	***A/G*****	***Skewness***	***Kurtosis***
rain	37	0.15	p > .20	***p < .05***	***0.94***	***0.05***	1.39	0.54	-0.70
pH	36	0.09	p > .20	p > .20	0.98	0.64	1.01	***-0.04***	0.27
Al	31	0.23	***p < .05***	***p < .01***	***0.73***	***0.00***	1.87	1.98	3.66
Ba	36	0.23	***p < .05***	***p < .01***	***0.71***	***0.00***	1.42	2.37	5.79
Ca	35	0.26	***p < .05***	***p < .01***	***0.77***	***0.00***	1.42	2.13	5.61
Cd	28	0.15	p > .20	***p < .10***	***0.90***	***0.01***	1.18	***-0.02***	-1.59
Co	27	0.14	p > .20	p < .10	0.93	0.09	1.15	***0.79***	0.14
Cr	18	0.12	p > .20	p > .20	0.90	0.06	1.45	1.16	2.09
Cu	36	0.13	p > .20	p < .15	0.95	0.08	1.12	0.87	1.41
Fe	37	0.23	***p < .05***	***p < .01***	***0.75***	***0.00***	1.81	1.87	3.04
K	37	0.27	***p < .01***	***p < .01***	***0.61***	***0.00***	1.57	3.37	13.60
Mg	36	0.20	p < .15	***p < .01***	***0.77***	***0.00***	1.51	2.03	4.45
Mn	37	0.23	***p < .05***	***p < .01***	***0.76***	***0.00***	1.56	1.80	2.94
Na	35	0.15	p > .20	p < .10	***0.89***	***0.00***	1.35	1.38	2.82
Ni	37	0.12	p > .20	p < .20	0.97	0.36	1.03	***0.48***	0.80
Pb	29	0.22	p < .15	***p < .01***	***0.80***	***0.00***	1.24	1.72	2.77
Sr	37	0.24	***p < .05***	***p < .01***	***0.65***	***0.00***	1.69	2.82	8.90
V	36	0.16	p > .20	***p < .05***	***0.93***	***0.02***	1.07	0.99	1.78
Zn	37	0.24	***p < .05***	***p < .01***	***0.60***	***0.00***	1.37	3.81	18.01

*:Valid number of samples, **:Ratio of arithmetic mean to geomethric mean.

Notes: The magnitude of deviations from normality of data is related these criterias:

[i].The higher values as max D, the more deviation from normality and, the more similarity to log-normal distribution. (Kolmogorov-Smirnov test values must also be significant for log-normal distribution).

[ii].p values (of Lilliefors test and others) are significant if the values are smaller 0.05. This indicates that the deviations from the normality are expressiable.

[iii].The more clossness to the value 1 in Shapiro-Wilk's W tests, the more expressiable of the normal distributions of data.

[iv].If the arithmetic mean values is equal to geometric mean or skewness is equal to the value "0", the deaviation from normality is minimal.

[v].Kurtosis test is related to sharpness of the frequency distribution curves.

Table 4.6.c. Test for distribution properties of Bornova in 2005-2006 sampling period (bold italic values are significant).

Parameters	***Valid N****	***max D***	***K-S***	***Lilliefors***	***W***	***p***	***A/G*** **	***Skewness***	***Kurtosis***
rain	34	0.21	p < .10	***p <.01***	***0.83***	***0.00***	1.63	1.08	-0.14
pH	34	0.12	p > .20	p > .20	0.93	0.04	1.00	-1.00	3.12
Al	30	0.31	***p <.01***	***p <.01***	***0.58***	***0.00***	2.26	2.70	6.94
Ba	34	0.23	p < .10	***p <.01***	***0.67***	***0.00***	1.78	3.05	11.86
Ca	33	0.21	p < .10	***p <.01***	***0.87***	***0.00***	1.62	0.95	-0.10
Cd	34	0.06	p > .20	p > .20	0.99	0.99	1.13	0.16	-0.39
Co	29	0.14	p > .20	p < .10	***0.95***	***0.14***	1.11	0.73	0.75
Cr	27	0.19	p < .20	***p <.01***	***0.75***	***0.00***	1.41	2.34	6.97
Cu	34	0.17	p > .20	***p <.05***	0.90	0.01	1.33	1.20	1.63
Fe	34	0.31	***p <.01***	***p <.01***	***0.51***	***0.00***	2.42	3.58	14.01
K	34	0.23	p < .10	***p <.01***	***0.79***	***0.00***	1.54	1.64	2.05
Mg	34	0.21	p < .15	***p <.01***	***0.80***	***0.00***	1.44	2.02	4.80
Mn	33	0.22	p < .10	***p <.01***	***0.75***	***0.00***	1.63	1.96	3.71
Na	34	0.17	p > .20	***p <.05***	***0.86***	***0.00***	1.42	1.09	0.34
Ni	34	0.15	p > .20	***p <.05***	***0.88***	***0.00***	1.17	1.21	0.90
Pb	34	0.26	***p <.05***	***p <.01***	***0.65***	***0.00***	1.23	3.39	14.62
Sr	34	0.17	p > .20	***p <.05***	***0.84***	***0.00***	1.41	1.57	2.66
V	34	0.17	p > .20	***p <.05***	***0.85***	***0.00***	1.32	1.37	1.66
Zn	32	0.25	***p <.05***	***p <.01***	***0.66***	***0.00***	2.10	2.50	6.46
Br	10	0.16	p > .20	p > .20	0.97	0.92	1.04	0.32	0.30
Cl	18	0.18	p > .20	p < .15	***0.83***	***0.00***	1.56	1.09	0.08
Fl	18	0.26	p < .20	***p <.01***	***0.84***	***0.01***	1.32	1.33	1.21
NO_3	18	0.17	p > .20	p < .20	0.90	0.06	1.28	0.69	-0.62
NO_2	18	0.28	p < .15	***p <.01***	***0.83***	***0.00***	1.26	1.10	0.25
PO_4	6	0.35	p > .20	***p <.05***	***0.75***	***0.02***	1.22	-0.96	-1.68
SO_4	18	0.20	p > .20	***p <.05***	***0.84***	***0.01***	1.38	1.06	0.01

*:Valid number of samples, **:Ratio of arithmetic mean to geomethric mean.

Notes: The magnitude of deviations from normality of data is related these criterias:

[i].The higher values as max D, the more deviation from normality and, the more similarity to log-normal distribution. (Kolmogorov-Smirnov test values must also be significant for log-normal distribution).

[ii].p values (of Lilliefors test and others) are significant if the values are smaller 0.05. This indicates that the deviations from the normality are expressiable.

[iii].The more clossness to the value 1 in Shapiro-Wilk's W tests, the more expressiable of the normal distributions of data.

[iv].If the arithmetic mean values is equal to geometric mean or skewness is equal to the value "0", the deaviation from normality is minimal.

[v].Kurtosis test is related to sharpness of the frequency distribution curves.

4.1.3 Güzelyalı

This sampling point was evaluated as an urban sampling point. This station takes part in a settling point near the Aegean Sea shoreline in İzmir.

Eighty three wet deposition samples were collected between January 2005 and June 2006 in this meteorological station.

Summaries of the descriptive statistics of the measured chemical parameters at Güzelyalı precipitation sampling station at 2004-2005 sampling period and 2005-2006 sampling period were presented in Table 4.7. Median values with 25-75 % percentiles, minimum and maximum values of all measured parameters at this station were also given Figure 4.5 as Box & Whisker plots. Also, all measured concentrations belong to parameters in the datasets were generally represented Figure 4.6 with confidence levels vs precipitation amount related to the samples.

Table 4.7.a. Summary of data handled from Güzelyalı in 2004-2006 sampling period (overall sampling periods).

Parameters	Sampling Periods	Valid N	VWMV[i]	Arithmetic Mean	Std.Dev.	Median	Min.	Max.	Confidence -%95	Confidence +%95	Geometric Mean
mm	06-11-04/ 19-05-06	71	-	12.25	12.21	7.80	0.20	54.70	9.58	14.91	7.26
pH		70	5.64	5.83	1.00	5.95	3.40	8.20	5.61	6.05	5.74
Al		61	118.92	201.90	420.30	66.40	12.83	2344.21	104.52	299.27	83.52
Ba		70	7.93	12.08	14.92	8.02	0.70	82.62	8.80	15.36	7.89
Ca		68	3249.27	4735.72	5262.42	3098.23	113.11	35973.87	3586.63	5884.80	2860.68
Cd		62	0.60	0.79	0.40	0.73	0.15	1.69	0.70	0.89	0.68
Co		56	0.47	0.88	0.56	0.79	0.20	2.90	0.73	1.02	0.74
Cr		45	0.59	1.24	1.13	0.87	0.21	5.54	0.94	1.54	0.91
Cu		70	8.07	10.27	5.36	10.87	0.87	25.28	9.07	11.47	8.41
Fe		71	103.38	143.81	268.52	55.06	7.35	1733.70	84.81	202.81	67.08
K		71	237.04	367.46	356.85	267.40	18.63	1904.00	289.54	445.38	258.36
Mg		70	409.45	550.53	627.15	348.80	49.89	3291.11	412.73	688.32	359.99
Mn		70	10.48	16.38	24.28	9.10	0.72	125.25	11.08	21.68	9.12
Na		69	1959.20	2357.37	2023.56	1688.37	37.49	11840.00	1915.51	2799.23	1662.38
Ni		71	4.29	4.95	2.16	4.70	1.50	12.62	4.48	5.43	4.52
Pb		63	6.08	8.84	9.49	6.57	1.49	66.07	6.64	11.04	6.90
Sr		71	10.21	15.31	25.70	7.57	1.08	191.29	9.67	20.96	8.52
V		70	5.70	6.20	4.07	4.98	1.14	18.93	5.31	7.10	4.88
Zn		69	18.90	30.84	39.49	17.19	1.48	223.72	22.22	39.46	17.41

Notes i.Volume weighted mean values.
ii.Unit for rain amount was given as mm, and units of concentration of all chemical parameters were given as ppb.

Table 4.7.b. Summary of data handled from Güzelyalı in 2004-2005 sampling period.

Parameters	Sampling Periods	Valid N	VWMV[i]	Arithmetic Mean	Std.Dev.	Median	Min.	Max.	Confidence -%95	Confidence +%95	Geometric Mean
mm	06-11-04/ 31-05-05	42	-	11.68	12.00	7.80	0.80	50.50	7.94	15.42	7.11
pH		42	5.45	5.64	1.20	5.82	3.40	8.20	5.26	6.01	5.51
Al		35	173.18	306.05	577.30	77.88	16.53	2344.21	107.74	504.36	111.24
Ba		41	8.65	14.52	19.92	7.84	0.70	82.62	8.23	20.81	7.68
Ca		42	2783.17	4367.24	6172.15	2249.20	113.11	35973.87	2443.86	6290.62	2187.82
Cd		29	0.24	0.59	0.42	0.44	0.15	1.66	0.43	0.75	0.47
Co		28	0.45	0.96	0.76	0.77	0.20	2.90	0.67	1.26	0.74
Cr		23	0.70	1.88	1.41	1.32	0.21	5.54	1.27	2.49	1.38
Cu		41	10.34	10.97	3.93	11.28	1.70	20.56	9.72	12.21	10.09
Fe		41	153.39	202.64	356.22	72.49	7.35	1733.70	90.20	315.08	81.11
K		42	222.97	390.54	378.13	255.59	18.63	1659.14	272.70	508.37	263.72
Mg		41	443.30	629.65	716.47	304.03	49.89	3291.11	403.51	855.80	381.74
Mn		42	13.50	21.84	32.38	9.84	0.72	125.25	11.75	31.93	9.95
Na		42	1988.83	2569.37	2081.26	1767.61	37.49	11840.00	1920.80	3217.94	1882.60
Ni		42	4.96	5.56	1.97	5.44	1.58	10.47	4.94	6.17	5.18
Pb		33	3.67	8.95	13.11	5.76	1.49	66.07	4.31	13.60	5.84
Sr		41	11.71	18.12	32.62	6.37	1.08	191.29	7.82	28.42	8.59
V		41	8.99	9.03	3.54	8.19	1.73	18.93	7.91	10.15	8.21
Zn		42	21.03	38.50	47.38	18.46	4.15	223.72	23.74	53.26	23.99

Notes i.Volume weighted mean values.
ii.Unit for rain amount was given as mm, and units of concentration of all chemical parameters were given as ppb.

Table 4.7.c. Summary of data handled from Güzelyalı in 2005-2006 sampling period.

Parameters	Sampling Periods	Valid N	VWMV[i]	Arithmetic Mean	Std.Dev.	Median	Min.	Max.	Confidence -%95	Confidence +%95	Geometric Mean
mm	16-09-05/ 19-05-06	41	-	12.82	12.54	7.80	0.20	54.70	8.87	16.78	7.41
pH		40	5.81	6.03	0.70	6.05	4.40	7.65	5.81	6.25	5.99
Al		39	69.28	108.42	149.02	51.05	12.83	661.70	60.11	156.73	64.58
Ba		41	7.27	9.64	6.46	8.52	2.72	33.58	7.60	11.68	8.10
Ca		41	3675.64	5113.18	4175.45	4406.00	867.60	17070.00	3795.25	6431.11	3765.03
Cd		41	0.94	0.94	0.32	0.88	0.50	1.69	0.83	1.04	0.88
Co		31	0.48	0.80	0.28	0.79	0.21	1.46	0.70	0.90	0.75
Cr		33	0.48	0.80	0.58	0.67	0.21	3.37	0.59	1.01	0.68
Cu		38	5.99	9.52	6.54	8.01	0.87	25.28	7.37	11.67	6.91
Fe		41	57.62	84.97	109.65	50.90	15.85	582.20	50.36	119.58	55.47
K		41	249.90	343.82	336.69	267.40	51.01	1904.00	237.55	450.10	252.98
Mg		41	378.48	471.40	519.90	355.60	64.57	3211.00	307.30	635.50	339.48
Mn		41	7.71	10.79	8.38	8.73	2.02	35.41	8.15	13.44	8.34
Na		41	1932.11	2140.20	1964.40	1523.00	81.16	9568.00	1520.16	2760.24	1463.48
Ni		41	3.67	4.34	2.19	3.81	1.50	12.62	3.64	5.03	3.93
Pb		41	8.28	8.75	5.18	8.12	3.21	36.50	7.11	10.38	7.89
Sr		41	8.84	12.51	16.04	7.60	2.78	77.36	7.44	17.57	8.46
V		41	2.68	3.38	2.16	2.88	1.14	13.18	2.70	4.06	2.90
Zn		41	16.95	23.00	27.77	13.28	1.48	129.40	14.23	31.76	12.53
Br	27-12-05/ 19-03-06	18	11.09	12.78	2.46	11.64	9.40	19.88	11.55	14.00	12.58
Cl		21	3881.42	3499.66	3248.32	2136.39	961.55	14634.06	2021.04	4978.27	2603.92
Fl		23	65.12	86.90	50.14	69.51	16.24	240.60	65.22	108.58	74.46
NO_3		22	1630.58	2126.48	1560.49	1628.58	516.40	7079.58	1434.60	2818.36	1763.66
NO_2		22	91.51	98.36	42.93	105.97	14.97	198.20	79.32	117.39	86.49
PO_4		7	97.89	277.16	104.76	313.58	79.26	390.52	180.28	374.05	250.76
SO_4		20	4862.65	6112.66	3182.95	5221.22	2750.56	12818.53	4623.00	7602.33	5464.76

Notes: i.Volume weighted mean values;
ii.Unit for rain amount was given as mm, and units of concentration of all chemical parameters were given as ppb.

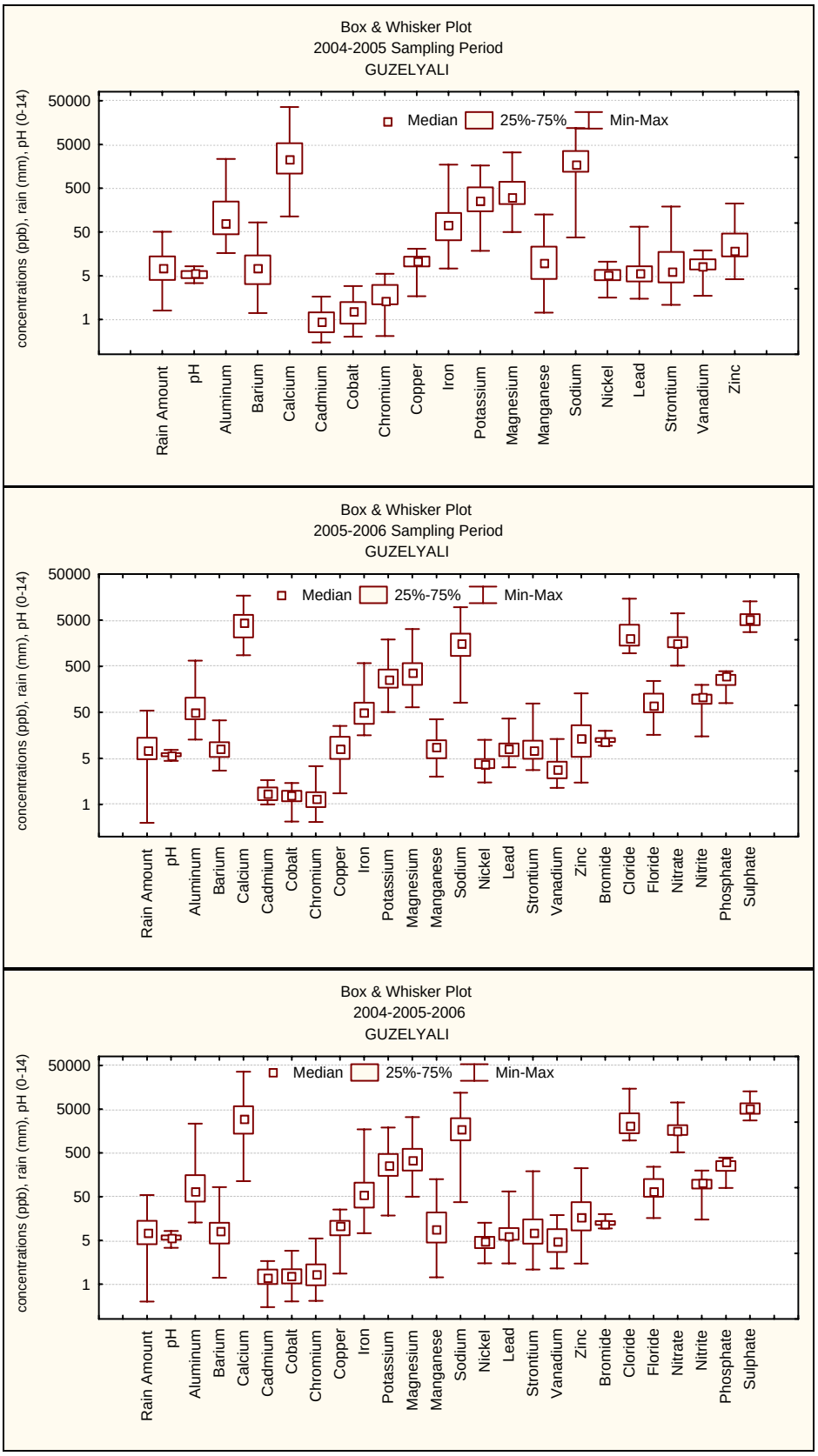


Figure 4.5 Box & Whisker plot for data handled from Güzelyalı sampling point for two sampling periods and over all periods.

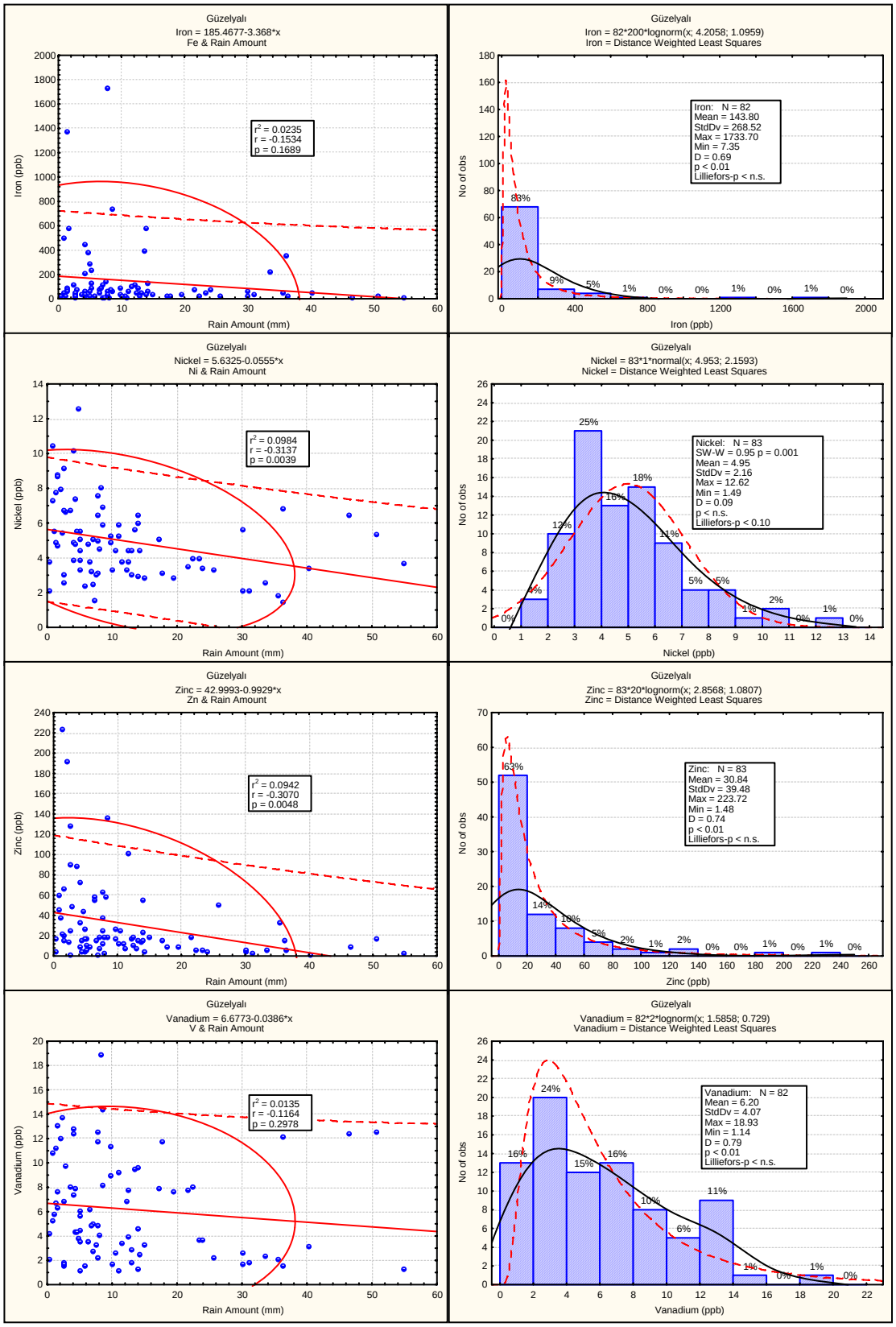


Figure 4.6 Distribution of all measured concentrations belongs to some chemical parameters versus rainwater amounts with also represented with frequency histograms (Güzelyali). Eliptic ranges with coefficient ±95 % and regression bans with prediction ±95 % were also given as straight and truncated lines, respectively, to observe confidence ranges for visual inspections in figures located left part of the page. Truncated lines on histograms indicate the fitted normal or log-normal distribution curves, and black ones show the distance weighted least squared curves.

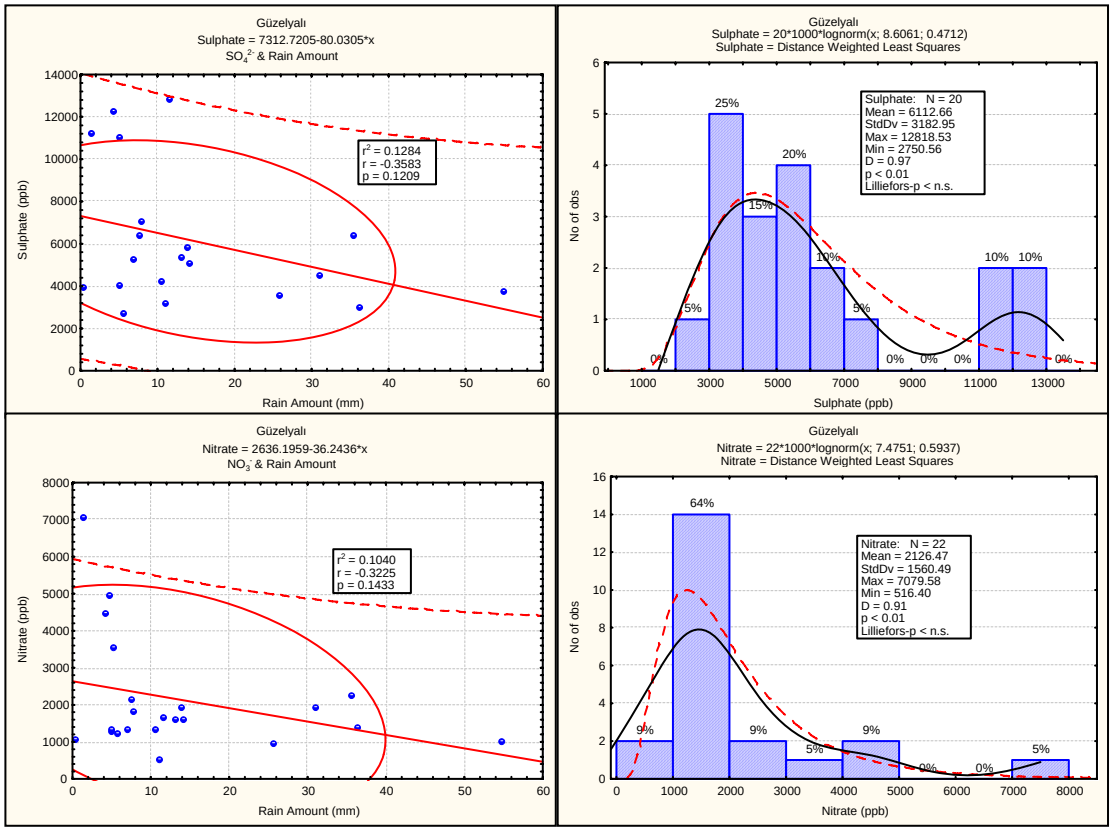


Figure 4.6 Continued.

Table 4.8 shows the result of other normality tests. Similar to Tınaztepe and Bprnova, many of the chemical parameters in Güzelyali site distributed asymmetrically. Statistical tests to explain the distributions of data infer that many of data fits log normally distributions as in Bornova and Tınaztepe. This indicates that transportation from distant regions and mixing play a major role in the distribution of concentrations. Frequency histograms and the fitted log normal and normal distribution curves with distances weighted least square curves for some measured parameters were given exemplary Figure 4.6 for visual inspection.

Table 4.8.a. Test for distribution properties of Güzelyalı in 2004-2006 sampling periods (overall sampling periods) (bold italic values are significant).

Parameters	***Valid N****	***max D***	***K-S***	***Lilliefors***	***W***	***p***	***A/G*****	***Skewness***	***Kurtosis***
rain	83	0.20	***p < .01***	***p < .01***	***0.81***	***0.00***	1.69	1.65	2.32
pH	82	0.10	p > .20	***p < .05***	0.97	0.07	1.02	***-0.32***	-0.15
Al	74	0.33	***p < .01***	***p < .01***	***0.44***	***0.00***	2.42	4.08	17.40
Ba	82	0.26	***p < .01***	***p < .01***	***0.59***	***0.00***	1.53	3.33	12.11
Ca	83	0.19	***p < .01***	***p < .01***	***0.71***	***0.00***	1.66	3.11	14.59
Cd	70	0.11	*p > .20*	***p < .05***	0.97	0.07	1.17	***0.32***	-0.73
Co	59	0.16	*p < .15*	***p < .01***	***0.82***	***0.00***	1.18	1.91	4.32
Cr	56	0.21	***p < .05***	***p < .01***	***0.76***	***0.00***	1.37	1.96	3.81
Cu	79	0.06	p > .20	p > .20	0.97	0.10	1.22	***0.32***	0.13
Fe	82	0.33	***p < .01***	***p < .01***	***0.48***	***0.00***	2.14	4.14	19.76
K	83	0.21	***p < .01***	***p < .01***	***0.73***	***0.00***	1.42	2.35	6.09
Mg	82	0.22	***p < .01***	***p < .01***	***0.67***	***0.00***	1.53	2.76	8.47
Mn	83	0.26	***p < .01***	***p < .01***	***0.54***	***0.00***	1.80	3.41	11.92
Na	83	0.17	***p < .05***	***p < .01***	***0.81***	***0.00***	1.42	2.10	6.24
Ni	83	0.09	p > .20	*p < .10*	***0.94***	***0.00***	1.10	0.99	1.23
Pb	74	0.29	***p < .01***	***p < .01***	***0.49***	***0.00***	1.28	4.51	22.79
Sr	82	0.29	***p < .01***	***p < .01***	***0.48***	***0.00***	1.80	4.70	27.73
V	82	0.13	*p < .15*	***p < .01***	***0.92***	***0.00***	1.27	0.75	-0.20
Zn	83	0.25	***p < .01***	***p < .01***	***0.66***	***0.00***	1.77	2.86	9.59

*:Valid number of samples, **:Ratio of arithmetic mean to geomethric mean.

Notes: The magnitude of deviations from normality of data is related these criterias:

[i].The higher values as max D, the more deviation from normality and, the more similarity to log-normal distribution. (Kolmogorov-Smirnov test values must also be significant for log-normal distribution).

[ii].p values (of Lilliefors test and others) are significant if the values are smaller 0.05. This indicates that the deviations from the normality are expressiable.

[iii].The more clossness to the value 1 in Shapiro-Wilk's W tests, the more expressiable of the normal distributions of data.

[iv].If the arithmetic mean values is equal to geometric mean or skewness is equal to the value "0", the deaviation from normality is minimal.

[v].Kurtosis test is related to sharpness of the frequency distribution curves.

Table 4.8.b. Test for distribution properties of Güzelyalı in 2004-2005 sampling period (bold italic values are significant).

Parameters	**Valid N***	**max D**	**K-S**	**Lilliefors**	**W**	**p**	**A/G****	**Skewness**	***Kurtosis***
rain	42	0.21	***p < .05***	***p < .01***	***0.79***	***0.00***	1.64	1.80	2.99
pH	42	0.11	p > .20	p > .20	0.97	0.40	1.02	***0.03***	-0.75
Al	35	0.31	***p < .01***	***p < .01***	***0.52***	***0.00***	2.75	2.89	7.71
Ba	41	0.27	***p < .01***	***p < .01***	***0.63***	***0.00***	1.89	2.49	5.71
Ca	42	0.25	***p < .05***	***p < .01***	***0.62***	***0.00***	2.00	3.61	16.67
Cd	29	0.18	p > .20	***p < .05***	***0.87***	***0.00***	1.26	1.14	0.52
Co	28	0.16	p > .20	***p < .05***	***0.83***	***0.00***	1.31	1.40	1.18
Cr	23	0.21	p > .20	***p < .01***	***0.89***	***0.01***	1.36	1.08	0.62
Cu	41	0.09	p > .20	p > .20	0.99	0.93	1.09	***-0.02***	0.08
Fe	41	0.33	***p < .01***	***p < .01***	***0.55***	***0.00***	2.50	3.12	10.35
K	42	0.23	***p < .05***	***p < .01***	***0.77***	***0.00***	1.48	1.88	3.24
Mg	41	0.24	***p < .05***	***p < .01***	***0.73***	***0.00***	1.65	2.16	4.83
Mn	42	0.27	***p < .01***	***p < .01***	***0.61***	***0.00***	2.19	2.43	4.97
Na	42	0.17	p < .20	***p < .01***	***0.80***	***0.00***	1.36	2.34	8.50
Ni	42	0.07	p > .20	p > .20	0.98	0.69	1.07	***0.29***	0.20
Pb	33	0.35	***p < .01***	***p < .01***	***0.46***	***0.00***	1.53	3.71	13.84
Sr	41	0.30	***p < .01***	***p < .01***	***0.49***	***0.00***	2.11	4.16	20.33
V	41	0.11	p > .20	p > .20	0.98	0.58	1.10	***0.21***	0.32
Zn	42	0.26	***p < .01***	***p < .01***	***0.65***	***0.00***	1.60	2.62	7.17

*:Valid number of samples, **:Ratio of arithmetic mean to geomethric mean.

Notes: The magnitude of deviations from normality of data is related these criterias:

[i].The higher values as max D, the more deviation from normality and, the more similarity to log-normal distribution. (Kolmogorov-Smirnov test values must also be significant for log-normal distribution).

[ii].p values (of Lilliefors test and others) are significant if the values are smaller 0.05. This indicates that the deviations from the normality are expressiable.

[iii].The more clossness to the value 1 in Shapiro-Wilk's W tests, the more expressiable of the normal distributions of data.

[iv].If the arithmetic mean values is equal to geometric mean or skewness is equal to the value "0", the deaviation from normality is minimal.

[v].Kurtosis test is related to sharpness of the frequency distribution curves.

Table 4.8.c. Test for distribution properties of Güzelyalı in 2005-2006 sampling period (bold italic values are significant).

Parameters	***Valid N****	***max D***	***K-S***	***Lilliefors***	***W***	***p***	***A/G*****	***Skewness***	***Kurtosis***
rain	41	0.22	***p < .05***	***p < .01***	***0.82***	***0.00***	1.73	1.56	2.18
pH	40	0.13	p > .20	p < .10	0.97	0.34	1.01	***-0.35***	0.40
Al	39	0.30	***p < .01***	***p < .01***	***0.58***	***0.00***	1.68	2.81	7.67
Ba	41	0.18	p < .15	***p < .01***	***0.80***	***0.00***	1.19	2.05	5.17
Ca	41	0.19	p < .15	***p < .01***	***0.84***	***0.00***	1.36	1.48	1.79
Cd	41	0.10	p > .20	p > .20	0.95	0.07	1.06	***0.41***	-0.72
Co	31	0.10	p > .20	p > .20	0.98	0.82	1.07	***0.34***	0.06
Cr	33	0.23	p < .10	***p < .01***	***0.70***	***0.00***	1.18	2.98	11.71
Cu	38	0.13	p > .20	p < .10	***0.93***	***0.03***	1.38	0.61	-0.18
Fe	41	0.30	***p < .01***	***p < .01***	***0.58***	***0.00***	1.53	3.18	11.22
K	41	0.19	p < .10	***p < .01***	***0.67***	***0.00***	1.36	3.11	11.93
Mg	41	0.22	***p < .05***	***p < .01***	***0.59***	***0.00***	1.39	3.99	19.69
Mn	41	0.25	***p < .05***	***p < .01***	***0.82***	***0.00***	1.29	1.40	1.13
Na	41	0.19	p < .15	***p < .01***	***0.80***	***0.00***	1.46	1.92	4.26
Ni	41	0.19	p < .15	***p < .01***	***0.82***	***0.00***	1.10	1.94	4.65
Pb	41	0.19	p < .10	***p < .01***	***0.62***	***0.00***	1.11	3.95	20.85
Sr	41	0.29	***p < .01***	***p < .01***	***0.54***	***0.00***	1.48	3.42	12.14
V	41	0.15	p > .20	***p < .05***	***0.78***	***0.00***	1.16	2.53	9.68
Zn	41	0.25	***p < .05***	***p < .01***	***0.73***	***0.00***	1.84	2.23	5.45
Br	18	0.24	p > .20	***p < .05***	***0.84***	***0.01***	1.02	1.60	3.11
Cl	21	0.24	p < .15	***p < .01***	***0.73***	***0.00***	1.34	2.31	6.29
Fl	23	0.18	p > .20	p < .10	***0.89***	***0.01***	1.17	1.35	2.56
NO_3	22	0.28	***p < .05***	***p < .01***	***0.74***	***0.00***	1.21	2.05	4.17
NO_2	22	0.10	p > .20	p > .20	0.98	0.86	1.14	***0.06***	0.31
PO_4	7	0.34	p > .20	***p < .05***	0.84	0.10	1.11	-1.33	1.41
SO_4	20	0.21	p > .20	***p < .05***	***0.83***	***0.00***	1.12	1.16	0.09

*:Valid number of samples, **:Ratio of arithmetic mean to geomethric mean.

Notes: The magnitude of deviations from normality of data is related these criterias:

[i].The higher values as max D, the more deviation from normality and, the more similarity to log-normal distribution. (Kolmogorov-Smirnov test values must also be significant for log-normal distribution); [ii].p values (of Lilliefors test and others) are significant if the values are smaller 0.05. This indicates that the deviations from the normality are expressiable; [iii].The more clossness to the value 1 in Shapiro-Wilk's W tests, the more expressiable of the normal distributions of data.

[iv].If the arithmetic mean values is equal to geometric mean or skewness is equal to the value "0", the deaviation from normality is minimal.

[v].Kurtosis test is related to sharpness of the frequency distribution curves.

4.1.4 Gaziemir

This sampling point was evaluated as a suburban sampling point. The campus was relatively far from any settlement zones or industrial facilities. This station take part in an airport (Adnan Menderes Airport Area) area 5 km far from nearest settling site and 14 km far from the Aegean Sea shoreline in İzmir.

Twenty-six wet deposition samples were collected between January 2005 and July 2005 in this meteorological station.

A summary of the descriptive statistics of the measured chemical parameters at Gaziemir precipitation sampling station at 2005-2006 sampling period was presented in Table 4.9. Median values with 25-75 % percentiles, minimum and maximum values of all measured parameters at this station was also given Figure 4.7 as Box & Whisker plots.

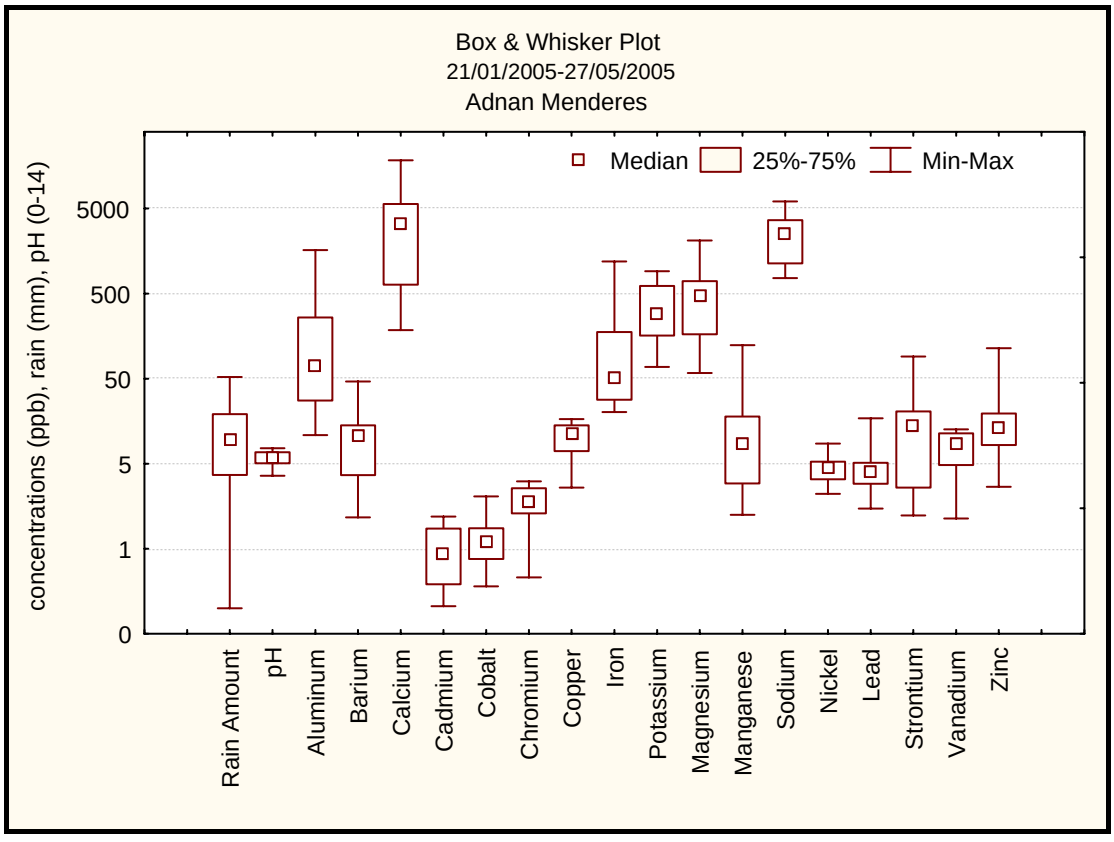


Figure 4.7 Box & Whisker plot for data handled from Gaziemir sampling point at 2004-2005 sampling period.

Table 4.9.Summary of data handled from Gaziemir in 2004-2005 rainy periods.

Parameters	Sampling Periods	Valid N	VWMV [i]	Arithmetic Mean	Std.Dev.	Median	Min.	Max.	Confidence -%95	Confidence +%95	Geometric Mean
mm	21/01/05-27/05/05	26	-	12.36	11.49	9.40	0.10	52.40	7.72	17.00	7.06
pH		25	4.90	5.85	1.15	6.00	3.60	7.60	5.37	6.32	5.73
Al		23	200.26	231.53	378.78	71.11	10.85	1629.73	67.73	395.33	86.08
Ba		26	11.91	12.25	11.32	10.48	1.17	46.35	7.68	16.82	7.87
Ca		26	3743.48	4230.25	4554.27	3384.03	186.21	18476.53	2390.74	6069.76	2192.53
Cd		16	0.28	0.53	0.39	0.44	0.11	1.20	0.33	0.74	0.40
Co		17	0.39	0.70	0.49	0.61	0.18	2.06	0.45	0.95	0.56
Cr		16	1.35	1.86	0.85	1.83	0.23	3.11	1.41	2.31	1.59
Cu		26	10.77	10.68	4.11	11.03	2.63	16.71	9.02	12.34	9.78
Fe		26	142.46	148.32	249.81	51.66	20.23	1193.43	47.42	249.22	73.43
K		26	387.64	370.32	251.83	293.60	68.50	916.40	268.60	472.03	289.51
Mg		26	550.62	523.05	471.79	459.78	58.36	2108.61	332.49	713.61	357.08
Mn		26	18.53	17.68	26.18	8.66	1.26	124.16	7.11	28.25	8.87
Na		25	3090.48	2711.92	1574.22	2594.00	762.19	6072.00	2062.12	3361.73	2260.17
Ni		26	3.97	4.50	1.40	4.50	2.22	8.62	3.93	5.06	4.29
Pb		20	4.01	4.67	3.39	3.98	1.49	17.10	3.08	6.25	3.95
Sr		26	18.33	19.41	24.01	13.67	1.23	91.32	9.71	29.11	9.82
V		26	7.30	7.95	3.80	8.66	1.14	12.68	6.41	9.49	6.64
Zn		26	15.42	17.91	21.28	13.01	2.68	114.33	9.32	26.51	13.09

Notes i.Volume weighted mean values.
ii.Unit for rain amount was given as mm, and units of concentration of all chemical parameters were given as ppb.

4.1.5 Çiğli

This sampling point was evaluated as a suburban sampling point. This station take part in a military aircraft area near the Aegean Sea shoreline in İzmir. This station was the nearest sampling point to the petrochemical platforms in Aliağa region and approximately 35 km far from Aliağa. Emission from Aliağa was another local factor affecting the air quality in this sampling site. Thirteen wet deposition samples were collected between January 2005 and May 2005 in this site.

A summary of the descriptive statistics of the measured chemical parameters at Çiğli precipitation sampling station at 2004-2005 sampling period was presented in Table 4.10. Median values with 25-75 % percentiles, minimum and maximum values of all measured parameters at this station were also given Figure 4.8 as Box & Whisker plots.

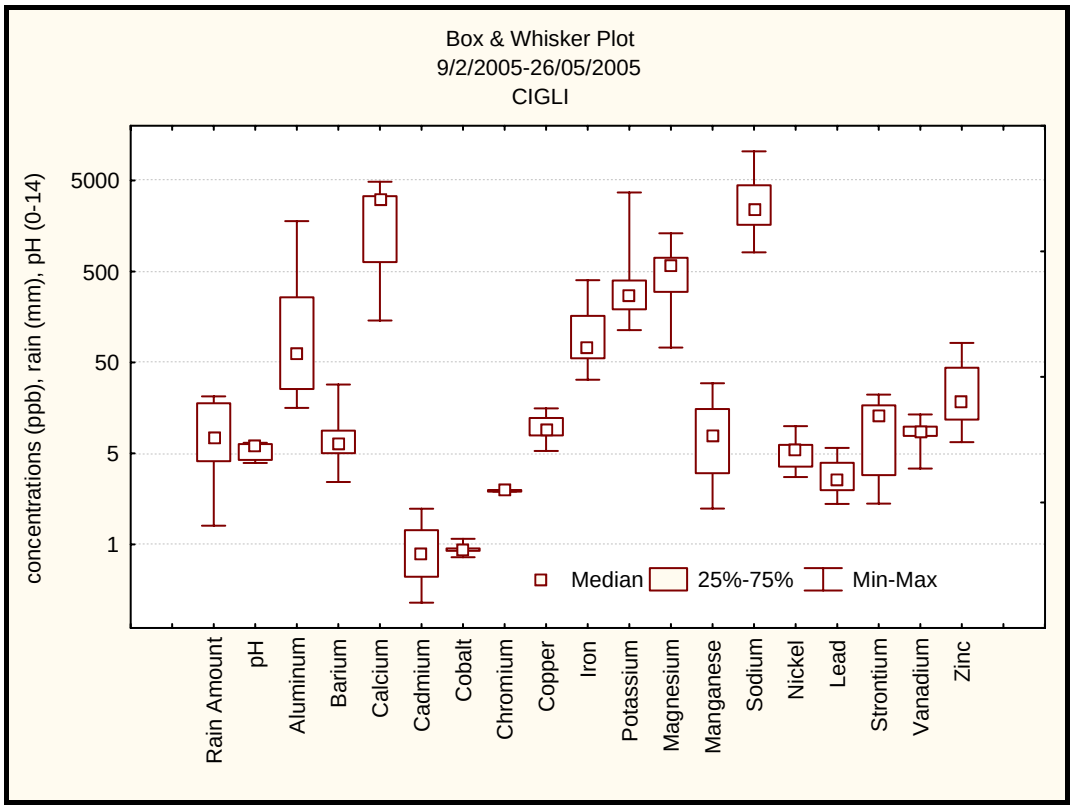


Figure 4.8 Box & Whisker plot for data handled from Çiğli sampling point at 2004-2005 sampling period.

Table 4.10 Summary of data handled from Cigli in 2004-2005 rainy period.

Parameters	Sampling Periods	Valid N	VWMV[i]	Arithmetic Mean	Std.Dev.	Median	Min.	Max.	Confidence -%95	Confidence +%95	Geometric Mean
mm	09-02-05/ 26-05-05	13	-	9.96	7.32	7.40	0.80	21.20	5.54	14.39	6.94
pH		13	4.90	5.43	1.06	5.94	3.92	6.55	4.79	6.06	5.32
Al		10	200.26	143.91	200.30	57.11	15.78	663.70	0.63	287.20	71.55
Ba		13	11.91	8.23	6.74	6.23	2.42	28.66	4.15	12.30	6.67
Ca		12	3743.48	2500.13	1539.73	3047.04	298.90	4855.83	1521.84	3478.43	1831.97
Cd		7	0.28	0.48	0.38	0.39	0.11	1.23	0.13	0.84	0.37
Co		5	0.39	0.45	0.08	0.44	0.36	0.57	0.35	0.55	0.45
Cr		2	1.35	1.94	0.05	1.94	1.90	1.97	1.49	2.39	1.94
Cu		13	10.77	9.90	2.99	9.21	5.32	15.66	8.09	11.70	9.49
Fe		13	142.46	124.20	112.22	71.81	32.21	401.60	56.38	192.01	91.39
K		13	387.64	727.11	1057.14	268.50	113.05	3692.22	88.28	1365.93	372.26
Mg		13	550.62	560.13	345.56	576.36	73.00	1314.96	351.31	768.95	447.69
Mn		13	18.53	10.82	8.79	7.75	1.23	29.53	5.52	16.13	7.36
Na		13	3090.48	3379.90	2640.68	2333.77	814.10	10481.90	1784.15	4975.65	2665.92
Ni		13	3.97	5.50	2.32	5.43	2.75	9.99	4.10	6.91	5.09
Pb		7	4.01	2.96	1.47	2.56	1.39	5.75	1.61	4.32	2.69
Sr		13	18.33	10.98	7.15	12.59	1.40	22.11	6.66	15.30	8.00
V		13	7.30	8.88	2.72	8.48	3.41	13.39	7.23	10.52	8.43
Zn		13	15.42	27.42	22.61	18.01	6.62	82.05	13.76	41.09	20.45

Notes i.Volume weighted mean values.
ii.Unit for rain amount was given as mm, and units of concentration of all chemical parameters were given as ppb.

4.2 Data Evaluations

4.2.1 Evaluations on concentration of measured parameters at İzmir

Concentrations of elements and ions of precipitation were shown in Tables 4.11.a and Table 4.11.b for 23 chemical species. Table 4.11.b presented data for ionic concentrations, while Table 4.11.a presented data for elemental concentrations. In both tables, values in parenthesis for our work and some compartment works were showed the arithmetic means. We tried to represent more of the values as volume weighted mean concentrations. The first three columns showed the result of our studies, the remaining columns allowed a comparison of the concentrations of measured species with those found by others in suburban and urban areas worldwide. Furthermore, visual inspections of comparison tables were given in Figure 4.9 and 4.10 for better perceptions.

Literature data that had similar sampling procedure and geographic properties, were selected for comparison. Most of suburban areas given in the following tables or figures were affected from some industrial areas near the sampling points similar to our sampling stations.

Concentrations of crustal elements in the literature were arranged differently due to geological properties. Concentrations of crustal elements (Ca, Mn, Al and Fe) measured in our stations had moderate values relative to other sites. High concentrations of some crustal elements in our samples (especially Mn) were due to sporadic, intense incursions of Saharan dust and the long dry summer season in the region which increases the atmospheric loading of soil particles which get washed out by precipitation. Concentrations of Ni were obtained moderately high relative to other sampling points. Kubilay & Saydam (1995) found anomalous Cr and Ni enrichments in the eastern Mediterranean aerosol and explained it to be due to the presence of Cr- and Ni-rich soil along the Mediterranean Coast of Turkey.

Table 4.11.a Comparisons of volume weighted mean concentrations or arithmetic mean concentrations of pH, main and trace elements as reported in the literatures and this work (ppb).

Parameter & Stations	This work[i]			Antalya[3,iii] (Suburban)	Ankara[6,iii] (Suburban)	Eastern Mediterranean Basin[16] (Suburban)	Athens[7,iii] (Suburban)	Ajlune[9] (Suburban)	Western Massach.[17] (Suburban)	Al-Hashimya[8,iii] (Urban)	Singapore[10] (Urban)	Worldwide Review[18]
	Tınaztepe (Suburban)	Güzelyalı (Urban)	Bornova (Urban)									
pH	5.8 (5.8)	5.6 (5.8)	6.5 (6.7)	5.2	4.7		6.5	6.4		7.5		
Al	84.5 (95.5)	118.9 (201.9)	129.4 (194.2)	580.0	980.0	73.0	5.9	382.0	53.0	386.0	18.4	
Ca	2328.2 (3018.5)	3249.3 (4735.7)	4818.6 (6841.2)		2640.0					12900.0		
Cd	0.9 (1.0)	0.6 (0.8)	0.8 (0.8)	4.5	9.5	4.3	0.2	0.4	0.31	11.8	0.3	0.5
Co	0.8 (0.8)	0.5 (0.9)	0.4 (0.6)								0.6	
Cr	0.4 (0.9)	0.6 (1.2)	0.8 (1.8)	9.0	3.0	3.7	1.3	0.8	0.14	6.2	1.6	0.44
Cu	7.8 (11.0)	8.1 (10.3)	9.7 (12.4)		6.1	3.1	15.4	3.1	0.95	9.9	5.6	5.4
Fe	56.5 (61.0)	103.4 (143.8)	114.2 (173.4)	530.0	750.0		4.4	92.0	65.0	363.0	23.9	
K	154.4 (253.0)	237.0 (367.5)	259.1 (423.0)	710.0	139.0					896.0		
Mg	275.5 (327.2)	409.5 (550.5)	328.3 (470.8)		240.0					820.0		
Mn	6.6 (7.5)	10.5 (16.4)	9.5 (14.0)			3.6	3.6	2.1	1.3	48.6	2.8	5.7
Na	1551.0 (1976.8)	1959.2 (2357.4)	1435.1 (1966.8)	10000.0	530.0					3717.0		
Ni	5.1 (5.8)	4.3 (5.0)	4.1 (4.8)		4.1	11.0	4.1	2.6	0.75		3.9	2.4
Pb	7.1 (8.3)	6.1 (8.8)	5.3 (7.6)		19.1	6.4	0.9	2.6	4.5	27.0	3.4	12
V	2.0 (2.3)	5.7 (6.2)	5.2 (6.7)	0.7	2.2			4.2	1.1		3.5	9
Zn	31.6 (48.7)	18.9 (30.8)	29.5 (42.4)	140.0	0.03	124.0	33.5	6.5	3.7	1230.0	7.2	36
Br	8.9 (15.4)	11.1 (12.8)	3.6 (14.7)	9.0								
Cl	3087.7 (3787.9)	3881.4 (3499.7)	2615.4 (3612.4)	18000.0	1460.0					7410.0		
NO_3	1551.3 (2006.3)	1630.6 (2126.5)	1454.2 (2044.7)	4900.0	2200.0					6020.0		
SO_4	3083.2 (4358.6)	4862.6 (6112.7)	5456.7 (8070.1)	6200.0	2500.0					20630.0		
NH_4				1300.0	1200.0					110.0		

Table 4.11.b Comparisons of volume weighted mean concentrations and arithmetic mean concentrations of pH, main cations and anions as reported in the literatures and this work (µeq/L).

Parameter & Stations	This work[i]			Menemen[1] (Suburban)	Cubuk[2] (Suburban)	Ankara[4] (Suburban)	Kaynarca[5,iii] (Suburban)	Patras[21] (Suburban)	Ajlune[9] (Suburban)	Galilee[20] (Suburban)	Albany[13,iii] (Suburban)	Germany[22,iii] (average values of 8 sites in different ecosystems)	Netherlands[12,iii] (Suburban)	Colmar[11,iii] (Suburban)	Pyrenees[19] (Suburban)
	Tınaztepe (Suburban)	Güzelyalı (Urban)	Bornova (Urban)												
pH	5.8 (5.8)	5.6 (5.8)	6.5 (6.7)	5.6	6.3	6.1	5.6		6.4	4.2	4.1	4.2	4.1	5.7	
Na^+	67.4 (86.0)[ii]	85.2 (102.5)[ii]	62.4 (85.5)[ii]	117.0	15.6	21.0	69.4	90.2	50.0	60.9	5.0	60.9	290.0	70.0	23.0
K^+	3.9 (6.5)[ii]	6.1 (9.4)[ii]	6.6 (10.8)[ii]	17.0	9.8	19.0	40.7	6.6	11.1	3.8	6.0	3.8	28.0	83.0	9.0
Mg^{+2}	22.7 (26.9)[ii]	33.7 (45.3)[ii]	27.0 (38.8)[ii]	101.0	9.3		23.1	30.4	30.7	13.2	3.0	13.2	90.0	16.0	8.0
Ca^{+2}	116.4 (150.9)[ii]	162.5 (236.8)[ii]	240.9 (342.1)[ii]	81.0	71.4	210.0	290.0	98.5	108.1	15.0	10.0	15.0	60.0	166.0	94.0
Ba^{+2}	0.05 (0.07)[ii]	0.20 (0.18)[ii]	0.12 (0.19)[ii]												
NH_4^+				43.0	86.4	12.0	40.7	16.3	14.8	27.8	17.0	27.8	78.0	140.0	22.0
Br^-	0.10(0.18)	0.10(0.41)	0.05(0.06)												
Cl^-	87.0(106.1)	109.3(151.8)	73.7(66.5)	117.0	20.4		91.0	114.3	37.0	38.4	8.0	38.4	313.0	167.0	20.0
F^-	1.4(1.6)	3.4(4.4)	2.7(3.6)				30.3								
NO_3^-	25.0(32.5)	26.3(37.0)	23.5(30.5)	23.0	29.2	62.0	31.6	19.4	75.5	42.3	45.0	42.3	47.0	78.0	18.0
SO_4^{-2}	66.8(94.1)	101.3(149.0)	113.5(141.9)	66.0	48.0	150.0	305.9	46.1	62.1	75.2	68.0	75.2	140.0	147.0	51.0

Notes: i.Values in parenthesis was given as arithmetic mean values.

ii. These values are represented the "µeq/L values" of the related parameters measured by ICP-OES.

iii. These values in these columns were given as arithmetic mean concentrations.

[1.] Al-Momani et al., 1995. [2.] Topcu et al., 2002. [3.] Al-Momani et al., 1997. [4.] Tuncel & Ungor, 1996. [5.] Okay et al., 2001. [6.] Kaya & Tuncel, 1997. [7.] Kanellopoulou, 2001. [8.] Al-Momani et al., 2002. [9.] Al-Momani, 2003. [10.] Balasubramanian & Hu, 2003. [11.] Sanusi et al., 1995. [12.] Schuurkes et al., 1988. [13.] Khwaja & Husain, 1990. [16.] Al-Momani et al., 1998. [17.] Dasch & Wolff, 1989. [18.] Galloway et al., 1982. [19.] Camarrero & Catalian, 1993. [20.] Herut et al., 2000. [21.] Glavas, 1988. [22.] Grömping et al., 1997.

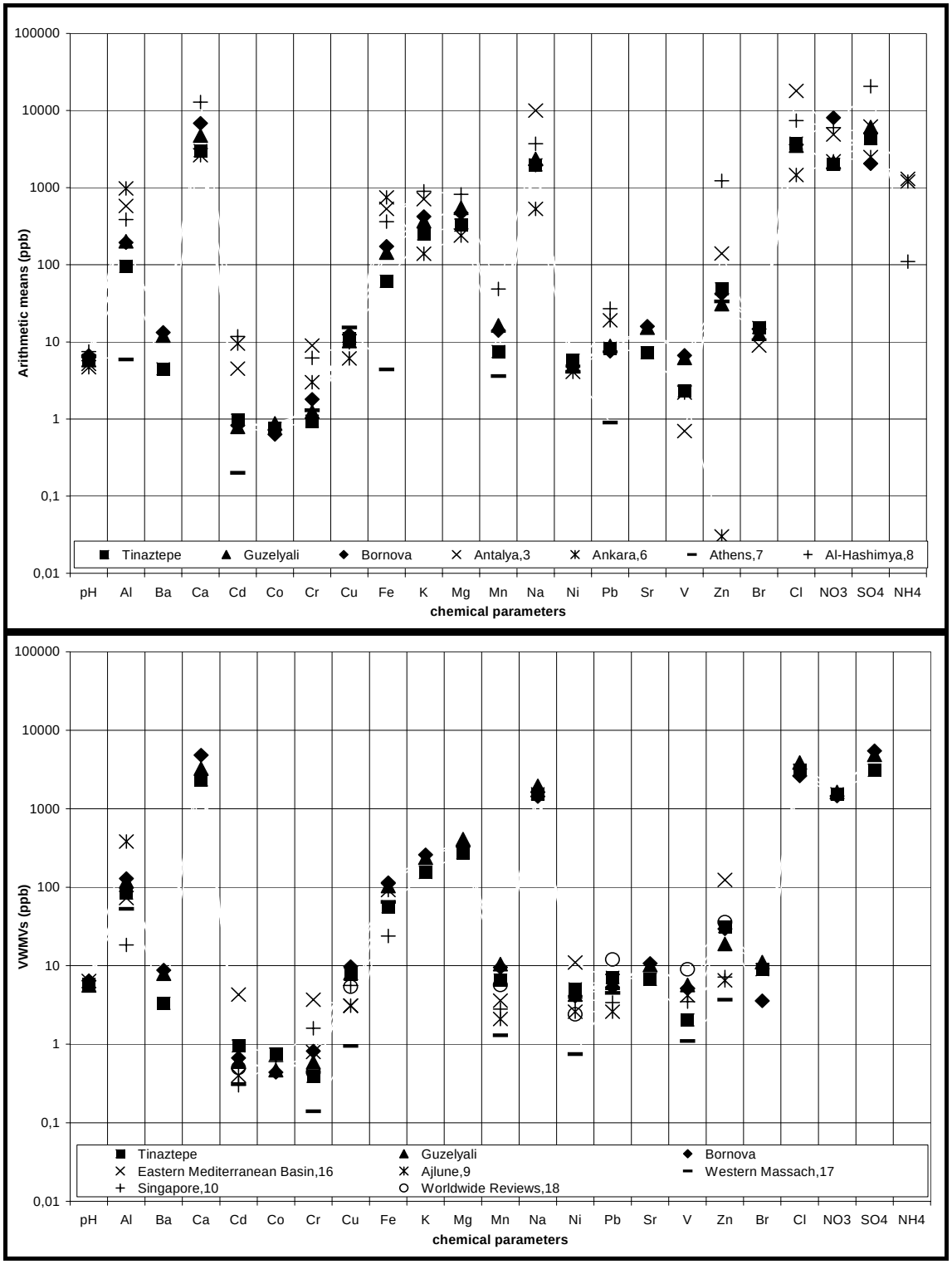


Figure 4.9 Graphical comparisons of chemical parameters into rainwaters detected by other studies in the world and our studies (Visual inspections of Table 4.11.a).

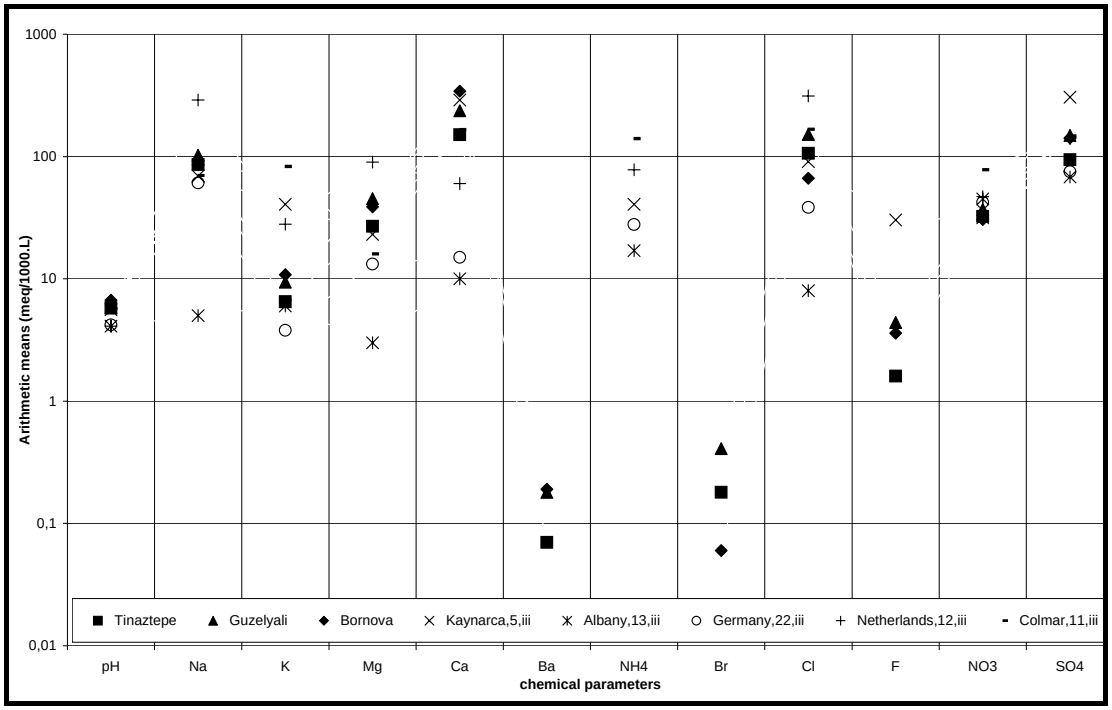
Concentrations of Ca was higher than those reported for more of the sites. This high concentrations were due to the large contribution of the local sources (soil or soil related industries) together with Saharan soil dust, which contains large fractions

of $CaCO_3$ (Singer et al., 1993). At this point, it can be suggested that these results were explained by the effect of cement industries surrounded the city, especially near Bornova sampling point. Therefore, the origin of calcium was considered to be mainly of natural sources due to calcareous nature of the soil, soil related sources and the frequent input of Saharan soil dust.

Concentrations of marine elements (Na, Mg and Cl) were not similar almostly coastal sites such as Eastern Mediterranean, Greece and Israel precipitation sampling points. Concentrations of these ions were obtained moderately low, but moderately similar nearly sampling points (Kaynarca and Menemen; Turkey, and Patras; Greece). It is important here geological properties of sampling points for example distances between sampling points and marine sources. Güzelyalı is the nearest station to the coast of Aegean Sea and high concentrations of these elements were obtained at this station as expected.

Summary of average values determined by evaluating of datasets of all stations (Bornova, Güzelyalı, Tınaztepe, Çiğli, and Gaziemir stations) were listed above in Table 4.12 to point out the general perspectives of chemical composition of raindroplets into İzmir atmosphere. Mean values handled from our five stations were ranged moderately according to other similar studies.

It is obvious that concentrations of trace metals have moderate values in our research when the literature values for urban or suburban areas were considered attentively. It was likely that trace elements have higher concentrations for an urban area than suburban areas. However, some trace elements, especially Pb, Cd, Zn, Co, have the highest values at our suburban sampling area between our sampling stations. This was an unexpected result. But the values obtained in our studies were not the highest values in the literature. Everyone of these pollution-derived trace elements refers to some common industrial sources and indicates similar transport mechanisms.



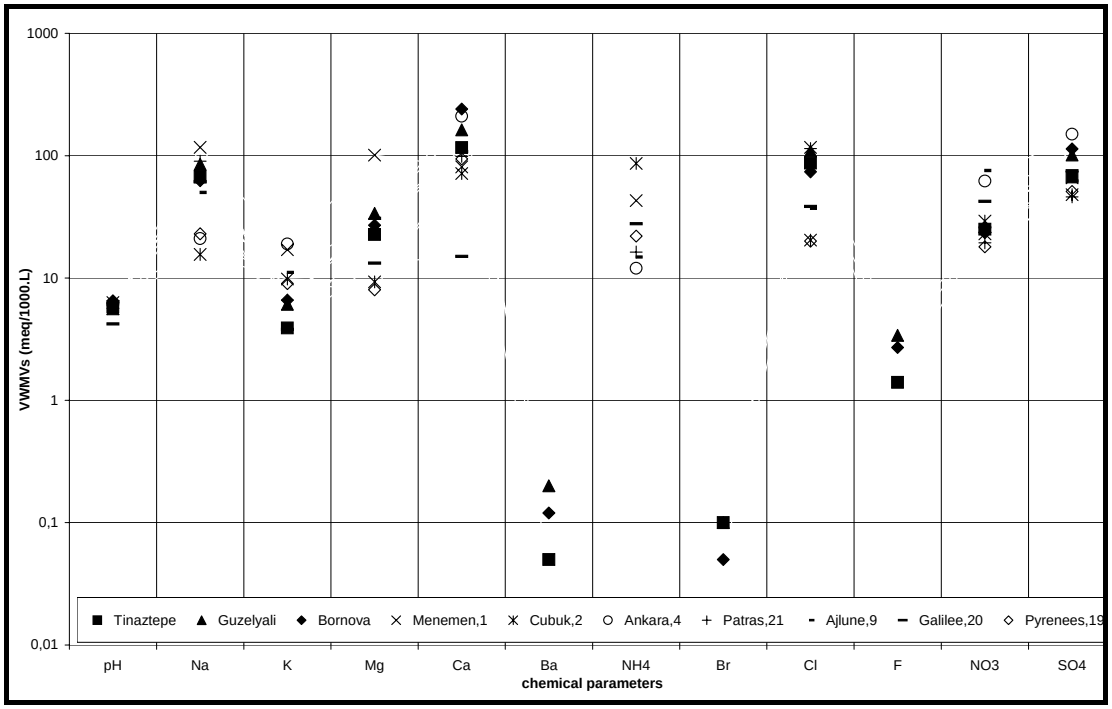


Figure 4.10 Graphical comparisons of chemical parameters into rainwaters detected by other studies in the world and our studies (Visual inspections of Table 4.11.b)**.**

Table 4.12 Summary of data handled from İzmir (average values of five stations).

Parameters	Samplind Periods	Valid N	VWMV[i]	Arithmetic Mean	Std.Dev.	Median	Min.	Max.	Confidence -%95	Confidence +%95	Geometric Mean
mm	06-11-04/30-04-06	226	-	12.79	12.02	8.90	0.10	70.40	11.22	14.37	7.99
pH		223	-	6.06	1.01	6.25	3.40	8.43	5.92	6.19	5.96
Al		200	96.25	191.49	346.60	69.04	10.85	2344.21	143.16	239.82	82.51
Ba		224	5.42	11.12	13.21	6.82	0.70	82.62	9.38	12.86	7.03
Ca		223	2469.58	4923.82	5262.65	3335.70	112.89	35973.87	4229.32	5618.33	2925.31
Cd		187	0.44	0.80	0.41	0.80	0.11	1.96	0.74	0.86	0.68
Co		163	0.34	0.74	0.44	0.68	0.18	2.90	0.67	0.81	0.64
Cr		144	0.48	1.44	1.25	1.06	0.21	7.71	1.24	1.65	1.04
Cu		219	6.16	11.10	5.99	11.16	0.87	39.00	10.30	11.90	9.22
Fe		225	72.23	140.40	233.67	59.42	6.04	1733.70	109.70	171.10	67.23
K		224	178.57	390.42	450.15	244.96	18.63	3692.22	331.15	449.70	258.63
Mg		224	266.80	490.09	505.24	331.85	34.09	3291.11	423.57	556.62	331.24
Mn		225	7.21	14.18	19.53	8.12	0.72	125.25	11.61	16.75	8.38
Na		222	1324.20	2280.92	1843.24	1700.85	37.49	11840.00	2037.12	2524.72	1640.98
Ni		225	3.05	5.00	2.37	4.56	1.05	14.91	4.68	5.31	4.50
Pb		197	3.91	7.71	7.27	6.04	1.39	66.07	6.69	8.73	6.15
Sr		225	7.42	14.54	20.92	7.60	1.08	191.29	11.79	17.29	8.55
V		222	3.57	6.18	4.02	5.41	1.13	18.93	5.64	6.71	4.80
Zn		224	16.78	35.32	43.24	18.46	1.37	284.66	29.63	41.01	20.73
Br	27-12-05/05-04-06	39	-	14.00	3.72	13.10	7.75	24.36	12.80	15.21	13.57
Cl		59	-	3631.75	3254.98	2335.89	374.44	14634.06	2783.50	4480.00	2393.15
Fl		61	-	61.93	49.59	44.92	2.18	240.60	49.23	74.63	43.50
NO_3		58	-	1931.74	1313.29	1618.11	320.24	7079.58	1586.42	2277.05	1591.98
NO_2		60	-	101.25	73.58	96.22	11.02	342.15	82.24	120.25	76.68
PO_4		19	-	212.97	131.20	291.03	30.14	390.52	149.74	276.21	159.90
SO_4		58	-	6115.28	5181.68	4072.93	630.33	23511.55	4752.82	7477.73	4577.56

Notes i.Volume weighted mean values.
ii.Unit for rain amount was given as mm, and units of concentration of all chemical parameters were given as ppb.

According to Table 4.11, highest pH value was measured in Bornova sampling point. It was seen from the figures that the total concentrations of neutralizing types (Ca, K, and Mg) had the highest value for the same station between our sampling stations. Also, the concentrations of SO_4 were highest value in Bornova. Differently NO_3 was the lowest value in Bornova. Although acidifying types necessitate the lower pH values, it was obtained that there was a positively correlation between pH and acidifying potentials. It is obviously explained that SO_4 into rain droplets was not originated from compounds with acidic characters such as (H_2SO_4, H_2SO_3, SO_2 SO_3, other organic or inorganic acidifying types) in atmosphere or neutralizing effects of $CaCO_3$ with high concentrations. When the correlation matrixes were evaluated to understand the origin of these anions, it can be said that there were good relations between these anions and elements originated from sea, soil and soil related industries. In this case, it might be said that airborne SO_4 and NO_3 did not cause decreasing in pH values because of high alkali concentrations as $CaCO_3$. Also, it is obviously said that the salts of Ca was the main responsible for neutralizing the acidity of rains in İzmir.

4.2.2 Evaluations on rainwater pH at İzmir

The acidity of precipitation expressed in terms of pH is a consequence of acid-base balances of chemical species from incorporation of atmospheric gases and aerosols by in-cloud and sub-cloud scavenging (Khwaja & Husain, 1990). The low pH levels are primarily due to the deposition of H_2SO_4 and HNO_3. Since these acids dissolve in water to give H^+, together with SO_4^{2-} and NO_3^-. In addition to these acidic species, CO_2 dissolves in rainwater resulting in the natural pH of precipitation at 5.6, as previously described. Furthermore, organic acids may contribute to the acidity of rainwater. Since the atmospheric burdens of all these parameters and meteorological conditions change significantly from one region to another, the acidity of the collected samples are highly variable both spatially and temporally.

Analyzing 226 samples from November 2004 to May 2006, the average, maximum and minimum pH values were summarised in Table 4.13 with respect to stations.

Table 4.13 Summary of pH data for all sampling stations and sampling periods.

Measured Parameter	pH									
Stations	2004-2005 Rainy Period (September-August)					2005-2006 Rainy Period (September-August)				
	Number of the Analysed Samples	Average pH	Maximum pH	Minimum pH	±95% Confidence Levels	Number of the Analysed Samples	Average pH	Maximum pH	Minimum pH	±95% Confidence Levels
Bornova	36	6.7	8.4	4.8	6.4-7.0	34	6.6	7.9	4.6	6.4-7.8
Güzelyalı	42	5.6	8.2	3.4	5.2-6.0	40	6.0	7.7	4.4	5.8-6.2
Tınaztepe	0	-	-	-	-	33	5.7	7.0	3.7	5.4-6.1
Çiğli	13	5.4	6.6	3.9	4.8-6.1	-	-	-	-	-
Gaziemir	25	5.8	7.6	3.6	5.3-6.3	-	-	-	-	-
Total	116	5.9	8.4	3.4	5.8-6.2	107	6.1	7.9	3.7	6.0-6.2

According to evaluations all of the samples, the relative frequency distribution of pH was given in Figure 4.11. 63 % of the samples had pH values between 5.5 and 7.0. Additionally, the pH of the samples were concentrated between 6.0 and 7.0. About 45 % of the pH values were found in this class. pH values below 3.4 and above 8.4 were not measured in the study. Only 11 % of the samples had pH values between 4.0 and 5.0, which can be considered as "slightly acidic", and only 5 % of the samples had pH values below 4.0, which could be considered as "acid rain".

Summary of the frequency of pH values measured at different stations were given in Table 4.14, and Figure 4.11 for visual inspection of distrubition of pH datasets due to sampling stations.

The pH of rainwater is a result of acid-base reactions in cloud droplets and in rain droplets. Sulphate and Nitrate are the main ions that increase the H^+ ion concentration in rain water, whereas NH_4^+, Ca^{2+} (usually in the form of $CaCO_3$), Mg^{2+}, K^+ ions are the common neutralizing species. The relative abundances of these ions determine the final pH of the rain that is sampled.

In addition to simple abundances of acid and base precursors in the atmosphere, several other factors also play role in the final pH of the rain.

Table 4.14 Frequency distribution of pH.

Periods and Stations	**Frequencies (%) of pH Values**					
	Intervals					
	3-4	**4-5**	**5-6**	**6-7**	**7-8**	**8-9**
(September 2004-August 2005)						
Bornova	0	3	14	***53***	23	8
Güzelyalı	12	24	24	***31***	7	2
Çiğli	23	16	15	***46***	0	0
Gaziemir	8	16	28	***32***	16	0
Total	9	15	21	***39***	13	3
September 2005-August 2006						
Bornova	0	3	6	***70***	21	0
Güzelyalı	0	7	43	***44***	6	0
Tınaztepe	6	15	36	***42***	0	0
Total	2	9	28	***53***	8	0
September 2004- August 2006						
Bornova	0	3	11	***61***	21	4
Güzelyalı	6	16	33	***38***	6	1
% Frequencies of all measured values at all stations	***5***	***11***	***25***	***45***	***11***	***2***

Since SO_4^{2-} and NO_3^- ions originated anthropogenically, their higher concentrations indicated that these group of samples was transported from regions with high anthropogenic emissions. However, it should be noted that SO_4^{2-} and NO_3^- concentrations were also high in many samples at our stations was a necessary but not sufficient condition to have acidic precipitation in stations. Since ions of NH_4^+, Ca^{2+}, Mg^{2+} and K^+ were involved in the neutralization of acidity in the precipitation, their low concentrations indicated that lack of neutralizing species was another requirement to have acidic precipitation. So, high concentration of neutralising spices in precipitations restrains forming of acidic rain droplets.

Below-cloud scavenging of neutralizing ions in samples with high precipitation volume could also result in low pH. The concentrations of elements associated with dust particles decreased rapidly in the first 10-20 minutes of the rain. Although the concentration of SO_4^{2-} and NO_3^- gradually decreased throughout the rain event, the decrease in the concentrations of SO_4^{2-} and NO_3^- ions were significantly smaller than the rates observed for ions such as Ca^{2+}, K^+ and Mg^{2+} due to association of these anthropogenic ions with fine particles which were not scavenged by rain droplets as efficiently as coarse particles (Tuncel & Ungor, 1996).

Low rainwater pH could simply be due to the low concentrations of neutralizing species in samples with high concentrations of acid precursors carried by long-range transport. In many cases, SO_4^{2-} and NO_3^- concentrations, which were greater than the background concentrations, were observed in the data set having pH values greater than 5. However, concentration of neutralizing species in these samples was also high leading to alkaline conditions. Consequently, assessment of relative abundances of acidifying and neutralizing species on an annual basis is needed to understand the neutralization process in our studies. Such an assessment could be made by calculating "acidifying" and "neutralizing" potential at our sampling site. Comparison of the ratio of these two parameters with the corresponding values measured pH values could simply provide information on observed high pH values in our stations.

From this discussion it can be concluded that the acidic rain in İzmir can be observed when emissions that had high concentrations of pollutants were transported with air masses through İzmir.and and when the atmospheric loading of neutralizing species were low. Acidic rain was observed only when these two conditions coincide.

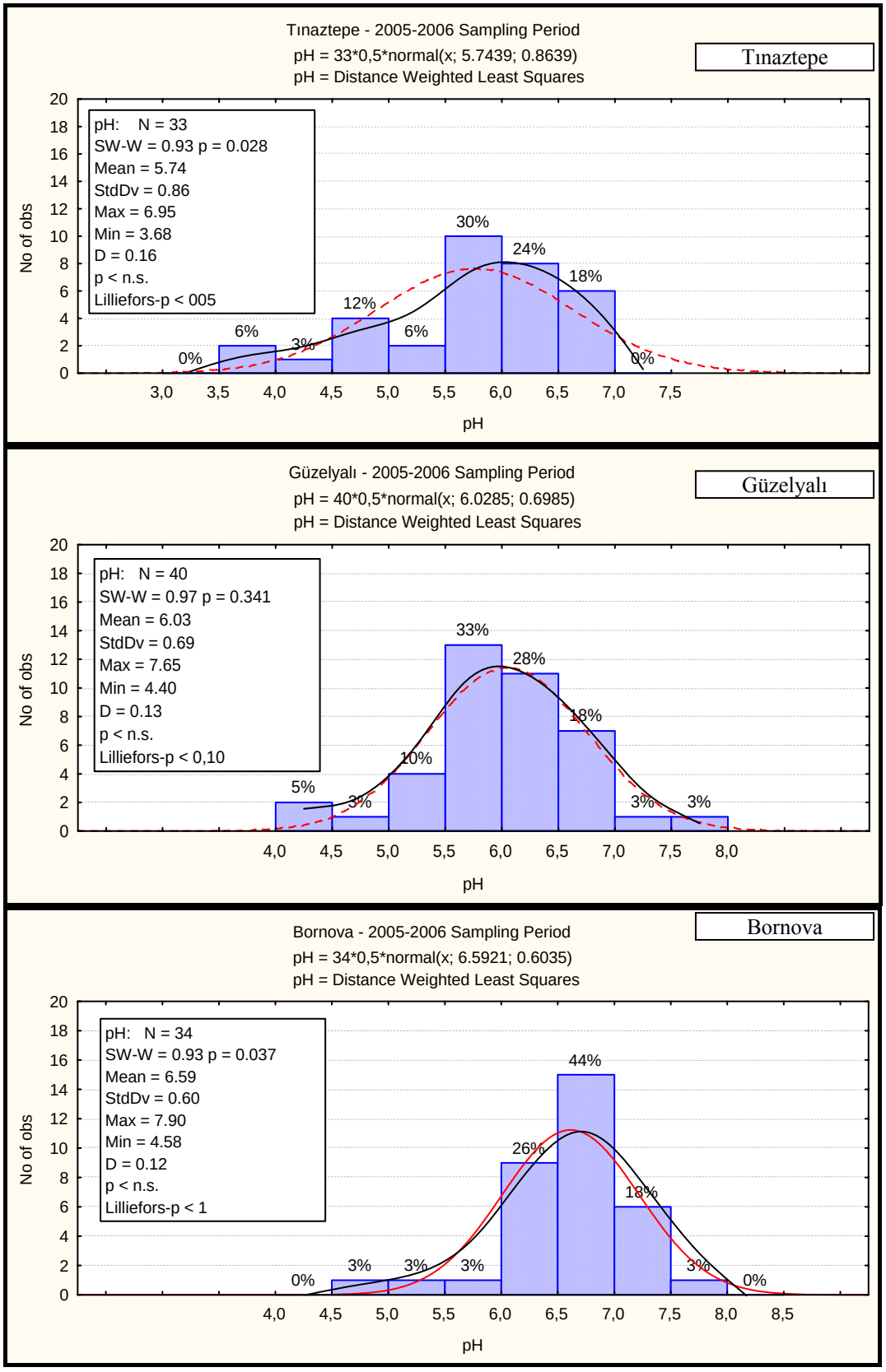


Figure 4.11 pH Histograms for three sampling points (T:Tınaztepe, B:Bornova, G:Güzelyalı) in 2005-2006 sampling period. Truncated lines on histograms indicate the fitted normal distribution curves, and black ones show the distance weighted least squared curves.

The terms acidifying and neutralizing potentials were introduced by Tsuruta (1989) and were further improved by Fujita et al. (2000). "Acidifying Potential" (AP) was defined as the sum of SO_4^{2-} and NO_3^-, which was used as an index of human activities, whereas "Neutralizing Potential" (NP) was defined as the sum of Ca^{2+} and NH_4^+, which was used as an index to demonstrate the effect of air masses containing basic species. Fujita et al. (2000) attributed the decrease in the [NP/AP] ratio to the production of NH_3 and Ca^{2+} over the continents and association with coarse particles, which rapidly decrease with distance from source regions.

Although the concept was attractive to understand the neutralization capacity of the atmosphere in İzmir, some modifications were needed because of our parameters measured at stations. The "AP" was used in this study as "AT" (Acidifying Types) and it was the sum of SO_4^{2-} and NO_3^- ions. However the neutralizing potential as "NT, Neutralising Types" was redefined as [Ca^{2+} + Mg^{2+} + K^+]. The reason for including Mg^{2+} and K^+ ions to the neutralization potential term was due to their correlation with SO_4^{2-} and NO_3^- (Al-Momani et al., 1997).

Table 4.15 Average pH values with average NT, AT, and NT/AT for five sampling stations and different sampling periods.

Measured Parameter	**pH, Ca, K, Mg, SO_4, NO_3**									
Periods	**2004-2005 Rainy Period (September-August)**					**2005-2006 Rainy Period (December-August)**				
Stations	*Number of the Analysed Samples*	*Average pH*	*Average NT, Total Measured Neutralizing Types (µeq/L)*	*Average AT, Total Acidifying Types (µeq/L)*	*Average NT/AT*	*Number of the Analysed Samples*	*Average pH*	*Average NT, Total Measured Neutralizing Types (µeq/L)*	*Average AT, Total Acidifying Types (µeq/L)*	*Average NT/AT*
Bornova	36	6.7	339	-	-	18	6.7	425	235	*1.81*
Güzelyalı	42	5.6	280	-	-	22	6.2	301	173	*1.74*
Tınaztepe	-	-	-	-	-	20	5.9	184	131	*1.40*
Çiğli	13	5.4	180	-	-	-	-	-	-	-
Gaziemir	25	5.8	264	-	-	-	-	-	-	-
Total	*116*	*5.9*	*229*	-	-	*60*	*6.3*	*303*	*303*	*1.70*

Statistical relations between pH and neutralizing (Ca^{2+}, Mg^{2+}, K^+), acidifying types (SO_4^{2-}, NO_3^-) in 5 stations were given as different sampling periods in same stations. Additionally, the values of average NT, AT and NT/AT ratio observed in rain periods

were given in Table 4.15. As expected, the acidity of rainwater was affected by high alkali concentrations, hence acidity decreased with increasing NT/AT ratio. This was expected because; increase in the ratio can be either due to abundance of neutralizing species in the precipitation or owing to lack of acid precursors. In either the case high NT/AT ratios were expected to correspond to low pH values.

Table 4.16 Statistical relations between pH, NT and AT values obtained in stations.

Period	***Stations /Parameters***	***Relationship (pearson "r" correlation coefficients with p values) between pH and neutralization types (Ca, Mg and K)***							
		∑NT=Ca+Mg+K		***Ca^{2+}***		***K^{+}***		***Mg^{2+}***	
		r	***p***	***r***	***p***	***r***	***p***	***r***	***p***
2004-2006		**0.5456**	**0.0000**	**0.5498**	**0.0000**	**0.2686**	**0.0000**	**0.3598**	**0.0000**
	Bornova	**0.4722**	**0.0000**	**0.4692**	**0.0000**	**0.3648**	**0.0000**	**0.3517**	**0.0000**
	Güzelyalı	**0.5675**	**0.0000**	**0.5682**	**0.0000**	**0.4253**	**0.0000**	**0.4652**	**0.0000**
2004-2005		**0.5031**	**0.0000**	**0.5037**	**0.0000**	**0.2262**	**0.0016**	**0.4122**	**0.0000**
	Bornova	0.3667	0.0360	0.3696	0.0340	0.4044	0.0200	0.2819	0.1120
	Güzelyalı	**0.5586**	**0.0000**	**0.5445**	**0.0000**	**0.4986**	**0.0010**	**0.5550**	**0.0000**
	Çiğli	**0.8487**	**0.0000**	**0.8658**	**0.0000**	0.2470	0.4160	**0.7270**	**0.0050**
	Gaziemir	**0.5507**	**0.0040**	**0.5180**	**0.0080**	0.4498	0.0240	**0.6557**	**0.0000**
2005-2006		**0.6266**	**0.0000**	**0.6346**	**0.0000**	**0.3936**	**0.0000**	**0.2909**	**0.0030**
	Bornova	**0.6723**	**0.0000**	**0.6675**	**0.0000**	0.4052	0.0190	**0.4575**	**0.0070**
	Güzelyalı	**0.6553**	**0.0000**	**0.6725**	**0.0000**	**0.4141**	**0.0070**	**0.4259**	**0.0050**
	Tınaztepe	**0.4976**	**0.0040**	**0.5289**	**0.0020**	0.2380	0.1970	0.0200	0.9150
Period	***Stations /Parameters***	***Relationship (pearson "r" correlation coefficients with p values) between pH and acidifying types (NO_3, SO_4)***					
		∑AT=NO_3+SO_4		***NO_3^-***		***SO_4^{2-}***	
		r	***p***	***r***	***p***	***r***	***p***
2005-2006		0.3120	0.0190	0.1945	0.0151	0.3201	0.0160
	Bornova	0.3519	0.1520	0.3444	0.1620	0.3487	0.1560
	Güzelyalı	0.0451	0.8500	0.0626	0.7930	0.0360	0.8800
	Tınaztepe	0.1066	0.6740	0.0514	0.8400	0.1156	0.6480

Relationship between pH and neutralizing or acidifying types were researched by obtaining linear correlation, pearson correlation coefficient with p values. Correlation between pH and neutralizing types were statistically meaningful and in some cases moderately and strongly correlations were obtained. However, any expressive statistical results were not covered between acidifying types and pH values. These

tests explained the neutralizing process of rainwater acidity but couldn't be able to explain the effects of acidifying types on rainwater. Statistical evaluations was given above in Table 4.16.

We also summarised the effect of alkali metals on neutralizing process by calculating Neutralization Factor (NF). The role of Ca^{2+}, K^{+} and Mg^{2+} has been validated by calculating neutralization factors (Thepanondh et al., 2005) using the equations as follows:

$$NF(x) = X /[NO_3] + [SO_4], \quad (4.1)$$

where; [X] = concentration of ion (x) of interest. For the above equations, equivalent concentrations of these cations have been used.

The average values of neutralization factor (NF) for Ca, and Mg and K were presented in Table 4.17. This feature indicates that major neutralization has occurred due to Ca^{2+}, and Mg^{2+} with K playing only a minor role.

Table 4.17 Average values of NF for Ca, Mg and K for our sampling stations.

Parameter & Stations	Tınaztepe	Güzelyalı	Bornova
pH	5.8	5.6	6.5
NF(Ca)	1.14	1.10	1.51
NF(Mg)	0.22	0.23	0.17
NF(K)	0.04	0.04	0.04

Understanding the mechanisms which take part in the neutralization of acidity was as important as understanding the transport of acidic species. The main bases which neutralize the acidity in precipitations can suggested Ca salts (especially $CaCO_3$) and NH_3 as in many of literatures. The main source of $CaCO_3$ was suspended soil particles. Since coarse particles rapidly sediment out from the atmosphere and hence have relatively short atmospheric residence times, neutralization by $CaCO_3$ was a local process, occurring by incorporation of $CaCO_3$ containing soil particles in rain primarily by below-cloud processes (Altwicker & Mahar, 1984). In our studies we had not any chance to measure NH_3 or NH_4 types in precipitation samples. Another important neutralising type of acidifying types in precipitation is NH_3. Sources of NH_3 are more variable than $CaCO_3$. On a global scale the ocean is the dominant

source (Vong, 1997), but on a regional scale the NH_3 present in precipitation was mostly due to livestock farming or the application of NH_4 containing fertilizers (Bridgman, 1992). The NH_3 can be incorporated in rainwater through both in-cloud and below-cloud processes. Studies of NH_4^+/Ca^{2+} ratio in rainwater processes (Altwicker & Mahar, 1984) and composition of sequentially sampled rain events (Lim et al., 1991) have shown that dissolution of gaseous NH_3 in cloud droplets is the main source of NH_4 ion in rainwater in remote areas. However, in regions with strong NH_3 source, such as agricultural areas and areas with extensive livestock farming, atmospheric NH_3 concentration is high and below-cloud scavenging of atmospheric NH_3 may become an important source for the observed NH_4 ion in rainwater (Crawley & Sievering, 1986).

Consequently, we can say that our stations were affected by many sources of Ca and NH_3. Especially measurements at Bornova Sampling station showed that Ca was major important material for neutralising of rainwater acidity as $CaCO_3$. Neutralising types as major alkali ions have very high concentrations in samples handled from this station and we also can follow a correlation between Ca concentrations and pH values positively. There were a lot of cement industries and stone ores for masonry industries around Bornova. Neutralization was realized to be a local process. Other factors must be NH_3 sources in neutralising processes. The main base responsible for the neutralization of acidity was found as NH_3 from fertilizer used in the region in a study achieved by Al-Momani et al. (1994). Through there were a lot of agricultural regions around Bornova, Çiğli (Menemen) and Tınaztepe, measurement of ions from agricultural activities should be realized simultaneously in our stations to prove this effect.

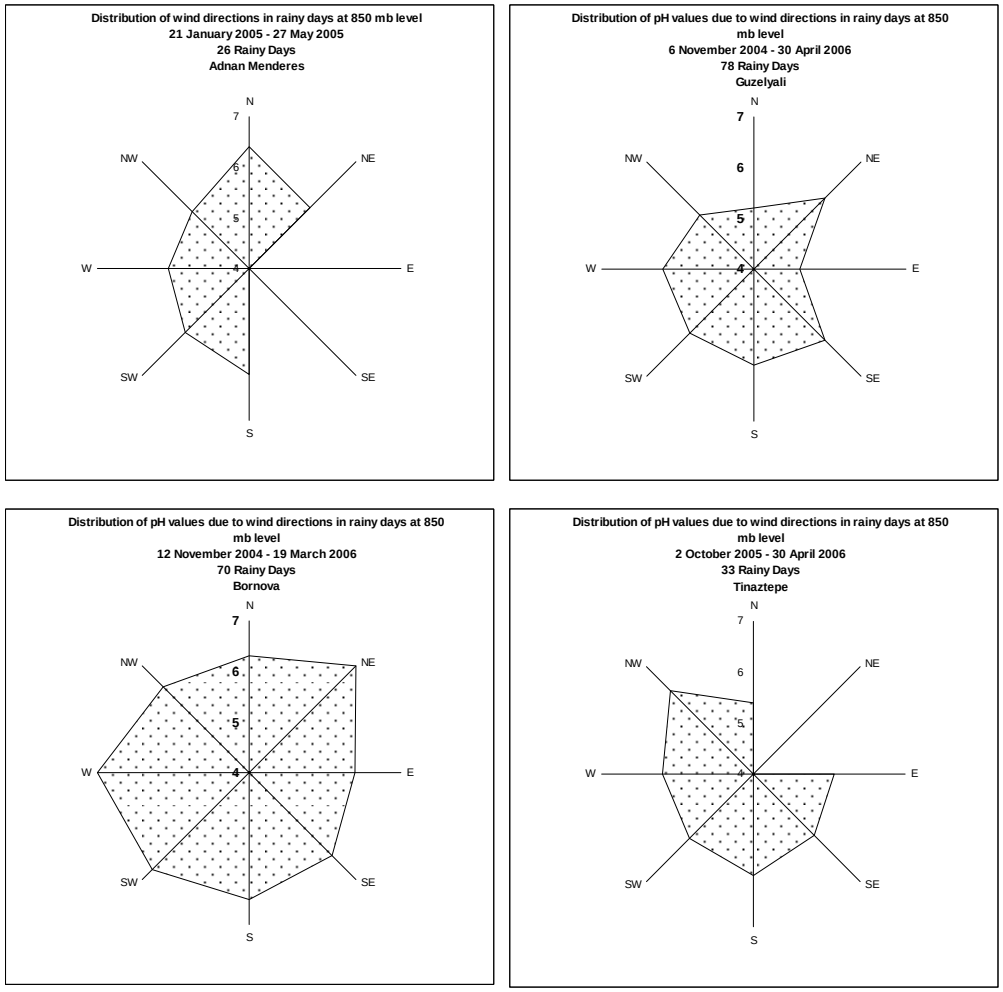


Figure 4.12 Distribution of average pH values due to wind direction during rainy days at 850 mb standard level.

Furthermore, upper atmospheric meteorological properties were evaluated for pH values to obtain factors of meteorological parameters on rainwater chemistry. Northerly and easterly winds were effective on decreasing pH values. In this case, it may be pronounced that long range transportation of acidifying and neutralizing types affects the pH values of rainwater at İzmir. These results in Figure 4.12 also suggest the direction of sources of rainwater components for our region, when an evaluation of datasets between metallic constituents and daily prevailing wind directions at sampling stations was realized.

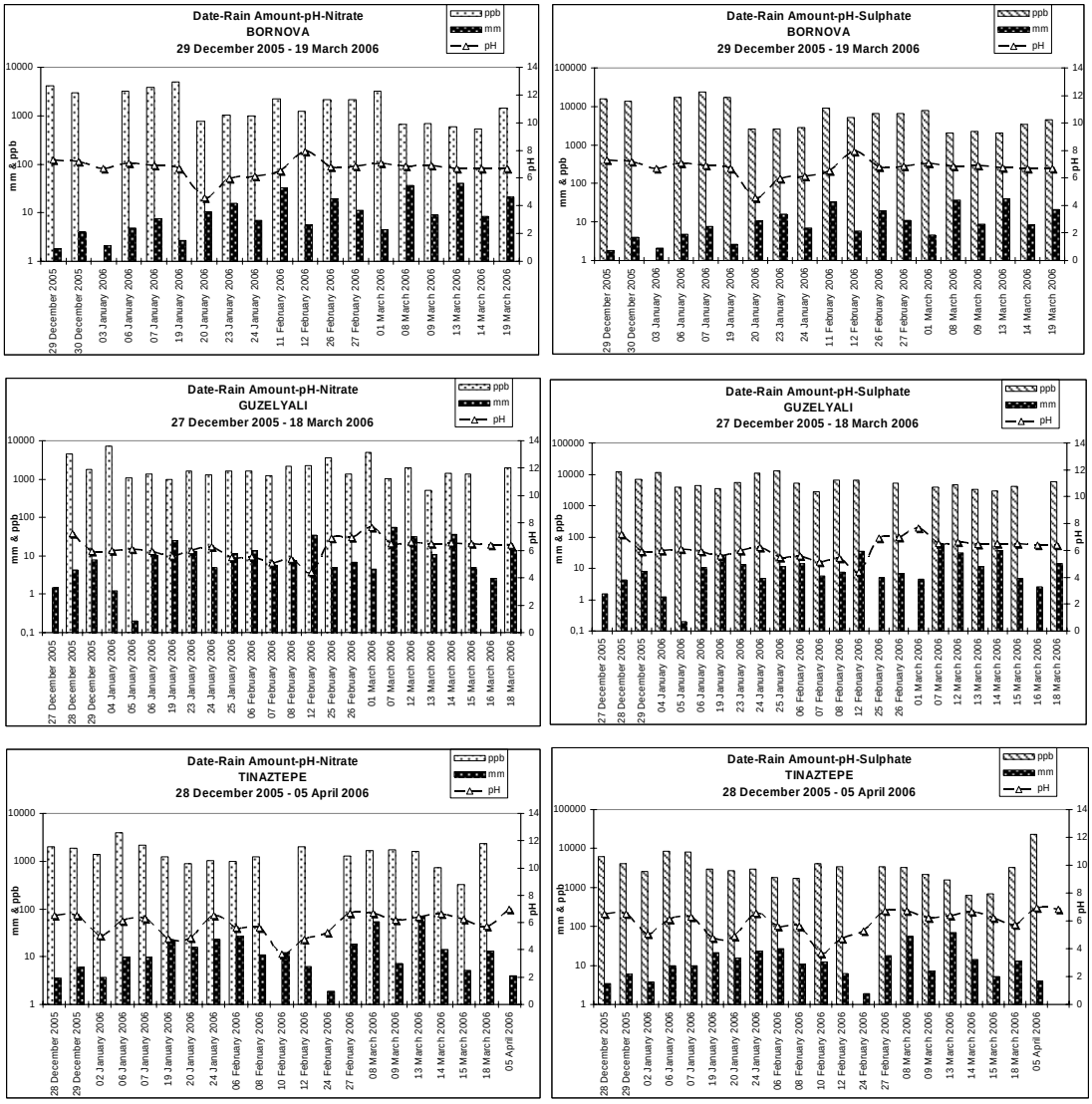
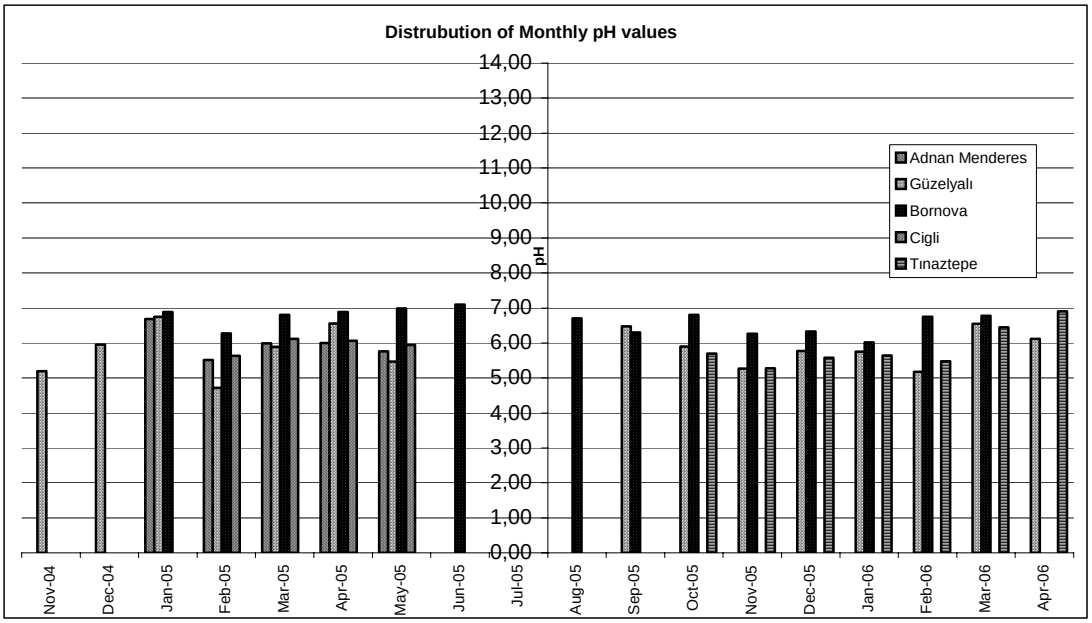


Figure 4.13 Periodical variations of SO_4 concentrations (ppb), NO_3 concentrations (ppb), rain amount (mm), pH values for three sampling points.

Periodical variations of SO_4 concentrations (ppb), NO_3 concentrations (ppb), rain amount (mm), pH values for three sampling point were given Figure 4.13. Any clear seasonal variations were not obtained for sulphate and nitrate constituents of rainwater because of shortness of sampling period owing to impossibilities of analysis instrumentations.

a.



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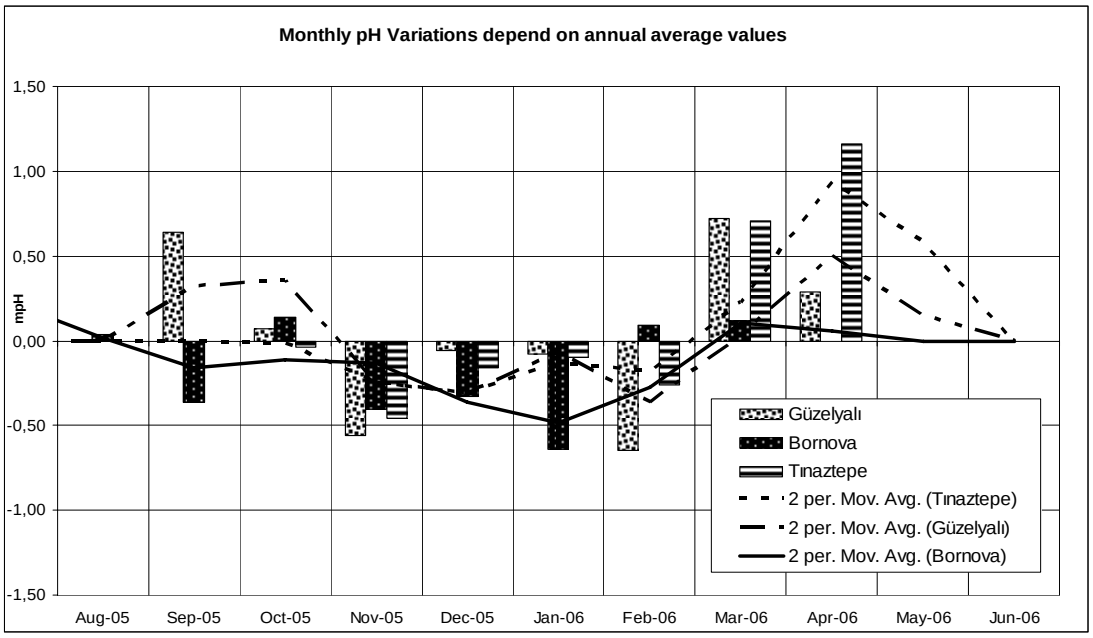


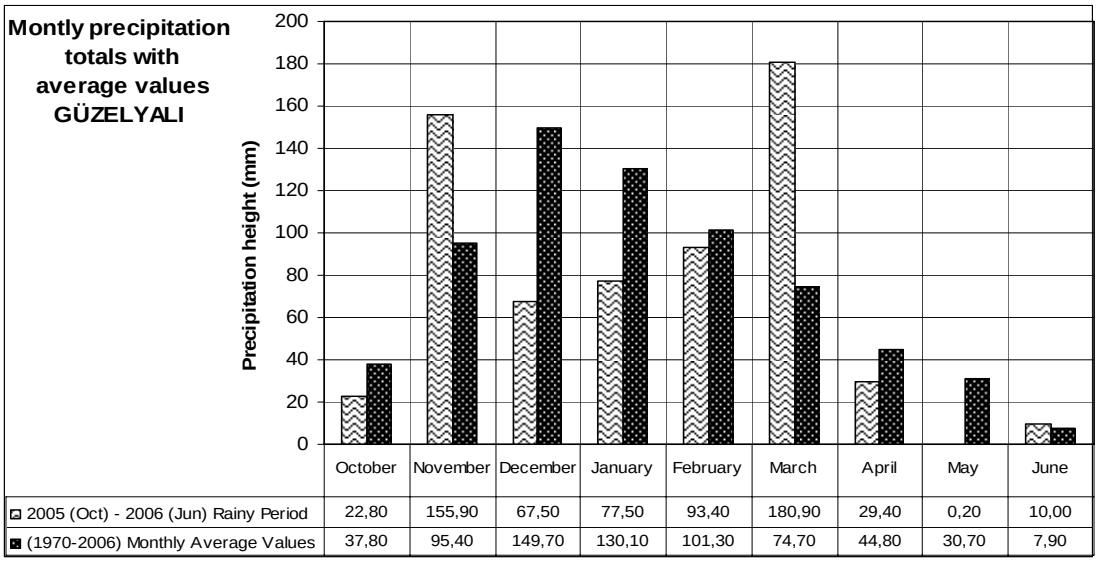
Figure 4.14 (a) Monthly average pH values for five stations; (b) alterations of differences between monthly average pH values and yearly average pH values.

Variations of pH values and rain amounts for all stations depend on sampling date were given in Figure 4.14.a, and periodical pH variations depend on sampling dates were given in Figure 4.14.b. It is obvious that there was a clean difference between winter times and summer times. In winter times, the monthly average pH values were generally below yearly average values for all stations. This result can clear up with the relation between air temperatures and consumption of fuels for heating in winter

times. The main acidifying types SO_4 and NO_3 must be simultaneously observed to obviously explain these results. In our research we could only measure anions in winter times, in a short time as approximately three months.

4.2.3 Evaluations on wet depositional fluxes at İzmir

Monthly wet deposition fluxes of trace metals were calculated as the product of the monthly volume-weighted precipitation concentrations and corresponding volume of the monthly precipitation depths (Figure 4.15).



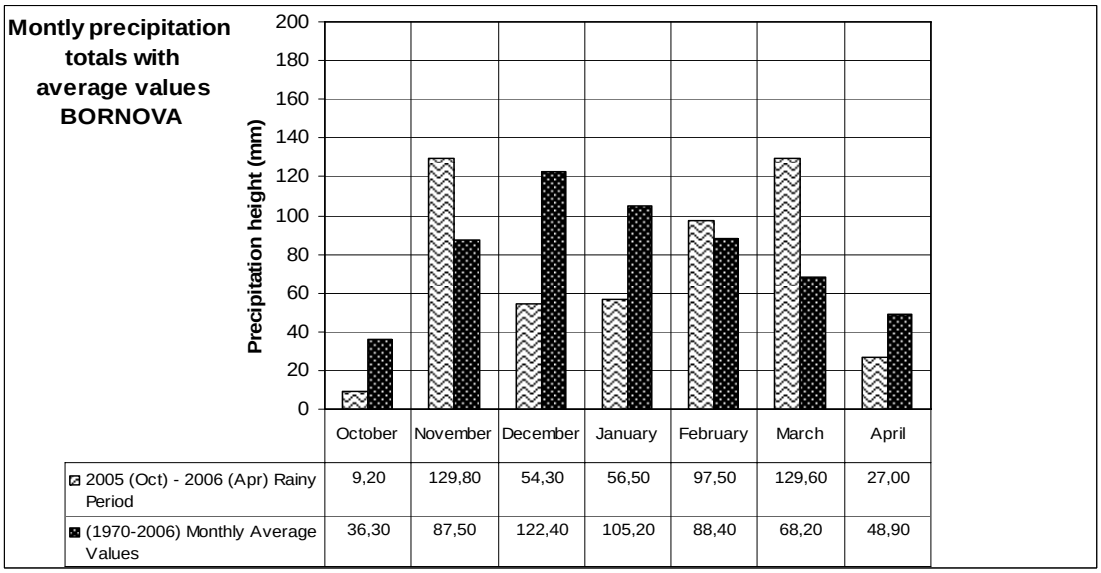


Figure 4.15 Monthly precipitation totals with average of monthly precipitation values in period of 1970-2005 for Bornova and Güzelyalı sampling points.

Monthly precipitation depths of Güzelyali and Bornova were given in Figure 4.15. Precipitation totals from September 2005 to April 2006 were 509.40 and 645.20 mm respectively for Bornova and Güzelyalı. Average values of that parameter due to long period evaluation approximately 30 years were 570.40 and 634.00 mm respectively. The total precipitation depth during our sampling period were lower the average values, and annual sampling recovery of Bornova also reached only 67 %. Therefore, average values of annual wet depositional fluxes values must be higher than our findings.

Similar competitions could be thought for the results of Güzelyalı and Tınaztepe. Although there was no clear difference between annual average precipitation depths and annual precipitation amount belong to one year period (2005-2006 rainy period), annual sampling recovery reached only 70 % at Güzelyalı. In this case, annual depositions at these two stations can be evaluated as a bit higher values. It can easily understandable from the Figure 4.15 that calculating higher monthly wet depositional fluxes is probable in November and March for stations.

The calculated monthly results of wet deposition fluxes of trace metals at İzmir were examined to see if there is any systematic deposition pattern during the year. Seasonal variations in the monthly wet deposition of trace elements have been reported in literature (Scudlark et al., 1994a; Kaya & Tuncel, 1997; Kim et al., 1999). These studies have demonstrated that different trace elements display different seasonal variations in their wet deposition fluxes depending on the nature and strength of their contamination sources, major wind directions, mixing depths, hours of dry weather, and monthly precipitation amounts.

In our study, there was no clear seasonal trend to the elemental or anionic depositions except highest depositions owing to monthly high loadings of precipitations. When distribution of monthly volume weighted mean concentrations as in Figure 4.17 were considered with monthly total depositions, higher wet deposition fluxes were determined for November, February and J-F-M (January-February-March) three months period for Bornova. Cd, Cu, Ni, Pb, V deposition fluxes reached the highest values in November; Ba, Cr, Zn, Na, Cl, and Mg wet

deposition fluxes in February; Fe, Al, Sr and Mn wet deposition fluxes reached the highest values as three months totally in a period of including J-F-M. These elements (Fe, Al, Sr and Mn) have similar monthly depositions in that period. Precipitation amount is the principal effective causing these depositions especially in November and March. Monthly volume weighted concentrations of SO_4, Br, NO_2, NO_3 showed decreasing trends during the sampling period. Highest monthly concentrations were calculated for SO_4, Br, F, NO_2, NO_3 in December. Although monthly concentrations couldn't behave a determinative factor obtaining monthly wet deposition fluxes, high values of monthly concentrations affects their deposition as in February.

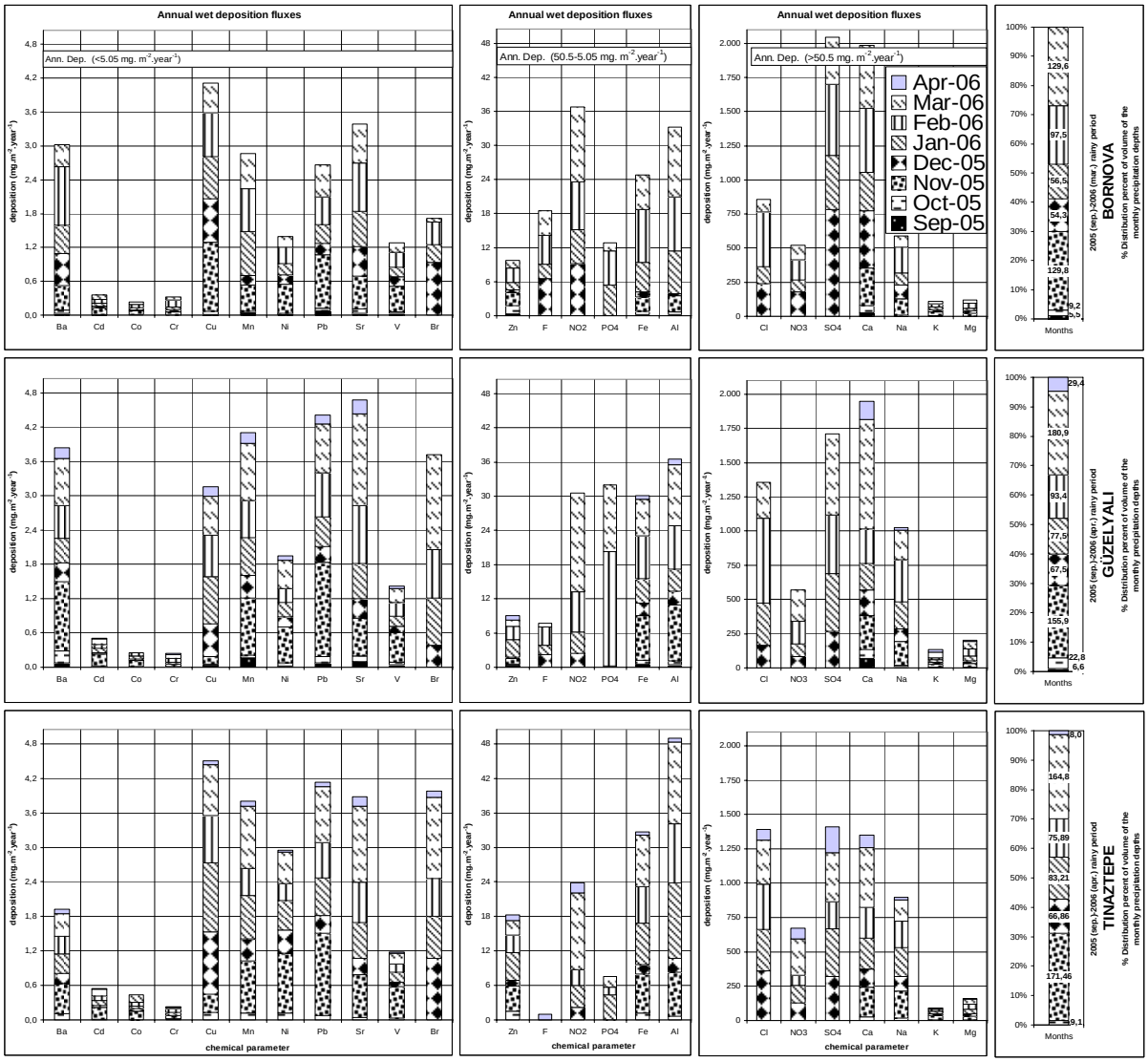


Figure 4.16 Annual wet deposition fluxes in period of 2005-2006.

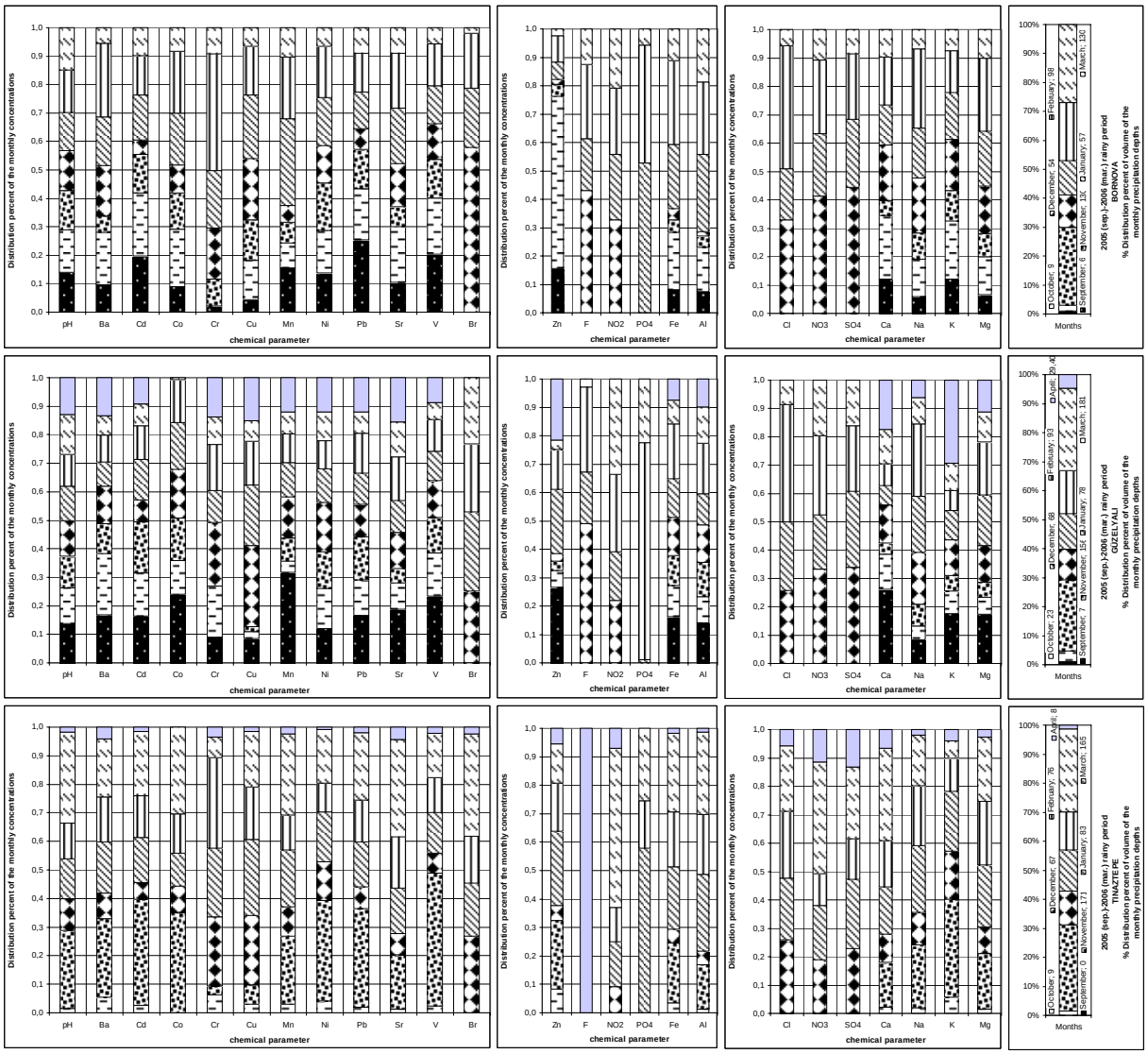


Figure 4.17 Distribution of monthly concentrations of chemical parameters with volume of the monthly precipitation depths in period of 2005 (Sep.) – 2006 (Apr.).

Precipitation depths have a bit more effective on deposition results for Güzelyalı and Tınaztepe. Similar results were gained during November, February, March and J-F-M period. Some highest depositions (Sr, Br, NO_2, Ca and SO_4) were determined in March due to highest loadings of precipitation to the stations. Under the prevailing wind conditions, industrial generated aerosols containing trace metals or naturally emissions of chemical types based on soil or biogenic activities to the atmosphere could be transported and scavenged by rain droplets at the sampling site. Alternatively, clouds reaching the sampling site might have traveled over the heavily industrialized, oceans and urban corridor in that sector and carried a heavier load of pollutants, than those reaching from other wind directions. In addition, the major

ongoing production of construction materials of Bornova, appear to have contributed to the increased concentration and deposition of the elements associated with soil dust. Golomb et al. (1996) also made similar observation at the Massachusetts Bay, U.S.A., in that wet deposition of metals did not display any discernable seasonal variations.

Based on the monthly volume-weighted concentration and cumulative precipitation depth, the annual atmospheric wet depositional fluxes of the measured trace elements were calculated and were given in Table 4.19 and Figure 4.16, along with the published values for other sites outside İzmir. The highest fluxes were observed for the elements Ca (1,716.15 $mg.m^{-2}.year^{-1}$) and Na (830.40 $mg.m^{-2}.year^{-1}$), and for the anions SO_4 (1,721.35 $mg.m^{-2}.year^{-1}$) and Cl (1,201.62 $mg.m^{-2}.year^{-1}$). Average values for annual wet deposition fluxes in İzmir were ranged 0.26-1,721.35 $mg.m^{-2}.year^{-1}$ as given Table 4.18.

Table 4.18 Average values of annual wet depositional fluxes of measured parameters at İzmir ($mg.m^{-2}.year^{-1}$).

SO_4	Ca	Cl	Na	NO_3	Mg	K	Al	NO_2	Fe	PO_4	Zn
1,721.35	1,716.15	1,201.62	830.40	587.00	157.49	105.15	39.20	30.37	29.01	17.44	12.07
F	**Sr**	**Cu**	**Pb**	**Mn**	**Br**	**Ba**	**Ni**	**V**	**Cd**	**Co**	**Cr**
9.07	3.90	3.87	3.68	3.52	3.13	2.87	2.07	1.28	0.47	0.30	0.26

Among the combustion-generated elements, the wet deposition fluxes of Zn, Cu, Pb, Ni were considerably higher than those of the other elements. Wet deposition fluxes of elements were functions of both their concentration and precipitation amount (frequency of rainfall and volume of rainwater). Consequently, the relatively higher wet deposition fluxes of both crustal and some non-crustal elements were due to the effect of abundant rainfall rather than the concentration of elements in İzmir by a majority. On the contrary, the lowest value of crustal elements fluxes found in Ankara (Turkey) was due to the effect of low precipitation amount rather than concentrations (Kaya & Tuncel, 1997). The much higher deposition fluxes of sea salts in this study as compared to those in other sites were consistent with the higher effective transportations from seas due to adjacency to the marine and prevailing wind directions. Prevailing winds at Bornova (Table 3.1) were not strengthening the

transportation from seas, so the deposition values of these salts were relatively lower at Bornova. Combustion emissions of anthropogenic origin (fuel oil and coal consumption, petrochemical industries) in this region were responsible the higher depositional fluxes of SO_4, NO_3, Zn, Pb, Cu, Br. Long range transportations from North Africa deserts can be effective on deposition of some crustal elements such as Fe, Al, Ni, and Cr. Natural or industrial (soil related industries – cement, stone quarries, and lime kiln) emissions based on soil minerals and biogenic minerals with were also playing a major role to obtain depositional fluxes of some constituents (Ca, Al, Sr, Fe, K, Mg, and Mn) of precipitation in İzmir.

Table 4.19 Annual wet deposition fluxes at various sites in the world and this work. (mg. m^{-2}. $year^{-1}$).

Points/Parameters		Al	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Sr	V	Zn	Br	Cl	F	NO_3	NO_2	PO_4	SO_4
This Work	**Bornova**	33.20	3.02	1.986.8	0.36	0.23	0.32	4.12	24.83	109.12	118.96	2.86	587.4	1.39	2.67	3.39	1.29	9.7	1.72	858.69	18.5	519.32	36.75	12.81	2.043.6
	Güzelyali	35.47	3.65	1.812.9	0.49	0.25	0.22	2.99	29.47	116.87	193.89	3.91	1.005.3	1.87	4.25	4.44	1.38	8.2	3.71	1.354.91	7.7	571.12	30.57	31.95	1.710.9
	Tınaztepe	48.94	1.93	1.348.8	0.55	0.43	0.23	4.50	32.73	89.47	159.61	3.80	898.5	2.95	4.13	3.88	1.18	18.3	3.97	1.391.27	1.0	670.55	23.78	7.57	1.409.4
Similar Works	**Singapore**[1]	47.80			0.78	1.56	4.16	14.56	62.40			7.28		10.1	8.84		9.10	18.7							
	Ankara[2]	3.40		254.0	1.32		0.16	0.45	0.68	13.00	14.00		43.9	0.20	0.87		0.21	2.8		216.00		345.00			883.0
	New Castle[3]	16.67			0.12	0.12	0.08	0.67	14.44					0.42	0.78		0.72	8.3							
	Chesapeake and Delaware Bay[4]	19.80			0.04		0.04	0.97	14.00			0.92		0.82	0.35			3.6							
	Bermuda[5]				0.02			0.07	1.60			0.14		0.08	0.31		0.07	0.7							
	New Zealand[6]							0.02	3.70			0.13			0.04			0.1							
	Massachusetts[7]	29.40			0.21	0.01	1.50	0.70	36.00			0.98		3.00	0.86			2.7							
	North Sea[8]						1.40	10.50							11.0			31.0							
	Japan[9]	0.09			0.09			0.89				2.35		0.42	1.78		0.33	6.8							
	Dutch Delta[10]				0.07			0.23						0.88	4.23			12.7							
	Menemen[11]			311.0						126.00	233.00		511.0							267.00					732.0
	Hong Kong[12]	62.10	6.04					4.44	67.20	398.82	131.22	3.85	943.0		8.28	2.63	2.55	32.7							
	Çubuk[13]			560.0						130.00	48.00		140.0							240.00		680.00			1.000.0
	Greece[14]			1.168.8						391.78	97.69		208.4									807.24			1.916.9

Notes: [1.] Balasubramanian et al., 2003. [2.] Kaya & Tuncel, 1997. [3.] Pike & Moran, 2001. [4.] Kim et al., 1999. [5.] Veron et al., 1992. [6.] Halstead et al., 2000. [7.] Golomb et al., 1996. [8.] Injuk et al., 1997. [9.] Takeda et al., 2000. [10.] Nguyen et al., 1990. [11.] Al-Momani et al,. 1995. [12.] Zheng et al., 2005. [13.] Tuncer et al., 2001. [14.] Tsitouridou. & Anatolaki, 2006.

4.3 Data Analysis

4.3.1 Parametric and non-parametric statistics

Parametric and non-parametric statistics were applied to obtain data quality and harmoniousness between our sampling points. For this purpose, results of simultaneously handled from all stations were subjected to these tests. Mann-Whitney U Test, Wald-Wolfowitz Runs Test, Kolmogorov-Smirnov Test (non-parametrics) and t-Tests (parametrics) were applied to 42 samples of Güzelyalı and Bornova, to 20 samples of Güzelyalı and Tınaztepe, and 19 samples of Bornova and Tınaztepe.

Significant results were given through all chemical parameters in Table 4.20, 4.21, and 4.22. Our datasets were generally represented as nonparametrics according to distribution properties of chemical parameters measured by our studies (Table 4.4, 4.6, and 4.8 together with Figure 4.2, 4.4 and 4.6).

There are certain differences on pH and Calcium values of Bornova and Güzelyalı according to Table 4.20. Also, it can be said that there was no good harmoniousness for Cobalt, Chromium, and Zinc results between Güzelyalı and Bornova. Parametric tests showed similar results for these two stations and same chemical parameters. We could say that there was a good relation between Bornova and Güzelyalı, although 5 chemical parameters had different statistical distributions.

pH, Calcium and Nitrite values showed different statistical distributions for Tınaztepe and Bornova according to all statistical tests results in Table 4.21 as expected. Especially high values for pH and Calcium concentration were the characteristics for Bornova. Nickel, Floride, Vanadium, Barium, and Sodium might be evaluated in a group, disunity, for other test results.

Table 4.20 Parametric or non-parametric test results (including t-test between stations) for Güzelyalı and Bornova sampling stations.

Parametric or Nonparametric Statistical Tests (Significant test results were given).
Independent Variables; G: Güzelyalı, B: Bornova.

T-test Statistics By Variable Group. Marked tests are significant at p <,05000

dependent variables	*Mean for G*	*Mean for B*	*t-value*	*df*	*p*	*Valid N for G/B*	*Std.Dev. For G*	*Std.Dev. For B*	*F-ratio variances*	*p variances*
pH	5.858	6.802	-4.62138	82	0.000014	42/42	1.115	0.713	2.4454	0.005104
Calcium	4588.707	7254.721	-2.20638	81	0.030189	41/42	4155.086	6557.462	2.4906	0.004630
Cobalt	0.939	0.678	2.00513	65	0.049117	35/32	0.657	0.345	3.6253	0.000487
Chromium	1.287	2.201	-2.14930	50	0.036475	28/24	1.170	1.864	2.5378	0.021653
Zinc	22.933	47.050	-2.21330	81	0.029690	42/41	31.772	62.875	3.9161	0.000029
	t separ. Var. Est.	*df*	*p 2-sided*	*Levene F(1.df)*	*df Levene*	*p Levene*	*Brn-Fors F(1.df)*	*df Brn-Fors*	*p Brn-Fors*	
pH	-4.62138	69.72797	0.000017	7.00184	82	0.009759	6.678875	82	0.011528	
Calcium	-2.21790	69.59470	0.029828	6.81204	81	0.010783	1.911126	81	0.170638	
Cobalt	2.05754	52.38085	0.044628	3.32749	65	0.072728	1.937649	65	0.168669	
Chromium	-2.07715	37.51453	0.044687	4.72496	50	0.034490	2.838489	50	0.098264	
Zinc	-2.19734	58.85930	0.031944	7.84529	81	0.006370	3.567567	81	0.062498	

Mann-Whitney U Test By variable Group. Marked tests are significant at p <,05000

dependent variables	*Rank Sum G*	*Rank Sum B*	*U*	*Z*	*p-level*	*Z adjusted*	*p-level*	*Valid N for G*	*Valid N for B*	*2*1sided exact p*
pH	1310.000	2260.000	407.0000	-4.24938	0.000021	-4.24990	0.000021	42	42	0.000012
Calcium	1499.000	1987.000	638.0000	-2.03114	0.042242	-2.03114	0.042242	41	42	0.042278
Chromium	622.000	756.000	216.0000	-2.20267	0.027619	-2.20267	0.027619	28	24	0.027398
Zinc	1496.000	1990.000	593.0000	-2.44101	0.014647	-2.44101	0.014647	42	41	0.014285

Wald-Wolfowitz Runs Test By variable Group. Marked tests are significant at p <,05000

dependent variables	*Valid N for G*	*Valid N for B*	*Mean for G*	*Mean for B*	*Z*	*p-level*	*Z adjstd*	*p-level*	*No. of runs*	*No. of ties*
pH	42	42	5.858	6.802	-2.85408	0.004316	2.744306	0.006064	30	8

Kolmogorov-Smirnov Test By variable Group. Marked tests are significant at p <,05000

dependent variables	*Max Neg Difference*	*Max Pos Difference*	*p-level*	*Mean for G*	*Mean for B*	*Std.Dev. For G*	*Std.Dev. For B*	*Valid N for G*	*Valid N for B*
pH	-0.476190	0.000000	p < .001	5.858	6.802	1.115	0.713	42	42
Calcium	-0.318815	0.012195	p < .05	4588.707	7254.721	4155.086	6557.462	41	42

Note: The detailed results belong to chemical parameters, which have p values below 0.05, were given in table.

Table 4.21 Parametric or non-parametric test results (including t-test between stations) for Tınaztepe and Bornova sampling stations.

Parametric or Nonparametric Statistical Tests (Significant test results were given). Independent Variables; B: Bornova, T: Tınaztepe.										
T-test Statistics By Variable Group. Marked tests are significant at p <,05000										
dependent variables	*Mean for B*	*Mean for T*	*t-value*	*df*	*p*	*Valid N for B/T*	*Std.Dev. For B*	*Std.Dev. For T*	*F-ratio variances*	*p variances*
pH	6.609	5.782	3.62373	36	0.000889	19/19	0.645	0.757	1.37454	0.506589
Barium	7.865	3.887	2.29991	35	0.027534	18/19	6.985	2.775	6.33822	0.000303
Calcium	7379.126	2411.095	3.27998	36	0.002309	19/19	6397.221	1632.430	15.35726	0.000000
Nickel	3.829	6.698	-2.61277	35	0.013146	19/18	2.392	4.109	2.95098	0.028147
Vanadium	3.983	2.258	2.10052	34	0.043175	19/17	3.261	0.942	11.98010	0.000008
Nitrite	154.510	69.070	2.20616	20	0.039233	11/11	119.272	47.669	6.26035	0.007693
	t separ. Var. Est.	*df*	*p 2-sided*	*Levene F(1.df)*	*df Levene*	*p Levene*	*Brn-Fors F(1.df)*	*df Brn-Fors*	*p Brn-Fors*	
pH	3.62373	35.12608	0.000910	1.57888	36	0.217014	1.45455	36	0.235666	
Barium	2.25383	21.99760	0.034506	13.67496	35	0.000741	9.50040	35	0.003990	
Calcium	3.27998	20.33427	0.003685	40.40160	36	0.000000	12.72815	36	0.001042	
Nickel	-2.57714	27.03569	0.015737	8.00082	35	0.007687	7.54973	35	0.009422	
Vanadium	2.20457	21.30655	0.038605	19.36609	34	0.000101	5.64290	34	0.023306	
Nitrite	2.20616	13.11522	0.045802	9.10160	20	0.006812	2.32832	20	0.142698	
Mann-Whitney U Test By variable Group. Marked tests are significant at p <,05000										
dependent variables	*Rank Sum B*	*Rank Sum T*	*U*	*Z*	*p-level*	*Z adjusted*	*p-level*	*Valid N for B*	*Valid N for T*	*2*1sided exact p*
pH	492.5000	248.5000	58.5000	3.56176	0.000368	3.56312	0.000367	19	19	0.000188
Calcium	454.0000	287.0000	97.0000	2.43776	0.014779	2.43776	0.014779	19	19	0.014139
Nickel	286.0000	417.0000	96.0000	-2.27901	0.022667	-2.27901	0.022667	19	18	0.022294
Floride	158.0000	95.0000	29.0000	2.06845	0.038599	2.06845	0.038599	11	11	0.039976
Nitrite	162.0000	91.0000	25.0000	2.33111	0.019748	2.33111	0.019748	11	11	0.019231
Wald-Wolfowitz Runs Test By variable Group. Marked tests are significant at p <,05000										
dependent variables	*Valid N for B*	*Valid N for T*	*Mean for B*	*Mean for T*	*Z*	*p-level*	*Z adjstd*	*p-level*	*No. of runs*	*No. of ties*
Sodium	19	19	1568.616	1787.626	-1.97351	0.048438	1.809050	0.070444	14	0
Vanadium	19	17	3.983	2.258	-2.35610	0.018469	2.186456	0.028783	12	0
Kolmogorov-Smirnov Test By variable Group. Marked tests are significant at p <,05000										
dependent variables	*Max Neg Difference*	*Max Pos Difference*	*p-level*	*Mean for B*	*Mean for T*	*Std.Dev. For B*	*Std.Dev. For T*	*Valid N for B*	*Valid N for T*	
pH	0.000000	0.526316	p < .025	6.609	5.782	0.645	0.757	19	19	
Calcium	0.000000	0.473684	p < .05	7379.126	2411.095	6397.221	1632.430	19	19	
Nitrite	0.000000	0.636364	p < .025	154.510	69.070	119.272	47.669	11	11	

Note: The detailed results belong to chemical parameters, which have p values below 0.05, were given in table.

Disunity between datasets from Güzelyalı and Tınaztepe had different characteristics through three sampling points. Parametric and non-parametric tests results between these two stations were nearly same as seen in Table 4.22. Güzelyalı as an urban area had naturally higher SO_4 values in its atmosphere as expected. Barium, Zinc, Floride, Nitrite, Sulphate, and Potassium did not show similar distribution properties for Güzelyalı and Tınaztepe.

Some differences were also obtained due to properties of sampling points, when our sampling stations were evaluated between themselves. Though the distances between sampling points in our study were not too much, concentrations were affected by the sampling sites geological properties and industrial activities around themselves. The highest values for crustal elements (Al, Ba, Fe, Sr, K, Cr and Ca) were fixed at Bornova sampling station. Elements and ions originated from marine (Na, Mg, Cl, Br, and F) were determined as the highest values in the samples handled from Güzelyalı. Values of Mn, V, NO_3 and PO_4 for Güzelyalı were also determined higher than Bornova and Tınaztepe. The anthropogenic elements Cd, Co, Ni, Pb and Zn have unexpectedly the highest values at Tınaztepe sampling station, although Tınaztepe sampling station is relatively far from anthropogenic sources than Güzelyalı and Bornova.

Table 4.22 Parametric or non-parametric test results (including t-test between stations) for Güzelyalı and Tınaztepe sampling stations.

Parametric or Nonparametric Statistical Tests (Significant test results were given).
Independent Variables; G: Güzelyalı, T: Tınaztepe.

T-test Statistics By Variable Group. Marked tests are significant at p <,05000

dependent variables	*Mean for G*	*Mean for T*	*t-value*	*df*	*p*	*Valid N for G/T*	*Std.Dev. For G*	*Std.Dev. For T*	*F-ratio variances*	*P variances*
Barium	8.217	4.517	2.99895	38	0.004759	20/20	3.620	4.164	1.322892	0.54789
Zinc	21.508	50.780	-2.15078	38	0.037917	20/20	29.747	53.103	3.186922	0.01514
Floride	72.264	25.280	4.50583	22	0.000175	12/12	32.382	16.006	4.092695	0.02772
Nitrite	87.338	51.897	2.35807	22	0.027674	12/12	40.150	33.147	1.467160	0.53554
Sulphate	6032.955	3136.553	2.69142	22	0.013333	12/12	2953.485	2274.722	1.685827	0.39978

	t separ. Var. Est.	*df*	*p 2-sided*	*Levene F(1.df)*	*df Levene*	*p Levene*	*Brn-Fors F(1.df)*	*df Brn-Fors*	*p Brn-Fors*
Barium	2.99895	37.27967	0.004805	0.130448	38	0.719968	0.152457	38	0.698378
Zinc	-2.15078	29.85496	0.039713	5.547133	38	0.023776	3.236200	38	0.079974
Floride	4.50583	16.07259	0.000355	3.865171	22	0.062043	3.267726	22	0.084349
Nitrite	2.35807	21.23852	0.028028	0.382867	22	0.542428	0.396895	22	0.535186
Sulphate	2.69142	20.65332	0.013792	0.683759	22	0.417174	0.608569	22	0.443640

Mann-Whitney U Test By variable Group. Marked tests are significant at p <,05000

dependent variables	*Rank Sum G*	*Rank Sum T*	*U*	*Z*	*p-level*	*Z adjusted*	*p-level*	*Valid N for G*	*Valid N for T*	*2*1sided exact p*
Barium	541.0000	279.0000	69.0000	3.54356	0.000395	3.54356	0.000395	20	20	0.000228
Zinc	321.0000	499.0000	111.0000	-2.40746	0.016065	-2.40746	0.016065	20	20	0.015478
Floride	208.0000	92.0000	14.0000	3.34863	0.000812	3.34863	0.000812	12	12	0.000371
Nitrite	187.0000	113.0000	35.0000	2.13620	0.032664	2.13620	0.032664	12	12	0.033241
Sulphate	198.0000	102.0000	24.0000	2.77128	0.005584	2.77128	0.005584	12	12	0.004513

Wald-Wolfowitz Runs Test By variable Group. Marked tests are significant at p <,05000

dependent variables	*Valid N for G*	*Valid N for T*	*Mean for G*	*Mean for T*	*Z*	*p-level*	*Z adjstd*	*p-level*	*No. of runs*	*No. of ties*
Potassium	20	17	242.829	188.568	-2.14143	0.032240	1.973561	0.048433	13	0
Floride	12	12	72.264	25.280	-2.92196	0.003479	2.713253	0.006663	6	0

Kolmogorov-Smirnov Test By variable Group. Marked tests are significant at p <,05000

dependent variables	*Max Neg Difference*	*Max Pos Difference*	*p-level*	*Mean for G*	*Mean for T*	*Std.Dev. For G*	*Std.Dev. For T*	*Valid N for G*	*Valid N for T*
Barium	-0.050000	0.600000	p < .005	8.217	4.517	3.620	4.164	20	20
Potassium	-0.073529	0.455882	p < .05	242.829	188.568	142.635	122.941	20	17
Floride	0.000000	0.750000	p < .005	72.264	25.280	32.382	16.006	12	12
Sulphate	0.000000	0.583333	p < .05	6032.955	3136.553	2953.485	2274.722	12	12

Note: The detailed results belong to chemical parameters, which have p values below 0.05, were given in table.

4.3.2 Correlations

The quantify relation between elemental concentrations, correlation matrixes were calculated. The correlation matrixes including Pearson "r" values ($p \leq 0.05$) of Bornova, Güzelyalı, and Tınaztepe sampling points were given in Table 4.23, 4.24, 4.25, respectively. Also, spearmen rank correlation matrixes were evaluated and similar results were reached as parametric or nonparametric alternatives. Following tables for parametric alternatives were listed. Good correlation coefficients between parameters were expressed in black field and high effective correlations were showed in grey fields.

The correlation matrix for Bornova was given in Table 4.23. Good correlations between soil (Alkali/Soil/Soil Alkali) elements were obtained. Al was significantly correlated with some soil elements (Fe, Mg, Mn, Ba, Ca, Sr), especially high correlated with Fe, Mg and Mn and some anthropogenic ones (Co, Cr, Cu, V, Ni, Pb). Similarly, Fe and Ba were correlated with the same elemental groups. Only Ba was high correlated also with Cr, Pb, and Br as anthropogenic elements. When this results were considered, it was obviously pointed that the origin of terrestrial elements were soil, soil related industries and anthropogenic sources such as fuel burning (Coal, fuel).

Ca also was high correlated with SO_4 ions. When the samples handled from Bornova sampling point were evaluated, this high correlation between Ca and SO_4 suggested that the origin of these parameters were same (Soil, soil industries) or pH neutralizing reactions between them ($CaCO_3$ and H_2SO_4). This result also represented that pH values were not decreased by increasing of SO_4 concentration. The highly significant ($p < 0.05$) SO_4 correlation values with Ca ($r = 0.71$) as well as high NO_3 correlation values $r = 0.69$ suggest a neutralization process affecting the rainwater chemistry.

Table 4.23 Correlations of values determined from all samples handled from Bornova in 2004-2005 and 2005-2006 rainy periods. Marked correlations (Pearson r values) are significant.

	pH	Al	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Sr	V	Zn
pH	1.00																	
Al	**0.30**	1.00																
Ba	**0.33**	**0.62**	1.00															
Ca	**0.47**	**0.45**	**0.79**	1.00														
Cd	0.09	0.01	0.10	0.17	1.00													
Co	0.04	**0.51**	**0.49**	0.27	0.19	1.00												
Cr	**0.41**	**0.60**	**0.77**	**0.59**	**0.33**	**0.41**	1.00											
Cu	0.21	**0.32**	**0.65**	**0.57**	0.05	0.25	**0.53**	1.00										
Fe	**0.25**	**0.95**	**0.81**	**0.57**	-0.02	**0.58**	**0.83**	**0.44**	1.00									
K	0.23	0.16	**0.66**	**0.74**	0.12	0.19	**0.39**	**0.61**	**0.47**	1.00								
Mg	**0.27**	**0.76**	**0.77**	**0.67**	-0.03	**0.52**	**0.58**	**0.38**	**0.82**	**0.67**	1.00							
Mn	**0.25**	**0.72**	**0.86**	**0.69**	0.09	**0.54**	**0.68**	**0.51**	**0.81**	**0.58**	**0.85**	1.00						
Na	**0.26**	0.25	**0.54**	**0.52**	0.05	**0.28**	0.30	**0.40**	**0.42**	**0.72**	**0.79**	**0.53**	1.00					
Ni	0.20	**0.35**	**0.69**	**0.60**	0.16	0.21	**0.55**	**0.71**	**0.51**	**0.66**	**0.49**	**0.59**	**0.44**	1.00				
Pb	0.06	**0.43**	**0.71**	**0.42**	**0.43**	**0.51**	**0.70**	**0.52**	**0.62**	**0.41**	**0.42**	**0.51**	0.25	**0.54**	1.00			
Sr	**0.28**	**0.68**	**0.82**	**0.72**	0.05	**0.46**	**0.70**	**0.36**	**0.79**	**0.64**	**0.88**	**0.88**	**0.62**	**0.48**	**0.45**	1.00		
V	0.18	**0.40**	**0.59**	**0.54**	0.02	0.12	**0.64**	**0.55**	**0.58**	**0.51**	**0.53**	**0.58**	**0.41**	**0.76**	**0.48**	**0.52**	1.00	
Zn	0.11	0.14	**0.37**	**0.26**	**0.30**	0.23	**0.58**	**0.32**	**0.26**	**0.27**	0.18	**0.24**	0.20	**0.36**	**0.50**	0.23	**0.29**	1.00
Br	0.50	0.03	**0.83**	0.63	-0.21	0.08	**0.70**	0.60	0.06	**0.87**	0.51	**0.71**	0.59	**0.66**	-0.21	**0.78**	0.46	**0.73**
Cl	0.13	-0.10	0.25	0.22	0.12	0.14	0.09	0.25	-0.03	**0.49**	**0.80**	0.30	**0.95**	0.34	0.00	**0.55**	0.24	0.26
F	0.35	-0.20	0.18	**0.67**	0.20	-0.48	0.26	0.34	-0.15	**0.80**	0.13	0.19	0.31	**0.49**	-0.16	0.43	**0.57**	0.15
NO_3	0.34	0.03	0.22	**0.69**	0.25	-0.25	0.24	0.33	0.00	**0.79**	0.46	0.37	**0.59**	**0.49**	-0.13	**0.69**	**0.60**	0.06
NO_2	0.40	-0.19	0.10	**0.59**	0.06	-0.41	0.14	0.16	-0.15	**0.57**	0.08	0.16	0.19	0.34	-0.18	0.39	0.46	0.02
PO_4	0.22	0.05	0.36	0.55	-0.26	-0.02	0.45	-0.35	0.06	0.45	0.55	0.00	**0.88**	0.07	0.15	0.44	0.52	0.40
SO_4	0.35	-0.11	0.21	**0.71**	0.22	-0.49	0.23	0.32	-0.08	**0.62**	0.23	0.28	0.36	0.45	-0.15	**0.56**	**0.59**	0.11

	Br	Cl	F	NO_3	NO_2	PO_4	SO_4
Br	1.00						
Cl	0.36	1.00					
F	0.61	0.30	1.00				
NO_3	**0.67**	0.44	**0.89**	1.00			
NO_2	0.24	0.14	**0.82**	**0.81**	1.00		
PO_4	**0.96**	0.82	0.46	0.63	0.56	1.00	
SO_4	0.24	0.27	**0.86**	**0.90**	**0.90**	0.62	1.00

Table 4.24 Correlations of values determined from all samples handled from Güzelyalı in 2004-2005 and 2005-2006 rainy periods. Marked correlations (Pearson r values) are significant.

	pH	Al	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Sr	V	Zn
pH	1.00																	
Al	**0.44**	1.00																
Ba	**0.50**	**0.91**	1.00															
Ca	**0.56**	**0.75**	**0.76**	1.00														
Cd	-0.04	0.09	0.17	0.21	1.00													
Co	**0.51**	**0.75**	**0.81**	**0.69**	0.07	1.00												
Cr	**0.37**	**0.68**	**0.71**	**0.42**	-0.05	**0.67**	1.00											
Cu	0.12	0.21	**0.31**	**0.30**	-0.12	0.22	**0.41**	1.00										
Fe	**0.50**	**0.95**	**0.91**	**0.62**	-0.09	**0.75**	**0.71**	**0.28**	1.00									
K	**0.41**	**0.57**	**0.68**	**0.74**	0.14	**0.72**	**0.44**	**0.41**	**0.49**	1.00								
Mg	**0.47**	**0.73**	**0.70**	**0.77**	0.06	**0.63**	**0.53**	**0.24**	**0.63**	**0.66**	1.00							
Mn	**0.49**	**0.86**	**0.92**	**0.72**	0.08	**0.87**	**0.69**	**0.33**	**0.90**	**0.64**	**0.67**	1.00						
Na	**0.26**	**0.39**	**0.36**	**0.41**	0.01	**0.36**	**0.45**	**0.29**	**0.35**	**0.51**	**0.81**	**0.34**	1.00					
Ni	0.07	0.21	**0.38**	**0.33**	0.00	**0.29**	**0.34**	**0.63**	**0.27**	**0.46**	**0.26**	**0.39**	0.18	1.00				
Pb	-0.01	**0.47**	**0.44**	**0.60**	**0.28**	**0.46**	**0.33**	0.13	0.14	**0.37**	**0.39**	**0.38**	0.12	0.22	1.00			
Sr	**0.43**	**0.84**	**0.79**	**0.92**	0.18	**0.70**	**0.54**	0.19	**0.77**	**0.66**	**0.84**	**0.76**	**0.47**	**0.24**	**0.59**	1.00		
V	-0.14	**0.30**	**0.33**	0.16	**-0.26**	**0.36**	**0.48**	**0.47**	**0.32**	0.20	**0.27**	**0.39**	**0.23**	**0.52**	0.20	**0.23**	1.00	
Zn	-0.05	0.21	**0.27**	**0.35**	0.17	0.22	**0.20**	**0.22**	-0.02	**0.46**	**0.43**	**0.26**	**0.33**	**0.36**	**0.44**	**0.36**	**0.26**	1.00
Br	0.03	0.42	0.23	0.19	0.18	-0.19	0.18	0.23	0.09	0.36	**0.55**	0.04	**0.71**	0.13	0.18	0.32	0.26	0.45
Cl	-0.40	-0.01	0.03	0.03	0.13	-0.11	0.12	0.13	-0.02	0.18	**0.79**	-0.05	**0.95**	-0.11	0.18	0.16	0.14	0.21
F	0.24	**0.68**	**0.81**	**0.72**	0.04	**0.51**	**0.87**	**0.60**	**0.75**	**0.43**	0.36	**0.67**	0.24	**0.63**	**0.72**	**0.49**	**0.89**	0.13
NO_3	0.29	0.37	**0.59**	**0.61**	-0.01	0.23	**0.73**	0.30	0.33	**0.59**	**0.49**	**0.45**	**0.55**	0.30	0.25	**0.48**	**0.76**	0.02
NO_2	**0.54**	**0.46**	**0.45**	**0.66**	-0.33	**0.61**	0.32	-0.25	0.34	0.41	0.34	0.38	0.26	0.15	0.11	**0.55**	0.39	-0.29
PO_4	0.31	0.54	0.10	0.34	-0.58	0.70	-0.17	-0.69	0.20	0.06	0.55	0.23	0.40	-0.68	0.19	0.50	-0.35	**-0.84**
SO_4	0.04	0.33	**0.68**	**0.55**	0.23	**0.56**	**0.65**	**0.55**	**0.45**	**0.45**	**0.49**	**0.50**	0.36	0.32	0.42	0.41	**0.74**	0.40

	Br	Cl	F	NO_3	NO_2	PO_4	SO_4
Br	1.00						
Cl	**0.61**	1.00					
F	0.16	0.12	1.00				
NO_3	0.37	0.38	**0.77**	1.00			
NO_2	-0.14	0.00	**0.58**	**0.56**	1.00		
PO_4	-0.20	0.22	-0.15	-0.16	0.62	1.00	
SO_4	0.09	0.37	**0.76**	**0.62**	0.36	-0.27	1.00

Table 4.25 Correlations of values determined from all samples handled from Tınaztepe in 2005-2006 rainy periods. Marked correlations (Pearson r values) are significant.

	pH	Al	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Sr	V	Zn
pH	1.00																	
Al	0.33	1.00																
Ba	**0.35**	**0.52**	1.00															
Ca	**0.48**	0.30	**0.65**	1.00														
Cd	-0.12	0.04	**0.47**	0.07	1.00													
Co	0.05	-0.05	-0.08	-0.23	0.28	1.00												
Cr	-0.14	0.04	0.13	0.03	0.10	0.00	1.00											
Cu	-0.06	0.02	0.31	0.12	-0.05	-0.21	-0.23	1.00										
Fe	0.32	**0.91**	**0.69**	**0.38**	0.27	0.10	0.18	0.06	1.00									
K	0.24	0.15	**0.80**	**0.43**	**0.37**	-0.06	0.12	**0.57**	0.33	1.00								
Mg	-0.02	**0.46**	**0.38**	**0.52**	0.03	-0.14	0.36	0.06	**0.42**	0.22	1.00							
Mn	**0.46**	**0.60**	**0.81**	**0.57**	0.29	-0.06	-0.02	0.27	**0.76**	**0.63**	0.21	1.00						
Na	-0.24	0.11	0.23	0.34	0.08	-0.13	0.28	0.16	0.08	0.26	**0.88**	-0.02	1.00					
Ni	-0.05	-0.14	**0.40**	0.05	0.32	-0.04	-0.19	**0.58**	0.03	**0.64**	-0.03	**0.43**	0.10	1.00				
Pb	0.07	0.19	0.32	0.11	0.25	0.21	0.13	-0.10	0.34	0.14	0.01	0.19	-0.02	-0.11	1.00			
Sr	**0.44**	**0.47**	**0.58**	**0.89**	0.06	-0.11	0.16	0.00	**0.50**	0.30	**0.72**	**0.51**	**0.45**	-0.03	0.00	1.00		
V	0.03	0.13	**0.66**	**0.45**	**0.60**	-0.03	0.20	0.10	0.34	**0.59**	0.20	**0.52**	0.13	**0.47**	**0.36**	**0.37**	1.00	
Zn	0.16	0.00	**0.67**	0.32	**0.58**	-0.06	0.07	0.25	0.28	**0.63**	0.13	**0.44**	0.27	**0.41**	**0.46**	0.18	**0.42**	1.00
Br	**-0.86**	-0.11	-0.24	-0.41	0.16	0.16	0.22	0.39	-0.15	0.05	0.40	-0.44	**0.82**	0.13	0.53	-0.46	-0.19	0.27
Cl	-0.35	0.15	**0.45**	0.44	0.08	0.05	0.43	0.15	0.13	0.47	**0.93**	0.00	**0.97**	0.08	-0.07	**0.55**	0.40	0.22
F	**0.48**	0.14	**0.78**	**0.86**	-0.05	0.30	0.06	-0.18	0.32	**0.53**	0.34	**0.58**	0.14	-0.09	0.29	**0.72**	**0.71**	0.39
NO_3	0.32	-0.03	**0.75**	**0.90**	0.20	-0.43	0.16	0.09	0.10	**0.70**	**0.50**	**0.56**	0.45	0.15	-0.06	**0.78**	**0.77**	0.38
NO_2	**0.57**	-0.05	**0.61**	**0.63**	-0.06	0.11	-0.02	0.02	0.11	**0.68**	0.10	**0.59**	-0.05	0.32	-0.03	**0.55**	**0.51**	0.44
PO_4	0.72	0.13	0.53	0.19	-0.63	0.34	-0.04	-0.78	0.30	**-0.83**	-0.68	0.22	-0.66	-0.47	**0.98**	-0.43	**0.92**	0.69
SO_4	0.28	0.02	**0.81**	**0.93**	0.17	-0.40	0.11	0.25	0.14	**0.80**	**0.51**	**0.57**	0.42	0.23	-0.04	**0.80**	**0.81**	**0.45**

	Br	Cl	F	NO_3	NO_2	PO_4	SO_4
Br	1.00						
Cl	**0.69**	1.00					
F	-0.40	0.29	1.00				
NO_3	-0.29	**0.54**	**0.80**	1.00			
NO_2	**-0.62**	0.03	**0.73**	**0.70**	1.00		
PO_4	0.94	-0.64	**0.90**	-0.69	**0.91**	1.00	
SO_4	-0.26	**0.50**	**0.78**	**0.97**	**0.69**	**-0.82**	1.00

The high correlation between Cl and Na suggests a common origin. However, Cl also had significant correlation with K ($r = 0.49$, $p < 0.05$) indicating that K and Cl found in rainwater were associated with a specific source. The Cl to Na correlation suggests a marine origin, while K is often associated with a specific source namely, biomass burning. Recent research has shown that K is also released by and accumulated on plant leaves during transpiration and dispersed into the atmosphere by wind action.

There was another high correlation between Ni and V due to it can be from the same anthropogenic origin. Zn and Br were originated from traffic emissions, petrochemical industries and heavy metal industries.

The correlation matrix for Güzelyalı was given in Table 4.24. Good correlations between soil (Alkali/Soil/Soil Alkali) elements were obtained as similarly Bornova.

Soil elements (Al, Fe, Mg, Mn, Ba, Ca, Sr) were significantly correlated between themselves. Al, Ba was correlated with some anthropogenic elements (Co, Cr, Pb, and V); especially highly correlated with some anthropogenic elements (Co, Cr). Differently, there was a weakly relation between Al and Na – K at Güzelyalı.

Ba and V were significantly correlated with SO_4 anions. Cu was not highly correlated with any element but moderately correlated with Ni and V. Therefore, we may consider that Cu, Ni and V were originated from the same sources.

Na, K, Mg and Cl may strongly represent the same sources as sea salts. Differently, F was correlated with mostly elements. But F has almost same correlation with the anions. Zn was not correlated with Br as in Bornova.

The correlation matrix for Tınaztepe was given in Table 4.25.

According to other two urban sampling points, less correlation was obtained between elements at Tınaztepe sampling point as a suburban area. Similarly, Al was only high correlated with Fe and Mn. Furthermore, trace elements were not correlated with soil related elements. Cd was correlated with V and Zn; Cu was

correlated with K and Ni. The sources of these trace elements may be evaluated in same anthropogenic group.

Ba, Ca, V, Sr have high correlation with anions (F, NO_2, NO_3, SO_4). Na was significantly correlated with Br like Cl as in two other urban sampling points.

The correlation matrix for whole datasets handled from Bornova, Güzelyalı and Tınaztepe was given in Table 4.26.

There were good correlations between soil (Alkali/Soil/Soil Alkali) elements. According to correlation matrixes determined from whole datasets of all sampling stations, Al was moderately correlated with some soil elements (Fe, Mg, Mn, Ba, Ca, Sr) and some anthropogenic ones (Co, Cr, Pb), but especially high correlated with Ba, Fe, Mg, Sr and Mn. Similarly, Fe and Ba were correlated with the same elemental groups and Cr, but Ba was high correlated also with Ca. Ca was highly correlated with K, Sr and SO_4 anion as general correlation perspectives between parameters.

Table 4.26 Correlations of all dataset determined from all stations in 2004-2005 and 2005-2006 sampling periods. Marked correlations (Pearson r values) are significant.

	pH	Al	Ba	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Sr	V	Zn
pH	1.00																	
Al	**0.36**	1.00																
Ba	**0.42**	**0.82**	1.00															
Ca	**0.53**	**0.61**	**0.75**	1.00														
Cd	-0.02	0.03	0.11	0.14	1.00													
Co	**0.21**	**0.65**	**0.61**	**0.40**	0.12	1.00												
Cr	**0.38**	**0.59**	**0.72**	**0.53**	0.15	**0.42**	1.00											
Cu	**0.17**	**0.21**	**0.44**	**0.41**	-0.01	0.11	**0.43**	1.00										
Fe	**0.39**	**0.95**	**0.86**	**0.56**	-0.07	**0.61**	**0.70**	**0.33**	1.00									
K	**0.33**	**0.41**	**0.67**	**0.70**	0.12	**0.37**	**0.40**	**0.53**	**0.47**	1.00								
Mg	**0.31**	**0.72**	**0.71**	**0.66**	0.00	**0.56**	**0.48**	**0.25**	**0.70**	**0.61**	1.00							
Mn	**0.37**	**0.82**	**0.88**	**0.64**	0.05	**0.74**	**0.59**	**0.33**	**0.86**	**0.57**	**0.72**	1.00						
Na	0.14	**0.33**	**0.39**	**0.38**	0.02	**0.31**	**0.31**	**0.28**	**0.35**	**0.53**	**0.79**	**0.36**	1.00					
Ni	0.02	**0.16**	**0.38**	**0.29**	**0.16**	**0.20**	**0.25**	**0.60**	**0.26**	**0.49**	**0.24**	**0.34**	**0.22**	1.00				
Pb	-0.01	**0.44**	**0.48**	**0.43**	**0.31**	**0.46**	**0.46**	**0.21**	**0.31**	**0.33**	**0.37**	**0.39**	0.14	**0.22**	1.00			
Sr	**0.36**	**0.80**	**0.80**	**0.79**	0.09	**0.58**	**0.60**	**0.23**	**0.77**	**0.61**	**0.85**	**0.79**	**0.50**	**0.22**	**0.51**	1.00		
V	0.08	**0.34**	**0.49**	**0.37**	-0.13	**0.21**	**0.57**	**0.44**	**0.46**	**0.38**	**0.37**	**0.46**	**0.26**	**0.42**	**0.26**	**0.36**	1.00	
Zn	0.07	0.13	**0.29**	**0.28**	**0.31**	0.15	**0.34**	**0.29**	0.11	**0.35**	**0.25**	**0.20**	**0.24**	**0.36**	**0.43**	**0.25**	**0.20**	1.00
Br	-0.21	0.07	**0.32**	0.08	0.14	-0.02	**0.44**	**0.42**	0.00	**0.46**	**0.38**	0.24	**0.64**	**0.38**	0.15	0.19	0.22	**0.53**
Cl	-0.21	0.00	0.16	0.17	0.11	0.04	0.16	0.18	0.00	**0.34**	**0.83**	0.11	**0.95**	0.13	0.04	**0.41**	0.17	0.23
F	**0.36**	0.18	**0.43**	**0.66**	-0.01	0.09	**0.36**	**0.30**	**0.26**	**0.60**	**0.33**	**0.47**	0.23	0.18	0.24	**0.51**	**0.69**	0.01
NO_3	**0.27**	0.13	**0.30**	**0.59**	0.06	-0.02	0.27	**0.27**	0.10	**0.62**	**0.46**	**0.39**	**0.51**	**0.32**	-0.13	**0.51**	**0.56**	-0.03
NO_2	**0.54**	0.02	**0.30**	**0.67**	-0.05	-0.02	0.22	0.10	0.05	**0.59**	0.16	**0.34**	0.10	0.18	-0.13	**0.39**	**0.53**	-0.01
PO_4	**0.47**	0.18	0.45	**0.49**	**-0.53**	0.37	0.01	**-0.52**	0.21	0.25	0.36	0.23	0.23	-0.31	0.29	0.45	0.37	-0.26
SO_4	**0.33**	0.01	**0.35**	**0.75**	0.18	-0.19	**0.28**	**0.34**	0.07	**0.67**	**0.37**	**0.41**	**0.35**	0.25	-0.08	**0.64**	**0.63**	0.19

	Br	Cl	F	NO_3	NO_2	PO_4	SO_4
Br	1.00						
Cl	**0.57**	1.00					
F	-0.03	0.16	1.00				
NO_3	0.25	**0.36**	**0.72**	1.00			
NO_2	-0.17	0.03	**0.70**	**0.60**	1.00		
PO_4	**-0.61**	0.15	**0.52**	0.27	**0.63**	1.00	
SO_4	-0.03	**0.33**	**0.78**	**0.74**	**0.79**	0.38	1.00

4.3.3 Enrichment factors

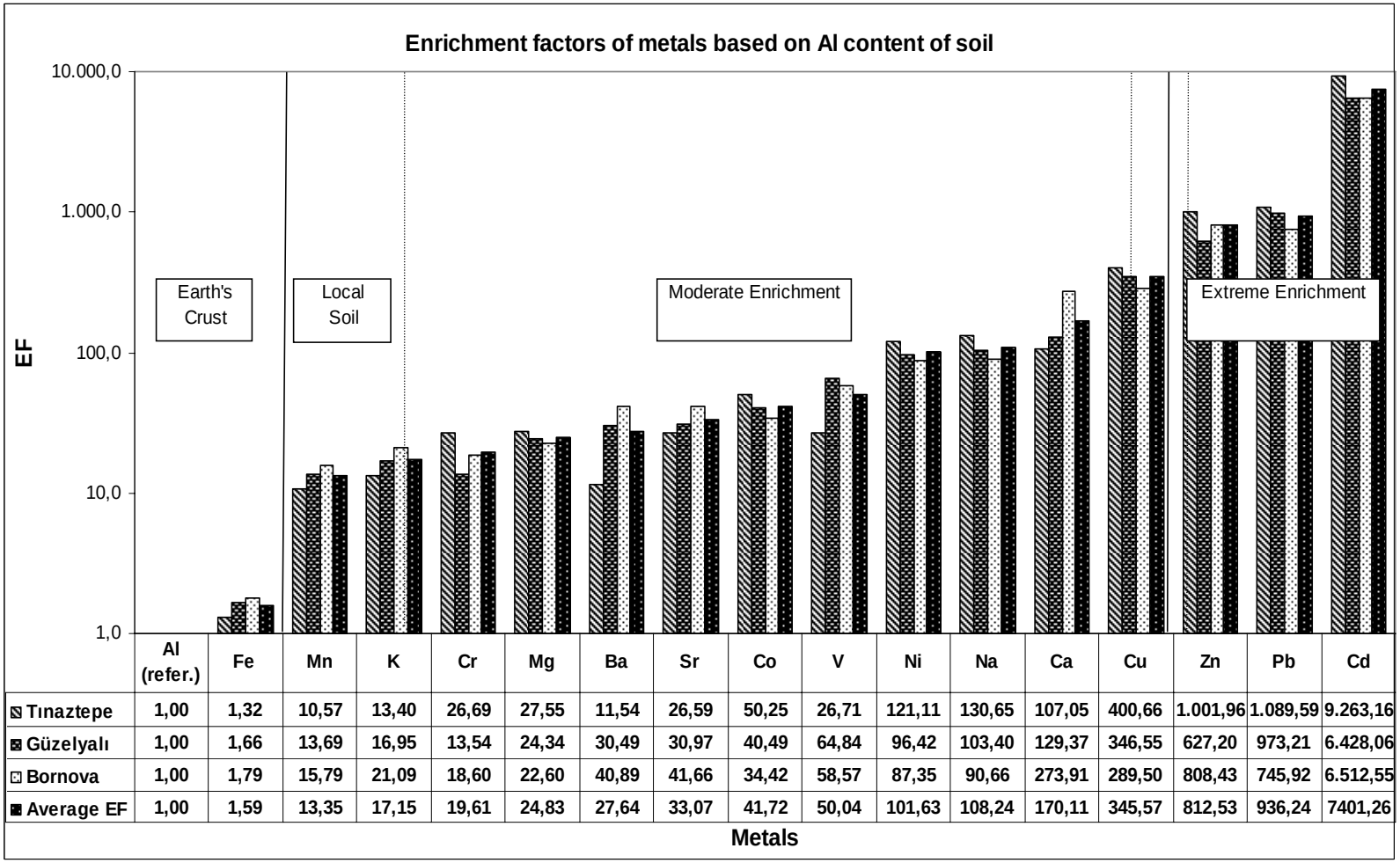
3.3.1 Contribution of Earth's Crust

In an attempt to determine whether the trace metals in the rain were due to natural or anthropogenic sources, enrichment factors were calculated from the data set. Enrichment factors are very good pollution indicators (natural or anthropogenic) with respect to upper-crust mean composition. The crustal enrichment factor (EF_c) of an element is calculated with Al normalization. This reference provides the compilation of the relative abundance of different trace metals in the earth's crust. For crustal sources, Al has been most commonly used as the source indicator element and the Earth's crust as the source material.

In EF_c equation, Al is the reference metal, which was hypothesized to originate exclusively from crustal materials (Al-Momani, 2003). Therefore, metals with EF_cs close to 1 must originate from weathering of the Earth's crust, and EF_cs between 1 and 10 might indicate the influence of the chemical composition of local soil (Al-Momani, 2003). Those between 10 and 500 denote moderate enrichment, indicating other sources in addition to crustal materials, and those greater than 500 are clear evidence of extreme enrichment, indicating severe contamination due to human activities (Poissant et al., 1994).

Figure 4.18 shows the EF_cs obtained, which were calculated from the water volume-weighted averages of metal concentrations in precipitations. EF_c values for all steps of our researchment determined using the average crustal ratios represented by Mason (1966) for Earth's crust.

The EF_cs differed slightly between the 3 sites, but the orders of the metals when arranged according to EF_cs were almost the same. EF_cs for Fe were close 1, whereas those for Pb, Cd, and Zn were greater than 500, which were regarded as extreme enriched. The remaining metals had EF_cs ranged between 10-500, and were classified as moderately enriched.



	Al (refer.)	Fe	Mn	K	Cr	Mg	Ba	Sr	Co	V	Ni	Na	Ca	Cu	Zn	Pb	Cd
Tınaztepe	1,00	1,32	10,57	13,40	26,69	27,55	11,54	26,59	50,25	26,71	121,11	130,65	107,05	400,66	1.001,96	1.089,59	9.263,16
Güzelyalı	1,00	1,66	13,69	16,95	13,54	24,34	30,49	30,97	40,49	64,84	96,42	103,40	129,37	346,55	627,20	973,21	6.428,06
Bornova	1,00	1,79	15,79	21,09	18,60	22,60	40,89	41,66	34,42	58,57	87,35	90,66	273,91	289,50	808,43	745,92	6.512,55
Average EF	1,00	1,59	13,35	17,15	19,61	24,83	27,64	33,07	41,72	50,04	101,63	108,24	170,11	345,57	812,53	936,24	7401,26

Metals

Figure 4.18 Crustal enrichment factors (EF_c) of metals, (X/Al)rain/(X/Al)crust, in rainwater. Metals were arranged form left to right in order of increasing average EF_c.

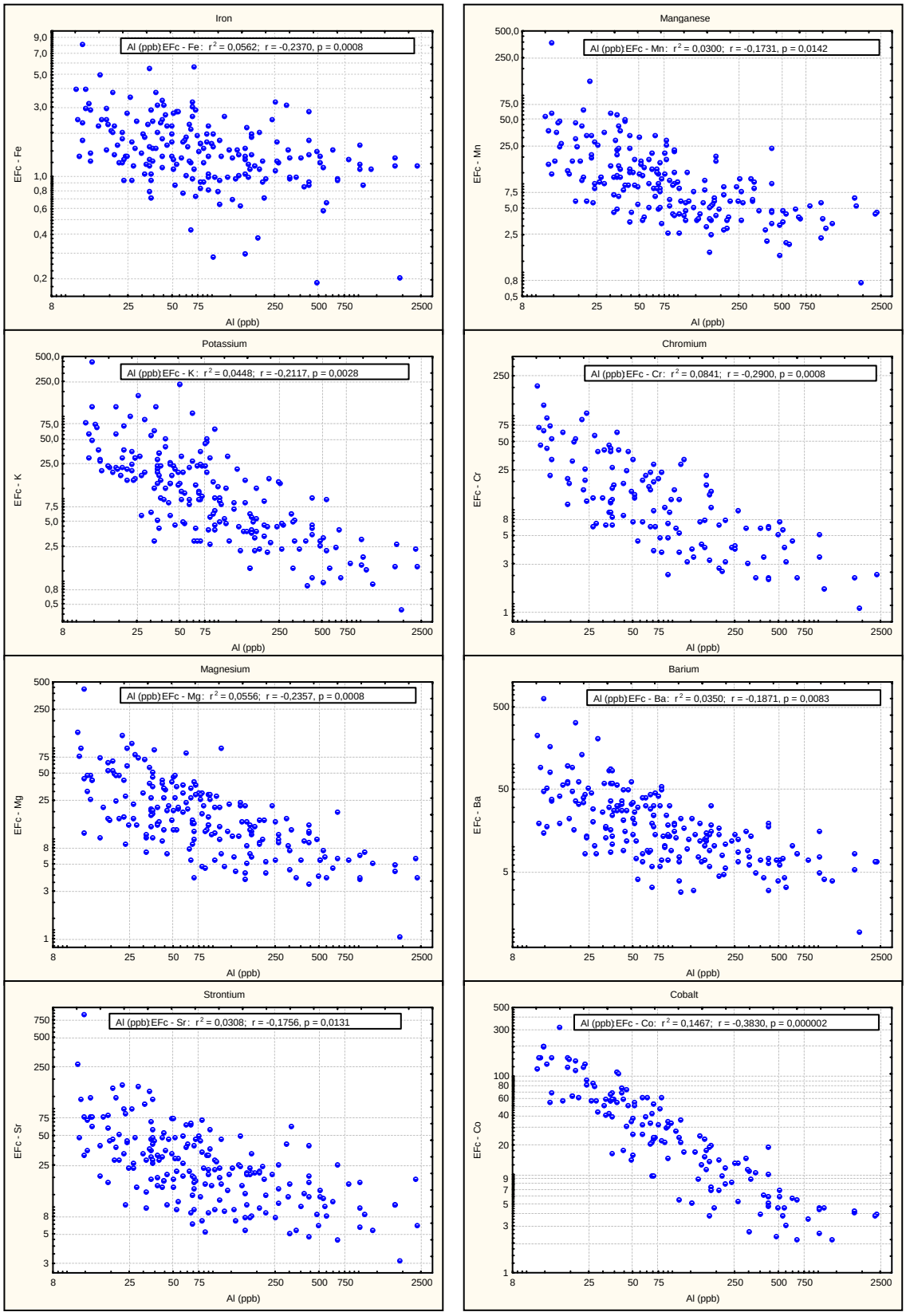


Figure 4.19 The crustal enrichment factors (EF_c) of metals versus Al content of rainwater.

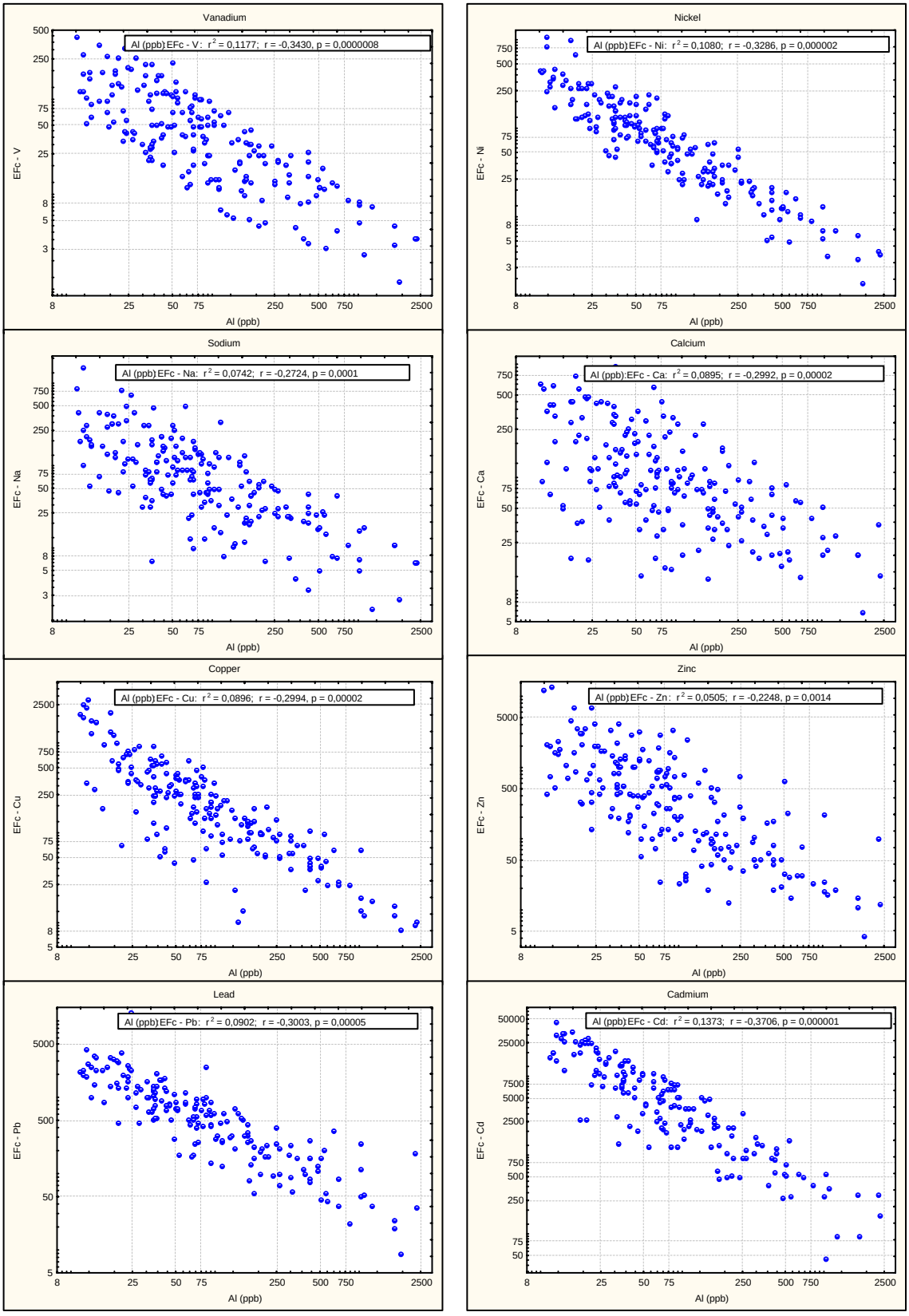


Figure 4.19 Continued.

Considering the fact that aluminium in precipitation has a single origin (crustal in nature), an enrichment factor close to unity reveals that the trace metal origin is predominantly crustal. Trace metals for which the earth's crust is the only source has an EF_c of unity. On the other hand, trace metals from sources other than crustal materials were expected to have enrichment factors greater than 1.0. However, since the types of crustal materials and soils are different in different areas and little was known about uncertainties concerning fractionation during weathering, enrichment factors were not resolvable within an order of magnitude ($EF_c < 10$) from crustal materials (Kaya & Tuncel, 1997). As a result, Fe and Mn could be grouped together with Al as crustal elements with the average EF_c being 1.7 and 13.4, respectively. Al, Fe, and Mn originated mainly from the earth's crust and were most enriched in coarse aerosols. Moreover, a good correlation between the Al and Fe fluxes in precipitation samples were observed. Fe/Al ratios in the earth's surface may be variable, depending on chemical enrichments, but a very good correlation was obtained between them for all of our sampling stations. Although Mn showed a similar trend with Al and Fe in periodical variation, its enrichment factors were calculated to be between 10 and 15 at three sites. Thought a good correlation between Mn and Fe, Al was defined previously, it can said that some anthropogenic contaminations occured for Mn. Based on the calculated EF_c, one can deduced that the remaining trace metals were mainly derived from anthropogenic sources.

To study the influence of crustal sources on rainwater in relation with contamination due to non-crustal sources, EF_c was investigated for all the metals as a function of Al concentration. When EF_c of an element in each sample is plotted against Al concentration, the resulting plot is a narrow horizontal belt close to unity for crustal elements. On the other hand, enrichment factors of non-crustal elements decreased with increasing Al concentrations. Figure 4.19 showed that the trace metals such as Pb, Cd and Zn have sources other than crustal material at low Al concentrations. Also, EF_c - Al diagrams in Figure 4.19 point that, EF_c values of some elements against to increasing of Al content of rain water showed decreasing disordered distribution. Although Zn, Ca, and Na had relatively higher crustal enrichment factors than others, crustal contribution of these elements to the rain

waters could not be rejected almost when decreasing properties of disordered distributions of these elements were considered.

However, EF_c - Al diagrams were indicated interestingly that Cr may have crustal sources beside anthropogenic sources such as oil-fuel combustions and steel industries. Furthermore, another pointer gained these evaluations that some alkali metals such as Ca, Sr, Mg, and Ba have an important anthropogenic source differently crustal source. The most likely source that can affect their concentrations in precipitation is the cement factory located environment of İzmir. Also another natural source as crustal particles may be accepted marine source based on oceanographic transportations.

The elements for which crustal source cannot be assigned even at high Al concentrations are Cd, Cu, Pb and Zn and V, particularly for Cd and Pb. Enrichment factor calculations showed that Pb, Cd and Zn in precipitation were non-crustal. In general, Pb and Cd were associated with fine particles which are generated as high-temperature combustion condensates and injected by smokestacks higher into the boundary layer (Lindberg, 1982; Scudlark et al., 1994a). Also, Fujita et al. (2000) pointed out that 99 % of the Pb and Cd in precipitation were non-crustal and were associated with fine particles (<1 μm). Leaded gasoline had been phased out in Turkey several years ago. Therefore, local vehicular emissions were unlikely to be the source of Pb. Thus, these elements were involved strongly with long-range transport and cloud condensation. Kim (1998) also confirmed that the source of stable Pb is mainly from the upper troposphere and thus its fluxes were more controlled by precipitation amounts.

However, emissions of both Pb and Cd could arise from waste incinerators due to the use of their metal oxides as pigments, stabilizers, and catalysts in plastic processing (Petrochemical Industry). In view of the continued use of leaded gasoline in some countries in the region and the presence of waste incinerators in the region, it was quite likely that some amounts of these two elements observed in this study could be derived from long-range transport and cloud condensation. Cu, V, and Zn had also a close relationship with high temperature processes (fossil fuel

combustion). Zn, Cu, elements in the atmosphere were mostly non-crustal based on the enrichment factor calculation. Since these elements were associated with both high- and low-temperature combustion, episodic local/regional contaminations must be more important sources.

Zn was known to be a marker element for burning fossil fuels, smelting non-ferrous metals, and sprinkling agrochemicals, and Zn released from such processes could be easily dissolved in rainwater (Halstead et al., 2000). As a result, they did not correlate with crustal elements, as is the case with Pb and Cd. Power plants, petroleum refineries, incinerator, industrial, residential and commercial boilers and furnaces, automobiles, trucks, aircraft, and ships could be accepted as fossil fuel combustion sources in İzmir as in the world.

Thus, this enrichment analysis confirmed the fact that the trace metals present in the İzmir rainwater resulted from a blend of crustal particles and particles derived from anthropogenic sources.

3.3.2 Contribution of Marine

In order to estimate the marine and non-marine contributions, various ratios and marine enrichment factors (Ef_m) have been calculated. For this purpose, Na has been taken as a reference element assuming that all Na were marine origin. This assumption was supported by comparing the average ratio of Cl to Na in seawater which is 1.166 (Millero, 1974; Akkoyunlu & Tayanc, 2003), to the corresponding value found in this study between 1.18-1.29. This indicated that Na and the majority of Cl ions in the rainwater of the study area originated from sea. The seawater ratios of Cl, SO_4, K, Ca and Mg with respect to Na were shown in Table 4.27. High ratios for the species Mg, K, especially Ca and SO_4 suggested a non-marine origin for these components.

Marine enrichment factors have been calculated and used to distinguish sources of major constituents of rainwater. The calculation was based on the elemental ratio found between ions collected in the atmosphere or in precipitation, compared with a similar ratio for a reference material.

Table 4.27 Comparison between seawater ratios of ions and rainwater ratios due to Na concentrations.

Parameter & Stations	[Cl]/[Na]	[SO_4]/[Na]	[K]/[Na]	[Mg]/[Na]	[Ca]/[Na]
Seawater Ratio[i]	1.17	0.06	0.02	0.11	0.02
Ratios in Rain (Tınaztepe)	1.09	1.14	0.06	0.34	1.73
Ratios in Rain (Güzelyalı)	1.08	1.43	0.07	0.40	1.91
Ratios in Rain (Bornova)	0.98	2.18	0.11	0.43	3.86

Note: i. Millero, 1974

Enrichment factors have been used to give useful indications about the source of the elements in precipitations and in the atmosphere (Vermette et al., 1988; Ahmed et al., 1990; Singer et al., 1993). These marine enrichment factors (EF_m) of different species with respect to Na were calculated using this equation:

$$EF_m(x) = ([x]/[Na])_{rain}/([x]/[Na])_{seawater},$$

Table 4.28 Average EF_m (Marine enrichment factor).

Parameter & Stations	Cl	Mg	K	SO_4	Ca
EF_m (Tınaztepe)	1.11	2.96	2.65	18.95	78.86
EF_m (Güzelyalı)	1.10	3.48	3.28	23.65	87.09
EF_m (Bornova)	1.01	3.81	4.85	36.22	176.28

The EF_m values were given in Table 4.28. Results indicated that most of the Ca was not of marine origin with EF_m(Ca) = 79-176, but most of Cl and a significant component of Mg was marine origine with EF_m(Cl) = 1-1.1 and EF_m(Mg) = 3-3.8, respectively. SO_4 was also enriched with respect to the sea (EF_m (SO_4) = 19-36), suggesting that the sea was not the main source of this ion. The calculated enrichment factors indicated the strong influence of local sources, possibly crustal sources, such as carbonate rocks and soil, and gaseous and particulate emission from the anthropogenic sources.

The sea salt fraction and non-sea salt fraction have also been calculated. The calculation of non-sea salt concentration using Na as a reference component can be expressed as in the equation:

$NSS(X) = Total[X]_{rain} - f_x[Na]_{rain}$, , where; f_x = correction factor for (X) component.

Average concentrations in sea water as presented by Weast (1975) and Bodek et al. (1988) yield the following f_x values for SO_4, Mg, Ca, and K as 0.0601, 0.1131, 0.0218 and 0.0212 respectively (Keene et al., 1999).

Volume weighted mean concentrations of the non-sea salts components were summarized in Table 4.29. This again indicated that the species, SO_4, K and Ca were predominantly of non-marine origin; Mg had a significant component, but not major, which was of non-marine origin while Cl appears to originate mainly from the sea. Approximately 87-93 % of SO_4 in rainwater samples was of non-sea salt origin (NSS-SO_4).

Table 4.29 Comparison of average total and non sea salt concentration of chemical components in precipitation.

Parameter & Stations	SO_4	Mg	Ca	K
Tınaztepe				
VWMCs[i]	32.11	11.50	58.20	3.95
Non-sea salt concentrations	28.06	3.41	56.73	2.52
Sea salt fraction (%)	12.62	70.37	2.53	36.20
Non-sea salt fraction (%)	87.38	29.63	97.47	63.80
Güzelyalı				
VWMCs[i]	50.66	17.04	81.23	6.08
Non-sea salt concentrations	45.54	6.82	79.37	4.27
Sea salt fraction (%)	10.11	59.98	2.29	29.71
Non-sea salt fraction (%)	89.89	40.02	97.71	70.29
Bornova				
VWMCs[i]	56.84	13.67	120.48	6.64
Non-sea salt concentrations	53.09	6.18	119.11	5.32
Sea salt fraction (%)	6.60	54.78	1.13	19.92
Non-sea salt fraction (%)	93.40	45.22	98.87	80.08

Notes: i. Volume Weighted Mean Concentrations;
ii. Concentration units was given as μmol/L.

4.3.4 Factor Analysis

Factor analysis (FA) was applied for three sampling sites; Bornova, Güzelyalı and Tınaztepe to obtain groups that contain elements with similar behaviours to identify possible sources of elements and anions. The analysis were done by using Varimax rotated principle component analysis (Eigenvalues>1). Only the significant loadings were indicated in the factors. The determination of factors that were given in the

second line of the table was done to according to the loadings of the elements in the factors. Because of some missing data, PO_4 was cancelled for FA.

Table 4.30 Results of factor analysis for whole dataset.

Parameters & Factors	**Factor 1**	**Factor 2**	**Factor 3**	**Factor 4**	**Factor 5**
	• *Soil*	• *Mineral Industries* • *Agricultural Activities*	•*Sea*	• *Fossil Fuel* • *Petrochemical Industries*	• *Steel Industries*
Al	0.93				
Fe	0.95				
Mn	0.84				
Ba	0.82				
Co	0.82				
Cr	0.59			0.46	
Cu				0.78	
Na			0.91		
Mg	0.69		0.69		
Ca	0.57	0.67			
Sr	0.76	0.46			
K		0.58			
V		0.53		0.52	
Ni				0.71	
Br			0.64	0.63	
Cl			0.98		
Zn				0.49	0.63
Cd					0.83
Pb					0.56
F		0.86			
NO_3		0.80			
NO_2		0.91			
SO_4		0.97			
Var. %	***40.5***	***14.5***	***11.4***	***7.9***	***6.2***
Cum. %	***40.5***	***55.0***	***66.4***	***74.3***	***80.5***

As the first experience, in a further attempt to assess the sources responsible for the observed pollution levels, factor analysis was applied to whole data set of total concentrations. Twenty three elements and ions which were detected in 33 samples were included in the analysis. Five interpretable factors were retained as given in Table 4.30. Incidentally, these five factors were the only ones with eigenvalues higher than unity. Totally, 80.5 % of the variance is explained by the five factors.

Factor 1 explains about 40.5 % of the total variance. The high loadings for Al, Mn, Fe, Mg, Ca, Sr, Ba, Co and Cr in this factor indicated a soil contribution. Associated with this factor were Co and Cr, which were usually emitted during fuel combustion. Recall that chromium had not enriched with respect to crustal

composition. Kubilay & Saydam (1995) found anomalous Cr and Ni enrichments in the eastern Mediterranean aerosol and explained it to be due to the presence of Cr- and Ni-rich soil along the Mediterranean coast of Turkey. This factor has been identified as “crustal factor”.

Factor 2 explained about 20.3 % of total variance. Ca, Sr and K were moderately enriched with respect to crustal composition, had moderate loadings in this factor due to the existence of crustal contribution for Ca and Sr. Soil related industries could suggested for these elements as another source. These sources can emanate fabrics of building outfits’ production for İzmir. These industries can be grouped in the title of mineral industries such as, cement, stone quarries, and lime kiln. Concrete plants and asphalts may be accepted as subsidiary sources on this factor. Agricultural activities may also be suggested as another source for anions with these metals, in addition to a secondary aerosol formation process, which associated with precursor gases SO_2 and NO_x. Also this result was observed for all stations. Very good correlations were obtained for all anions for all studies.

Factor 3 had high loadings of most sea salts and is named ‘‘sea factor’’. This factor showed high loading for Cl, Na and Mg and explained about 11.4 % of the total variance.

Factor 4, with loading for Cr, Cu, Ni, V, Zn and Br explained about 7.9 % of the total variance. This factor is attributed to combustion of fossil fuels such as, coal, fuel oil, and gasoline for vehicles. It also can be said that these trace metals were the production of some combustion products of some metal and petrochemical industries.

Factor 5 was strongly loaded by Pb, Cd and moderately loaded by Zn and explained 6.2 % of the total variance. Both Pb and Zn used to characteristic of road traffic emissions. These results agree with the results of Huang et al. (1994), which indicated Zn as a new potential marker element for motor vehicle. However, the moderate loading for Zn in this factor indicated the presence of other anthropogenic sources contributing to this factor. If we also consider that Pb-free fuel oil have been used in Turkey for several years, we have another source for these trace metals.

These sources may some industries which are using some chemical process (have Pb, Cd and Zn rich combustion production). Steel furnaces with electrical arc were evaluated as another possible source for these metals especially Pb and Cd. Pb and Cd were also involved strongly with long-range transport and cloud condensation (Kim, 1999).

3.4.1 Bornova

The results of factor analysis of Bornova sampling point were given in Table 4.31. Five factors were detected for Bornova sampling station. These factors for Bornova explained 88.91 % of the variance.

First factor consisted of Al, Sr, V, Mn, Co, Cr, Ba, Fe, Mg, Pb and Ca with high loadings, and explained 46.40 % of the total variance. This factor strongly indicated the soil contributions on rainwater chemistry of İzmir at Bornova.

The second factor represented especially mineral industries with minor effects of agricultural industries. K salts pointed to agricultural influences such as application of fertilizer. If the Ammonium could have been investigated, that might have been be said this factor strogly indicates to agricultural activities. Also, burning process of some mineral industries must be effective in this factor. The explanation of this factor was half of the first factor as 20.28 %.

The third factor was selected as sea since it contained Mg, Cl and Na. It was expected to obtain a factor of marine, since Na only correlated with Mg and Cl given in correlation matrixes. The explanation of Factor 3 was 8.76 %.

The fourth factor was selected as traffic emission and petrochemical industry because of high loadings of Zn and Br. Combustion processes of petrochemical industries may affect this group positively as is the case of Factor 4 obtained from evaluation of whole datasets.

The fifth factor may be evaluated as another industry source as steel industries differently from Factor 4. The explanations of Factor 4 and Factor 5 were 7.24 % and 6.23 %, respectively.

Table 4.31 Results of factor analysis for Bornova.

Parameters & Factors	**Factor 1**	**Factor 2**	**Factor 3**	**Factor 4**	**Factor 5**
	• *Soil*	• *Agricultural Activities* • *Mineral Industries*	• *Sea*	• *Traffic* • *Petrochemical Industries*	*Steel Industries*
Al	0.94				
Sr	0.73				
V	0.52	0.53			
Mn	0.81				
Co	0.58				
Cr	0.66			0.58	
Cu				0.61	
Ba	0.76			0.55	
Fe	0.99				
Mg	0.76		0.67		
Cl			0.99		
Na			0.86		
Cd					0.91
Pb	0.60				0.66
Zn				0.82	
Ni				0.56	
Br				0.86	
Ca	0.58	0.61			
K		0.59			
F		0.94			
NO_3		0.90			
NO_2		0.93			
SO_4		0.98			
Var. %	***46.40***	***20.28***	***8.76***	***7.24***	***6.23***
Cum. %	***46.40***	***66.68***	***75.44***	***82.68***	***88.91***

It was seen from the factor analysis; Bornova was mostly affected from crustal components and soil related industries (mineral industries). It can also be said that agricultural activities may have lower effect on rainwater chemistry of Bornova.

3.4.2 Güzelyalı

The results of factor analysis of Güzelyalı sampling point were given in Table 4.32. Six factors were detected for Güzelyalı sampling station. These factors for Güzelyalı explained 93.82 % of the variance. Although the total explanation of variances for Güzelyalı was better than Bornova, factors couldn't be separated certainly as various sources.

First factor may be obtained as burning fossil fuels such as coal, fuel oil and traffic emission, since Factor 1 consisted of Cr, Br, Ni, Ba, V, Ca, NO_2, NO_3, SO_4

with high loadings, and Br is the pointer of the traffic emission. This factor explained 36.50 % of the total variance.

Table 4.32 Results of factor analysis for Güzelyalı.

Parameters & Factors	**Factor 1** • *Fossil Fuel* • *Traffic*	**Factor 2** • *Soil* • *Steel Industry*	**Factor 3** • *Sea*	**Factor 4** • *Petrochemical Industry*	**Factor 5** • *Industry*	**Factor 6** • *Soil Related Industry*
Cu					0.94	
K					0.84	
Mn		0.55			0.63	
Fe		0.91				
Al		0.86				
Pb		0.68				
Sr		0.41				0.83
Cd		0.70		0.44		
Zn				0.96		
Cr	0.79					
Br	0.45		0.53			
Cl			0.97			
Mg			0.88			
Na			0.96			
Co					0.74	
SO_4	0.53			0.44	0.66	
Ba	0.50	0.70			0.45	
Ni	0.50				0.83	
V	0.85				0.43	
Ca	0.44				0.67	0.49
NO_2	0.80					
F	0.90					
NO_3	0.84					
Var. %	***36.50***	***22.82***	***13.26***	***8.51***	***7.58***	***5.15***
Cum. %	***36.50***	***59.32***	***72.59***	***81.10***	***88.68***	***93.82***

The second factor may represent soil and contribution of steel industries. Factor 2 consisted of Mn, Fe, Al, Ba, and Sr elements originated from soil with high loadings and explained 22.82 % of the total variance. Pb and Cd input this factor as the influence of emissions from steel industries.

The third factor was selected as sea since it contained Mg, Cl and Na. It was expected to obtain a factor of marine, since Na only correlated with Mg and Cl given in correlation matrixes. The explanation of Factor 3 was 13.26 %.

The fourth factor was selected as petrochemical industry. Because Cd, Zn were used in petrochemical industry as catalyzes. But a certain source for this factor

couldn’t be obtained from these results. A mix of some antropogenic sources can be suggested for Factor 4. The explanation of Factor 4 was 8.51 %.

The fifth factor may be evaluated as a mix of some natural or anthropogenic sources. Components of this factor were not pointer of a prominent source. The explanations of Factor 5 were 7.58 %.

The sixth factor can be selected as soil related industry. Sr and Ca were major terrestrial elements of soil and soil related industry. The explanation of Factor 6 was 5.15 %.

It was seen from the factor analysis; Güzelyalı was mostly affected from combustion of fossil fuels, steel industries. Other effective sources were accepted soil and marine.

3.4.3 Tınaztepe

The results of factor analysis of Tınaztepe sampling point were given in Table 4.33. Six factors were detected for Tınaztepe sampling station like Güzelyalı. These factors for Tınaztepe explained 92.41 % of the variance.

First factor may be obtained as agricultural and soil related industries. K and Ca salts were highly correlated with anions. In this case K salts can be evaluated in agricultural group and Ca salts can be evaluated as coming from soil related industries as in Bornova sampling station. The explanation of Factor 1 was obtained highly as 39.68 % of total variance.

The second factor was selected as sea since it contained Mg, Cl and Na. It was expected to obtain a factor of marine, since Na only correlated with Mg and Cl given in correlation matrixes. The explanation of Factor 2 was 16.07 %.

The third factor can be determined as an unknown industry. But it can be considered as metal industry since Ni and Cu were used as catalysis in metal industry. The correlation value between Cu and Ni was also higher than correlation

value of K. So it can be said that relation between K and other elements (Ni and Cu) may be sourced from a different industry. The explanation of Factor 3 was 12.86 %.

The fourth factor was selected as soil since Al, Fe, Ba, Mn, Sr and Ca were major components of soil. The explanation of Factor 4 was 11.10 %. The fifth factor may be evaluated as steel industry source. The explanations of Factor 5 were 7.58 %. Also, some combustion processes may affect this factor accepted as unknown industry. The sixth factor can be selected as fossil fuel. Cr and V were accepted as indicator elements of fossil fuel. The explanation of Factor 6 was 4.84 %. And also, steel industry may be effective on this factor.

Table 4.33 Results of factor analysis for Tınaztepe.

Parameters & Factors	**Factor 1**	**Factor 2**	**Factor 3**	**Factor 4**	**Factor 5**	**Factor 6**
	• *Soil Related Industry* • *Agricultural Industry*	• *Sea*	• *Industry*	• *Soil*	• *Steel Industry*	• *Fossil Fuel*
K	0.56		0.64			
Ni			0.85			
Cu			0.89			
Mn	0.55			0.65		
Fe				0.95		
Al				0.98		
Ba	0.67			0.49		
Pb					0.96	
Zn					0.58	
Br		0.74			0.50	
Na		0.98				
Mg		0.88				
Cl		0.97				
Cr						0.47
Cd						0.86
V	0.62					0.62
Sr	0.76			0.42		
Ca	0.88			0.46		
F	0.93					
NO_3	0.93					
NO_2	0.87					
SO_4	0.92					
Var. %	***39.68***	***16.07***	***12.86***	***11.10***	***7.87***	***4.84***
Cum. %	***39.68***	***55.74***	***68.60***	***79.70***	***87.57***	***92.41***

It was seen from the factor analysis; Tınaztepe was mostly affected from agricultural and Soil related industry.

CHAPTER FIVE
CONCLUSIONS

In this thesis, the chemical composition of wet deposition in İzmir, Turkey is studied by collecting rainwater samples more than a 1-year period. Concentrations of the trace or major elements (Na, Mg, Ca, K, Al, Fe, Mn, Sr, Ba, Cr, Cd, V, Zn, Pb, Co, Ni, and Cu) were determined by ICP-OES, and anions (Cl, NO_3, PO_4, F, Br, NO_2 and SO_4) were determined by IC.

Many of measured parameters in ther study showed us that distributions of the chemical parameters are generally asymmetric. Not determining of normal distributions in histograms of measured parameters shows that emissions of these parameters into İzmir atmosphere don't originate from only one source and realize regular amounts. Statistical tests to explain the distributions of data infer that many of data fit log normally distributions. This indicates that transportation from distant regions and mixing of air masses play a major role in the distribution of concentrations.

Non-linear relationships were obtained between parameters and rain amounts as expected. According to graphics figured as chemical parameters versus rainwater amount, the relation between those rainwater and chemical parameters can be identified as logarithmical. While rain amount were increasing, the concentrations of chemical parameters were generally decreasing. This effect can be explained as scavenging of particulate materials into the atmosphere by raindrops.

The average pH value for İzmir was found to be 6.1 as arithmetic mean value due to the neutralization, a bit more than the widely accepted background pH of precipitation, 5.6. High precipitation acidity was generally associated with winter days, when ambient anthropogenic smog levels were also high. The variability of pH was found to be very high during autumns and springs, leading to extreme pH values of 3.40 (Güzelyalı) and 8.43 (Bornova). The lower seasonal pHs were observed in the winter times.

According to the Spearman or Pearson correlation coefficient, an meaningful correlation is not obtained between pH values and SO_4 or NO_3 values. The Pearson correlation coefficient between sulphate anions and calcium cations is found to be 0.94, which is one of the highest correlations detected between the concentrations of anions and cations. Thus, it can be stated that the main reason of not having high acidity in the precipitation of İzmir was the high calcium deposition. Only about 5 % of the rain samples have a pH below 4.0 and about 16 % of the rain samples have a pH below 5.0. This reflects strong inputs of alkaline species to rainwater samples in this location. The average pH of the samples higher than 5.6 observed in one of the urban plants (Bornova) of İzmir is due to high loading of calcium ions because of the alkaline nature of the soil that is typical in Turkey. Although Bornova is accepted as an urban area, another effective factor in handling these results is the construction industries surrounding the sampling point. Highest Ca depositions are determined in this area. This expected result can be explained with high loadings of alkali ions in this area previously mentioned. When all evaluations on pH are considered, it can be said that the neutralization is realized to be a local process. Other factors must be NH_3 sources in neutralising processes. Through there are a lot of agricultural regions around Bornova and Çiğli, measurement of ions from agricultural activities should be realized simultaneously in our stations to prove this effect.

The order of volume-weighted concentrations of the trace metals in this study is Ca > Na > Mg > K > Al > Fe > Zn > Sr > Mn > Cu > Ba > Pb > V > Ni > Cr > Cd > Co. There is no clear seasonal variation in the monthly wet deposition of the trace metals. The wet deposition of crustal and some non-crustal elements reached peak values in some months (especially in November, February and March), mainly due to the amount of precipitation depths, transportations of contaminated air masses from the heavily industrialized area and sea surfaces, and emissions from locally natural or anthropogenic impurities in İzmir. The measured highest fluxes are observed for the elements Ca (1,716.15 $mg.m^{-2}.year^{-1}$) and Na (830.40 $mg.m^{-2}.year^{-1}$), and for the anions SO_4 (1,721.35 $mg.m^{-2}.year^{-1}$) and Cl (1,201.62 $mg.m^{-2}.year^{-1}$). Average values for annual wet deposition fluxes in İzmir are ranged 0.26-1,721.35 $mg.m^{-2}.year^{-1}$.

The order of wet depositional fluxes of the metals in this study is SO_4 > Ca > Cl > Na > NO_3 > Mg > K > Al > NO_2 > PO_4 > Zn > F > Sr > Cu > Pb > Mn > Br > Ba > Ni > Fe > V > Cd > Co > Cr. The measured annual deposition fluxes of Ca, Na, Cl, and SO_4 are considerably higher those reported in literature for other sites outside İzmir, which are mainly attributed to oceanographic transportations, local soil properties and anthropogenic activities.

In order to determine the contribution of sea and soil to the chemical composition of precipitation, enrichment factors for sea and soil are calculated. Al is selected as base element to determine EF_c values of parameters, and Na is selected as base elements to determine EF_m values of parameters. It is found that the majority of chlorine is of marine origin, as expected. Average EF_m of major ions Ca, SO_4, K, Mg, and Cl are 113.7, 26.2, 3.6, 3.5, 1.1, respectively, implying that the majority of the Ca and SO_4 come from the another sources. Non-sea salt values and non-sea salt fractions are estimated. Non-sea salt fractions of SO_4 ranged from 87-93 %, indicating that SO_4 emissions from fossil-fuel combustion are the dominant sources affecting the composition of wet deposition. Very high non-sea salt fractions of Ca revealed the importance of limestone as a source.

Ef_c values were obtained as in order, Fe(1.59) < Mn(13.35) < K(17.15) < Cr(19.61) < Mg(24.83) < Ba(27.64) < Sr(33.07) < Co(41.72) < V(50.04) < Ni(101.63) < Na(108.24) < Ca(170.11) < Cu(345.57) < Zn(812.53) < Pb(936.24) < Cd (7401.26). It can be said that the crustal enrichment is decreasing towards high Ef_c values; high Ef_c values show anthropogenic enrichments. While Cu, Zn, Pb, and Cd are accepted as non crustal elements, Fe and Mn are strongly enriched by soil components. Other elements are moderately enriched by Earth's crust according to our studies.

In our study, concentrations of crustal elements have moderate values relative to the reported values in the literature except Ca for Bornova. Contribution of marine cations and anions into rain waters is similar to between coastal sites. Na, Cl, Mg, and K concentrations are arranged similar to values determined by Okay et al. (2001) at Kaynarca, Turkey and Glavas (1988) at Patras, Greece. NO_3 and SO_4 values are

also moderate relative to similar studies. It is obvious that concentrations of trace metals have moderate values in our research. However some trace elements (Pb, Cd, Co and Zn) have the highest values at Tınaztepe sampling point in our studies but these values of trace metals were not the highest values in the literatures.

Correlation matrixes are computed one by one for every sampling station and for overall dataset. Furthermore, factor analysing is applied to correlation matrixes step by step. Similar results are obtained from these two data analysis applied to obtain origin of chemical parameters. Six factors for Tınaztepe and Güzelyalı, five factors for Bornova and whole dataset were found as similar sources indicated to contribution of soil, mineral industries, agricultural activities, marine, fossil fuels (with traffic effect), petrochemical industries, and steel industries. Total variance of factor analysis are considered, the major contribution in to precipitations due to location properties of stations are soil and soil related industries (mineral industries) for Bornova; agricultural and soil related industries for Tınaztepe; fossil fuels, steel industries, marine and soil for Güzelyalı.

Illustration of probable sources affecting composition of rainwater at the region together with prevailing wind directions are given in Figure 5.1, indiscriminately.

Results show us that two effective sources could be suggested, soil related industries with agricultural activities and oceanographic transportations playing major role to form of chemical characters of region atmosphere. And local industrial activities may be pointed as secondary sources affecting to the quality of atmosphere.

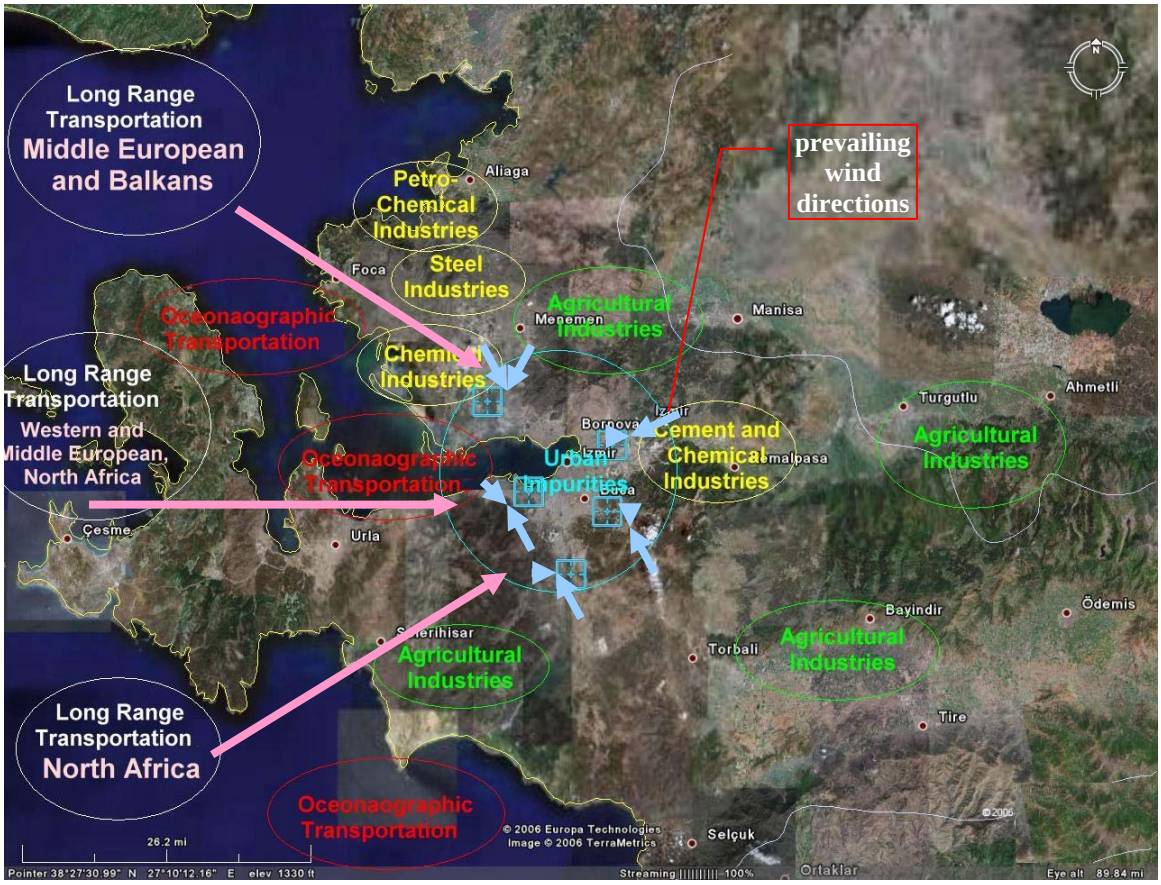


Figure 5.1 Illustration of probable sources affecting composition of rainwater at the region together with prevailing wind directions.

According to t-Test statistics together with non-parametrics of experimental results, harmoniousness between two stations, Güzelyalı and Bornova as urban areas, is better than between Tınaztepe and thems. It can be accepted that Bornova sampling station has similar atmospheric properties with Güzelyalı sampling station except Ca content. In this case, Bornova sampling site may be canceled in a further research. And probable sources located in the north of the region may be considered in a group, causing chemical impurities (affecting human health and quality of atmosphere) into atmosphere of İzmir. To obtain this probable effect, similar studies must be simultaneously realized in north region of İzmir together with our studies in our present sampling points.

By the highlights of these studies, the quality of precipitation in the region is detected chemically. Acidic characters of rain droplets are obtained and major and trace metals in precipitation samples are also investigated. All chemical parameters

examined during sampling periods play very important roles by forming of chemical composition of precipitations in the region, and affect the natural structure of the region atmosphere. It is thought that carrying on these studies will present many environmental profits because of the causes mentioned above.

A widespread meteorological observation network is operated by Turkish State Meteorological Service. This broad network of meteorological observation stations can also be used as air monitoring stations. Our studies are realized by the collaboration between İzmir Regional Meteorological Office and Department of Environmental Engineering of Dokuz Eylül University . Sample collections are achieved by the personnel of meteorological offices. Some sampling stations in meteorological offices are cancelled mandatory because of difficulties sampling and transportation steps and deficiencies of the number of meteorological personnel. When the conditions for sampling are adequate, handling of precipitation samples could be even realized by manually at meteorological offices. Sampling procedure of wet deposition can be effortless applied by meteorological personnel when automated samplers are located to the meteorological stations in Turkey. Consequently, the composition of the rain waters in Turkey can be obtained to have a board information net about country atmosphere by using these possibilities, when transportation problems are solved successively.

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APPENDIX

Appendix 1. Register Form for Rainwater Samples

Precipitation Samples Information Form													
Year:						***Station***							
Month:													
Sample Box Number	**Sampling Date**	**Location time of the sampling apparatus**	**Starting/Ending time of precipitation**	**Dislocation time of the sampling apparatus**	**Precipitation amount (mm)**	**Measured pH values (If pH-meter is located to the station.)**	**Name of personnel sampled precipitation**	**Daily Meteorological Parameters**					
								Temperature (°C)	**Humidity (%)**	**Pressure (mb)**	**Predominat daily wind direction (Degree)**	**Predominat daily wind average speed (m/s)**	