

T.R.
BOLU ABANT İZZET BAYSAL UNIVERSITY
INSTITUTE OF GRADUATE STUDIES
Department of Chemistry



**EVALUATION OF CHEMICAL COMPOSITION AND
SOURCE APPORTIONMENT OF FRACTIONAL RAIN
SAMPLES COLLECTED IN URBAN AND SEMI-URBAN
SITES OF BOLU**

MASTER OF SCIENCE

FATİH ÇINAR

ACADEMIC SUPERVISOR
Prof. Dr. Serpil YENİSOY-KARAKAŞ

BOLU, OCAK - 2023

APPROVAL OF THE THESIS

EVALUATION OF CHEMICAL COMPOSITION AND SOURCE APPORTIONMENT OF FRACTIONAL RAIN SAMPLES COLLECTED IN URBAN AND SEMI-URBAN SITES OF BOLU submitted by **Fatih ÇINAR** and defended before the Examining Committee Members listed below in partial fulfillment of the requirements for the degree of **Master of Science** in **Department of Chemistry, Institute of Graduate Studies of Bolu Abant İzzet Baysal University** in **6.01.2022** by

Examining Committee Members

Signature

Supervisor
Prof. Dr. Serpil YENİSOY-KARAKAŞ
Bolu Abant İzzet Baysal University

.....

Member
Prof. Dr. Azra BOZCAARMUTLU-BÜKEN
Bolu Abant İzzet Baysal University

.....

Member
Assoc. Prof. Dr. Mihriban CİVAN
Kocaeli University

.....

Prof. Dr. İbrahim KÜRTÜL
Director of Institute of Graduate Studies

ETHICAL DECLARATION

In this thesis dissertation that was properly prepared according to the Thesis Writing Rules of Bolu Abant İzzet Baysal University of the Institute of Graduates Studies, I hereby declare that;

- All data, information, and documents presented in the thesis were obtained in accordance with the academic and ethical rules,
- All data, documents, assessments, and results were presented in accordance with the scientific ethical and moral rules,
- All works that were benefitted in the thesis were appropriately cited,
- No alteration was made in the data used,
- Study presented in this thesis is original,

Otherwise, I declare that I accept the loss of all my rights in case any contradiction that may arise against me.

Based on the plagiarism report that was generated on the date of 30/01/2023 by using predetermined filtrations set by Directorate of Institute of Graduate Studies of the Turnitin programme, a plagiarism detection software, the similarity index detected was 23 %.

Fatih ÇINAR

ABSTRACT

EVALUATION OF CHEMICAL COMPOSITION AND SOURCE APPORTIONMENT OF FRACTIONAL RAIN SAMPLES COLLECTED IN URBAN AND SEMI-URBAN SITES OF BOLU

MSC THESIS

FATİH ÇINAR

BOLU ABANT IZZET BAYSAL UNIVERSITY

INSTITUTE OF GRADUATE STUDIES

DEPARTMENT OF CHEMISTRY

(SUPERVISOR: PROF. DR. SERPİL YENİSOY-KARAKAŞ)

BOLU, JANUARY 2023

xv + 118

In this study, the volume-based wet deposition samples were collected fractionally in May and June of 2020. The 167 samples were obtained from two different districts of Bolu. One hundred twenty-one samples were obtained from the city center of Bolu, the urban site, and forty-six samples were obtained from the Bolu Abant Izzet Baysal University campus, the semi-urban site. Major ions (F^- , Cl^- , NO_2^- , Br^- , NO_3^- , PO_4^{3-} , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}) and elements (Ag, Al, As, Ba, Bi, Cd, Co, Cr, Cs, Cu, Fe, Ga, Li, Mg, Mn, Mo, Ni, Pb, Sb, Sn, Sr, V, Zn) were determined by using IC and ICP-MS, respectively. The results showed that Bolu had not suffered acid rain during the sampling period. The mean pH value for the urban site was 6.29, while the mean pH value for the semi-urban site was 6.79. The VWM (volume-weighted mean) concentrations of anions and cations were 176 $\mu eq/L$ and 202 $\mu eq/L$ for the urban area and 524 $\mu eq/L$ and 798 $\mu eq/L$ for the semi-urban area, respectively. Furthermore, The VWM concentrations of elements were 68.5 mg/L and 103 mg/L for the urban and semi-urban areas, respectively. The neutralization potential is dominant in both areas. Calcium and NH_4^+ greatly impacted the neutralization of both areas. The Na^+ % and SAR (sodium adsorption ratio) values demonstrated that the precipitation in Bolu had good quality and had no risk of using irrigation in agricultural activities. Using positive matrix factorization (PMF 5.0), six sources for urban sites and five for semi-urban areas were identified. The major sources affecting the urban area were the iron-steel factories (37%), Bolu cement factory (6%), the biomass burning (10%), the transportation from Anatolia (14%), the coal burning (17%), and the urban atmosphere (16%). Likewise, the major sources affecting the semi-urban area were the long-range transportation (16%), the nitrate factor (5%), the iron-steel factory (39%), the biomass burning (12%), and the mixture of vehicular emission and coal burning (28%).

KEYWORDS: Rainwater, Fractional Sampling, PMF, Trace Elements, Major Ions

ÖZET

**BOLU'NIN KENT VE YARI-KENT ALANLARINDA TOPLANAN
FRAKSİYONEL YAĞMUR ÖRNEKLERİNİN KAYNAK PAYLAŞIMININ
VE KİMYASAL KOMPOZİSYONUNUN DEĞERLENDİRİLMESİ
YÜKSEK LİSANS TEZİ
FATİH ÇINAR
BOLU ABANT İZZET BAYSAL ÜNİVERSİTESİ
LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ
KİMYA ANABİLİM DALI
(TEZ DANIŞMANI: PROF. DR. SERPİL YENİYOS-KARAKAŞ)**

BOLU, OCAK - 2023

xv + 118

Bu çalışmada hacim bazlı yağ çökelme örnekleri 2020 yılı Mayıs ve Haziran aylarında fraksiyonel olarak toplanmıştır. Toplamda 167 örnek Bolu'nun iki farklı ilçesinden elde edilmiştir. Kentsel alan olan Bolu il merkezinde 121 örnek, yarı-kentsel alan olan Bolu Abant İzzet Baysal Üniversitesi yerleşkesinden ise 46 örnek alınmıştır. Ana iyonlar (F^- , Cl^- , NO_2^- , Br^- , NO_3^- , PO_4^{3-} , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}) ve iz elementler (Ag, Al, As, Ba, Bi, Cd, Co, Cr, Cs, Cu, Fe, Ga, Li, Mg, Mn, Mo, Ni, Pb, Sb, Sn, Sr, V, Zn) sırasıyla IC ve ICP-MS kullanılarak belirlenmiştir. Sonuçlar, Bolu'nun örnekleme döneminde asit yağmuruna maruz kalmadığını göstermiştir. Kentsel alan için ortalama pH değeri 6,29 iken, yarı-kentsel alan için ortalama pH değeri 6,79'dur. Anyon ve katyonların hacim ağırlıklı ortalama konsantrasyonları kentsel alan için sırasıyla 176 $\mu eq/L$ ve 202 $\mu eq/L$ ve yarı kentsel alan için sırasıyla 524 $\mu eq/L$ ve 798 $\mu eq/L$ olarak bulunmuştur. Ayrıca, elementleri VWM konsantrasyonları kentsel ve yarı-kentsel alanlar için sırasıyla 68,5 mg/L ve 103 mg/L olarak bulunmuştur. Nötralizasyon potansiyeli her iki alanda da baskındır. Kalsiyum ve NH_4^+ , her iki alanın nötralizasyonunu büyük ölçüde etkilemiştir. Na^+ ve SAR değerleri, Bolu'da yağışın iyi kalitede olduğunu ve tarımsal faaliyetlerde sulama suyu olarak kullanma riskinin olmadığını göstermiştir. PMF modelleme yöntemi kullanılarak, kentsel alan için altı ve yarı-kentsel alan için beş kaynak belirlenmiştir. Kentsel alanı etkileyen başlıca kaynaklar demir-çelik fabrikaları (%37), Bolu çimento fabrikası (%6), biyokütle yakımı (%10), Anadolu'dan taşınım (%14), kömür yakımı (%17) ve kent atmosferi (%16) olarak belirlenmiştir. Aynı şekilde, yarı-kentsel alanı etkileyen başlıca kaynaklar, uzun mesafeli taşınım (%16), nitrat faktörü (%5), demir-çelik fabrikaları (%39), biyokütle yakımı (%12) ve taşıt emisyonu ile kömür yakımı karşımı (%28) olarak belirlenmiştir.

ANAHTAR KELİMELELER: Yağmur Suyu, Fraksiyonel Örnekleme, PMF, İz Elementleri, Ana İyonlar

TABLE OF CONTENTS

	PAGE
APPROVAL OF THE THESIS	III
ETHICAL DECLARATION	IV
ABSTRACT	V
ÖZET	VI
TABLE OF CONTENTS	VII
LIST OF FIGURES	IX
LIST OF TABLES	XI
LIST OF PICTURES.....	XIII
LIST OF ABBREVIATIONS AND SYMBOLS	XIV
1. INTRODUCTION.....	1
1.1 A Brief Examination on Air Pollution.....	3
1.1.1 Types of Atmospheric Pollutants	3
1.1.1.1 Particulate Matter	3
1.1.1.2 Gaseous Species	4
1.1.2 Sources of Atmospheric Pollutants	5
1.1.3 Effects of Atmospheric Pollutants on the Other Environmental Compartments	9
1.1.4 Health Effects of Atmospheric Pollutants.....	10
1.2 Acidification of Soil, Water, and Atmosphere	13
1.3 Rainwater Chemistry	15
1.3.1 Deposition Phenomena.....	16
1.3.1.1 Wet Deposition	16
1.3.1.2 Dry Deposition	17
1.4 Analysis of Samples	18
1.4.1 Ion Chromatography	18
1.4.2 ICP-MS	20
2. AIM AND SCOPE OF THE STUDY	23
3. MATERIALS AND METHODS.....	24
3.1 Study Area	24
3.2 Meteorological Parameters	25
3.3 Sample Collection.....	29
3.4 Reagent and Material.....	32
3.5 Analysis	32
3.5.1 IC Analysis for Ions	32
3.5.2 ICP-MS Analysis for Elements.....	34

3.6	Quality Control and Quality Assurance.....	35
3.6.1	Detection and Quantification Limits.....	38
3.7	Source Apportionment.....	39
3.7.1	Back Trajectory Analysis.....	40
3.7.2	Positive Matrix Factorization.....	40
4.	RESULTS AND DISCUSSIONS	42
4.1	Statistical Evaluation	42
4.2	Ion Balance	51
4.3	The Volume-Weighted Mean Concentrations of Ions.....	53
4.4	The Volume-Weighted Mean Concentrations of Elements.....	55
4.5	Evaluation of Rainwater Acidity	56
4.5.1	Neutralization Factor.....	58
4.5.2	Multiple Linear Regression.....	58
4.5.3	Fractional Acidity.....	60
4.5.4	Ammonium Availability Index	60
4.5.5	The Ratio of Neutralization Potential and Acidic Potential.....	61
4.5.6	Evaluation of Some Ratios.....	61
4.6	Suitability of Rainwater for Irrigation and Cultivation	62
4.7	Comparison of Results with Literature.....	63
4.7.1	Comparison of Ions with Literature	63
4.7.2	Comparison of Elements with Literature	67
4.8	Source Apportionment.....	69
4.8.1	Crustal Enrichment Factor	69
4.8.2	Positive Matrix Factorization.....	70
4.8.2.1	The PMF Results for the Urban Area	72
4.8.2.2	The PMF Results for the Semi-urban Area	86
5.	CONCLUSIONS AND RECOMMENDATIONS	100
6.	REFERENCES	104
7.	APPENDICES	114

LIST OF FIGURES

	<u>Page</u>
Figure 1.1. Illustration of the interrelationship of Earth's compartments by a common pollutant, sulfur dioxide (1).....	1
Figure 1.2. Effect of atmospheric pollutants on other environmental compartments (49).....	9
Figure 1.3. Classification of atmospheric precipitation (49).....	17
Figure 1.4. Schematic diagram of ion chromatography (80)	19
Figure 1.5. Elements analyzed by ICP-MS (82)	21
Figure 1.6. Individual components of ICP-MS instrument (84,85)	21
Figure 3.1. The city map of Bolu (85).....	24
Figure 3.2. Daily minimum-maximum-average temperatures for the city center of Bolu	28
Figure 3.3. Daily minimum-maximum-average temperatures for the BAIBU campus.....	28
Figure 3.4. Average humidity and total rainfall amount for the city center of BOLU	29
Figure 3.5. Average humidity and total rainfall amount for the BAIBU campus	29
Figure 3.6. Sampling points	30
Figure 3.7. The number of fractions collected from the city center and the date of the fraction.....	31
Figure 3.8. The number of fractions collected from the BAIBU campus and the date of the fraction.....	31
Figure 3.9. Calibration curves for anions.....	36
Figure 3.10. Calibration curves for cations	37
Figure 4.1. The number of fractions of rainwater samples collected in the urban and semi-urban areas	42
Figure 4.2. Relationship between the sum of anions and cations for the urban area	52
Figure 4.3. Relationship between the sum of anions and cations for the semi-urban area	52
Figure 4.4. The VWM concentrations of major ions for the urban area ($\mu\text{eq/L}$).	53
Figure 4.5. The VWM concentrations of major ions for the semi-urban area ($\mu\text{eq/L}$).....	54
Figure 4.6. pH ranges for the urban area.....	57
Figure 4.7. pH ranges for the semi-urban area.....	57
Figure 4.8. The mean neutralization factors for Ca^{2+} , Mg^{2+} , NH_4^+ , K^+ , and Na^+ for the urban and semi-urban areas	58
Figure 4.9. Crustal enrichment factor results for the urban area.....	70
Figure 4.10. Crustal enrichment factor results for the semi-urban area.....	70
Figure 4.11. G score values of fractions for Factor 1.....	72

Figure 4.12. The back trajectory of the highest G score for Factor 1	72
Figure 4.13. PMF results for Factor 1	73
Figure 4.14. G score values of fractions for Factor 2.....	74
Figure 4.15. The windrose for the highest G score value	74
Figure 4.16. PMF results for Factor 2	75
Figure 4.17. G score values of fractions for Factor 3.....	76
Figure 4.18. The windrose for the highest G score value	76
Figure 4.19. PMF results for Factor 3	77
Figure 4.20. G score values of fractions for Factor 4.....	78
Figure 4.21. The back trajectories of the highest G scores for Factor 4	79
Figure 4.22. PMF results for Factor 4	80
Figure 4.23. G score values of fractions for Factor 5.....	81
Figure 4.24. The back trajectory of the highest G score for Factor 5	82
Figure 4.25. The windrose for the highest G score value	82
Figure 4.26. PMF results for Factor 5	83
Figure 4.27. G score values of fractions for Factor 6.....	84
Figure 4.28. The back trajectory of the highest G score for Factor 6	84
Figure 4.29. PMF result for Factor 6.....	85
Figure 4.30. G score values of fractions for Factor 1.....	86
Figure 4.31. The back trajectories of the highest G scores for Factor 1	87
Figure 4.32. PMF results for Factor 1	88
Figure 4.33. G score values of fractions for Factor 1.....	89
Figure 4.34. The windrose for the highest G score values.....	89
Figure 4.35. PMF results for Factor 2	90
Figure 4.36. G score values of fractions for Factor 3.....	91
Figure 4.37. The back trajectory of the highest G score for Factor 3	91
Figure 4.38. The windrose for the highest G-score value	92
Figure 4.39. PMF results for Factor 3	93
Figure 4.40. G score values of fractions for Factor 4.....	94
Figure 4.41. The windrose for the highest G score value	94
Figure 4.42. PMF results for Factor 4	95
Figure 4.43. G score values of fractions for Factor 5.....	96
Figure 4.44. The back trajectories of highest G scores for Factor 5	97
Figure 4.45. The windrose for the highest G-score value	97
Figure 4.46. PMF results for Factor 5	98
Figure 4.47. Percent contribution of each factor for urban area	99
Figure 4.48. Percent contribution of each factor for semi-urban area.....	99

LIST OF TABLES

	<u>Page</u>
Table 1.1. Six common air pollutants and volatile organic compounds (46).....	7
Table 1.2. Sources of heavy metals and metalloids (46).....	8
Table 1.3. Health effects of heavy metals and metalloids (46)	11
Table 1.4. The classification of heavy metal carcinogenicity (55,56).....	13
Table 1.5. Environmental effects of acidification processes by anthropogenic emissions (60).....	14
Table 3.1. Dominant daily wind directions and wind speeds (m/s) for the city center covering the sampling period.....	26
Table 3.2. Dominant daily wind directions and wind speeds (m/s) for the BAIBU campus covering the sampling period	27
Table 3.3. Microwave oven program	32
Table 3.4. The operation program for the Dionex ICS-1100 system	33
Table 3.5. Operation parameters of ICP-MS.....	34
Table 3.6. Analysis results of SRM for elements (concentrations are in mg/L) ..	38
Table 3.7. R ² , MDL, MQL values for ions (concentrations are in (µg/mL)	38
Table 3.8. MDL and MQL values of elements (concentrations are in µg/mL)....	39
Table 4.1. Statistical treatment values of major ions for the urban area (units are in µg/L).....	43
Table 4.2. Statistical treatment values of elements for the urban area (units are in µg/L).....	44
Table 4.3. Statistical treatment values of major ions for the semi-urban area (units are in µg/L).....	45
Table 4.4. Statistical treatment values of elements for the semi-urban area (units are in µg/L).....	46
Table 4.5. Distribution parameters of elements and ions for the urban area.....	49
Table 4.6. Distribution parameters of elements and ions for the semi-urban area	50
Table 4.7. Linear regression analysis results for the urban and semi-urban areas	51
Table 4.8. The VWM concentrations of elements for the urban and semi-urban areas (units are in µg/L).....	56
Table 4.9. Multiple linear regression parameters of SO ₄ ²⁻ and NO ₃ ⁻ for the urban area	59
Table 4.10. Multiple linear regression parameters of SO ₄ ²⁻ and NO ₃ ⁻ for the semi-urban area	59
Table 4.11. The classification scheme for the suitability of rainwater.....	63
Table 4.12. Literature comparison of major ions (units are in µeq/L), pH, and acidity	66
Table 4.13. Comparison of trace metals concentrations (units are in µg/L) with literature.....	68
Table 4.14. The base model results for the urban and semi-urban areas.....	71

Table 4.15. Urban area DISP analysis	71
Table 4.16. Semi-urban area DISP analysis	71
Table 7.1. Sampling information for the city center of Bolu	114
Table 7.2. Sampling information for the BAIBU Campus.....	117



LIST OF PICTURES

	<u>Page</u>
Picture 3.1. Manual system for collection of rainwater samples	30
Picture 3.2. A photo of Ion Chromatography system in the laboratory	33
Picture 3.3. A photo of the Perkin-Elmer ELAN DRC-e model ICP-MS system in the laboratory.....	34



LIST OF ABBREVIATIONS AND SYMBOLS

AAI	: Ammonium Availability Index
AAS	: Atomic Absorption Spectroscopy
AP	: Acidic Potential
EF	: Enrichment Factor
EPA	: Environmental Protection Agency
FA	: Fractional Acidity
IC	: Ion Chromatography
ICP-MS	: Inductively Coupled Plasma Mass Spectrometry
NF	: Neutralization Factor
NP	: Neutralization Potential
PAH	: Poly Aromatic Hydrocarbon
PM	: Particulate Matter
PM_{0.1}	: Ultrafine Mode Particulate Matter
PM_{2.5}	: Fine Mode Particulate Matter
PM₁₀	: Coarse Mode Particulate Matter
PMF	: Positive Matrix Factorization
SAR	: Sodium Adsorption Ratio
VWM	: Volume Weighted Mean
WHO	: World Health Organization

ACKNOWLEDGEMENTS

The author wishes to express his deepest gratitude to his supervisor Prof. Dr. Serpil YENİSOY-KARAKAŞ for her guidance, advice, criticism, encouragements and insight throughout the research.

The author would also like to thank Assoc. Prof. Dr. Duran KARAKAŞ for his suggestions and comments.

I would like to thank to my family for their support and sacrifices.

Many thanks to Dr. Hatice KARADENİZ for her contribution to the collection of samples on campus, and for her endless support during my thesis period.

I am also thankful to Dr. Murat KILIÇ for analyzing the elements by ICP-MS.

1. INTRODUCTION

Earth's environment consists of five interrelated compartments; hydrosphere, atmosphere, geosphere, anthroposphere, and biosphere. These compartments comprise water, air, rock and soil, human-modified part of the Earth, and living organisms, respectively (1). Therefore, contamination of one of these components with toxic substances also affects the other components. For example, mining coal from the geosphere and burning it in power plants release sulfur dioxide into the atmosphere (Figure 1.1). Atmospheric chemical processes lead to produce sulfuric acid, H_2SO_4 . The sulfur dioxide in the atmosphere may have detrimental effects on living organisms in the biosphere and the human respiratory system. The sulfuric acid in the precipitation may accelerate the corrosion of materials and be toxic to plants. Finally, the sulfuric acid gets into a sink which can be soil in the geosphere or a body of water in the hydrosphere. At this point, sulfuric acid continues to have other detrimental effects in the geosphere and hydrosphere (1).

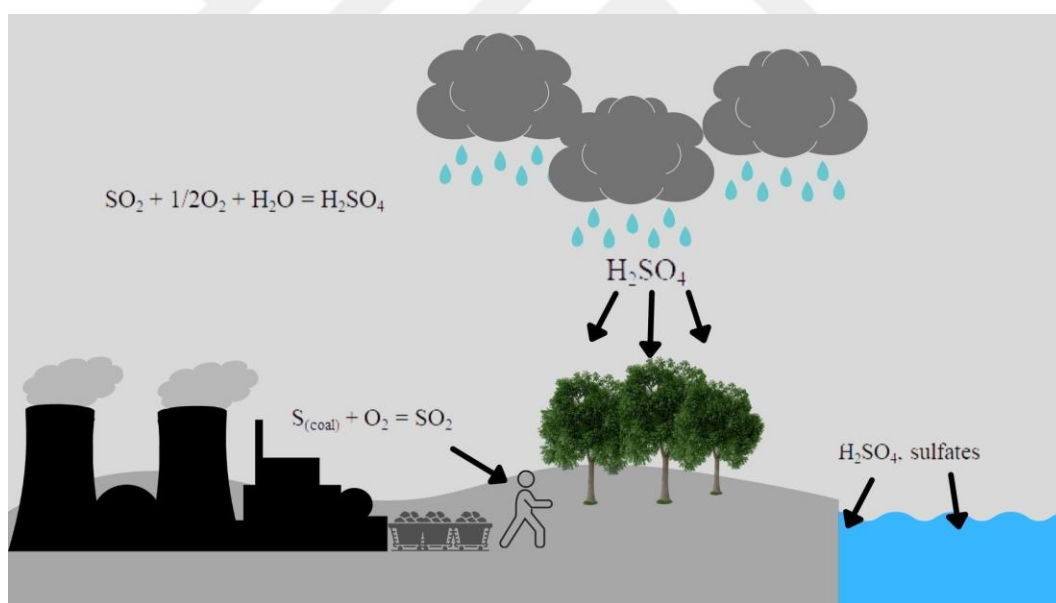


Figure 1.1. Illustration of the interrelationship of Earth's compartments by a common pollutant, sulfur dioxide (1)

Pollution is the contamination of the environment with toxic substances that have detrimental effects on living organisms. Pollutants may be solids, liquids, or gases (2). Although environmental components such as water, air, and soil are essential for the sustainability of life on Earth (3), industrialization, urbanization,

economic growth, increasing population concentration, and traffic development have enhanced the release of pollutants into the environment (4). Therefore, pollutants have been causing the deterioration of environmental quality (3). Pollution in the water, air, and soil can be defined as;

- Water pollution comes from the input of toxic substances such as heavy metals, herbicides, insecticides, phosphates, nitrogen compounds, and biodegradable organic compounds (1). Surface water (oceans, rivers, lakes) and groundwater (found in Earth's aquifers) constitute the water sources. However, the amount of freshwater is only 2.5% on our planet. For that reason, contamination of these water sources with pollutants reduces the water quality, leads to water scarcity, and be toxic for livings (3).
- Soil pollution reflects the contamination with toxic chemicals such as fertilizers, radioactive pollutants, industrial waste, and urban waste (5). These pollutants alter the structure and system of the soil, leading to a decrease in its productivity, making it unsuitable for agriculture and susceptible to drought. Moreover, the soil is a natural sink for pollutants; therefore, the accumulation of pollutants in the soil adversely affects humans, animals, and plants (6).
- Air pollution comes from the hanging of noxious chemicals in the air. According to the EPA's criteria, these chemicals are particulate matter, nitrogen oxides, sulfur dioxides, ozone, carbon monoxide, and lead (7). Once these pollutants are released into the air, they can cause many harmful effects on the environment. For example, precipitation transports air pollutants to the soil and water, affecting their quality (8,9). Also, global warming and climate change alter the ecosystem, leading to problems such as animal extinction and melting glaciers (10).

The aforementioned environmental components are of vital importance for all livings. They need to be preserved from all pollutants. Therefore, some measures should be taken, and environmental awareness should be given to people.

1.1 A Brief Examination on Air Pollution

As stated by the WHO, the increasing concentration of six major pollutants in the air (particulate matter, sulfur dioxide, nitrogen oxides, carbon monoxide, ozone, and lead) causes air pollution. These air pollutants have been steadily increasing since the industrial revolution (2). Moreover, anthropogenic activities such as high-energy consumption, agricultural processes, municipal waste burning, crop residue burning, and using vehicles have caused to increase in pollutants concentration in the air that affects people around the world (11,12). Air pollution is the most important among the other pollutants due to the harmful effects on climate change, the economy, humans, plants, and animals (13). It may also contaminate the other compartments of the environment and affect everyone in low- and high-income countries (14).

Nowadays, the world has suffered from COVID-19. Industrial and human activities have reduced throughout the pandemic, and the effects of these activities in terms of air pollution have shown more visible. For the first time in many years, blue skies and starry nights appeared around the world. Improving trends have shown in air quality owing to a considerable reduction in nitrogen dioxide (NO₂) emissions and fine particle air pollutants (PM_{2.5}) during the shutdown. On the contrary, ozone has had a higher concentration, probably due to the decrease in the concentration of nitrogen dioxide and the change in meteorological conditions (15).

1.1.1 Types of Atmospheric Pollutants

Air pollutants can be examined under two major groups as particulate matter and gaseous pollutants.

1.1.1.1 Particulate Matter

Particulate matters are solid particles or liquid droplets, generally occurring through atmospheric chemical reactions. Solid particles may be divided into two categories: small particles such as black carbon, sea salt nuclei, and combustion nuclei; large particles such as cement and aeolian dust, foundry powder, and pulverized coal. Liquid particles include mist, fog, haze, and raindrops. Particulate matters are present in the atmosphere as either primary (released directly into the atmosphere) or secondary (formed through atmospheric chemical reactions in the atmosphere) air pollutants. The main reason for the availability of primary particulate matter is the dust incursions from arid regions, and likewise, vehicular

emissions and industrial activities are the main reasons for the secondary particulate matter in the atmosphere.

According to the aerodynamic diameter, particulate matter in the atmosphere may be classified as coarse mode particles (PM_{10}), fine mode particles ($PM_{2.5}$), and ultrafine mode particles ($PM_{0.1}$) (16). The aerodynamic diameter of fine mode particles is less than $2.5\text{ }\mu\text{m}$ (17), and they are composed of sulfate, SO_4^{2-} ; nitrate, NO_3^- ; ammonium, NH_4^+ ; hydrogen ion, H^+ , elemental carbon, EC; organic compounds; PAH; metals, Pb, Cd, V, Ni, Cu, Zn; particle-bound water; and biogenic organics (18). $PM_{2.5}$ comes from the combustion of fossil fuels; transformation products of nitrogen oxides, sulfur dioxide, and organics; high-temperature industrial applications (19). The residence time of fine-mode particles in the air is very long because their lifetimes may be days to weeks (18), and they have a 100-1000 km travel distance (19). On the contrary, the aerodynamic diameter of coarse mode particles is less than $10\text{ }\mu\text{m}$ (17), and they are composed of resuspended dust, soil dust, street dust; coal and oil fly ash; metal oxides of Si, Al, Mg, Ti, Fe; $CaCO_3$, sea salt; pollen, mold spores, and plant parts (18). Coarse mode particles have a short lifetime (minutes to hours) (18), so they cannot stay in the air for an extended period, and they have a 1-10 km travel distance (19). The aerodynamic diameter of ultrafine particles is less than $0.1\text{ }\mu\text{m}$, and they are composed of organic compounds, trace metal oxides, elemental carbon, sulfate, nitrate, ammonium ion, sodium, and chloride. $PM_{0.1}$ frequently comes from mobile and stationary fuel combustion sources (20).

1.1.1.2 Gaseous Species

The most critical polluting atmospheric gases are ozone, nitrogen oxides, carbon monoxide, and sulfur dioxide. Those may cause serious environmental and health problems.

- Ozone is both natural and anthropogenic gas found in the stratosphere (formed naturally) and troposphere (formed by photochemical reactions of NO_x and VOCs). Although it helps to maintain life on the Earth by filtering harmful UV rays from outer space in the stratosphere, it has detrimental effects on humans and plants in the troposphere (21).

- Carbon monoxide is a harmful gas that results from burning fossil fuels. It prevents oxygen transportation from blood to tissues, and it leads to death at higher levels, and has some symptoms in humans, such as dizziness, confusion, and unconsciousness (22).
- Nitrogen oxides (NO_x : NO and NO_2) emissions usually arise from fossil fuels and biomass burning. The oxidation of NO_x forms nitric acid, which contributes to acid rain in the atmosphere (23,24).
- Sulfur dioxide (SO_2) comes from sulfur-containing fuels. The oxidation of SO_2 forms sulfuric acid (H_2SO_4), which is the primary precursor of acid rain (25,26).

1.1.2 Sources of Atmospheric Pollutants

Due to large-scale activities, anthropogenic emissions such as industrial activities, power plants, and cars are responsible for most air pollution. Although today cars are liable for almost 80 percent of pollution (27), anthropogenic emissions, such as planting processes, petrol stations, fuel tank heaters, and hygiene processes, may also affect the atmosphere (28). The pollutants may enter the atmosphere through both natural and anthropogenic sources. However, anthropogenic emissions have serious consequences. In the atmosphere, natural sources may be soil and rock, sea spray, forest decomposition, and volcanic activities, while anthropogenic sources may be fossil fuel combustion, agricultural activities, industrial activities, and biomass burning (29,30). Because the air pollutants arise from different source producers, they may be classified according to the four primary sources:

- Major sources originate from foundries, refineries, power plants, chemical industries, smelters, and incineration of municipal waste.
- Indoor area sources originate from cleaning agents, dry cleaners, glues and solvents, tobacco smoke, and paints.
- Mobile sources originate from motor vehicles such as buses, trucks, automobiles, railways, and airways.
- Natural sources originate from biomass burning, volcanic activities, and dust incursions (2).

Some salient pollutants' sources can be summarized as follows: Natural sources of SO₂ are sea salt, marine phytoplankton, and volcanoes, while anthropogenic source comes from fossil fuel combustion (31). For NO_x, power plants, vehicles, industrial production, and fossil fuel combustion are the anthropogenic sources, while forest wildfires, vegetation, and soils are the natural sources (32). Another important atmospheric pollutant is ammonia emitted from poultry waste, fossil fuel combustion, fertilizer, and agricultural waste (33). The sources of six common air pollutants and volatile organic compounds are shown in Table 1.1.

Heavy metals may enter the ecosystem through primary and secondary sources and natural sources. Primary sources comprise metal-based industries such as mining, smelting, and foundries. Besides the industries, the leaching of metals from various wastes and landfills, runoffs, livestock manure, and cars are also primary sources. Secondary sources come from using metal-containing chemicals in agriculture, such as pesticides, fertilizers, insecticides, and more. Natural sources include volcanic activity, metal corrosion, evaporation of metals from the soil and water and sediment, soil erosion, geological weathering, and re-suspension (34–40). Trace metals, mainly emitted from anthropogenic origins, have more harmful effects because they have a small size distribution (0.1-1 µm); therefore, they can stay in the atmosphere for an extended period and be carried extended distances by wind (41). Vehicular emissions have a significant contribution to the increase of trace elements in the atmosphere. For instance, Zn comes from tires, Mn from moving parts, and Cu from brake linings (42). On the other side, V is a tracer of fuel emissions (43), and Cr, Zn, Pb, As, Cd, Mn, Zn, and Ni exist in the atmosphere due to industrial, agricultural, and mining activities (44,45). Some sources of heavy metals and metalloids are shown in Table 1.2.

Table 1.1. Six common air pollutants and volatile organic compounds (46)

Pollutants and Examples	Main source	Persistence and Transformations
Carbon monoxide (CO)	Incomplete combustion of fossil fuels or biomass	Residency time in the atmosphere averages approximately two months
Nitrogen oxides (NO_x)	Burning of coal, oil, gasoline, and biomass; soil bacteria	Converted to nitric acid (HNO ₃) via a series of reactions in the atmosphere
Sulfur dioxide (SO₂)	Burning of coal, oil, and gasoline; metal smelting; volcanic eruptions	Converted to sulfuric acid (H ₂ SO ₄) via a series of reactions in the atmosphere
Ozone	Forms in the lower atmosphere (troposphere) via a series of reactions, in the presence of sunlight, between oxygen, water, NO _x , carbon monoxide, and volatile organic compounds	Residence time in the lower atmosphere averages a few months
Particulate matter	Fossil fuel and biomass burning; wind and water erosion associated with agricultural and construction activity	Removal of suspended particulates from either air or water-related to size, with the smallest particulates having the longest residence time in the medium
Lead	Coal-burning, metal smelting, oil, sewage	Persistent; biomagnifies in food chains
VOCs, acetone, benzene, formaldehyde, toluene	Evaporation of solvents, paints, gasoline, and other fuels; leaking underground storage tanks; improper disposal of household products; degassing of particleboard	Reacts with NO _x to produce ozone

Table 1.2. Sources of heavy metals and metalloids (46)

Heavy metal	Symbol	Source
Cadmium	Cd	Coal and municipal waste burning; emissions from metal plants
Arsenic	As	Erosion of natural deposits; agricultural and industrial particles; coal burning
Copper	Cu	Occurs in natural ores with other metals; emissions from metal smelters and refineries; coal burning
Chromium	Cr	Refining of metal ores and several industrial processes; coal burning
Mercury	Hg	Coal-burning; industrial processes; consumption of contaminated fish and shellfish
Lead	Pb	Paints in older buildings and furniture; plumbing; metal smelters; coal burning
Nickel	Ni	Oil and coal burning; metal smelters; nickel metal refining; sewage sludge incineration; industrial processes; contaminated food
Molybdenum	Mo	Coal-burning; metal smelters and refineries; mines; dust from contaminated soils; sewage sludge; contaminated food
Zinc	Zn	Coal and waste burning; sewage sludge; metal smelters; mining, dust from contaminated soils; contaminated food and water; galvanized pipes
Selenium	Se	Erosion of natural deposits; discharge of refineries containing petroleum and metal; burning of coal; contaminated food and water

Sources of atmospheric pollutants can be examined into three major groups: (i) marine sources, (ii) terrestrial sources, and (iii) anthropogenic sources (47). For instance, Na^+ and Cl^- ions are abundant in coastal areas, whereas Ca^{2+} , Mg^{2+} , and HCO_3^- are abundant in inland regions. Also, anthropogenic emissions such as SO_4^{2-} and NO_3^- primarily come from industrial and urbanized areas. Additionally, K^+ is a tracer of biomass burning (48).

1.1.3 Effects of Atmospheric Pollutants on the Other Environmental Compartments

Pollution in the atmosphere has an influence unfavorably on the natural environment. Atmospheric pollutants can be dispersed and transported to different environmental compartments due to the dynamic nature of the atmosphere. The most important effects of atmospheric pollutants on the other environmental compartments are shown in Figure 1.2 (49).

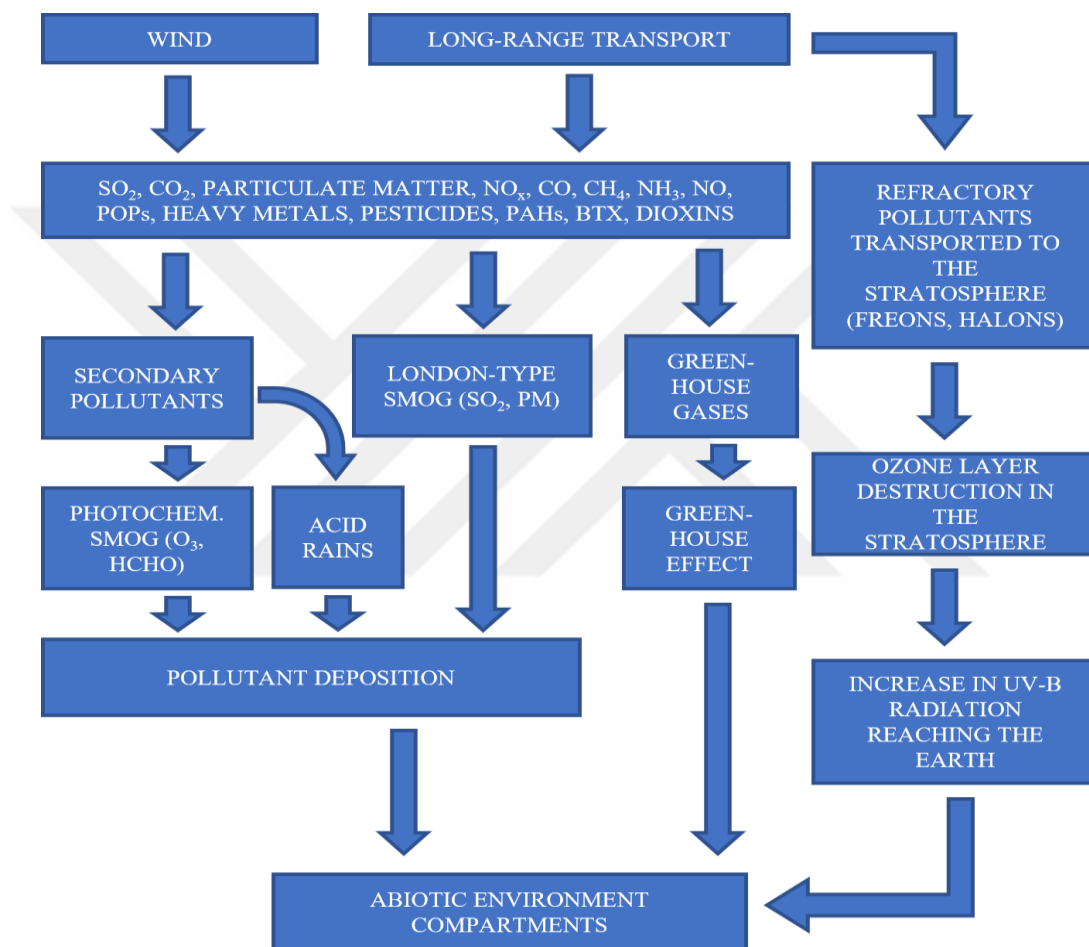


Figure 1.2. Effect of atmospheric pollutants on other environmental compartments (49)

Acid rain consists of secondary pollutants like SO₂ and NO_x, and it can be wet (snow, fog, rain) and dry (gases and particulate matters) forms. It strongly influences the soil and water environment and damages forests, buildings, monuments, and constructions. Haze, which causes reduced visibility of the atmosphere, is composed of fine particulate matter dispersed in the air. Gas emissions from anthropogenic sources are the primary reasons for the occurrence

of haze (2). Fog also causes reduced visibility of the atmosphere and consists of suspended droplets that have settled or evaporated. Fog takes place in the lowest parts of the atmosphere and extends up to 1000 m altitude (50).

1.1.4 Health Effects of Atmospheric Pollutants

Studies have shown that pollution in the air has lots of assorted impacts on human health. For instance, air pollutants have a negative role in vitamin D deficiency and bone mass (51); inhalation of them causes problems in the respiratory system, such as cough and sneezing (52); and also associated with a mind such as cognitive impairment, a decrease in IQ, and even memory loss (53). Further, the worst effect of air pollution is its association with lung, neck, and head cancer (13). Nowadays, air pollution has become the fourth risk factor that leads to early death more than alcohol use, malnutrition, and high body mass index. Moreover, millions of people died in 2019 from diseases, such as heart and respiratory diseases and lung cancer, led by air pollution (54).

Carbon monoxide may bind irreversibly to hemoglobin and reduce the oxygen-carrying capacity of the blood. Therefore, it causes dizziness and nausea at low concentrations, whereas it causes death at high concentrations. Lead causes problems in central nervous system function and development. For children, it reduces their IQ and learning capacity. Nitrogen oxides lead to irritation problems in the eyes, nasal passages, and lungs; they also increase the risk of lung infections. Ozone and particulate matter affect the respiratory system, causing breathing difficulties and irritation in the lungs. Sulfur dioxide causes breathing difficulties, especially for people with asthma (46).

Metalloids covalently bond with organic groups, and they cause the formation of lipophilic ions and compounds. The binding of these ions to non-metallic elements of cellular macromolecules causes the formation of toxic effects (55). Heavy metal uptake by humans occurs in four ways: Ingestion of contaminated food, inhalation from the atmosphere, drinking contaminated water, and skin contact from agriculture, pharmaceutical, manufacturing, residential and industrial areas (55,56). Since metals are not biodegradable and cannot be destroyed, the active element is either kept inside a protein or deposited in intracellular granules as an insoluble form for excretion or storage. Inhalation or ingestion of heavy metals causes bioaccumulation in our bodies, and hence

biological and physiological complications (54). The health effects of heavy metals and metalloids are shown in Table 1.3 (46).

Table 1.3. Health effects of heavy metals and metalloids (46)

Heavy metal	Symbol	Health effect
Cadmium	Cd	Animal studies indicate potential damage to the kidney, liver, lung, and bone; interferes with neurological development; probable carcinogen
Arsenic	As	Hemiplegia; stomach pain, nausea, vomiting; associated with cancer of the bladder, lung, and skin; thickening and discoloration of the skin
Copper	Cu	Irritation of nose, mouth, and eyes; stomach distress, vomiting; kidney and liver damage
Chromium	Cr	Irritation of the lungs; shortness of breath; decreased lung function; lung cancer
Mercury	Hg	Impaired neural development in developing infants and children; impairment of speech, hearing, and walking; muscle weakness in people of all ages; kidney damage, respiratory failure, and death at higher exposure
Lead	Pb	Developmental disorders, especially of the central nervous system; hearing problems; headaches; slowed growth in children; joint and muscle pain in adults
Nickel	Ni	Itching of fingers, hands, and forearms; stomach distress; lung and kidney damage; increased risk of nasal and lung cancers
Molybdenum	Mo	Weakness; fatigue; headaches; liver damage; mental disorientation; swollen and painful joints
Zinc	Zn	Stomach discomfort; skin irritations; anemia; damage to the pancreas
Selenium	Se	Irritation of the mucous membranes; bronchitis, bronchial pneumonia; loss of hair and nails; tooth decay; circulation problems; reduced mental alertness

Essential elements, which have biochemical and physiological functions in our bodies, are required to maintain life, but they may have detrimental effects when

they exist in large quantities. Essential elements can be categorized into three groups (55):

1. Major elements include hydrogen, carbon, nitrogen, and oxygen. They are essential for building blocks.
2. Macrominerals include sodium, magnesium, phosphorous, sulfur, chlorine, potassium, and calcium. They are needed for the ionic balance of structural compounds (amino acids and nucleic acids).
3. Trace elements include silicon, chromium, manganese, iron, cobalt, copper, zinc, selenium, molybdenum, and iodine.

The importance of essential elements can be listed as follows;

- Maintenance of skeletal structure formation,
- Acid-base equilibrium regulation,
- Maintenance of the colloidal system,
- Being constituents of crucial enzymes, structural proteins, and hormones (56,58,59).

Although essential elements benefit the human body, all metals may cause diseases when humans are exposed to excess amounts. Heavy metals affect cellular organelles and cell components, and the interaction of metals with DNA and nuclear proteins damages DNA, and therefore some problems occur like cancer formation and the death of cells. The classification of heavy metal carcinogenicity is shown in Table 1.4 (55,56).

Table 1.4. The classification of heavy metal carcinogenicity (55,56)

Group	Carcinogenicity Level	Heavy metal classification
Group 1	Carcinogenic	Compounds of arsenic, chromium VI, cadmium, nickel
Group 2A	Probably carcinogenic	Inorganic lead compounds
Group 2B	Possibly carcinogenic	Molybdenum trioxide, lead, metallic nickel and alloys, cobalt, molybdenum trioxide
Group 3	Carcinogenicity not classifiable	Compounds of chromium III, metallic chromium, selenium, copper, mercury
Group 4	Probably not carcinogenic	Manganese, silver, zinc

1.2 Acidification of Soil, Water, and Atmosphere

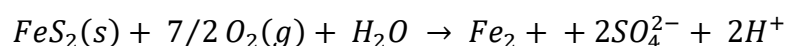
Frequently, acidity in the environment is derived from (i) power plants via the utilization of fossil fuels, (ii) extraction of resources via mining operations, and (iii) food production via fertilizer application. All of these processes cause acidification of the atmosphere, soils, and waters. Notably, increasing human population and resource consumption enhances acidification and eventually causes alteration of the Earth's environmental quality (60).

Generally, the oxidation-reduction reactions of carbon, iron, nitrogen, and sulfur-containing compounds cause an increase in acidity in the atmosphere, soil, and water.

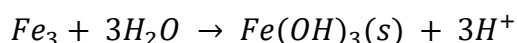
Table 1.5. Environmental effects of acidification processes by anthropogenic emissions (60)

Element oxidized	Means of human exacerbation	Environmental effect	Scale of effect	Nature of effect
S oxidation generates	Fossil fuel combustion	Acidic atmospheric deposition	Regional	Acidified receiving waters (freshwater); acidified soils
S oxidation generates strong acid, H ₂ SO ₄	Mining coal and base-metal sulfides: processing and smelting metal-sulfide ores	Acid mine drainage	Local	Acidified receiving waters (freshwater)
Free protons, H ⁺ , come from the hydrolysis and oxidation of Fe				
Oxidation of C causes weak acid, H ₂ CO ₃ , formation	Fossil fuel combustion; deforestation; cement manufacturing; biofuel development	Elevated CO ₂ in the atmosphere	Global	Acidification of oceans
Oxidation of N causes strong acid, HNO ₃ , formation	Fossil-fuel combustion; production and use of N fertilizers	Acidic atmospheric deposition	Regional	Acidified receiving waters (freshwater); acidified soils

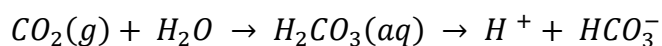
In the aquatic environment, if the pyrite rocks come into contact with O₂ and water, sulfide in pyrite rocks can be oxidized to form acidity, and oxidative dissolution of marcasite and pyrrhotite can be explained by this reaction.



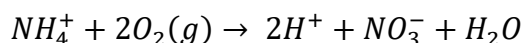
The cation formed by the dissolution of a mineral solid in water undergoes a hydrolysis reaction, which causes the formation of ferric oxyhydroxide in the solid phase, and the H⁺ ion resulting from the dissolution of H₂O is released in the water, leading to acidification.



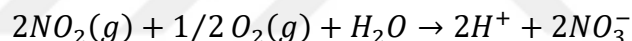
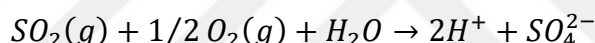
Furthermore, dissolution, hydration, and dissociation of CO₂ lead to the formation of carbonic acid, which contributes to the natural weathering reactions.



Biomasses decomposed by microbial organisms reveal ammonium which can be volatilized to the atmosphere as gaseous NH_3 or stayed in the soil as NH_4^+ . In the soil, a nitrification reaction can occur in the presence of oxygen, which leads to the acidification of the soil (60).



The unpolluted atmosphere is in equilibrium with water, and it naturally contains CO_2 . Therefore, the unpolluted atmosphere has a slightly acidic character and approximately has pH 5.6 (61,62). In response to this, anthropogenic emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x : $\text{NO} + \text{NO}_2$) cause the acidification of the atmosphere because of the oxidation and hydration reactions of S and N compounds that occur in the atmosphere (63). After that point, strong acids, H_2SO_4 and HNO_3 , form in the atmosphere, and they turn back to the Earth as H^+ , SO_4^{2-} , and NO_3^- with atmospheric deposition (64). These reactions can be written as;



1.3 Rainwater Chemistry

Rainwater chemistry includes complex interactions between cloud dynamics, microphysical processes, and atmospheric chemical reactions (65). The chemical content of rainwater is mainly composed of major and minor ions. Major constituents are sodium, potassium, magnesium, calcium, chloride, bicarbonate, sulfate ions, nitrate, nitrite, and other nitrogen compounds. In contrast, minor constituents are iodine, bromine, boron, iron, alumina, and silica (66). The chemical content of rainwater is mainly affected by anthropogenic emissions such as vehicle emissions, road dust, metal smelter processes, fossil-fuel combustion, and domestic heating (67–69). Because rainwater is a primary potable water source on Earth (70), contamination of rainwater with pollutants may cause strong effects on the terrestrial and aquatic ecosystem in the environment (71). For that reason, it is vital to understand the chemical composition of the atmosphere, especially in some large cities with high atmospheric pollution, because in this way, control measures can be taken to reduce air pollution (72).

1.3.1 Deposition Phenomena

Atmospheric deposition is an effective and important process for removing pollutants, including gases and particulate matters, from the atmosphere. On the other side, atmospheric pollutants are transported to terrestrial and aquatic parts of Earth (73). Therefore, it may cause environmental problems such as acidification and the eutrophication of natural ecosystems (74). Eutrophication is a process of accumulating nutrients in the ecosystem due to anthropogenic activities. As a consequence of eutrophication, there is an increase in nutrients, sediments, and growth of aquatic plants, whereas there is a decrease in oxygen, lake depth, and biodiversity (46). Atmospheric deposition of pollutants can occur through wet and dry deposition.

1.3.1.1 Wet Deposition

Wet deposition is crucial for the scavenging of atmospheric pollutants. Pollutants can be scavenged by clouds, liquid, and solid precipitation processes. After scavenging, the pollutants turn back to Earth's surface (49). Wet deposition is affected by many conditions (75);

- Meteorological and topographic features,
- Precipitation type and amount,
- Interaction of aerosols, clouds, and gaseous pollutants,
- Availability of cloud condensation nuclei,
- The concentration of the particulate atmospheric substance,
- The solubility of a particulate atmospheric substance,
- Availability of substances acting as catalysts.

Wet deposition might appear in different ways, such as atmospheric precipitation, surface condensation, and direct deposition. Although different forms of atmospheric precipitation, including liquid, solid, and freezing, have an essential role in transferring atmospheric pollutants to the ground, other forms of wet deposition should not be disregarded. For example, direct surface condensation appears after water vapor is condensed or sublimated due to contact with radiation-cooled surfaces, such as dew and hoar frost. On the contrary to precipitation, others are formed near the surface of the atmosphere. Comprehensive information for the classification of wet deposition is shown in Figure 1.3 (49).

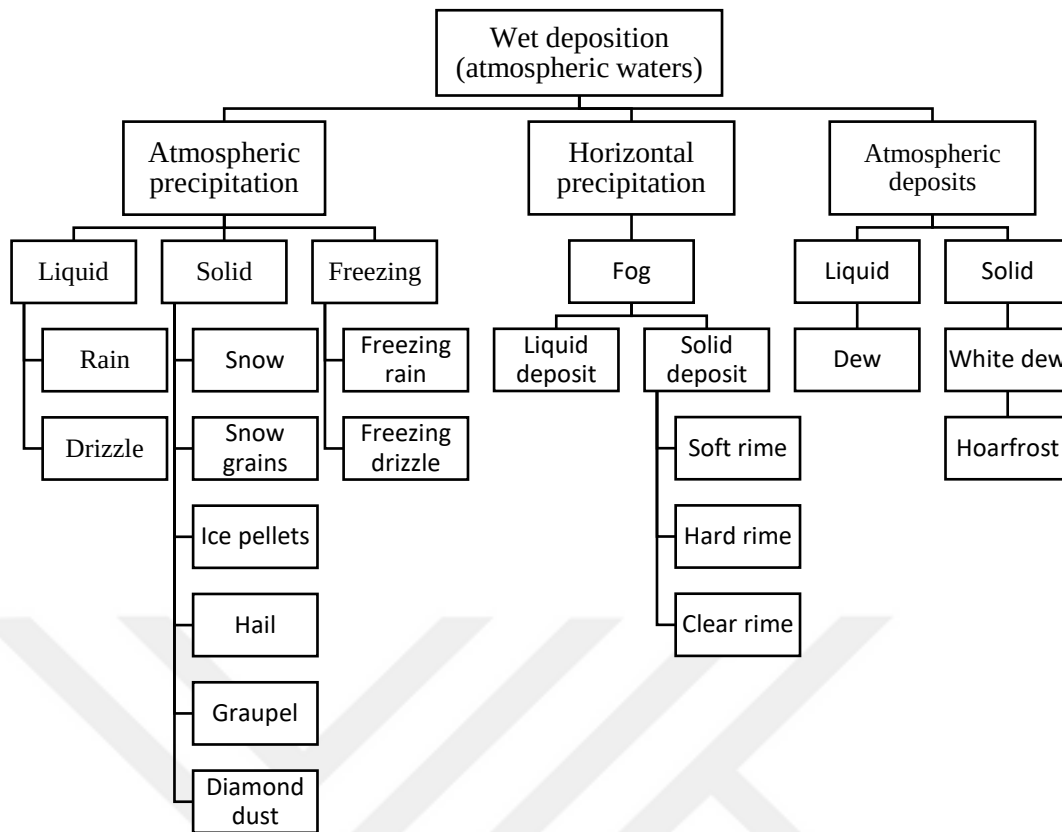


Figure 1.3. Classification of atmospheric precipitation (49)

Pollutants are scavenged from the atmosphere by three mechanisms: in-cloud scavenging, below-cloud scavenging, and nucleation.

- In-cloud scavenging takes place when diffusive and inertial collisions occur between aerosol and particles.
- Below-cloud scavenging occurs by rain, hail, or snow, and it takes place when aerosol particles larger than 1 μm scavenged inertially or gases are absorbed.
- Nucleation occurs through water condensation on the surfaces of aerosol particles that act as cloud condensation nuclei (49).

1.3.1.2 Dry Deposition

Dry deposition is also an important route for removing particles from the atmosphere in dry weather through the control of inertial impaction, Brownian diffusion, and gravitational sedimentation processes (76). Dry deposition is measured quantitatively by using the dry deposition flux (F) ($\mu\text{g}/\text{area time}$),

$$F = V(d) \times C,$$

which is a function of dry deposition velocity (V_d) (cm s^{-1}) and concentration of a chemical in the air (C) ($\mu\text{g m}^{-3}$). Dry deposition velocity (V_d) may be calculated by using the resistance model that is based on the resistance to transport for each step in the process,

$$V(d) = \frac{1}{r(a)+r(b)+r(c)} + v(g),$$

where $r(a)$, $r(b)$, and $r(c)$ are the resistance to aerodynamic transport, transport through the boundary sublayer, and the collection by the surface, respectively (73). Dry deposition velocity $V(d)$, which is a function of particle size and wind speed, increases with decreasing particle diameter when particle size range is $<0.1 \mu\text{m}$; is at minimum when particle size range is between $0.1\text{--}1 \mu\text{m}$; increases with increasing particle diameter when particle size range is $>1 \mu\text{m}$ (77).

Atmospheric parameters, surface properties, and particle characteristics have an impact on particle deposition. The most important atmospheric parameters are wind speed, humidity, stability, and temperature, whereas the most important surface properties can be given as chemical and biological reactivity, the geometry of roughness elements, terrain characteristics, and wetness. Lastly, particle characteristics also affect the dry deposition, and these can be listed as the size, shape, density, reactivity, hygroscopicity, and solubility of particles (73).

1.4 Analysis of Samples

1.4.1 Ion Chromatography

Ion chromatography is a commonly used and efficient method for separating, identifying, and determining ions (78). The general scheme of ion chromatography is illustrated in Figure 1.4. The analysis of ions in a solution is an analytical problem. Although quick and sensitive analytical methods such as AAS, ICP, and polarography for cation analysis have been present for a long while, high-sensitive methods have not been available for anion analysis before ion chromatography. The classical methods (titration, photometry, gravimetry) were laborious, complicated, and time-consuming for anion analysis. On the contrary, ion chromatography provides the following advantages (79):

- Speed
- Sensitivity
- Selectivity
- Simultaneous detection
- Stability of the separator columns

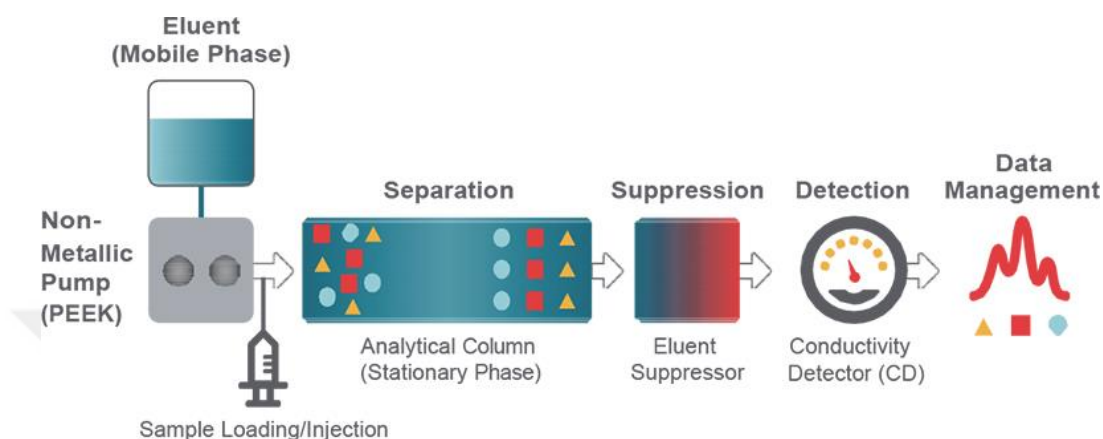


Figure 1.4. Schematic diagram of ion chromatography (80)

The method is based on the interaction of ions with the stationary phase (resin) and the mobile phase (eluent). The stationary phase is a polymeric resin modified with ion-exchange groups. Generally, the sulfonic acid group $-\text{SO}_3^-\text{H}^+$, a strong acid, and the carboxylic acid group $-\text{COO}^-\text{H}^+$, a weak acid, are used as an active site of cation-exchange resins, whereas tertiary amine groups $-\text{N}(\text{CH}_3)_3^+\text{OH}^-$, a strong base, and primary amine groups NH_3^+OH^- , a weak base, is used as an active site of anion-exchange resins (78).

The mobile phase is transferred to the system by a pump. The valve injector syringes the sample into the system, as shown in Figure 1.4. The sample injection is loaded into the system under atmospheric pressure, and then the mobile phase carries the sample to the column. Although injected volume is between 5 and 100 μL in general, the smaller injection volume can be used for capillary-scale ion chromatography and the larger volume for manual injection. The separatory column is the most significant component of the system. Therefore, the choice of an appropriate stable phase and chromatographic conditions are needed for high-quality analysis. As a heart of ion chromatography, the suppressor improves the signal-to-noise ratio. After separation, the eluent conductivity is reduced with a suppressor by exchanging the eluent and sample counter ions with suppressor-

derived ions. This process also reduces the associated noise while increasing the conductivity response of most analytes. Furthermore, the detector is used for the detection and quantification of the analytes. The performance of a detector depends on some criteria:

- Sensitivity
- Linearity
- Resolution (detector cell volume)
- Noise (detection volume)

Quantitative results obtained from chromatographic signals displayed as the chromatogram are evaluated according to the areas or heights of the peak. Finally, inert and non-metallic materials must be used for all components of the ion chromatography system due to protect them from the corrosive effects of the strong acids and bases (79).

1.4.2 ICP-MS

Inductively coupled plasma-mass spectrometry (ICP-MS) is a very efficient and popular technique for analyzing most of the elements in the periodic table. Environmental, geological, semiconductor, biomedical, and nuclear application fields constitute 80% of the use of ICP-MS. The elements shown in color in Figure 1.5 can be analyzed by ICP-MS, while elements with white color are either unmeasurable or have no isotopes (81).

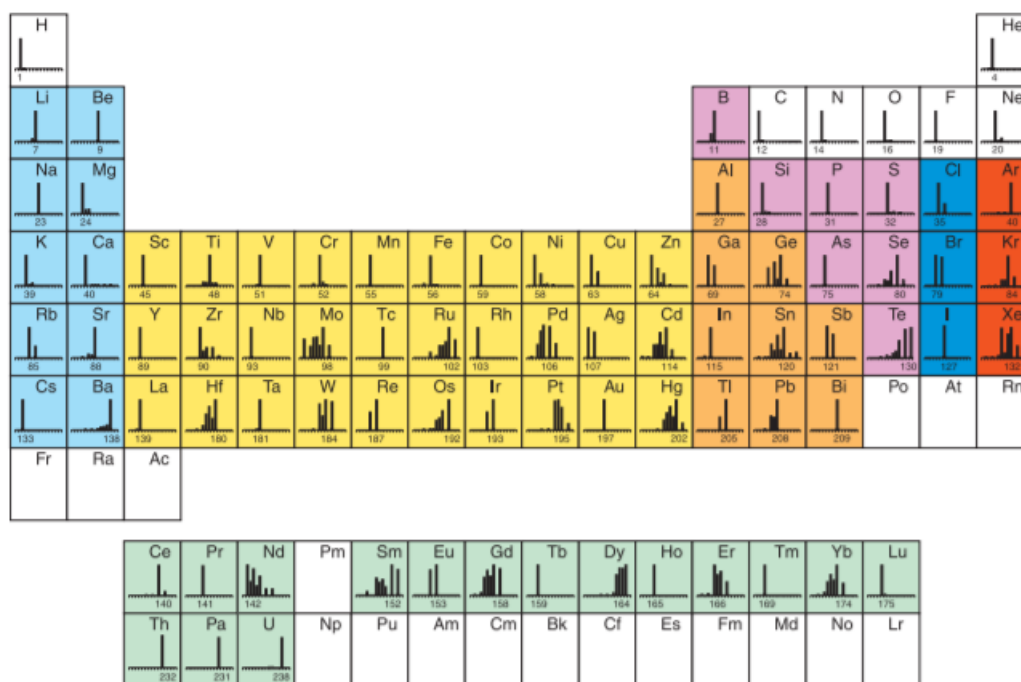


Figure 1.5. Elements analyzed by ICP-MS (82)

The other atomic spectroscopic methods, such as flame atomic absorption (FAA), electrothermal atomization (ETA), and inductively coupled plasma-optical emission spectrometry (ICP-OES), also determine the elements (81). However, compared to others, ICP-MS has some advantages, such as highly sensitive analysis – lower detection limits (ppt to ppq) for most elements, simultaneous multi-elemental analysis, the possibility of isotopic analysis, and quick determination of quality and quantity (83). ICP-MS consists of the following parts, as seen in Figure 1.6.

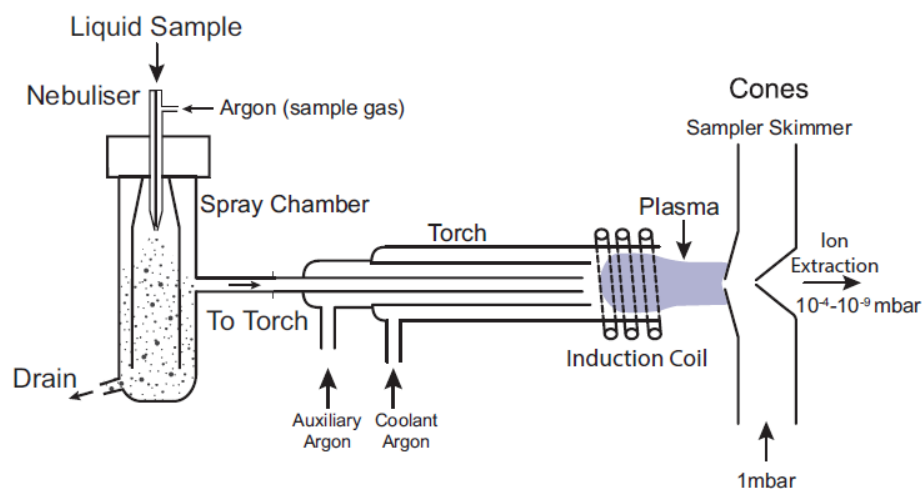


Figure 1.6. Individual components of ICP-MS instrument (84,85)

The components of ICP-MS are briefly described below (82):

- The sample introduction system transfers the samples into the system. It includes a nebulizer and a spray chamber.
- The ICP torch and RF coil produce the argon plasma, which is the ion source of the ICP-MS.
- Interface links the atmospheric pressure ICP ion source to the high vacuum mass spectrometer.
- The vacuum system creates a high vacuum for ion optics, quadrupole, and detector.
- Collision/reaction cell helps to remove interferences that may reduce the detection limits.
- Ion optics ensures neutral species and photons are ejected from the ion beam and directs the desired ions to the quadrupole.
- The mass spectrometer is a mass filter and classifies ions by their mass-to-charge ratio (m/z).
- The ions coming out of the quadrupole are counted by the detector.
- Data handling and system controller enables all aspects of instrument control and data processing to be controlled to achieve the final concentration of results.
- ICP-MS cones are composed of a sampler and skimmer cone. The interface, formed from cones, is located between the ICP and MS, and it effectively transports the ions to the mass spectrometer.

2. AIM AND SCOPE OF THE STUDY

Air pollutants such as sulfur dioxide, nitrogen oxides, and heavy metals have adverse impacts on human health and the ecosystem, both directly and indirectly. For example, high exposure to lead, arsenic, and chromium may cause different types of cancer. On the other hand, sulfur dioxide and nitrogen oxides are the primary acid precursors, and they may have destructive effects on the ecosystem. For that reason, it is vital to determine the air pollution level and sources of air pollutants. In this way, some control measures can be taken to reduce pollution levels.

Therefore, the primary purpose of this study is to gain information about the sources of air pollutants in urban and semi-urban sites, either local or long-range transport. Moreover, this study focused on the following objectives:

- To evaluate and compare the acidity of rainwater samples collected in urban and semi-urban areas of Bolu.
- To quantify and examine the major ions and trace elements variability in rainwater samples.
- To compare the spatial variability of the chemical composition of rainwater samples.
- To understand the neutralization capacity of rainwater.
- To check data quality by calculating the anion-to-cation ratio and explaining the differences of the sampling site.
- To evaluate the level of air pollution in Bolu in comparison with the literature.
- To evaluate the effects of various air masses on rainwater chemistry by using the Back Trajectory Model.
- To evaluate whether rainwater is suitable for agriculture and soil.

3. MATERIALS AND METHODS

3.1 Study Area

Bolu, one of the provinces affiliated with the North Central Anatolia Clean Air Center, is located in the Western Black Sea Part of the Black Sea Region. Its surface area is 1,524 km². The average altitude is 1,000 m, and the altitude of the central district is around 725 m. It is located between 40° 06' and 41° 01' north latitudes and 30° 32' and 32° 36' east longitudes. Bolu is surrounded by Zonguldak, Düzce, Sakarya, Eskişehir, and Ankara from the north, northwest, west, south, and southeast and east, respectively. Bolu has nine districts, including the city center, as shown in Figure 3.1.

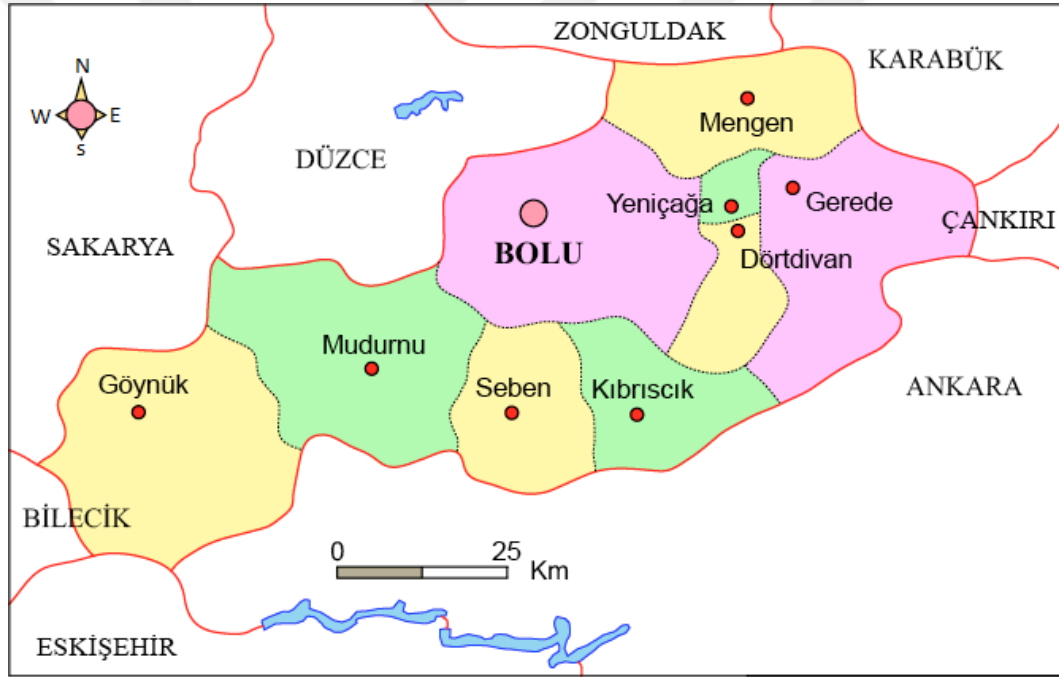


Figure 3.1. The city map of Bolu (85)

Bolu has many natural lakes and ponds. The mountains surrounding the city center of Bolu prevent the dispersion of pollutants and cause them to accumulate, especially in stagnant conditions. The mountain heights within the city border increase from North to South and West to East. The Bolu Mountains are located just after the mountains running parallel to the Black Sea coast. The highest points of the Bolu Mountains are Çele peak (1,980 m) and Naldöken hills (1,911 m) (85).

The province's general population was 316,126, the urban population was 233,379, and the rural population was 82,747 in 2019. While the ratio of the urban

population to the total population was 73.8%, the ratio of the rural population to the total population was 26.2%. Bolu City Center Population was 180,197 (86).

The distribution of the industrial sector, which is described as a point source, is dominant in the city center, Gerede, Mengen, Göynük, and Mudurnu districts of Bolu. Bolu mixed, and textile specialized organized industrial zone, cement factory, and small industrial site are located in the central district on the Ankara-Istanbul highway. In addition, there is an organized industrial zone where the wood-furniture industry, textile, and electronics sectors are among the important active producers. Two Organized Industrial Zones, where forest products production and leather processing sectors operate, are located in the Gerede district. The poultry sector and wood processing facilities are mainly located in the Mudurnu and Mengen districts. In the Göynük district, there are small-scale poultry facilities and a thermal power plant (Aksa Göynük Enerji Santrali) with a power of 270 MW (85).

Although the Black Sea climate type (semi-humid and semi-arid) is commonly effective in the province of Bolu, the Anatolian climate type is dominant in the southern parts of the Göynük district. Bolu is generally warm in summer, cold in winter, and rainy in all seasons. There are different climatic subzones from place to place in Bolu, Gerede, Seben, and Kıbrısık (87).

3.2 Meteorological Parameters

The daily meteorological parameters for the city center of Bolu and the BAIBU campus, including average wind direction, minimum-average-maximum temperatures (°C), total rainfall amount (mm), and average humidity (%), have been obtained for the sampling period from the Bolu meteorology directorate and are given in Tables 3.1, 3.2, and Figures 3.2, 3.3, 3.4 and 3.5.

Table 3.1. Dominant daily wind directions and wind speeds (m/s) for the city center covering the sampling period

1.05.2020	WSW	2.1	11.05.2020	W	1.5	21.05.2020	S	6.7	31.05.2020	WSW	0.0	10.06.2020	WSW	0.0	20.06.2020	SW	0.0
2.05.2020	W	5.1	12.05.2020	S	4.6	22.05.2020	SSW	1.0	1.06.2020	SSE	0.0	11.06.2020	W	0.0	21.06.2020	S	0.0
3.05.2020	ENE	0.0	13.05.2020	S	1.5	23.05.2020	WNW	0.0	2.06.2020	SSE	0.0	12.06.2020	SSW	0.0	22.06.2020	NW	0.0
4.05.2020	S	3.1	14.05.2020	S	3.6	24.05.2020	W	1.0	3.06.2020	SSW	0.0	13.06.2020	W	0.0	23.06.2020	W	13
5.05.2020	SW	0.5	15.05.2020	W	4.1	25.05.2020	WSW	2.1	4.06.2020	SSE	0.0	14.06.2020	E	0.0	24.06.2020	W	8.2
6.05.2020	W	3.1	16.05.2020	SW	5.7	26.05.2020	SSE	0.0	5.06.2020	SSW	0.0	15.06.2020	SSW	0.0	25.06.2020	S	7.2
7.05.2020	WSW	2.6	17.05.2020	W	1.5	27.05.2020	SW	1.0	6.06.2020	SSE	2.1	16.06.2020	NNW	0.0	26.06.2020	SW	6.2
8.05.2020	W	1.0	18.05.2020	SW	2.1	28.05.2020	SSE	0.0	7.06.2020	SSE	1.0	17.06.2020	E	0.0	27.06.2020	SW	6.7
9.05.2020	W	3.1	19.05.2020	E	2.1	29.05.2020	NW	0.0	8.06.2020	S	0.0	18.06.2020	SE	0.0	28.06.2020	SSW	7.7
10.05.2020	W	1.0	20.05.2020	W	7.7	30.05.2020	ENE	0.0	9.06.2020	N	0.0	19.06.2020	S	0.0	29.06.2020	SSW	5.7

Table 3.2. Dominant daily wind directions and wind speeds (m/s) for the BAIBU campus covering the sampling period

1.05.2020	NNW	6.9	11.05.2020	NNW	6.8	21.05.2020	NNW	11	31.05.2020	NW	6.6	10.06.2020	NNW	7.4	20.06.2020	NNW	8.4
2.05.2020	NNW	7.9	12.05.2020	S	7.5	22.05.2020	NW	11	1.06.2020	NW	7.5	11.06.2020	NNW	5.7	21.06.2020	NNW	7.0
3.05.2020	NNW	5.5	13.05.2020	NNW	8.2	23.05.2020	NNW	7.3	2.06.2020	NW	5.1	12.06.2020	NW	7.4	22.06.2020	N	7.3
4.05.2020	NW	7.6	14.05.2020	NNW	8.3	24.05.2020	NW	7.0	3.06.2020	SE	7.5	13.06.2020	SSE	5.1	23.06.2020	NNW	12
5.05.2020	NNW	8.8	15.05.2020	NNW	6.6	25.05.2020	SE	7.2	4.06.2020	SE	6.7	14.06.2020	NW	6.4	24.06.2020	WNW	6.2
6.05.2020	NW	9.5	16.05.2020	NW	7.6	26.05.2020	NW	3.4	5.06.2020	NW	6.3	15.06.2020	NW	4.6	25.06.2020	NNW	7.3
7.05.2020	NW	6.5	17.05.2020	NW	5.3	27.05.2020	NNW	9.1	6.06.2020	NNW	8.5	16.06.2020	NW	6.8	26.06.2020	NNW	7.7
8.05.2020	NNW	9.1	18.05.2020	NW	8.0	28.05.2020	NW	7.1	7.06.2020	NNW	9.6	17.06.2020	NW	7.3	27.06.2020	NW	8.2
9.05.2020	NNW	8.0	19.05.2020	NW	6.9	29.05.2020	NNW	6.0	8.06.2020	SE	8.7	18.06.2020	NW	8.0	28.06.2020	NNW	7.7
10.05.2020	NNW	6.5	20.05.2020	NNW	9.1	30.05.2020	NW	6.4	9.06.2020	NW	8.0	19.06.2020	SE	8.8	29.06.2020	NW	8.1

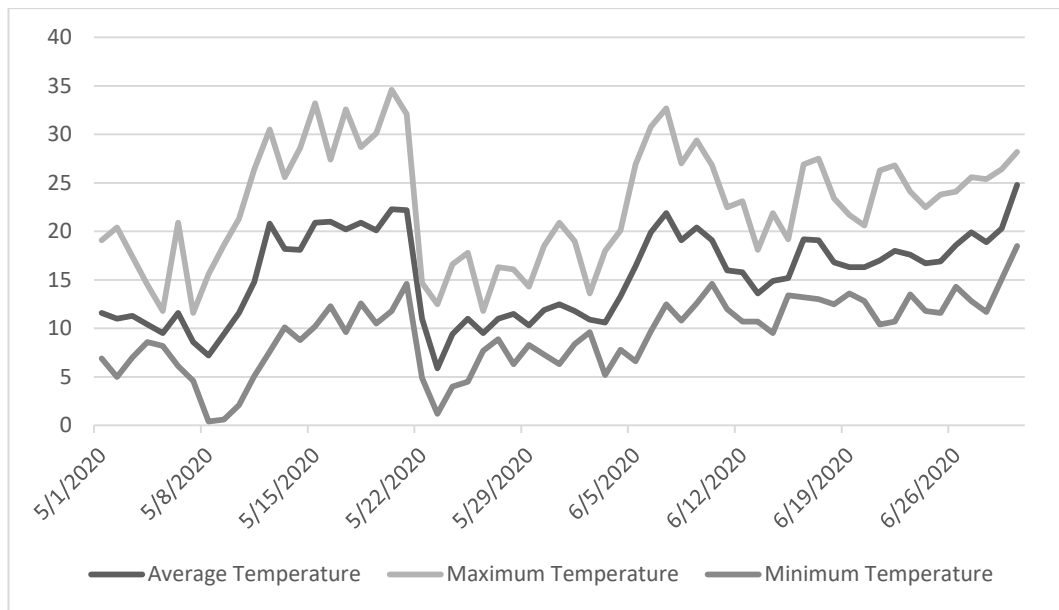


Figure 3.2. Daily minimum-maximum-average temperatures for the city center of Bolu

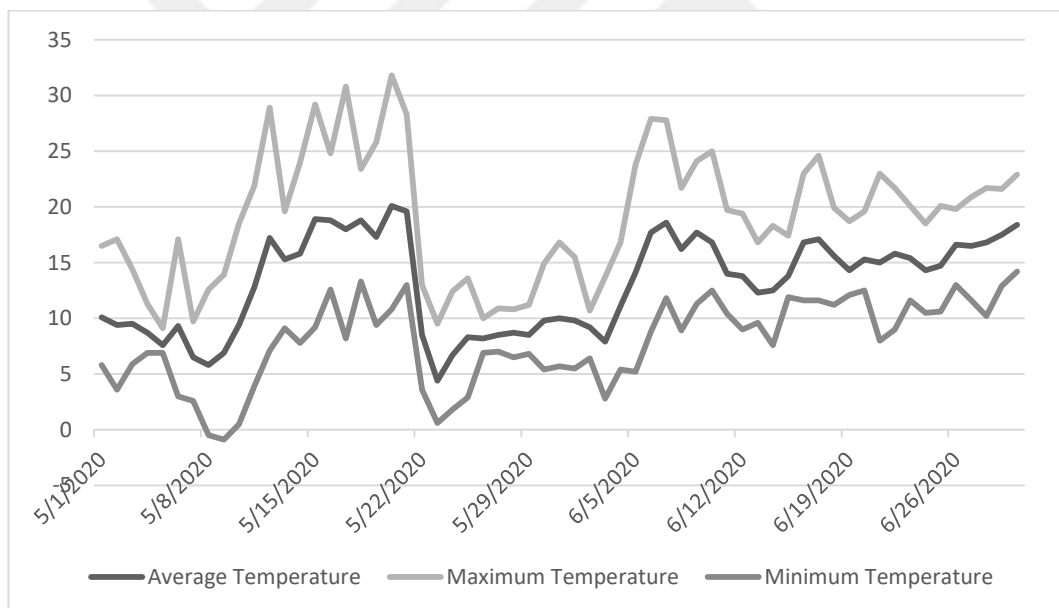


Figure 3.3. Daily minimum-maximum-average temperatures for the BAIBU campus

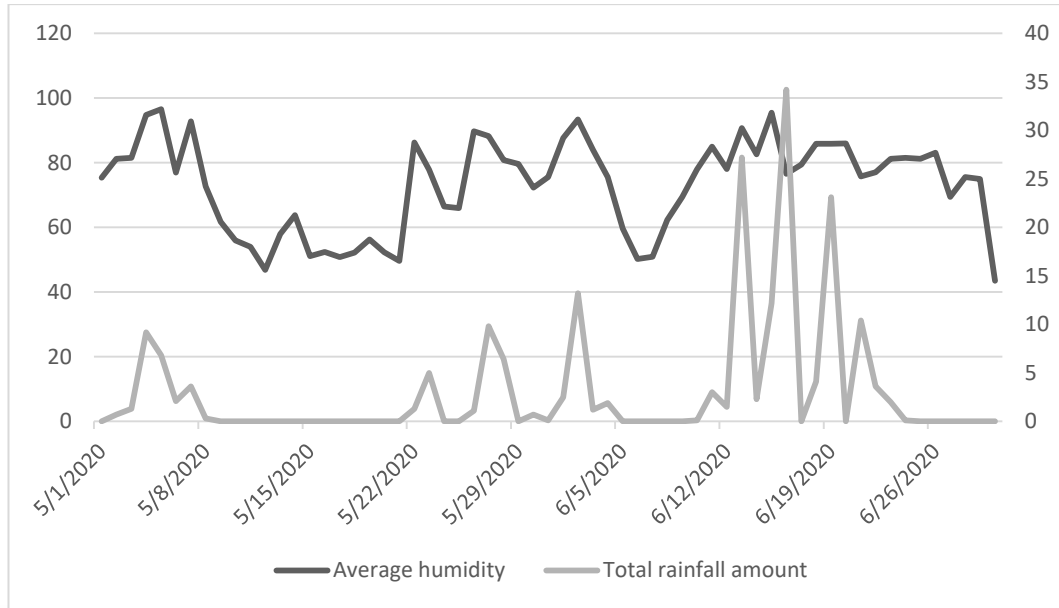


Figure 3.4. Average humidity and total rainfall amount for the city center of BOLU

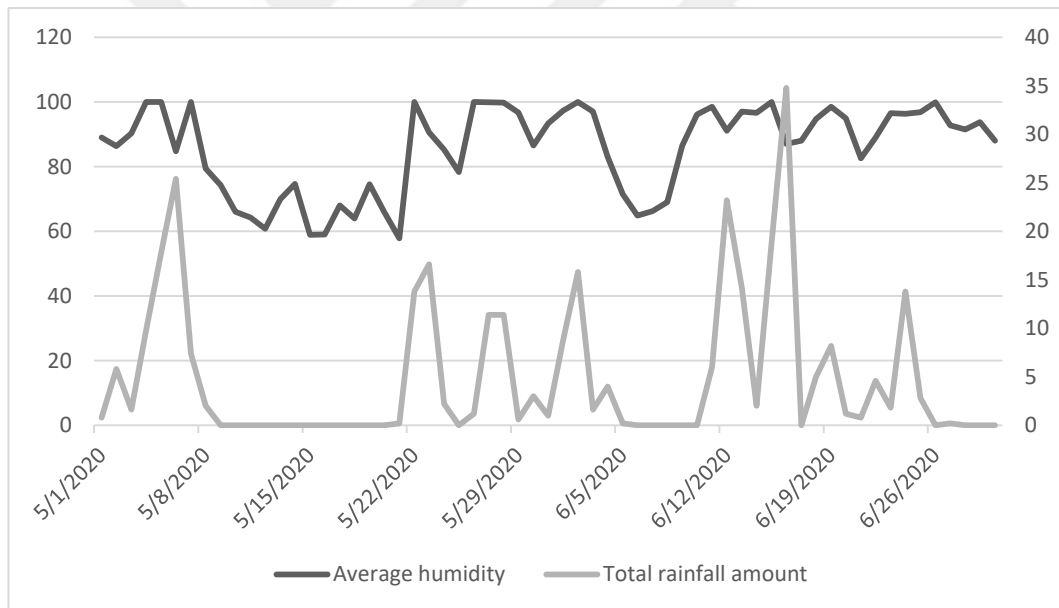


Figure 3.5. Average humidity and total rainfall amount for the BAIBU campus

3.3 Sample Collection

Volume-based fractional wet deposition samples were collected at two locations in Bolu between May 2020 and June 2020. The first sampling point was located in the city center of Bolu on the 40°43'40.8"N, 31°36'07.2"E coordinates, and 742 m above sea level. The second sampling point was located in the Bolu Abant Izzet Baysal University Campus (BAIBU) on the 40°42'42.6"N,

31°30'33.5"E coordinates, and 842 m above sea level. The map of sampling points is shown in Figure 3.6.

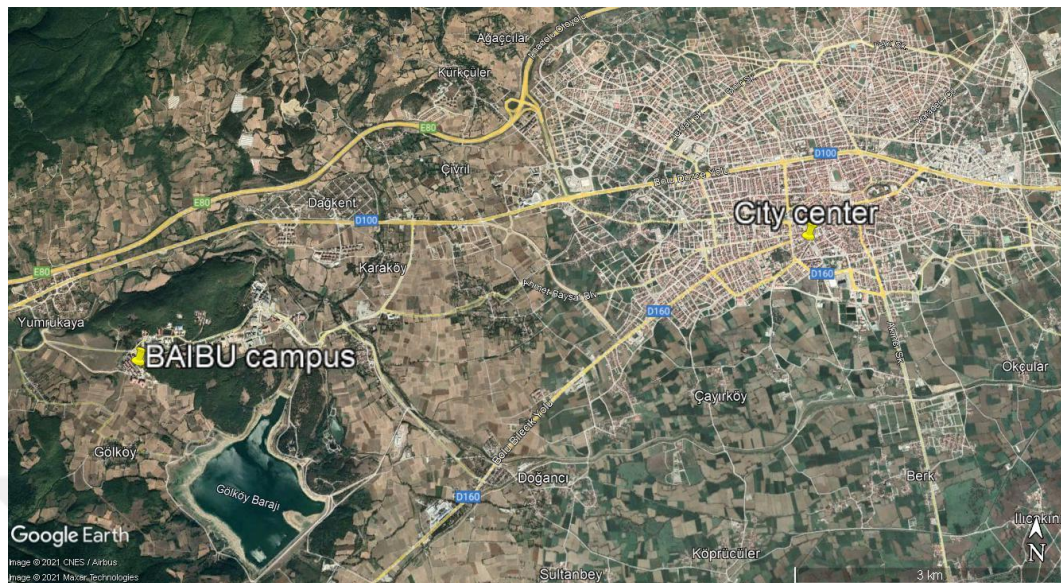


Figure 3.6. Sampling points

A total of one hundred sixty-seven samples were manually collected during two months by using 100 mL high-density polyethylene bottles with a funnel (Picture 3.1).



Picture 3.1. Manual system for collection of rainwater samples

One hundred twenty-one samples were collected in the city center, the urban area in Bolu. Forty-six samples were collected in Bolu Abant Izzet Baysal University Campus, a semi-urban area in Bolu. The number of fractions collected from the city center and BAIBU campus and the date of the fraction are shown in Figure 3.7 and Figure 3.8, respectively.

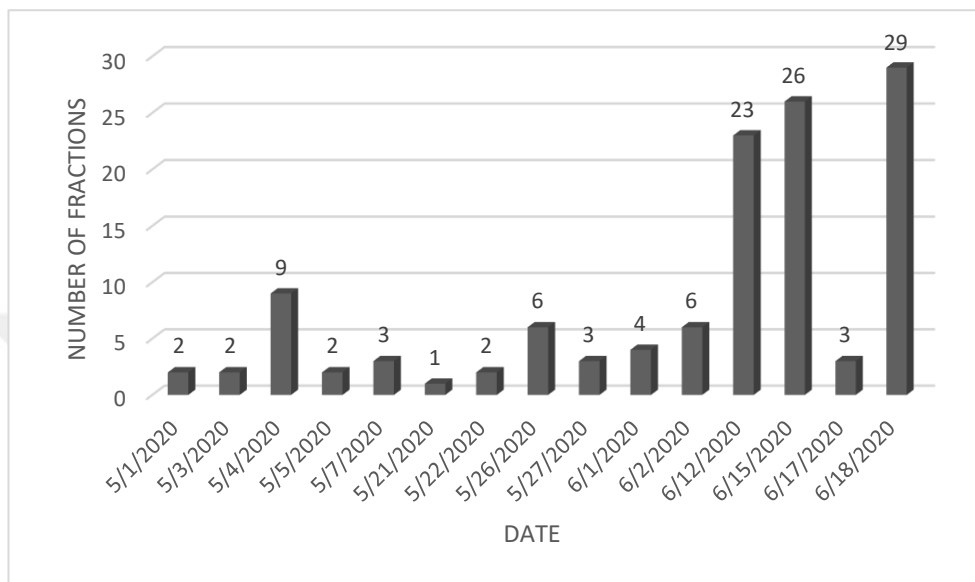


Figure 3.7. The number of fractions collected from the city center and the date of the fraction

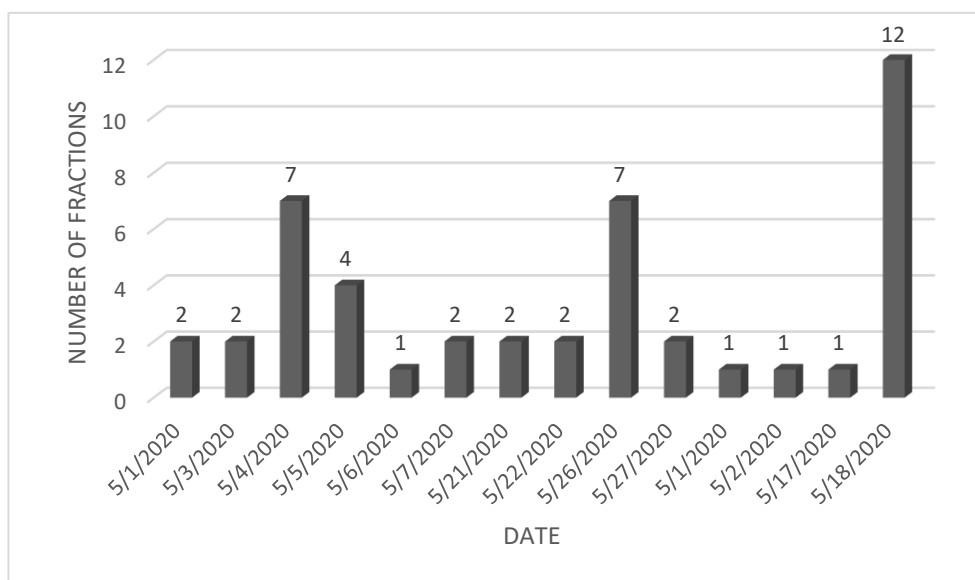


Figure 3.8. The number of fractions collected from the BAIBU campus and the date of the fraction

3.4 Reagent and Material

Reagents and chemicals were in analytical grade for this study. The mixed calibration standard-3 solution was purchased from Perkin Elmer and used to calibrate ICP-MS. The anions standard solutions that contain anion mix seven components and cation mix six components were purchased from Thermo Fisher Scientific and used for IC analyses.

In the laboratory, the pH and the volume of the samples were measured soon after each sampling. Then, 15.0 mL from all samples were filtered into the plastic centrifuge tubes using a 0.220 μm cellulose acetate filter, and 5.00 mL of samples were transferred to vials for ions analysis. The remaining parts were stored at 4.00 $^{\circ}\text{C}$ in the refrigerator for the analysis of elements.

For the element analysis, 20.0 mL was taken from the samples and acidified using 3.00 mL 60.0 % supra pure HNO_3 (Merck, Germany), 1.00 mL supra pure 30.0 % HCl (Merck, Germany), and 0.500 mL 40 % supra pure HF (Merck, Germany). After acidification, the samples were digested according to the procedure given in the water EPA 3015 method in the microwave digestion oven (MILESTONE Ethos One), and the final volumes of the samples were completed to 25 mL with deionized water. Then, the samples were concentrated to 5.00-7.50 mL in an 80.0 $^{\circ}\text{C}$ water bath, and the final volumes of the samples were completed to 10.0 mL with deionized water. The microwave oven program is shown in Table 3.3.

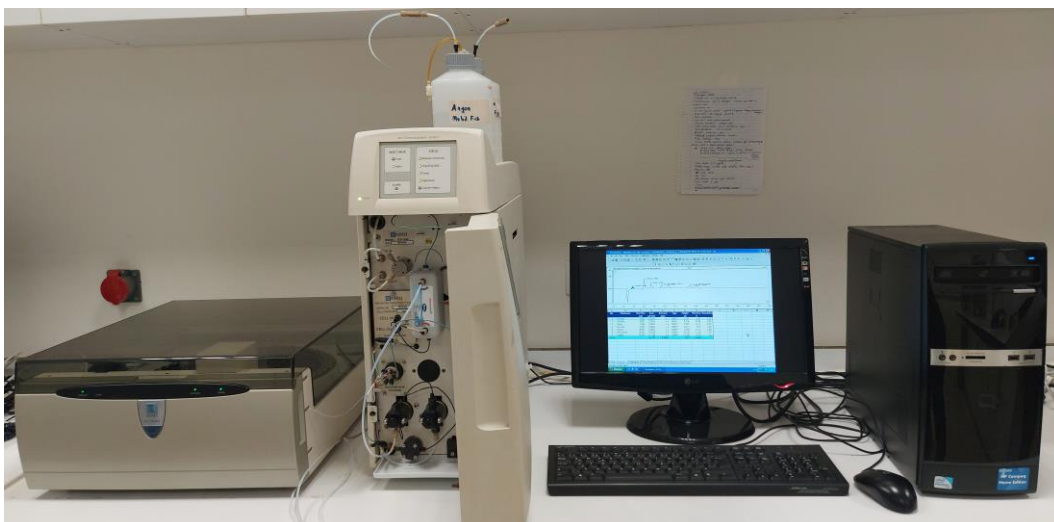
Table 3.3. Microwave oven program

Stage	Temperature ($^{\circ}\text{C}$)	Ramp (mm:ss)	Hold (mm:ss)	Pressure (psi)	Power (W)
1	175	10:00	10:00	50.0	90.0

3.5 Analysis

3.5.1 IC Analysis for Ions

Determination of anions (fluoride, chloride, nitrite, bromide, nitrate, phosphate, sulfate) and cations (lithium, sodium, ammonium, potassium, magnesium, calcium) was performed by using DIONEX 1100 model ion chromatography system (Picture 3.2).



Picture 3.2. A photo of Ion Chromatography system in the laboratory

AS9-11C column and AC9-HC guard column were utilized for anions, and sodium carbonate was used as an eluent. CS12-A column and CG12-A guard column were utilized for cations, and methanesulfonic acid was used as an eluent. The other properties of the operation program for the IC system are shown in Table 3.4.

Table 3.4. The operation program for the Dionex ICS-1100 system

	Anion	Cation
Mobile phase	9.00 mM Na ₂ CO ₃ (250 x 4 mm)	20.0 mM Methanesulfonic acid
Column	Ionpac AS9-11C	Ionpac CS12-A (250 x 4 mm)
Guard column	Ionpac AG9-HC (50.0 x 4.00 mm)	Ionpac CG12-A (50.0 x 4.00 mm)
Suppressor	ASRS – 4.00 mm	CSRS – 4.00 mm
Suppressor current	45.0 mA	65.0 mA
Detector	Conductance detector	Conductance detector
Pressure (psi)	2000-3000	2000-3000
Oven temperature	30.0 °C	30.0 °C
Background conductance	< 30.0 µS	0.500 – 2.00 µS
Flow rate	1.00 mL/min	1.00 mL/min
Injection volume	500 µL	1000 µL
Rate of data transfer	5.00 Hz	5.00 Hz
Duration	30.0 min	15.0 min

3.5.2 ICP-MS Analysis for Elements

Determination of elements (Ag, Al, As, Ba, Bi, Cd, Co, Cr, Cs, Cu, Fe, Ga, Li, Mg, Mn, Mo, Ni, Pb, Sb, Sn, Sr, V, Zn) was performed by using Perkin-Elmer ELAN DRC-e model ICP-MS system equipped with a Scott Spray Chamber (Picture 3.3).



Picture 3.3. A photo of the Perkin-Elmer ELAN DRC-e model ICP-MS system in the laboratory

Peak hopping was used as a scanning mode, and the standard mode was ^{107}Ag , ^{27}Al , ^{75}As , ^{137}Ba , ^{209}Bi , ^{112}Cd , ^9Co , ^{52}Cr , ^{133}Cs , ^{63}Cu , ^{57}Fe , ^{69}Ga , ^7Li , ^{24}Mg , ^{55}Mn , ^{98}Mo , ^{58}Ni , ^{208}Pb , ^{123}Sb , ^{120}Sn , ^{82}Se , ^{88}Sr , ^{51}V , ^{66}Zn . The other operation parameters of ICP-MS are shown in Table 3.5.

Table 3.5. Operation parameters of ICP-MS

Parameter	Value
Sample introduction	Quartz cyclonic DRC spray chamber
RF power	1100
Skimmer cone	Nickel
Sampler cone	Nickel
Nebulizer	Micromist nebulizer (0.4 mL/min)
Nebulizer gas flow	0.810 (L/min)
Auxillary gas flow	1.20 (L/min)
Plasma gas flow	19.0 (L/min)
Number of sweeps/reading	20
Number of readings/replicate	1
Number of replicates	3
Autosampler	CETAX ASX-520
Dwell time per AMU	50 ms
Sample flush time and speed	50 s, (+/- rpm) -48
Read delay time and speed	15 s, (+/- rpm) -20

3.6 Quality Control and Quality Assurance

Strict quality control protocols were applied to ensure data quality during sampling, handling, storage, preparation, and measurement of the samples. The deionized water with a resistivity of 18.2 M Ω cm was used in this study. All containers were washed at least three times with deionized water. Also, after the sampling was completed, the sampling system was cleaned with deionized water, and the funnel lid was opened and closed just before and after the rain events, respectively to prevent possible contamination problems. The samples collected after the sampling were stored in the refrigerator at 4.00 °C and analyzed as soon as possible. The prepared field and laboratory blanks were used to correct possible contamination and processed as samples. Also, in each set of 10 digestion vessels, a reagent blank was added and digested with the samples.

The calibration of the instruments was performed before starting the analysis of the samples. The calibration curve was created by plotting peak areas versus concentrations, and the deviation of the calibration was controlled by analyzing a standard in every ten samples. If the standard concentration was not in the range of 10 % error in the calibration standard, a new calibration was done. The calibration curve for elements was prepared using seven concentrations of 2, 5, 10, 25, 50, 100, and 200 ppb. The calibration curve for ions was prepared using six concentrations such as 0.1, 0.25, 0.5, 1.0, 2.0, and 5.0 ppm. The calibration curves for anions and cations are shown in Figure 3.9 and Figure 3.10, respectively.

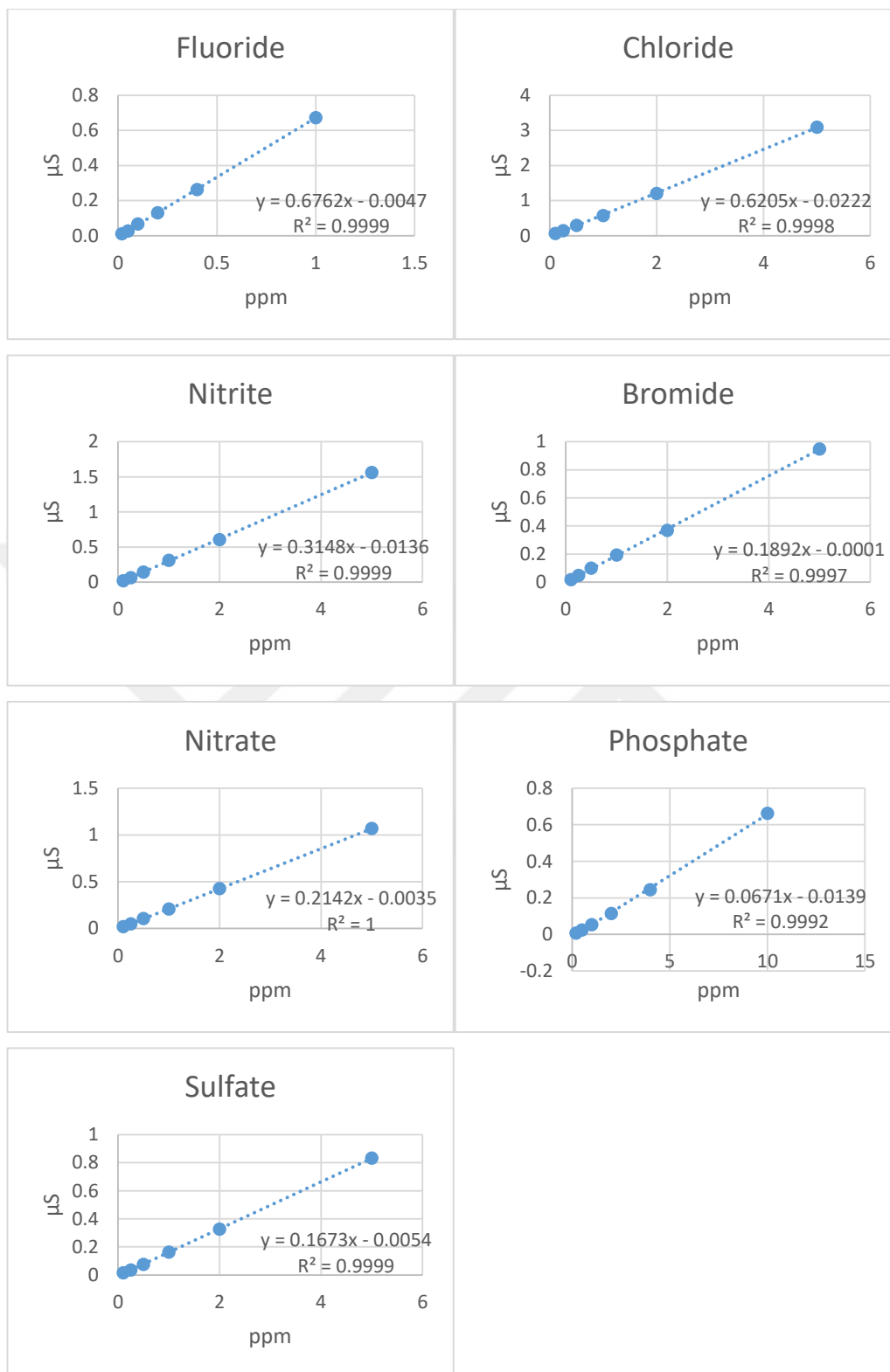


Figure 3.9. Calibration curves for anions

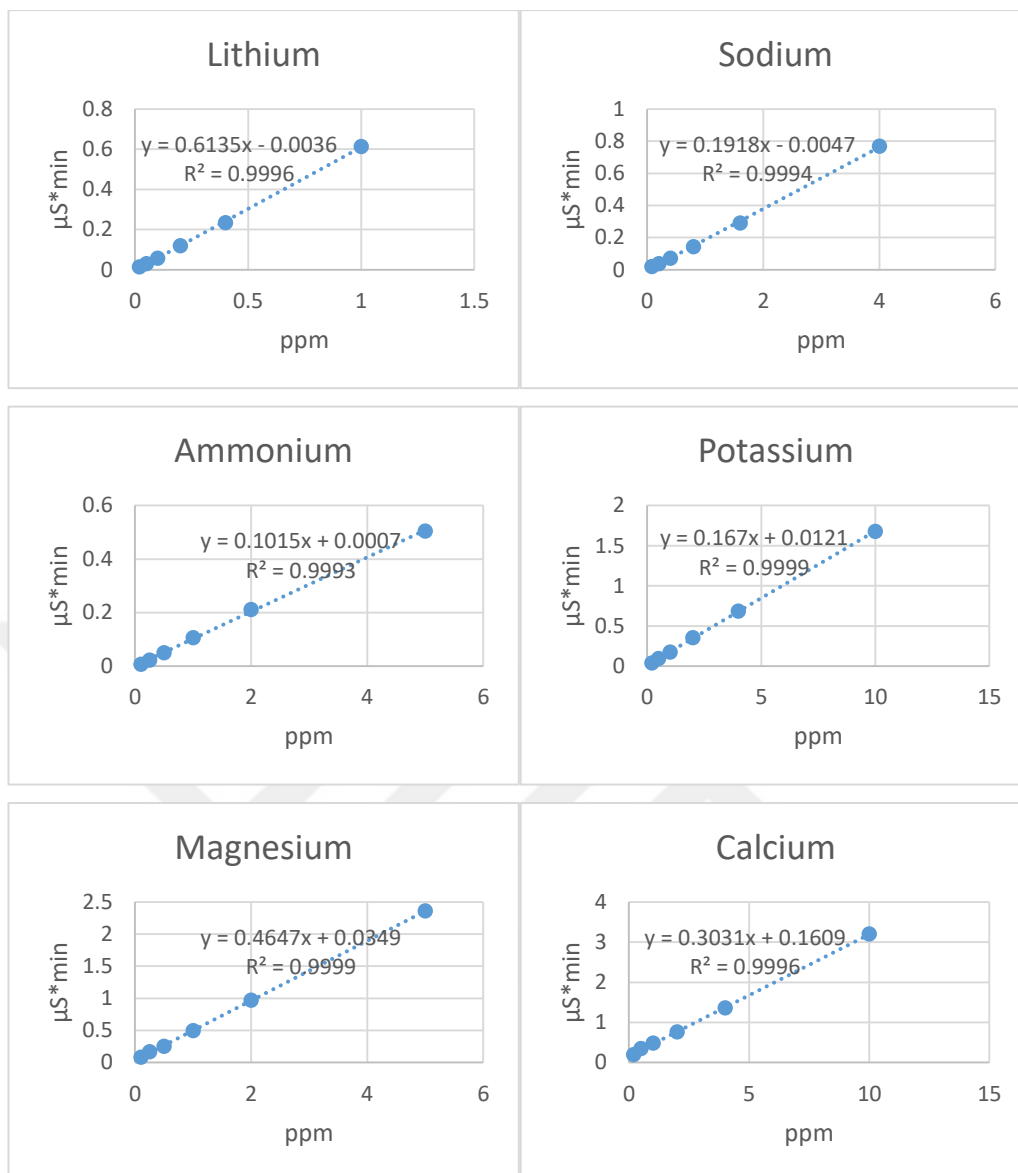


Figure 3.10. Calibration curves for cations

For the trueness of the analysis method of elements, the standard reference material (SRM) was analyzed using the same digestion procedure with samples, and the results of the SRM are listed in Table 3.6.

Table 3.6. Analysis results of SRM for elements (concentrations are in mg/L)

Parameter	Certified value	Arithmetic mean	Standard deviation	Error %
Al	0.296	0.332	34.3	-5.74
As	0.122	0.117	3.66	1.94
Ba	0.777	0.691	27.2	5.84
Be	0.0490	0.0500	3.73	-1.47
Cd	0.0490	0.0520	1.56	-2.55
Co	0.0370	0.0387	1.23	-1.59
Cr	0.242	0.242	15.8	-0.0220
Cu	0.487	0.495	37.3	-0.810
Fe	0.469	0.502	26.6	-3.40
Mn	0.109	0.107	2.59	0.710
Mo	0.197	0.194	4.06	0.720
Ni	0.242	0.249	17.1	-1.39
Pb	0.193	0.184	7.77	2.29
Sb	0.0510	0.0510	2.64	-0.370
Se	0.115	0.114	2.83	0.220
Sr	0.363	0.375	5.32	-1.66
V	0.376	0.353	9.18	3.19
Zn	2.42	2.47	134	-1.04
Ti	0.0790	0.073	4.39	3.99

3.6.1 Detection and Quantification Limits

The method detection limit (MDL) and the method quantification limit (MQL) was calculated to be three times and ten times the standard deviation of the field blank values, respectively. The MDL and MQL values for major ions and elements are given in Tables 3.7 and 3.8, respectively.

Table 3.7. R², MDL, MQL values for ions (concentrations are in (µg/mL))

	R ²	MDL	MQL
F ⁻	0.9999	0.0340	0.114
Cl ⁻	0.9998	0.0600	0.201
NO ₂ ⁻	0.9999	0.0190	0.0630
Br ⁻	0.9997	0.0350	0.118
NO ₃ ⁻	1.0000	0.286	0.953
PO ₄ ³⁻	0.9992	0.104	0.346
SO ₄ ²⁻	0.9999	0.156	0.521
Na ⁺	0.9994	0.381	1.27
NH ₄ ⁺	0.9993	0.0750	0.251
K ⁺	0.9999	0.0280	0.0930
Mg ²⁺	0.9999	0.0280	0.0940
Ca ²⁺	0.9996	0.464	1.55

Table 3.8. MDL and MQL values of elements (concentrations are in µg/mL)

Element	MDL	MQL	Element	MDL	MQL
Ag	0.00100	0.00200	Li	0.00900	0.0310
Al	0.858	2.86	Mg	0.549	1.83
As	0.00500	0.0170	Mn	0.0320	0.107
Ba	0.00500	0.0170	Mo	0.00800	0.0260
Bi	0.000500	0.00200	Ni	0.00300	0.0110
Cd	0.000200	0.00100	Pb	0.00300	0.0110
Co	0.00100	0.00200	Sb	0.0000500	0.000200
Cr	0.00300	0.0110	Sn	0.00100	0.00400
Cs	0.000500	0.00200	Sr	0.00300	0.00900
Cu	0.0310	0.105	V	0.00700	0.0240
Fe	2.56	8.53	Zn	0.0180	0.0600
Ga	0.0940	0.313			

3.7 Source Apportionment

Source apportionment is the practice of deriving information about pollution sources and their contribution to ambient air pollution levels. Quantification of pollution arises from long-range transport, transboundary transport, natural sources, winter sanding, and salting.

Different approaches are used to determine and quantify the impacts of air pollution sources on air quality (88). Commonly used source apportionment techniques are:

- Explorative methods use superficial mathematical relationships and several assumptions to achieve a preliminary estimation of the source contribution.
- Emission inventories are detailed compilations of the emissions from all source categories in a particular geographical area and within a specific year. Emissions are estimated by multiplying the intensity of each relevant activity by a pollutant-dependent proportionality constant.
- Inverse modeling estimates the air quality model parameters by fitting the model to the observations.
- Artificial neural networks are sets of interconnected simple processing elements which can exhibit complex global behavior.
- Lagrangian models use a moving frame of reference to describe the trajectories of single or multiple particles as they move in the atmosphere.
- Gaussian models assume that turbulent dispersion can be described using a Gaussian distribution profile.

- Eulerian models encompass equations of motion, chemistry, and other physical processes that are solved at points arranged on a 3D grid.
- Receptor models focus on the properties of the ambient environment at the point of impact, as opposed to the source-oriented dispersion models, which account for transport, dilution, and other processes between the source and the sampling or receptor site.

3.7.1 Back Trajectory Analysis

Back trajectory analysis provides information about the air masses' starting point and helps form relationships between source and receptor. Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) model provides convenience for computing simple air parcel trajectories, chemical transformation, dispersion, transport, and deposition simulation .(89) Therefore, the HYSPPLIT is the most extensively used model in the atmospheric sciences. The model calculating method is a hybrid between the Lagrangian approach, using a moving frame of reference for the advection and diffusion calculations as the trajectories or air parcels move from their initial location, and the Eulerian methodology, which uses a fixed three-dimensional grid as a frame of reference to compute pollutant air concentrations.

3.7.2 Positive Matrix Factorization

Two matrices are identified with a multivariate factor analysis tool (PMF), which dissociates an identified sample data matrix. These matrices are factor contributions (G) and factor profiles (F) and are used to determine the source types. Also, uncertainty data, derived from sample data, and the sample concentration are parameters used by the PMF model to strengthen individual points. Factor contributions and profiles are derived by the PMF model minimizing the objective function Q (90):

$$Q = \sum_{i=1}^n \sum_{j=1}^m \left[\frac{x_{ij} - \sum_{k=1}^p g_{ik} f_{kj}}{u_{ij}} \right]^2$$

Q is a critical parameter for PMF, and two versions of Q are displayed for the model runs.

- Q(true) is the goodness-of-fit parameter calculated, including all points.

- $Q(\text{robust})$ is the goodness-of-fit parameter calculated excluding points not fit by the model, defined as samples for which the uncertainty-scaled residual is greater than 4.

The difference between $Q(\text{true})$ and $Q(\text{robust})$ is a measure of the impact of data points with high-scaled residuals. These data points may be associated with peak impacts from sources that are not consistently present during the sampling period. In addition, the uncertainties may be too high, which results in similar $Q(\text{true})$ and $Q(\text{robust})$ values because the uncertainty scales the residuals (90).

Because each PMF run can affect factor profiles, each run evaluations and error estimates must be made by users to ensure the stability of results. Three methods help to evaluate PMF variability (91).

1. Bootstrap analysis (BS) is used to identify whether a small set of observations can disproportionately influence the solution. BS error intervals include effects from random errors and partially include effects of rotational ambiguity.
2. Displacement analysis (DISP) is an analysis method that helps the user understand the selected solution in finer detail, including its sensitivity to small changes. DISP error intervals include effects of rotational ambiguity but do not include effects of random errors in the data.
3. BS-DISP analysis (a hybrid approach) error intervals include effects of random errors and rotational ambiguity. As a result, BS-DISP results are more robust than DISP results.

4. RESULTS AND DISCUSSIONS

A total of one hundred sixty-seven volume-based fractional wet deposition samples were collected in the city center of Bolu (urban area) and Bolu Abant Izzet Baysal University Campus (semi-urban area) between May 2020 and June 2020. The samples were analyzed for ions (F^- , Cl^- , NO_2^- , Br^- , NO_3^- , PO_4^{3-} , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}) and elements (Ag, Al, As, Ba, Bi, Cd, Co, Cr, Cs, Cu, Fe, Ga, Li, Mg, Mn, Mo, Ni, Pb, Sb, Sn, Sr, V, Zn). The collection dates and the number of fractions of rainwater samples are shown in Figure 4.1.

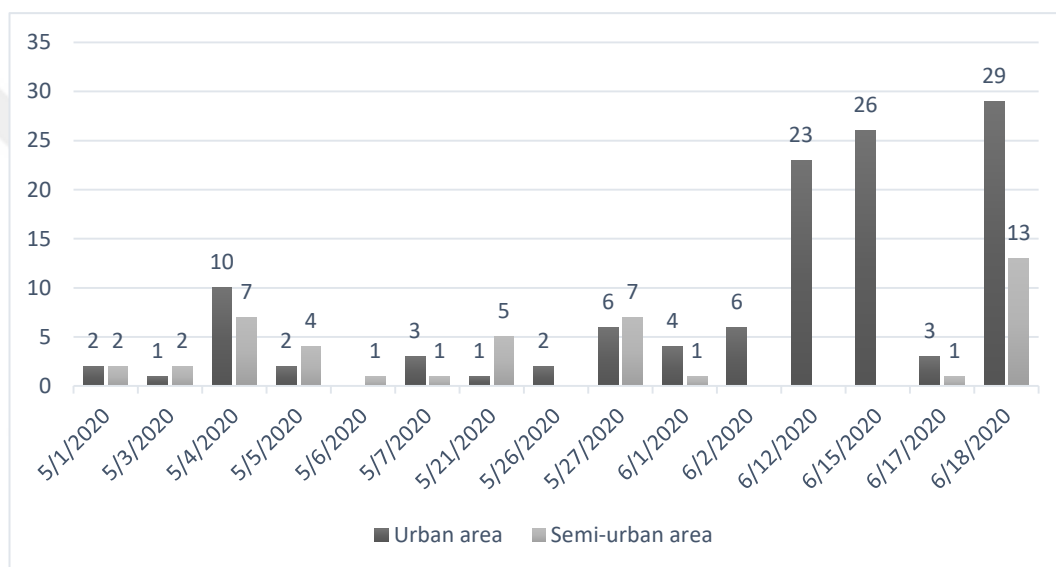


Figure 3.11. The number of fractions of rainwater samples collected in the urban and semi-urban areas

4.1 Statistical Evaluation

A comprehensive statistical evaluation was performed to investigate the chemical composition of rainwater samples. The statistical data was formed by calculating the observed value, mean, median, geometric mean, minimum, maximum, and standard deviation for each element and major ions. The value of N indicated the number of detected samples. The statistical data of major ions and elements for the urban area are given in Table 4.1 and Table 4.2, and the semi-urban area in Table 4.3 and Table 4.4, respectively. The data showed a generally log-normal distribution, and the geometric mean and median values are close to each other.

Table 3.9. Statistical treatment values of major ions for the urban area (units are in µg/L)

Major ions	N	Mean	Geometric mean	Median	Standard deviation	Minimum	Maximum
F ⁻	59.0	0.189	0.0660	0.282	0.160	0.000234	0.534
Cl ⁻	107	3.75	1.10	0.682	8.75	0.222	49.2
NO ₂ ⁻	17.0	0.0471	0.0326	0.0333	0.0473	0.00154	0.208
Br ⁻	6.00	0.0567	0.0127	0.0110	0.107	0.000681	0.273
NO ₃ ⁻	107	1.18	0.828	0.886	1.07	0.0130	5.00
PO ₄ ³⁻	42.0	0.0845	0.0485	0.0585	0.0920	0.00131	0.406
SO ₄ ²⁻	107	1.45	1.10	1.21	1.04	0.112	5.30
HCO ₃ ⁻	107	1.35	0.696	0.768	2.26	0.0160	19.3
Na ⁺	106	0.306	0.261	0.267	0.178	0.00789	1.34
NH ₄ ⁺	98.0	0.671	0.434	0.515	0.557	0.00100	2.90
K ⁺	102	3.58	0.567	0.360	8.29	0.0181	44.2
Mg ²⁺	50.0	0.0889	0.0458	0.0550	0.113	0.00338	0.536
Ca ²⁺	102	1.36	0.809	0.872	1.59	0.00659	9.35
H ⁺	107	0.00121	0.000509	0.000461	0.00281	0.0000183	0.0220

Table 3.10. Statistical treatment values of elements for the urban area (units are in µg/L)

Elements	N	Mean	Geometric mean	Median	Standard deviation	Minimum	Maximum
Ag	32.0	0.00234	0.00134	0.00172	0.00245	0.000102	0.0106
Co	40.0	0.0461	0.0219	0.0334	0.0481	0.000795	0.190
As	103	0.0907	0.0433	0.0705	0.0809	0.000304	0.239
Cr	67.0	3.78	0.500	0.540	5.86	0.00105	26.4
Pb	79.0	0.0692	0.0201	0.0189	0.177	0.000304	1.17
Ga	36.0	0.156	0.129	0.137	0.0874	0.0284	0.380
V	77.0	0.0963	0.0564	0.0511	0.0767	0.000917	0.230
Cd	32.0	0.000407	0.000189	0.000199	0.000444	0.0000127	0.00147
Mn	81.0	0.236	0.0605	0.0453	0.384	0.00263	1.98
Fe	41.0	21.9	9.52	13.6	23.5	0.0980	94.1
Ni	103	0.903	0.150	0.0981	1.74	0.00224	9.08
Cu	52.0	0.0580	0.0264	0.0297	0.0762	0.000281	0.374
Zn	54.0	0.144	0.0247	0.0236	0.543	0.000427	3.90
Al	94.0	38.3	17.7	25.7	34.2	0.0592	145
Ba	103	0.588	0.0358	0.0369	3.92	0.000378	33.4
Mo	35.0	0.0606	0.0384	0.0529	0.0547	0.00204	0.237
Sb	32.0	0.00218	0.00190	0.00180	0.00117	0.000707	0.00532
Sn	34.0	0.00507	0.00334	0.00386	0.00606	0.000174	0.0361
Sr	103	0.0622	0.0364	0.0361	0.0777	0.00214	0.500
Mg	92.0	3.64	1.56	2.17	3.69	0.0198	16.2
Cs	34.0	0.0364	0.0267	0.0361	0.0190	0.000120	0.0956
Bi	34.0	0.00354	0.00176	0.00152	0.00633	0.000108	0.0352
Li	58.0	0.312	0.0844	0.238	0.341	0.000392	1.61

Table 3.11. Statistical treatment values of major ions for the semi-urban area (units are in µg/L)

Major ions	N	Mean	Geometric mean	Median	Standard deviation	Minimum	Maximum
F ⁻	18.0	0.0477	0.0170	0.0131	0.0904	0.00305	0.305
Cl ⁻	38.0	4.87	1.71	1.44	12.2	0.211	73.7
NO ₂ ⁻	25.0	0.984	0.0762	0.055	2.38	0.000882	10.5
Br ⁻	6.00	0.0192	0.0139	0.017	0.0145	0.00325	0.0398
NO ₂ ⁻	35.0	2.66	1.63	1.63	3.31	0.289	15.3
PO ₄ ³⁻	20.0	2.12	0.304	0.272	3.89	0.00131	12.7
SO ₄ ²⁻	38.0	14.6	6.75	7.92	24.3	0.695	110
HCO ₃ ⁻	38.0	5.45	2.29	2.32	13.3	0.0823	82.3
Na ⁺	38.0	0.929	0.698	0.767	0.735	0.151	3.38
NH ₄ ⁺	22.0	4.20	1.74	1.93	5.66	0.119	18.4
K ⁺	37.0	6.03	2.386	3.31	11.7	0.0204	69.1
Mg ²⁺	34.0	0.304	0.166	0.189	0.321	0.00136	1.40
Ca ²⁺	38.0	10.8	6.60	8.49	9.74	0.155	39.8
H ⁺	38.0	0.000395	0.000154	0.000153	0.000851	0.00000430	0.00430

Table 3.12. Statistical treatment values of elements for the semi-urban area (units are in µg/L)

Elements	N	Mean	Geometric mean	Median	Standard deviation	Minimum	Maximum
Ag	23.0	0.00262	0.00146	0.00144	0.00521	0.000144	0.0262
Co	33.0	0.0862	0.0597	0.0647	0.0852	0.0129	0.444
As	42.0	0.0809	0.0154	0.00876	0.172	0.000346	0.694
Cr	37.0	11.7	4.01	7.79	19.6	0.0190	119
Pb	42.0	0.0180	0.0111	0.0105	0.0209	0.000631	0.110
Ga	29.0	0.0808	0.0578	0.0819	0.0578	0.00418	0.245
V	34.0	0.0869	0.0372	0.0320	0.122	0.00212	0.519
Cd	21.0	0.000601	0.000417	0.000427	0.000811	0.0000907	0.00401
Mn	41.0	0.636	0.210	0.489	0.692	0.000126	3.52
Fe	34.0	41.7	24.8	35.0	39.1	0.342	202
Ni	42.0	3.18	1.06	2.09	3.66	0.0137	19.4
Cu	34.0	0.0602	0.0230	0.0307	0.0901	0.000252	0.474
Zn	35.0	0.0918	0.0203	0.0241	0.172	0.000208	0.687
Al	42.0	31.3	16.0	19.7	46.1	2.47	223
Ba	42.0	0.0544	0.0324	0.0298	0.0644	0.00380	0.313
Mo	32.0	0.115	0.0756	0.0833	0.133	0.0131	0.746
Sb	19.0	0.000356	0.000205	0.000225	0.000330	0.00000950	0.00106
Sn	32.0	0.0185	0.00582	0.00529	0.0607	0.000647	0.348
Sr	42.0	0.194	0.0609	0.0500	0.537	0.0121	2.75
Mg	41.0	5.38	3.22	4.38	5.74	0.0830	33.7
Cs	32.0	0.0232	0.0102	0.0246	0.0279	0.00111	0.152
Bi	31.0	0.00338	0.00120	0.00124	0.00506	0.00000700	0.0228
Li	37.0	0.255	0.111	0.199	0.352	0.00917	2.05

From the statistical treatment of data, fluoride, nitrate, sulfate, sodium, gallium, vanadium, molybdenum, antimony, and cesium had higher standard deviation values than the arithmetic mean values in the urban area. Likewise, bromide, sodium, calcium, cobalt, gallium, iron, and antimony had a higher standard deviation values than the arithmetic mean values in the semi-urban area. Hence, it can be said that there are wide fluctuations and/or spikes in their concentrations due to the metrological changes, the effect of different sources or the long range transportation. On the contrary, ions and elements with lower standard deviation values represent stable variations in their concentration values due to constant effect of local sources.

Furthermore, Kolmogorov-Smirnow's goodness-of-fit statistic was performed to determine the distribution types of elements and ions by using Statgraphics Centurion XVII software. Because the samples can be fully described by their mean and standard deviation if they have a normal distribution. Standardized skewness and standardized kurtosis are two statistics that are used to find the distribution types of samples.

1. Skewness measures whether the distribution is symmetrical. For instance, if a distribution of skewness is zero, it can be said that it has symmetric distribution. A distribution can have both positive and negative skewness. Distributions have positive skewness when the values are higher than the peak, and distributions have negative skewness when the values are lower than the peak (92).
2. Kurtosis is used to measure the sharpness of the peak of a distribution. For instance, if the kurtosis value is zero, it can be said that it has a normal or bell-shaped curve. Moreover, positive kurtosis comes from a peaked distribution, and negative kurtosis comes from a flatter distribution (92).

The standardized skewness and kurtosis values must be between -2 to +2 for the normal distribution. If these statistic values are outside the range, it indicates deviation from normality. In that case, the p-value and DN value should be checked to determine the distribution type. The DN value states the absolute difference between the hypothesized and real distribution. The DN value is in the range of 0 to 1, and it is calculated from Statgraphics Centurion XVII software because log-normal distribution is selected as a distribution function. The Statgraphics

Centurion XVII software only determines the distribution types for p-value greater than 0.05. On the contrary, the distribution type must be chosen according to the smallest DN value.

In the present study, the distribution types obtained from Statgraphics Centurion XVII were primarily examined for the precipitation data. Then standard skewness and standard kurtosis were examined to determine whether the distribution type was normal. Finally, the p-value and DN value were examined to determine the distribution type. If the p-value was greater than 0.05, the distribution type determined by the software was selected. If the p-value was lower than 0.05, the distribution type with the smallest DN value was selected. The distribution parameters for the urban area and semi-urban area are listed in Tables 4.5 and 4.6, respectively.

According to Table 4.5 and Table 4.6, all elements and ions had positive skewness and kurtosis values except for fluoride, which had negative skewness and kurtosis values and negative kurtosis value, and arsenic and vanadium, which had negative kurtosis values, in the urban area. Likewise, bromide was the only ion with a negative kurtosis value on the semi-urban area.

In the city center, Al, Cd, Co, Cu, Fe, Ga, Li, Mo, Sn, V, NO_2^- , SO_4^{2-} , and NH_4^+ showed weibull distribution, and Cr, Cu, Ga, Li, Mg, Mn, Mo, Ni, Sb, Na^+ , K^+ , Mg^{2+} , Ca^{2+} showed weibull distribution in the campus. That means they had been affected by mostly constant emission sources during the sampling period. The rest of the species showed a log-normal distribution for the two sampling points except for Cs and F^- , which had a normal distribution type in the urban area. They had been affected by different parameters such as meteorological conditions, physical and chemical conversions, and various pollution sources.

Table 3.13. Distribution parameters of elements and ions for the urban area

Parameters	Skewness	Kurtosis	DN value	P-value	Distribution Type
Ag	14.68	44.1	0.103	0.826	log-normal
Al	3.90	0.493	0.0960	0.281	weibull
As	1.49	-3.35	0.162	0.00400	log-normal
Ba	35.1	143	0.151	0.0100	log-normal
Bi	11.1	28.0	0.160	0.283	log-normal
Cd	7.57	15.4	0.120	0.690	weibull
Co	3.91	2.80	0.0990	0.775	weibull
Cr	6.76	6.10	0.115	0.253	log-normal
Cs	1.81	2.88	0.112	0.727	normal
Cu	7.69	9.34	0.0900	0.721	weibull
Fe	3.79	2.42	0.120	0.504	weibull
Ga	1.84	0.469	0.0840	0.942	weibull
Li	4.68	4.72	0.178	0.0280	weibull
Mg	4.15	0.805	0.113	0.139	log-normal
Mn	10.6	17.5	0.104	0.284	log-normal
Mo	3.78	3.20	0.0950	0.881	weibull
Ni	17.0	43.4	0.0900	0.308	log-normal
Pb	17.4	42.4	0.112	0.203	log-normal
Sb	2.68	1.04	0.0810	0.973	log-normal
Sn	11.0	29.1	0.141	0.466	weibull
Sr	13.0	22.4	0.0530	0.894	log-normal
V	0.595	-3.02	0.251	0.00	weibull
Zn	21.6	78.3	0.0700	0.930	log-normal
F⁻	-0.247	-2.65	0.266	0.00	normal
Cl⁻	15.7	30.2	0.175	0.00300	log-normal
NO₂⁻	4.74	7.51	0.233	0.318	weibull
Br⁻	2.36	2.82	0.156	0.999	log-normal
NO₃⁻	8.95	9.37	0.116	0.110	log-normal
PO₄³⁻	4.96	4.44	0.136	0.428	lognormal
SO₄²⁻	5.38	3.62	0.0700	0.666	weibull
HCO₃⁻	23.3	82.1	0.0720	0.628	log-normal
Na⁺	9.78	20.9	0.0880	0.383	log-normal
NH₄⁺	7.07	8.25	0.0970	0.319	weibull
K⁺	13.6	22.5	0.124	0.0850	log-normal
Mg²⁺	7.13	9.11	0.107	0.616	log-normal
Ca²⁺	11.4	19.0	0.0770	0.583	log-normal

Table 3.14. Distribution parameters of elements and ions for the semi-urban area

Parameters	Skewness	Kurtosis	DN value	P-value	Distribution Type
Ag	9.02	21.3	0.180	0.455	log-normal
Al	7.40	10.4	0.155	0.263	log-normal
As	6.55	6.75	0.220	0.0350	log-normal
Ba	5.99	7.41	0.116	0.628	log-normal
Bi	5.61	7.63	0.0980	0.928	log-normal
Cd	7.59	16.5	0.140	0.804	log-normal
Co	6.04	10.5	0.0810	0.982	log-normal
Cr	12.1	33.5	0.139	0.482	weibull
Cs	7.42	16.8	0.214	0.108	normal
Cu	8.12	16.5	0.0930	0.932	weibull
Fe	5.46	9.13	0.0820	0.977	weibull
Ga	2.61	2.32	0.110	0.873	weibull
Li	9.42	23.6	0.206	0.086	weibull
Mg	8.57	19.0	0.099	0.820	weibull
Mn	5.35	8.21	0.127	0.542	weibull
Mo	8.51	19.7	0.0870	0.969	weibull
Ni	6.31	11.1	0.147	0.324	weibull
Pb	6.97	11.3	0.121	0.574	log-normal
Sb	1.89	0.0700	0.0850	0.999	weibull
Sn	12.7	35.7	0.122	0.725	log-normal
Sr	11.3	23.7	0.190	0.097	log-normal
V	4.99	4.88	0.0900	0.945	log-normal
Zn	6.15	7.35	0.119	0.708	log-normal
F⁻	4.47	4.82	0.143	0.854	log-normal
Cl⁻	13.0	36.4	0.0880	0.930	log-normal
NO₂⁻	6.62	11.5	0.105	0.948	log-normal
Br⁻	0.380	-0.863	0.226	0.919	log-normal
NO₃⁻	6.61	9.45	0.124	0.656	log-normal
PO₄²⁻	4.11	3.78	0.122	0.927	log-normal
SO₄³⁻	8.46	14.5	0.0960	0.873	log-normal
HCO₃⁻	13.9	40.7	0.136	0.493	log-normal
Na⁺	4.50	4.93	0.0680	0.995	weibull
NH₄⁺	3.32	1.74	0.0860	0.997	log-normal
K⁺	11.7	30.6	0.152	0.361	weibull
Mg²⁺	5.71	7.80	0.121	0.703	weibull
Ca²⁺	4.15	3.49	0.0860	0.940	Weibull

4.2 Ion Balance

The charge balance between anions and cations was calculated to assess the data quality and reliability by using the following formula:

$$Balance = \frac{\sum \mu eq \text{ cations} - \sum \mu eq \text{ anions}}{\sum \mu eq \text{ cations} + \sum \mu eq \text{ anions}} \times 100$$

According to EPA, the data were assumed to be acceptable if the balance ratio was in the range of $\pm 30\%$ and the total concentrations of ions were greater than 100 $\mu eq/L$ (93). However, some samples may not meet the quality criteria because H^+ , HCO_3^- , and organic acids (e.g., formic and acetic acid) are not included in the calculation (94). For that reason, the concentrations of H^+ and HCO_3^- were calculated according to the following equations (95,96):

$$[HCO_3^-] = 10^{-11.24+pH}$$

$$[H^+] = 10^{-pH}$$

The data have shown better quality after adding the concentrations of H^+ and HCO_3^- to the samples, the mean values for the ratio of the sum of anions to the sum of cations were 1.01 and 0.738 for the urban area and the semi-urban area, respectively. Moreover, the linear regression analysis was applied to the total anions and cations concentrations for the urban and semi-urban areas, and the results are shown in Table 4.7, Figure 4.2, and Figure 4.3.

Table 3.15. Linear regression analysis results for the urban and semi-urban areas

urban area				
Parameter	Estimate	Standard error	t Statistic	p-value
Intercept	-17.4	8.22	-2.11	0.0370
Slope	1.04	0.0260	40.0	0.00
R ²	0.938			
semi-urban area				
Parameter	Estimate	Standard error	t Statistic	p-value
Intercept	-180	102	-1.75	0.0880
Slope	0.915	0.0928	9.86	0.00
R ²	0.730			

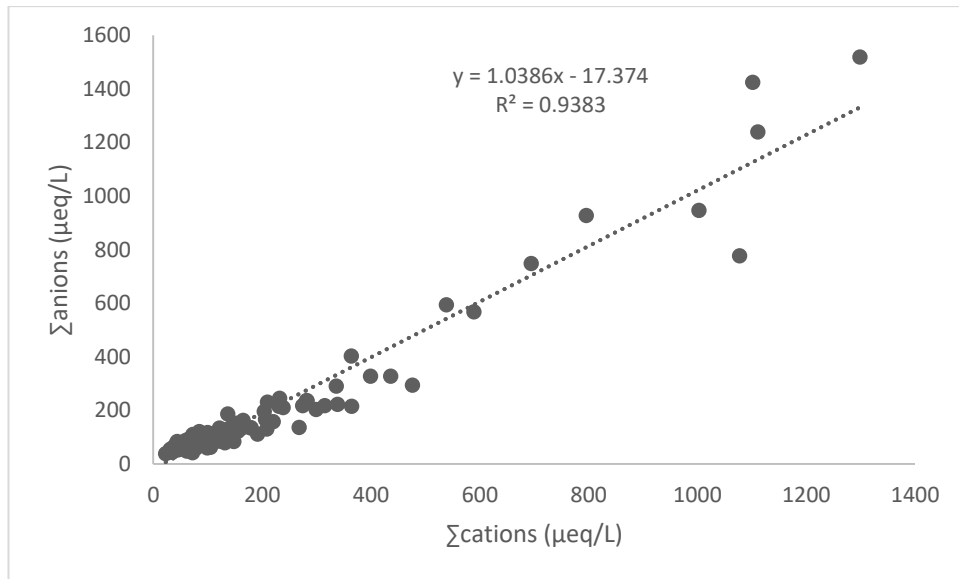


Figure 3.12. Relationship between the sum of anions and cations for the urban area

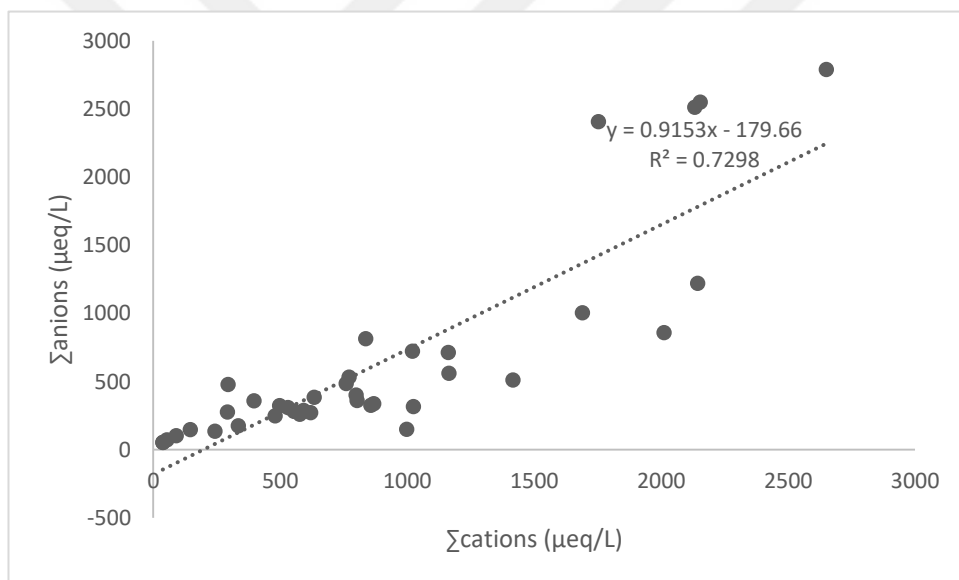


Figure 3.13. Relationship between the sum of anions and cations for the semi-urban area

The outputs showed the results of fitting a linear model to describe the relationship between the anions and cations. Since the p-value for the slope was less than 0.05, there was a statistically significant relationship between the anions and cations at the 95.0% confidence level for the urban and semi-urban areas. Also, the R-square values indicated that the model explained 93.8% and 72.9% of the variability in anions for the urban and semi-urban areas, respectively.

4.3 The Volume-Weighted Mean Concentrations of Ions

The volume-weighted mean concentration (VWM) is calculated as,

$$C_{vwm} = \frac{\sum(C_i \times P_i)}{\sum P_i}$$

where C_{VWM} is the volume weight mean concentration ($\mu\text{eq L}^{-1}$); C_i is the ionic concentration of the i^{th} event-based sample ($\mu\text{eq L}^{-1}$); P_i is the amount of precipitation (mm) from the i^{th} precipitation event (29).

The VWM concentrations of ions are shown in Figure 4.4 and Figure 4.5 for the city center and the BAIBU campus, respectively. In general, the total VWM concentrations of anions and cations were 176 $\mu\text{eq/L}$ and 202 $\mu\text{eq/L}$ for the urban area and 524 $\mu\text{eq/L}$ and 798 $\mu\text{eq/L}$ for the semi-urban area. Chloride was the most abundant anion in the urban area, followed by SO_4^{2-} , HCO_3^- , NO_3^- , F^- , PO_4^{3-} , and NO_2^- , while K^+ was the most abundant cation and was followed by Ca^{2+} , NH_4^+ , Na^+ , and Mg^{2+} . Likewise, SO_4^{2-} had the highest VWM concentration among the anions in the semi-urban area and was followed by Cl^- , HCO_3^- , NO_3^- , PO_4^{3-} , NO_2^- , and F^- , while Ca^{2+} had the highest VWM concentration among the cations and was followed by NH_4^+ , K^+ , Na^+ , and Mg^{2+} .

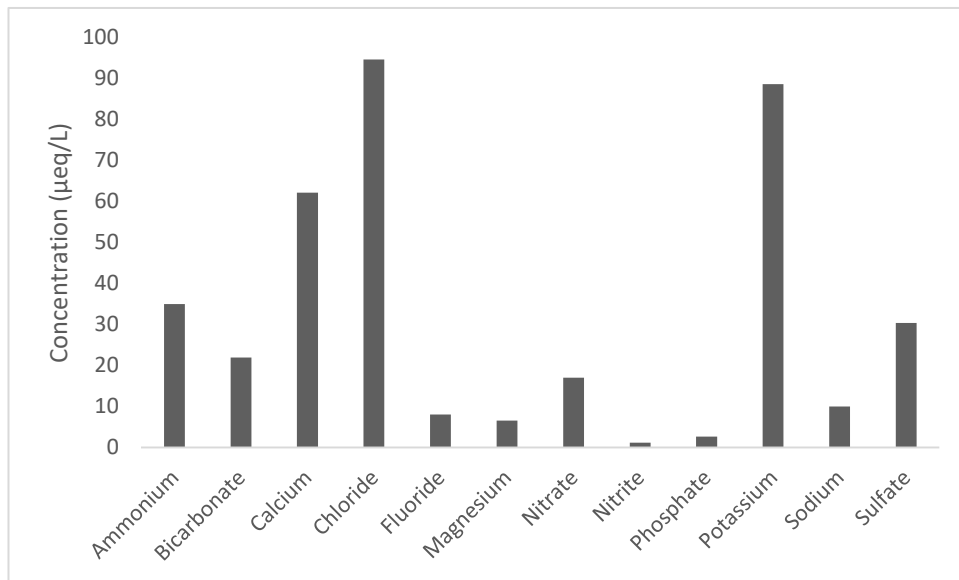


Figure 3.14. The VWM concentrations of major ions for the urban area ($\mu\text{eq/L}$)

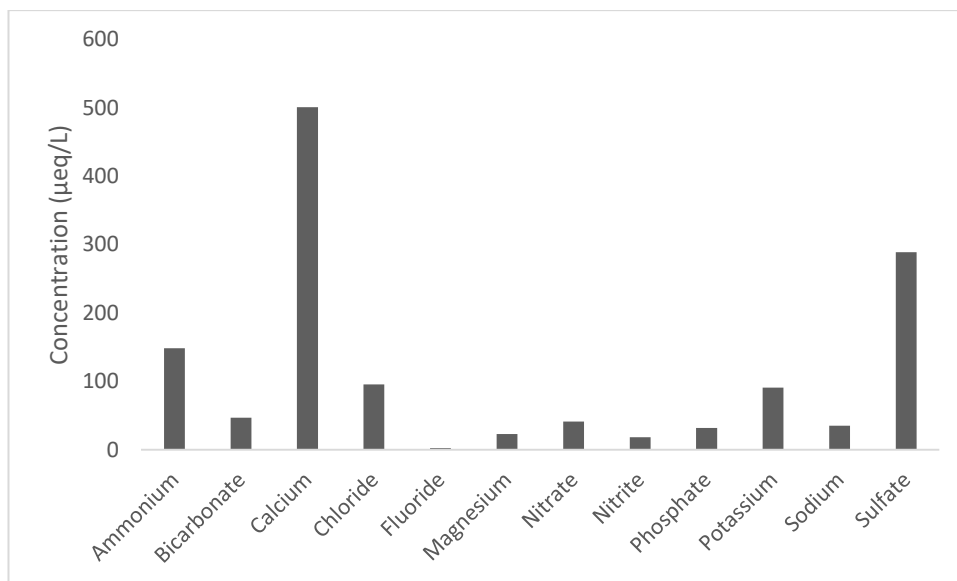


Figure 3.15. The VWM concentrations of major ions for the semi-urban area (µeq/L)

The VWM concentrations of calcium and bicarbonate ions in the semi-urban area were higher than in the urban area. The reason behind this might be the effect of the suspension of calcareous soil dust in the cereal grown agricultural areas in the semi-urban area. The ammonium in the semi-urban area showed a higher concentration than in the urban area because of the intensive agricultural activities around the campus area. The ammonium might also come from fertilizing processes, livestock, and cattle waste dump. Potassium, which showed nearly the same concentration in the two areas, is an indicator of biomass burning and various anthropogenic emissions. Sodium and Mg also had a high concentration in the semi-urban area, and this might be the effect of resuspension from the earth's crust as calcium. The concentration of chloride was almost similar in the two areas. The concentration of chloride might be related to the effect of marine aerosols and the earth's crust in two areas. In the urban area, anthropogenic emissions (e.g., vehicle emissions and industrial activities) might release sulfur dioxide into the atmosphere, and sulfur dioxide is converted to sulfate ions with atmospheric chemical reactions. Despite that, coal burning might be the main reason for the higher sulfate concentration in the semi-urban area. Nitrate might also come with the atmospheric conversion of NO_2 released from the vehicle exhaust. In other words, this study was conducted during the lockdown period of the COVID-19 pandemic. However, vehicles were more actively used in the semi-urban area than in the urban area,

which might be another reason why sulfate and nitrates were high in the semi-urban area. The long-range transportation of sulfate and nitrate was also a possible source in the semi-urban area. Fluoride showed a higher concentration in the urban area, which might be caused by producing construction materials from clay (e.g., bricks and tiles) (72).

4.4 The Volume-Weighted Mean Concentrations of Elements

The VWM concentrations of elements are given in Table 4.8 for the urban and semi-urban areas. The total VWM concentration of elements was 68.5 $\mu\text{g/L}$ for the urban area and 103 $\mu\text{g/L}$ for the semi-urban area. The VWM concentrations of trace elements in the urban area were in the order of $\text{Al} > \text{Fe} > \text{Mg} > \text{Cr} > \text{Ni} > \text{Ba} > \text{Li} > \text{Mn} > \text{Ga} > \text{Zn} > \text{V} > \text{As} > \text{Sr} > \text{Mo} > \text{Pb} > \text{Cu} > \text{Co} > \text{Cs} > \text{Sn} > \text{Bi} > \text{Ag} > \text{Sb} > \text{Cd}$, while in the semi-urban area were in the order of $\text{Fe} > \text{Al} > \text{Cr} > \text{Mg} > \text{Ni} > \text{Mn} > \text{Sr} > \text{Li} > \text{Mo} > \text{Zn} > \text{As} > \text{V} > \text{Co} > \text{Ga} > \text{Cu} > \text{Ba} > \text{Pb} > \text{Cs} > \text{Sn} > \text{Bi} > \text{Ag} > \text{Cd} > \text{Sb}$. Aluminum had the highest VWM concentration (38.4 $\mu\text{g/L}$) for the urban area, while Fe had the highest VWM concentration 44.7 $\mu\text{g/L}$ for the semi-urban area. Also, Fe for urban area and Al for semi-urban were the second-highest elements, with VWM concentrations of 20.0 $\mu\text{g/L}$ and 35.2 $\mu\text{g/L}$, respectively. On the contrary, Cd and Sb were the lowest concentration elements with VWM concentrations of 0.000446 $\mu\text{g/L}$ and 0.00229 $\mu\text{g/L}$ for the urban area and 0.000578 $\mu\text{g/L}$ and 0.000351 $\mu\text{g/L}$ for the semi-urban area, respectively. The VWM concentrations of Al, Fe, and Sr were higher in the semi-urban area than in the urban area, and Li had a high concentration in the urban area. Aluminum, Fe, Sr, and Li are the tracer elements found in the earth's crust. Nevertheless, Al, Fe, and Sr had been highly affected from the mechanical abrasion of brakes and tires of vehicles in the semi-urban area. The vehicle emissions from TEM and D-100 highways had higher contribution to Al, Fe, and Sr concentrations in the semi-urban area. Chromium had a higher concentration in the semi-urban area (12.7 $\mu\text{g/L}$) than in the urban area (3.48 $\mu\text{g/L}$). The VWM concentrations of Mg and Ni showed higher concentrations for the semi-urban area with VWM concentrations of 5.18 $\mu\text{g/L}$ and 3.19 $\mu\text{g/L}$ in comparison with the urban area of 3.80 $\mu\text{g/L}$ and 0.846 $\mu\text{g/L}$. The remaining elements had shown quite low VWM concentrations in the two sites of Bolu. However, the semi-urban area has shown higher VWM concentrations for almost all remaining elements.

Table 3.16. The VWM concentrations of elements for the urban and semi-urban areas (units are in $\mu\text{g/L}$)

Urban area		Semi-urban area	
Elements	Concentration	Elements	Concentration
Al	38.4	Fe	44.6
Fe	20.0	Al	35.2
Mg	3.80	Cr	12.7
Cr	3.48	Mg	5.18
Ni	0.846	Ni	3.19
Ba	0.616	Mn	0.619
Li	0.357	Sr	0.217
Mn	0.221	Li	0.173
Ga	0.162	Mo	0.127
Zn	0.153	Zn	0.117
V	0.108	As	0.110
As	0.0982	V	0.106
Sr	0.0607	Co	0.0926
Mo	0.0552	Ga	0.0744
Pb	0.0547	Cu	0.0617
Cu	0.0519	Ba	0.0612
Co	0.0411	Pb	0.0198
Cs	0.0380	Cs	0.0165
Sn	0.00501	Sn	0.00839
Bi	0.00353	Bi	0.00365
Ag	0.00245	Ag	0.00229
Sb	0.00229	Cd	0.000578
Cd	0.000446	Sb	0.000351

4.5 Evaluation of Rainwater Acidity

In general, the pH of rainwater is 5.60 in a pristine environment because of the dissolved carbon dioxide in the atmosphere. The rainwater pH below 5.60 shows an acidic character, which means the contribution of mainly H_2SO_4 and HNO_3 to the atmosphere from anthropogenic emissions. On the contrary, the rainwater pH above 5.60 shows an alkaline character, indicating the contribution of the terrigenous sources such as weathering rocks. The pH ranges for the urban and semi-urban areas are shown in Figure 4.6 and Figure 4.7, respectively.

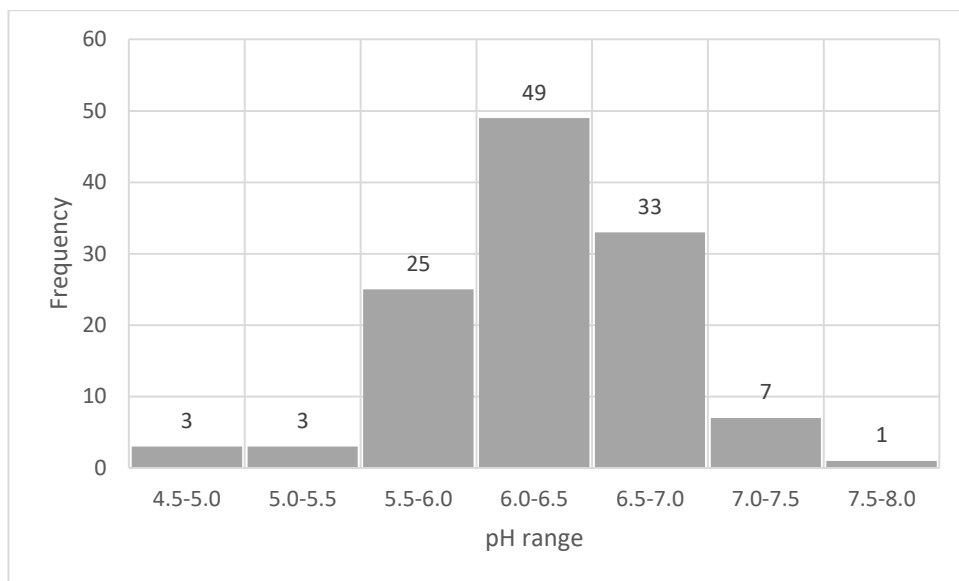


Figure 3.16. pH ranges for the urban area

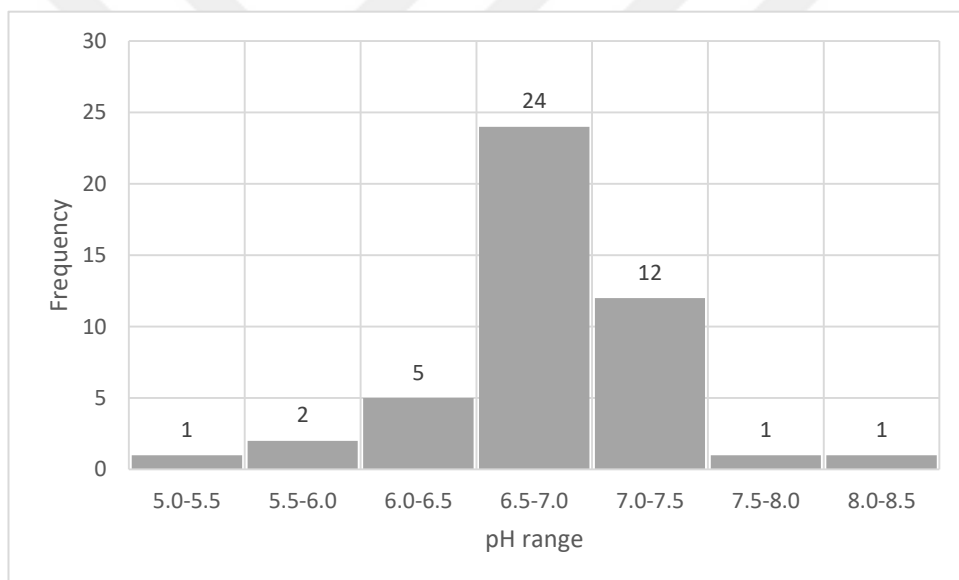


Figure 3.17. pH ranges for the semi-urban area

The measured acidity of rainwater for the urban area was in the range of 4.66 and 7.74 with a median value of 6.29, while for the semi-urban area was in the range of 5.37 and 8.37 with a median value of 6.79. On average, the pH showed an alkaline character in both areas because of the high concentrations of cations, especially Ca^{2+} , NH_4^+ , and K^+ . However, the urban area has been exposed to acid rain, as much as the 7.40% of total fractions, while 4.30% for the semi-urban area.

4.5.1 Neutralization Factor

The neutralization factor (NF) was calculated to evaluate the neutralization capacity of the cations according to the following equation:

$$NF = X_i / ([SO_4^{2-}] + [NO_3^-])$$

X_i is the concentration of the alkaline components expressed in $\mu\text{eq/L}$. Therefore, the neutralizing trend of any alkaline component in the rain can be explained as a neutralizing factor (97,98). The neutralization factor was applied to the Ca^{2+} , Mg^{2+} , K^+ , NH_4^+ , and Na^+ , and the results are shown in Figure 4.8.

The high calcium and potassium concentrations may be the reason for showing a high neutralization factor, which will be discussed in the next section.

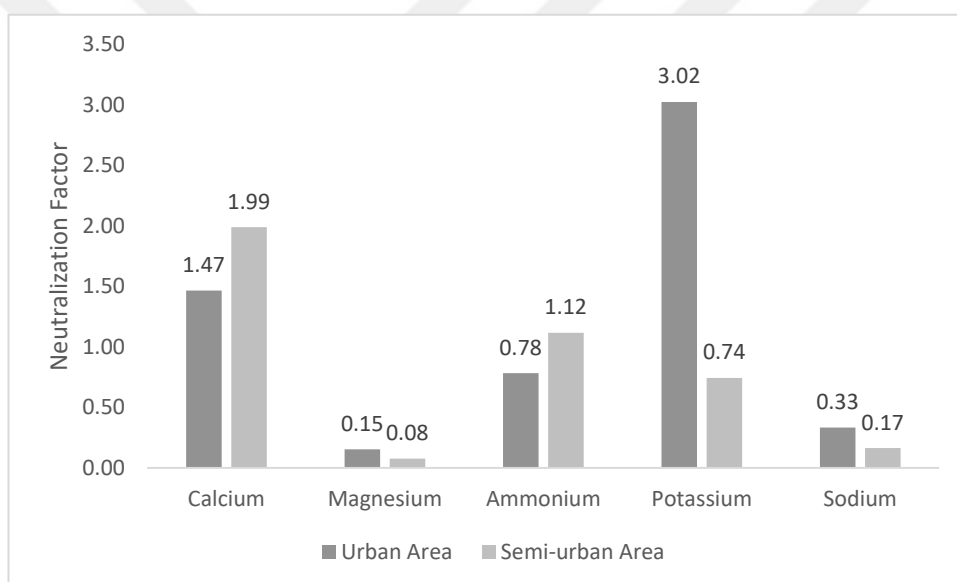


Figure 3.18. The mean neutralization factors for Ca^{2+} , Mg^{2+} , NH_4^+ , K^+ , and Na^+ for the urban and semi-urban areas

4.5.2 Multiple Linear Regression

The relationship between acidic and alkaline species was examined using multiple linear regression analysis. In the analysis, SO_4^{2-} and NO_3^- were used as dependent variables, while NH_4^+ , Ca^{2+} , Mg^{2+} , K^+ , and Na^+ as independent variables. The multiple linear regression parameters are given in Table 4.9 and Table 4.10 for the urban and semi-urban areas, respectively.

Table 3.17. Multiple linear regression parameters of SO_4^{2-} and NO_3^- for the urban area

$[\text{SO}_4^{2-}] = a + \alpha_1[\text{NH}_4^+] + \alpha_2[\text{Ca}^{2+}] + \alpha_3[\text{Mg}^{2+}] + \alpha_4[\text{K}^+] + \alpha_5[\text{Na}^+]$			
A	5.30	% of r^2	82.9
α_1	0.301	% of r^2 explained by NH_4^+	27.8
α_2	0.236	% of r^2 explained by Ca^{2+}	72.0
α_3	-0.0993	% of r^2 explained by Mg^{2+}	0.00
α_4	0.00127	% of r^2 explained by K^+	0.21
α_5	-0.214	% of r^2 explained by Na^+	0.00
$[\text{NO}_3^-] = b + \beta_1[\text{NH}_4^+] + \beta_2[\text{Ca}^{2+}] + \beta_3[\text{Mg}^{2+}] + \beta_4[\text{K}^+] + \beta_5[\text{Na}^+]$			
B	-0.594	% of r^2	87.1
β_1	0.255	% of r^2 explained by NH_4^+	23.8
β_2	0.258	% of r^2 explained by Ca^{2+}	76.2
β_3	-1.08	% of r^2 explained by Mg^{2+}	0.00
β_4	-0.000248	% of r^2 explained by K^+	0.00
β_5	-0.138	% of r^2 explained by Na^+	0.00

Table 3.18. Multiple linear regression parameters of SO_4^{2-} and NO_3^- for the semi-urban area

$[\text{SO}_4^{2-}] = a + \alpha_1[\text{NH}_4^+] + \alpha_2[\text{Ca}^{2+}] + \alpha_3[\text{Mg}^{2+}] + \alpha_4[\text{K}^+] + \alpha_5[\text{Na}^+]$			
A	3.69	% of r^2	82.0
α_1	0.0121	% of r^2 explained by NH_4^+	0.76
α_2	0.195	% of r^2 explained by Ca^{2+}	80.1
α_3	0.678	% of r^2 explained by Mg^{2+}	3.93
α_4	0.0437	% of r^2 explained by K^+	0.47
α_5	1.18	% of r^2 explained by Na^+	14.8
$[\text{NO}_3^-] = b + \beta_1[\text{NH}_4^+] + \beta_2[\text{Ca}^{2+}] + \beta_3[\text{Mg}^{2+}] + \beta_4[\text{K}^+] + \beta_5[\text{Na}^+]$			
B	62.3	% of r^2	3.76
β_1	-0.0389	% of r^2 explained by NH_4^+	2.00
β_2	-0.0197	% of r^2 explained by Ca^{2+}	0.00
β_3	0.661	% of r^2 explained by Mg^{2+}	98.0
β_4	0.0530	% of r^2 explained by K^+	0.00
β_5	-0.645	% of r^2 explained by Na^+	0.00

For the urban area, the independent variables explained SO_4^{2-} and NO_3^- at 82.9% and 87.1%. In the urban area, Ca^{2+} contributed the most to the neutralization of SO_4^{2-} and NO_3^- with percentage values of 72.0 and 76.2, respectively. Further, NH_4^+ had a contribution of 27.8% for SO_4^{2-} and 23.8% for NO_3^- . The remaining

cations had no contribution to the neutralization process of the SO_4^{2-} and NO_3^- , except for K^+ , which had a small contribution to the neutralization of SO_4^{2-} with a percentage value of 0.210 in the urban area.

For the semi-urban area, the neutralization of 82.0% of SO_4^{2-} and 3.76% of NO_3^- were explained with the NH_4^+ , Ca^{2+} , Mg^{2+} , Mg^{2+} , K^+ , and Na^+ . The results also showed that the largest contribution to the neutralization of SO_4^{2-} was made by Ca^{2+} , followed by Na^+ (14.8%), Mg^{2+} (3.93%), NH_4^+ (0.760%), and K^+ (0.470%). Although there was no great effect of cations on the neutralization of NO_3^- , only 2.00% of NH_4^+ and 98.0% of Mg^{2+} have contributed to the explained part of NO_3^- .

4.5.3 Fractional Acidity

The relationship between acidic and neutralization species was assessed using the following formula (99). The key acidifying components in precipitation are H_2SO_4 , HNO_3 , and organic acids.

$$FA = H^+ / ([\text{SO}_4^{2-}] + [\text{NO}_3^-]) \text{ (units are in } \mu\text{eq/L)}$$

An FA value of 1 indicates that the acidity is not fully neutralized, whereas a value near zero shows the maximum neutralization condition (100). The mean fractional acidity for the urban area was 0.0244 and for the semi-urban area was 0.00135. The results have shown that the alkaline species neutralized the acidity for both areas because the FA values were near zero.

4.5.4 Ammonium Availability Index

The ratio between ammonium ions and the sum of the sulfate and nitrate ions is expressed as an ammonium availability index (AAI) (101).

$$AAI = \{[\text{NH}_4^+] / 2[\text{SO}_4^{2-}] + [\text{NO}_3^-]\} \times 100 \text{ (units are in } \mu\text{eq/L)}$$

The AAI ratio shows the neutralization capacity of ammonium to neutralize acidic ions such as SO_4^{2-} and NO_3^- . The ratio below 100% indicates the deficiency of NH_4^+ , which means NH_4^+ does not completely neutralize acidic ions, or other cations are contributed to the neutralization of acidity, or there is the occurrence of acidic precipitation. The ratio above 100% indicates the full neutralization of acidity by ammonium and the formation of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 (102). In this study, the mean AAI ratio was 43.0% for the urban area and 46.3% for the semi-

urban area. The results indicated that ammonium had contributed to almost half of the neutralization of acidity in urban and semi-urban areas. Furthermore, it was observed that agricultural activities had an intense impact on the rainwater of Bolu.

4.5.5 The Ratio of Neutralization Potential and Acidic Potential

The evaluation of stability between the alkaline and acidic ions was carried out by using the neutralization potential to the acidic potential (NP/AP) ratio (103):

$$\frac{NP}{AP} = \frac{(Ca^{2+} + Mg^{2+} + K^+ + NH_4^+)}{(SO_4^{2-} + NO_3^-)}$$

In the present study, the mean ratio of neutralization potential to the acidic potential was 4.40 for the urban area and 3.70 for the semi-urban area. The results had indicated that the neutralization potential was dominant over the acidic potential in the study period for both sites.

4.5.6 Evaluation of Some Ratios

The ratio of NO_3^-/SO_4^{2-} indicates whether sulfuric acid or nitric acid contributes more to the rainwater acidity and also gives information about the sources. The ratio above 1.00 shows the greater contribution of vehicular emissions, while the ratio below 1.00 shows the greater contribution of industrial activities and coal burning (96). The mean values of the ratio were 0.620 and 0.520 for the urban and semi-urban areas. The results indicated that sulfuric acid was dominant, and industrial activities and coal burning were effective sources in the rainwater of Bolu.

The ratio of $(Ca^{2+} + NH_4^+)/(NO_3^- + SO_4^{2-})$ demonstrates the role of calcium and ammonium ions in the neutralization process of rainwater acidity. The ratio above 1.00 shows that calcium and ammonium ions provide the neutralization of rainwater acidity to a large extent. In another case, the ratio below 1.00 shows that other cations play a role in neutralizing rainwater acidity (96). The ratio of $(Ca^{2+} + NH_4^+)/(NO_3^- + SO_4^{2-})$ were 2.08 and 2.98 for the urban and semi-urban areas. The results had shown that Ca^{2+} and NH_4^+ had a prominent role in the neutralization process of rainwater acidity.

The ratio of $(SO_4^{2-} + NO_3^-)/(Ca^{2+} + Mg^{2+})$ indicates whether the rainwater is acidic or alkaline. If the ratio is greater than 1.00, the rainwater has acidic nature, and If the ratio is lower than 1.00, the rainwater has alkaline nature (96). The

average values of $(\text{SO}_4^{2-} + \text{NO}_3^-)/(\text{Ca}^{2+} + \text{Mg}^{2+})$ were calculated as 0.830 and 0.870 for the urban and semi-urban areas, indicating again the alkaline nature of the rainwater.

4.6 Suitability of Rainwater for Irrigation and Cultivation

The evaluation of rainwater suitability for irrigation and cultivation activities can be assessed using parameters such as sodium adsorption ratio (SAR) and percent sodium ($\text{Na}^+\%$) (104).

The SAR is used to determine the suitability of rainwater for irrigation by measuring the alkaline sodium ratio, which is dangerous for crops because the osmotic activity of crops decreases in the presence of high salinity, and nutrients cannot sufficiently be uptaken with water (105). The high concentration of Na^+ in the irrigation water reduces the permeability of the soil and causes weak drainage. Because the clay particles, which are displaced with Mg^{2+} and Ca^{2+} , absorb the ions. Alkaline and saline soils can be formed in the presence of excessive Na^+ since the combination of Na^+ with CO_3^{2-} and Cl^- , and these soils are not suitable for crop growth (106). Therefore, the SAR and $\text{Na}^+\%$ values are estimated according to the following formulas:

$$\text{SAR} = \text{Na}^+ / \sqrt{(\text{Ca}^{2+} + \text{Mg}^{2+})/2}$$

$$\text{Na}^+\% = \{(\text{Na}^+ + \text{K}^+)/(\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+)\} \times 100$$

where the concentration of the ionic constituents is expressed in meq/L.

The suitability categorizations of rainwater for irrigation and cultivation according to the SAR and $\text{Na}^+\%$ and calculated values are listed in Table 4.11.

Table 3.19. The classification scheme for the suitability of rainwater

Parameter	Thresholds	Class	Urban area	Semi-urban area
SAR	<10	Excellent	0.660	0.720
	10-18	Good	-	-
	18-26	Fair	-	-
	>26	Poor	-	-
Na⁺%	<20	Excellent	-	-
	20-40	Good	36.9	24.6
	40-60	Permissible	-	-
	60-80	Doubtful	-	-
	>80	Unsuitable	-	-

From the table, the mean Na⁺% was 36.9 and 24.6 for the urban and semi-urban areas, respectively. Also, the SAR values were calculated as 0.660 and 0.720 for the urban and semi-urban areas, respectively. The results indicated that the rainwater had good quality and had no risk for crop growth, and it can be used for irrigation in agricultural activities.

4.7 Comparison of Results with Literature

In the present study, the results of major ions and elements were used for the comparison with the studies conducted in various sampling areas in different countries to investigate the pollution level in our sampling areas. The results for the VWM concentrations of major ions, pH, neutralization factor values, and fractional acidity values are given in Table 4.12, and the results for the VWM concentration of trace elements are given in Table 4.13.

4.7.1 Comparison of Ions with Literature

The study conducted by Yenisoy-Karakaş et al. (2012) event based rain samples were collected using wet-only sampler in the semi-urban area (BAIBU Campus) of Bolu between June 2011 and June 2012. In this study, fifty-two samples were collected and analyzed for major ions and trace elements. The pH value showed that the acidity in Bolu's atmosphere was lower in 2011-2012. Also, the total VWM concentrations of anions in 2011-2012 were lower than in 2020, while the cations were almost the same in both studies. Pollution levels have increased in

8-9 years in the semi-urban site of Bolu. According to the NF values, the main neutralizing ions were Ca^{2+} and NH_4^+ in both studies (107).

Bayramoğlu Karşı et al. (2018) studied rainwater chemistry in the city center of Bolu. They manually collected thirty-three precipitation samples and analyzed them for major anions with ion chromatography. The total VWM mean concentrations of anions and cations in 2018 were five and ten times higher than in the present study. Also, the measured pH was almost the same, and it showed that Bolu's atmosphere had not suffered from acid rain during the two sampling periods (108). The present study was conducted during the lockdown period of COVID-19. This may be the reason to obtain low concentration of ions in the present study in the city center.

Karadeniz et al. (2020) manually collected six-hour rain samples in the semi-urban area of Bolu (BAIBU Campus), Turkey, from March to May 2019. The samples were analyzed for major ions by using ion chromatography. When the VWM concentrations of major ions were compared, it was observed that the major anions were three times and major cations were two times higher in the same area in 2019. The present study was conducted during the lockdown period of COVID-19, and human activities were less intense compared to 2019. Therefore, the effect of reduced human activities on pollutants has also been observed when comparing these two studies in the campus. Nevertheless, the pH values have revealed no difference in the alkalinity in the atmosphere of the semi-urban area over two sampling periods. Also, the neutralization capacity of Ca^{2+} was higher than the other cations in both studies (109).

In the study performed by Liyandeniya et al. (2020), the event-based precipitation samples were collected manually in Kelaniya, located in the Gampaha District of Sri Lanka, from October 2012 to July 2014. The total VWM results of cations found in Kelaniya were close to ours in the urban area, while the total VWM results of anions were almost two times lower than ours. Also, the linear regression coefficient analysis showed that most of the explained part of the sulfate appears as CaSO_4 , like in Bolu's urban atmosphere. For nitrate, it appeared as $\text{Ca}(\text{NO}_3)_2$ in Kelaniya's atmosphere and MgSO_4 in Bolu's urban atmosphere. Similar to our results, the pH of Kelaniya's atmosphere has shown an alkaline character and was not suffer from acid rain in the sampling period (72).

Rao et al. (2016) studied the precipitation chemistry to characterize and perform source apportionment in two urban areas (Pune and Delhi) in India from 2011 to 2014. The collected samples ($n = 127$) in Pune and ($n = 106$) in Delhi were analyzed for anions and cations. The concentrations of ions in our sites were generally greater than the sites in India. The mean pH values showed that the precipitation in both studies had an alkaline nature. Like the present study, the FA values in Pune and Delhi were close to zero, demonstrating the neutralization of acidity by alkaline ions. In addition, the NF value revealed that the Ca^{2+} ion has a dominant neutralization capacity in Pune and Delhi, but in the urban area of the present study, K^+ was the dominant ion (110).

The study was performed by Wu et al. (2016) at three rural sites from April to October 2008 in Hebei Province, North China. A total of 122 precipitation samples were analyzed for major ions. The VWM concentration results of sulfate and nitrate in the three rural areas were higher in the range of two to three times than in our sites. Also, the measured pH values in the three regions were lower than in our urban and semi-urban areas (111).

The rainwater samples were collected by Martins et al. (2019) in Limeira, Brazil, from September 2013 to March 2014. A total of 30 samples were each collected at a 24-h interval and analyzed by using ion chromatography for the determination of major ions. The total concentration of anions (especially K^+ , SO_4^{2-} , and Cl^-) was nearly 2-10 times lower than our urban sites. The concentrations of Na^+ and Mg^{2+} in Limeira were 2-3 times greater than that in our urban site. Nevertheless, the pH in Limeira was lower than in the urban area of Bolu (29).

Zhang et al. (2020) investigated precipitation chemistry by collecting rainwater samples in Taiyuan, North China. In this study, 350 rainwater samples were collected from April 2011 to November 2018. According to the results, the total VWM concentrations in Taiyuan were nearly two times higher than in the urban area of Bolu, and the acidity of both atmospheres was nearly equal. Additionally, K^+ highly contributed to the neutralization process in Bolu, while the most important alkaline ion for the neutralization process in Taiyuan was Ca^{2+} (71).

Table 3.20. Literature comparison of major ions (units are in $\mu\text{eq/L}$), pH, and acidity

Region (Country)	Sampling type	Region type	N	pH	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ²⁺	NF _{NH4+}	NF _{K+}	NF _{Mg2+}	NF _{Ca2+}	FA
Bolu (This study) (Türkiye)	Fractional	Urban Semi-urban	121 46.0	6.29 6.79	8.00 2.17	94.6 95.4	17.0 41.1	30.4 289	9.95 34.8	34.9 149	88.6 90.6	6.57 22.6	62.1 501	0.780 1.12	3.02 0.74	0.153 0.0777	1.47 1.99	0.024 0.0014
Bolu (Türkiye(107))	Event based	Semi-urban	52.0	5.93		65.9	29.6	82.5	137	131	5.81	28.2	492	2.12	0.150	0.510	7.66	0.054
Bolu (Türkiye(108))	Fractional	Urban	33.0	6.0		137	158	381	136	57.0	45.0	125	1177	0.130	0.095	0.250	2.30	
Bolu (Türkiye(109))	6-hour interval	Semi-urban	21.0	6.33		556	333	476	694	36.7	54.0	80.2	665	0.0440		0.110	0.850	0.0100
Kelaniya Sri (Lanka(72))	Event based	Urban	78.0	6.54	1.17	37.0	13.2	35.5	94.0	18.7	9.15	16.2	55.0					
Pune Delhi (India(95))	Event based	Urban Urban	127 106	6.33 6.35			26.8 50.5	39.7 91.6		19.5 23.7	5.30 5.30	19.1 69.2	93.4 199	0.290 0.170	0.10 0.04	0.29 0.49	1.40 1.40	0.0200 0.080
Chicheng Huailai Xuanhua (China(111))	Event based	Rural Rural Rural	36.0 47.0 39.0	5.50 5.77 5.23	7.18 10.9 7.06	63.9 71.4 66.2	86.5 169 117	162 289 213	10.9 22.2 18.9	92.4 57.7 117	17.7 12.3 15.8	47.6 70.9 49.3	183 391 210	0.370 0.130 0.350	0.07 0.03 0.05	0.19 0.16 0.15	0.740 0.860 0.640	
Limeira (Brazil(29))	24-h interval	Urban	30.0	5.62		7.06	14.7	15.5	22.4	34.4	5.68	17.4	54.9					
Taiyuan (China(71))	Event based	Urban	350	6.12	12.5	36.1	80.4	210	22.1	163	12.1	35.4	201	0.120		0.560	0.690	

4.7.2 Comparison of Elements with Literature

In another study conducted by Yenisoy-Karakaş et al. (2012) in semi-urban site (BAIBU campus) of Bolu, the event based rainwater samples were collected between June 2011 and June 2012 and analyzed to determine trace elements by ICP-MS. The comparison of two different years in the same sampling areas showed that the total VWM concentrations of trace elements in 2011-2012 were around ten times higher than in the urban area and the semi-urban area in 2020. The results have demonstrated that during the lockdown period, the concentrations of elements were decreased gradually.

The study that was performed by Samayamanhula et al. (2021) collected rainwater samples in 12 different areas, which include industrial and urban areas, in Kuwait, between November 2018 and March 2019. Thirty-one samples were analyzed to determine 16 trace elements using ICP-OES. The results demonstrated that Kuwait's total trace elements concentration was considerably higher than in Bolu's urban and semi-urban areas. Nevertheless, the concentrations of Al and Cr in Kuwait city were partially lower than our results (112).

In the city of Denizli in Türkiye, Cukurluoglu (2017) collected precipitation samples between December 2011 and November 2012, and samples were analyzed to determine 14 trace elements using ICP-OES. The comparison of results demonstrated that the total concentration of trace elements in Denizli was four times and three times higher than in Bolu's urban and semi-urban areas (113).

In the study conducted by Rivera-Rivera et al. (2020), fifty-two precipitation samples were collected in six regions in Mexico from March 2016 to April 2017. The samples were analyzed for ten trace metals by using Atomic Absorption Spectrometer. The total concentration of analyzed trace metals in six different regions was significantly (10-10000 times) higher than in Bolu's urban and semi-urban areas (114).

Table 3.21. Comparison of trace metals concentrations (units are in µg/L) with literature

Region	Bolu (This Study)		Bolu	Gustavo A. Madero	Tula	Pachuca	Tulancingo	Agua Blanca	Molango	Kuwait City	Pamukkale	Jiaozhou Bay
Country	Türkiye		Türkiye(107)	Mexico(114)						Kuwait(112)	Denizli(113)	China(115)
Region type	Urban	Semi- urban	Semi-urban	Urban	Industrial	Urban	Peri-urban	Rural	Rural	Coastal	Urban	Coastal
Al	38.4	35.2	258							30.4	39.0	34.0
As	0.0982	0.110	1.07	3.00	4.00	3.00	3.00	3.00	2.00	<3.70		
Ba	0.616	0.0612	2.074							95.2	17.0	
Bi	0.00353	0.00365	0.476									
Cd	0.000446	0.000578	0.100	4.00	2.00	1.00	2.00	2.00	1.00	0.31	13.0	0.15
Co	0.0411	0.0926	0.0410	9.00	15.0	13.0	17.0	14.0	13.0	<0.70	11.0	0.10
Cr	3.48	12.7	20.7	35.0	36.0	30.0	38.0	58.0	55.0	1.74	5.90	0.77
Cs	0.0380	0.0165	0.0423									
Cu	0.0519	0.0617	5.62	37.0	45.0	41.0	46.0	32.0	47.0	6.13	21.0	
Fe	20.0	44.6	119	371	472	292	406	379	448	4.69	24.0	16.0
Li	0.357	0.173	0.360								12.0	
Mg	3.80	5.18	217									
Mn	0.221	0.619	6.79	44.0	74.0	75.0	98.0	59.0	148	13.0	22.0	28.0
Mo	0.0552	0.127	0.585							2.00		
Ni	0.846	3.19	16.1	19.0	33.0	12.0	14.0	29.0	12.0	2.80	4.60	
Pb	0.0547	0.0198	22.6	33.0	28.0	20.0	31.0	45.0	31.0	3.10	10.0	2.60
Sb	0.00229	0.000351	0.0575									
Sn	0.00501	0.00839	3.18									
Sr	0.0607	0.217	10.1							188	16.0	
V	0.108	0.106	0.325							2.30		
Zn	0.153	0.117	129	952	137	1174	1892	799	282	17.0	90.0	28.0
Number of samples	121	46.0	40.0	52.0						31.0	45.0	49.0

4.8 Source Apportionment

4.8.1 Crustal Enrichment Factor

The crustal enrichment factor (EF_{crust}) is used to determine the possible contribution of crustal weathering to any element and ions in rainwater samples. The crustal enrichment factor values for each element and ion were calculated using the following equation (116):

$$EF_{crust} = \left(\frac{C_x}{C_{Ref}} \right)_{sample} / \left(\frac{C_x}{C_{Ref}} \right)_{crust}$$

where C_x is the concentration of the related element and ion in rainwater samples and continental crust, and C_{ref} is the concentration of reference element in rainwater samples and continental crust. In this study, Sr was used as a reference element, and the classification of EF_{crust} values was carried out in three ways:

1. Nonenriched: $EF_{crust} < 10$.
2. Moderately enriched: $10 < EF_{crust} < 100$.
3. Highly enriched: $EF_{crust} > 100$.

The crustal enrichment factor results for elements are shown in Figure 4.9 and Figure 4.10 for the urban and semi-urban areas. Copper, Fe, Al, Zn, Ba, Mn, and Mg were the non-enriched elements for the urban area, whereas Fe, Mn, Cu, Pb, Zn, V, Al, Mg, and Ba for the semi-urban area, indicating the crustal sources. Antimony, Ni, Ga, V, Co, Sn, Cd, and Pb were the moderately enriched elements for the urban area, whereas Sb, Ni, Ga, V, Co, Sn, Cd, and Pb for the semi-urban area, showing the contribution of both crustal and anthropogenic sources. The highly enriched elements (coming from anthropogenic sources) were Bi, Cr, Mo, Ni, and Ag and Bi, Cr, Mo, Ni, and Ag for the urban and semi-urban areas, respectively.

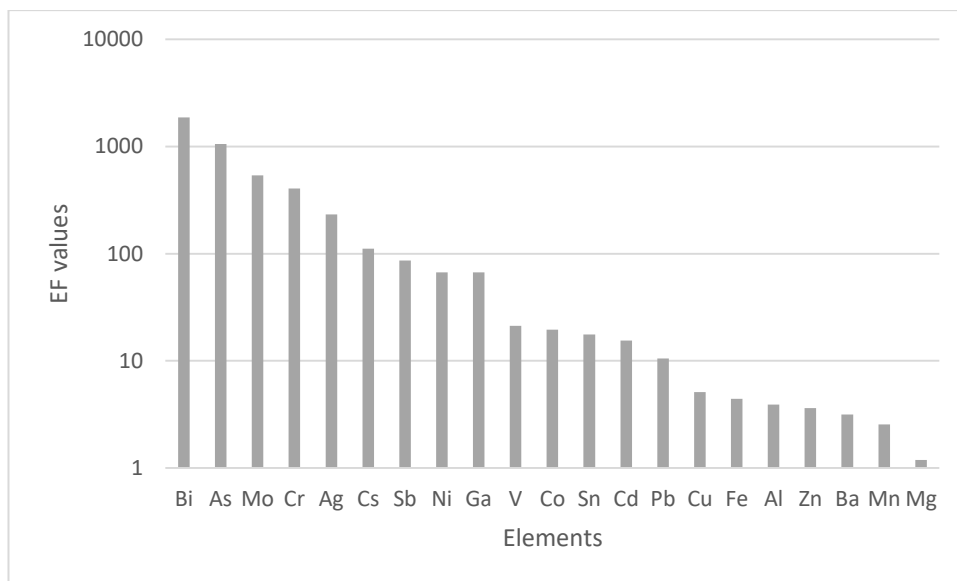


Figure 3.19. Crustal enrichment factor results for the urban area

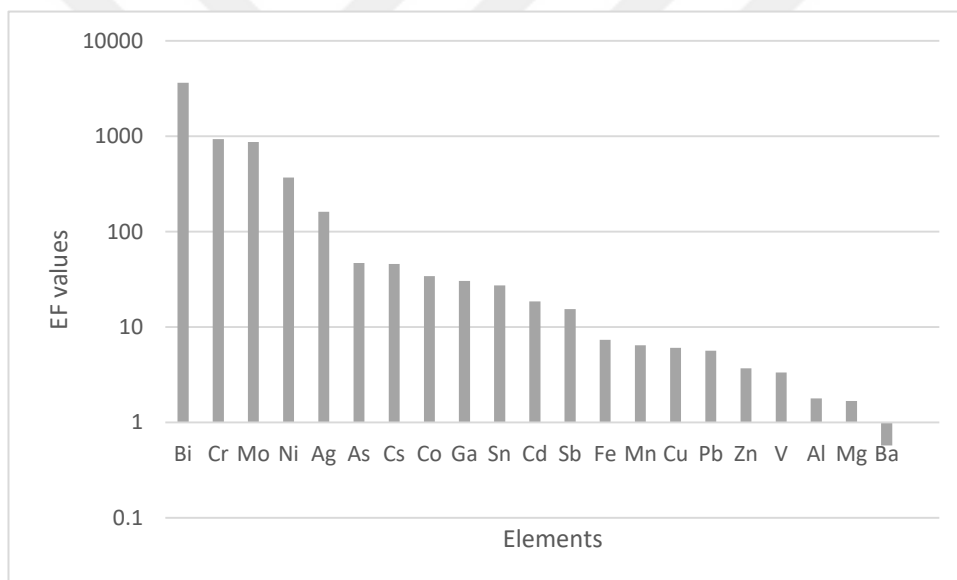


Figure 3.20. Crustal enrichment factor results for the semi-urban area

4.8.2 Positive Matrix Factorization

The PMF model is a multivariate receptor modeling tool used to do source apportionment. The matrix of designated sample data is decomposed into two matrices (factor contribution and factor profile) to determine the source contribution of the factor. The categorization of species was evaluated as weak, bad, and strong after controlling the r^2 values. For the urban area, Co, Cr, Pb, Cd, Mn, Fe, Ni, Cu, Al, Mo, Sb, Sr, Mg, F^- , Cl^- , NO_3^- and K^+ were categorized as strong, and As, Sn, SO_4^{2-} , Na^+ and Ca^{2+} was categorized as weak, and Zn, Ba, Cs, Bi, and

Li was categorized as bad. For the semi-urban area, Cr, As, Cr, Pb, Mn, Fe, Ni, Cu, Zn, Ba, Mo, Sr, Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, K⁺, and Ca²⁺ were categorized as strong, and Al, Mg, Bi, and Li was categorized as bad.

The Q values are shown in Table 4.14 and the DISP analysis results are shown in Table 4.15 and Table 4.16 for urban and semi-urban areas, respectively. The DISP analysis result was valid because the first line value was 0, meaning no error. The second value was the largest observed drop of Q during DISP.

Table 3.22. The base model results for the urban and semi-urban areas

Factor Number	Q _{theoretical}	Q _{true}	Q _{robust}	Q _{robust} / Q _{theoretical}	Q _{true} / Q _{robust}
Urban area					
6	492.0	747.0	808.0	1.640	0.9240
Semi-urban area					
5	430.0	1784	2444	5.680	0.7300

Table 3.23. Urban area DISP analysis

		0	-0.027		
0	0	0	0	0	0
0	0	0	0	0	0
0	0	0	0	0	0
0	0	0	0	0	0

Table 3.24. Semi-urban area DISP analysis

		0	-0.015		
0	0	0	0	0	0
0	0	0	0	0	0
0	0	0	0	0	0
0	0	0	0	0	0

Finally, six factors were obtained for the urban area and named iron-steel factories, Bolu cement factories, biomass burning, transportation from Anatolia, coal burning, and urban atmosphere for the urban area. Five factors were obtained for the semi-urban area: long-range transportation, nitrate factor, iron-steel factories, biomass burning, and the mixture of vehicular emissions and coal burning.

4.8.2.1 The PMF Results for the Urban Area

Iron-steel industries release many elements into the atmosphere, such as Fe, Cr, Cu, and Ni (112–114). Cobalt, Cr, Mn, Fe, Ni, Cu, Mo, and Sn were observed in Factor 1. The most contributing element in Factor 1 was Fe, with 78.9%, followed by Co, Mn, Cr, Ni, Mo, Cu, and Sn. Because of the high contribution of these elements, Factor 1 was attributed to iron-steel industries. Furthermore, G score values were examined in Figure 4.11, and the highest G score value was observed on 02/06/2020. The back trajectory was generated for this date and is shown in Figure 4.12. It has been observed that the air mass at 500 m and 1000 m comes from the Ereğli, which is located in the Black Sea Region and has many iron-steel factories known as ERDEMİR. The PMF results for Factor 1 are shown in Figure 4.13.

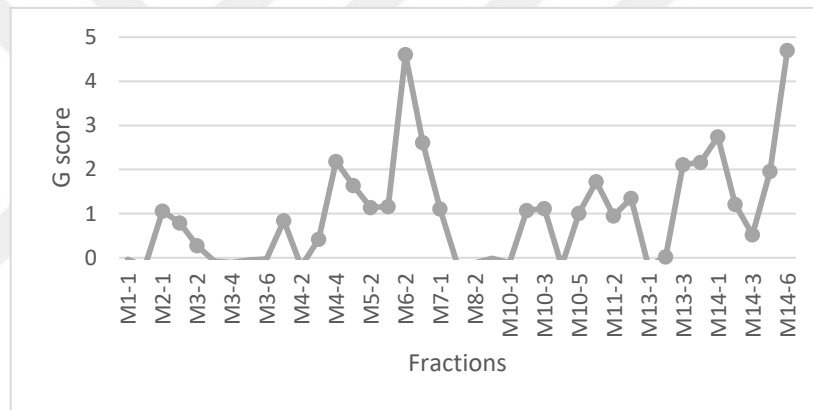


Figure 3.21. G score values of fractions for Factor 1

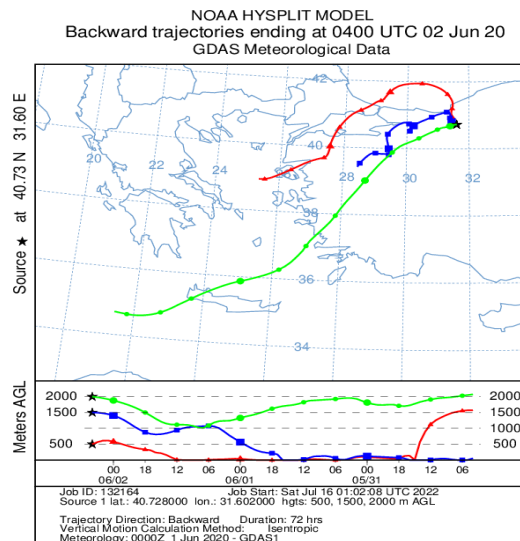


Figure 3.22. The back trajectory of the highest G score for Factor 1



Figure 3.23. PMF results for Factor 1

The sampling area has a big cement factory known as the Bolu Cement Factory. In factor 2, it was observed that F^- had the highest contribution, with 70.8%, followed by Na^+ , Ca^{2+} , and As. Although they might come from various sources, the cement factory is a common source for them and provides the greatest contribution to these species in the sampling area (14,72,117). Since the cement factory is a local source, the wind rose was created for the highest G score value. The windrose and G score values are shown in Figure 4.14 and Figure 4.15, respectively. Despite the dominant wind direction being NNW, the air mass has been coming from the direction of the cement factory (ENE, E, and ESE) during the sampling time. For that reason, Factor 2 was named the Bolu Cement Factory, and the PMF results for this factor are shown in Figure 4.16.

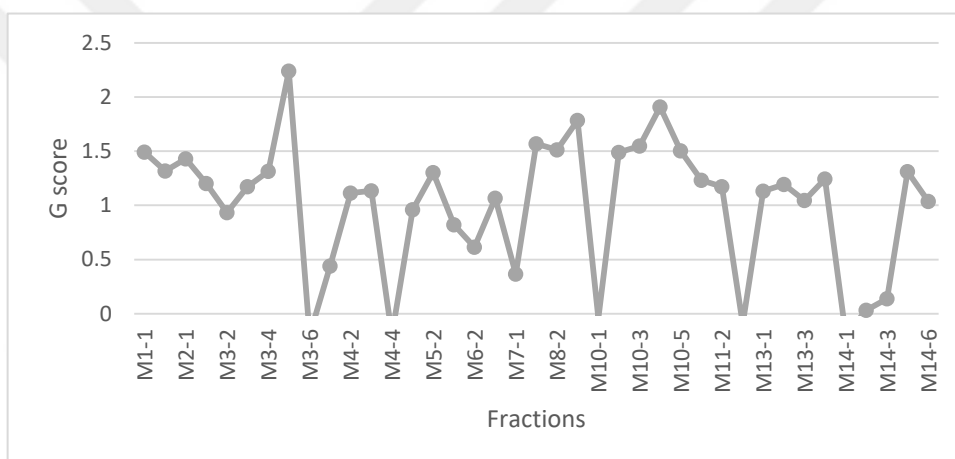


Figure 3.24. G score values of fractions for Factor 2

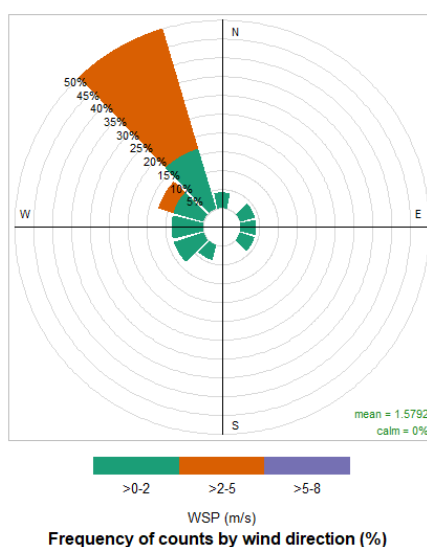


Figure 3.25. The windrose for the highest G score value

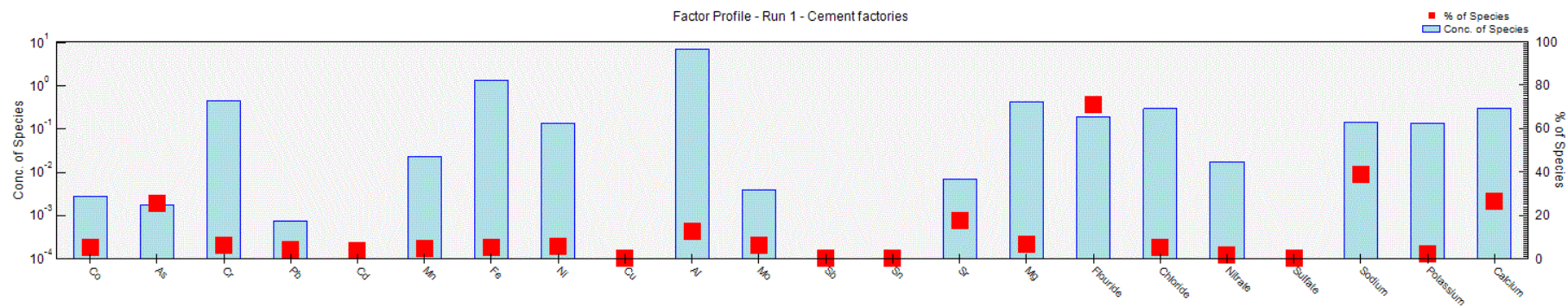


Figure 3.26. PMF results for Factor 2

Potassium is mainly a tracer of biomass burning, such as the burning of crops and wildfires (71). Chloride also comes from biomass burning (118). Hence, the source of Factor 3 was identified as biomass burning, and the results of PMF are illustrated in Figure 4.19. Because biomass burning was affected by local sources, the airmass was examined according to the highest G score value. The highest G score value was observed on 07/05/2020. The G score values are shown in Figure 4.17, and the wind rose is shown in Figure 4.18. The wind rose showed that air masses came from NNW and SSE sectors on a large scale, and many villages are located in these directions, which might release the K^+ and Cl^- .

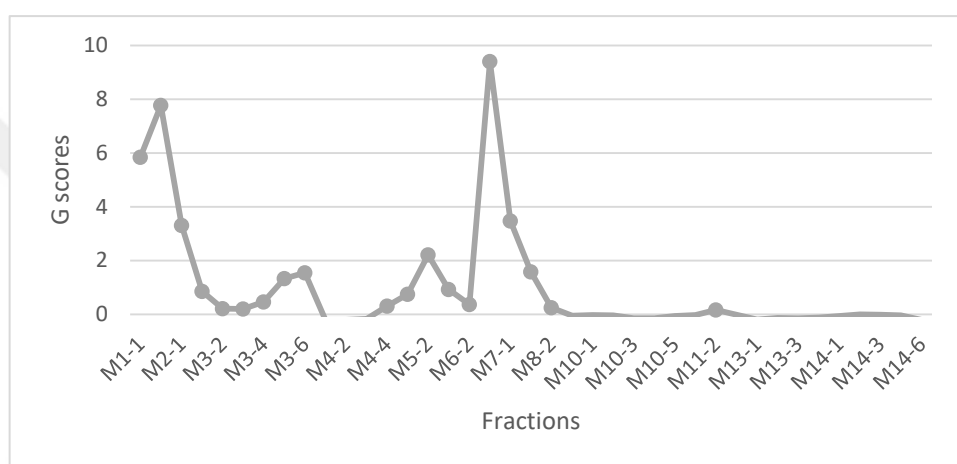


Figure 3.27. G score values of fractions for Factor 3

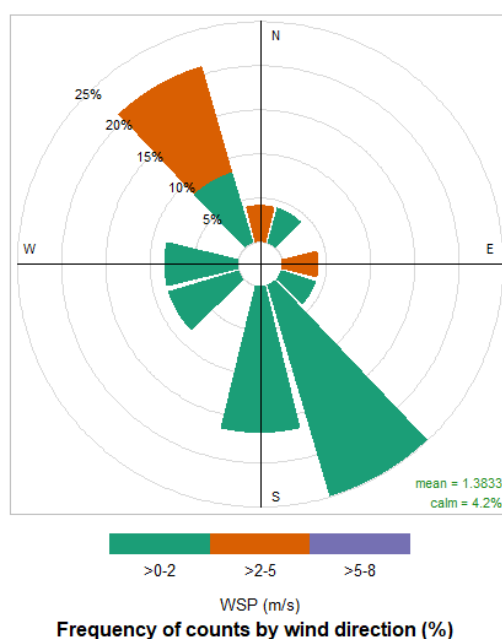


Figure 3.28. The windrose for the highest G score value

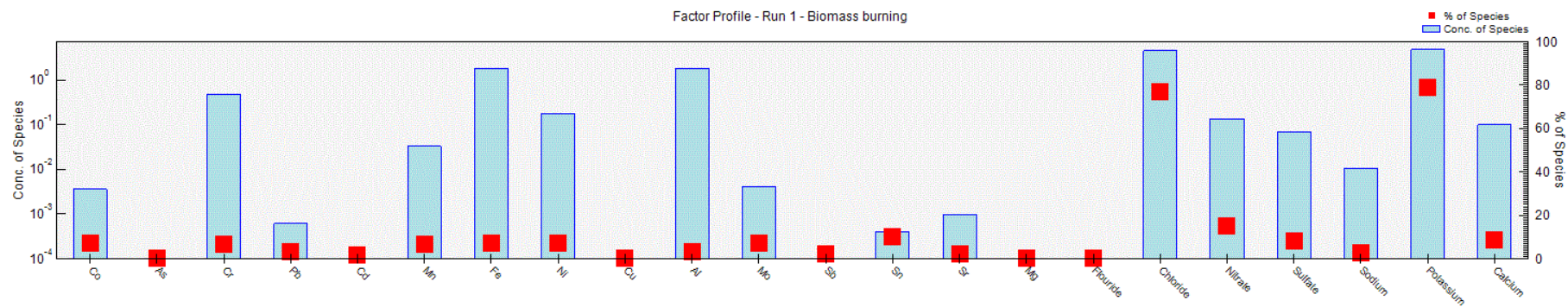


Figure 3.29. PMF results for Factor 3

As illustrated in Figure 4.22, SO_4^{2-} , NO_3^- , Ca^{2+} , and Na^+ showed the highest contribution for Factor 4. They can come from many different sources, such as coal burning, vehicle exhaust, natural weathering, soils, and long-range transportation. For that reason, the back trajectories for the highest G score values were generated for Factor 4. The results of G score values and the back trajectories are shown in Figure 4.20 and Figure 4.21, respectively. The highest G score values were observed on 21/05/2020, 27/05/2020, and 01/06/2020. The back trajectories showed air masses coming from the Aegean and Mediterranean regions to the Türkiye and passed through Central Anatolia by scavenging the pollutants and arriving at the sampling point. For that reason, Factor 4 was designated as transportation from Anatolia. However, one exception occurred on 27/05/2020 at 500 m above the ground level. The air mass at this point traveled through the Black Sea region before arriving at the sampling point. Therefore, the Na^+ contribution could be slightly affected by sea-salt contributions.

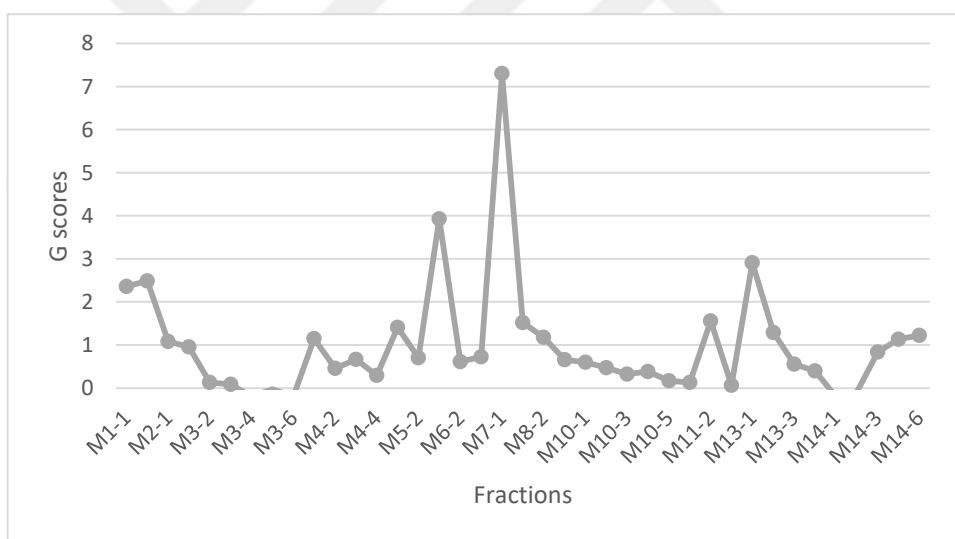


Figure 3.30. G score values of fractions for Factor 4

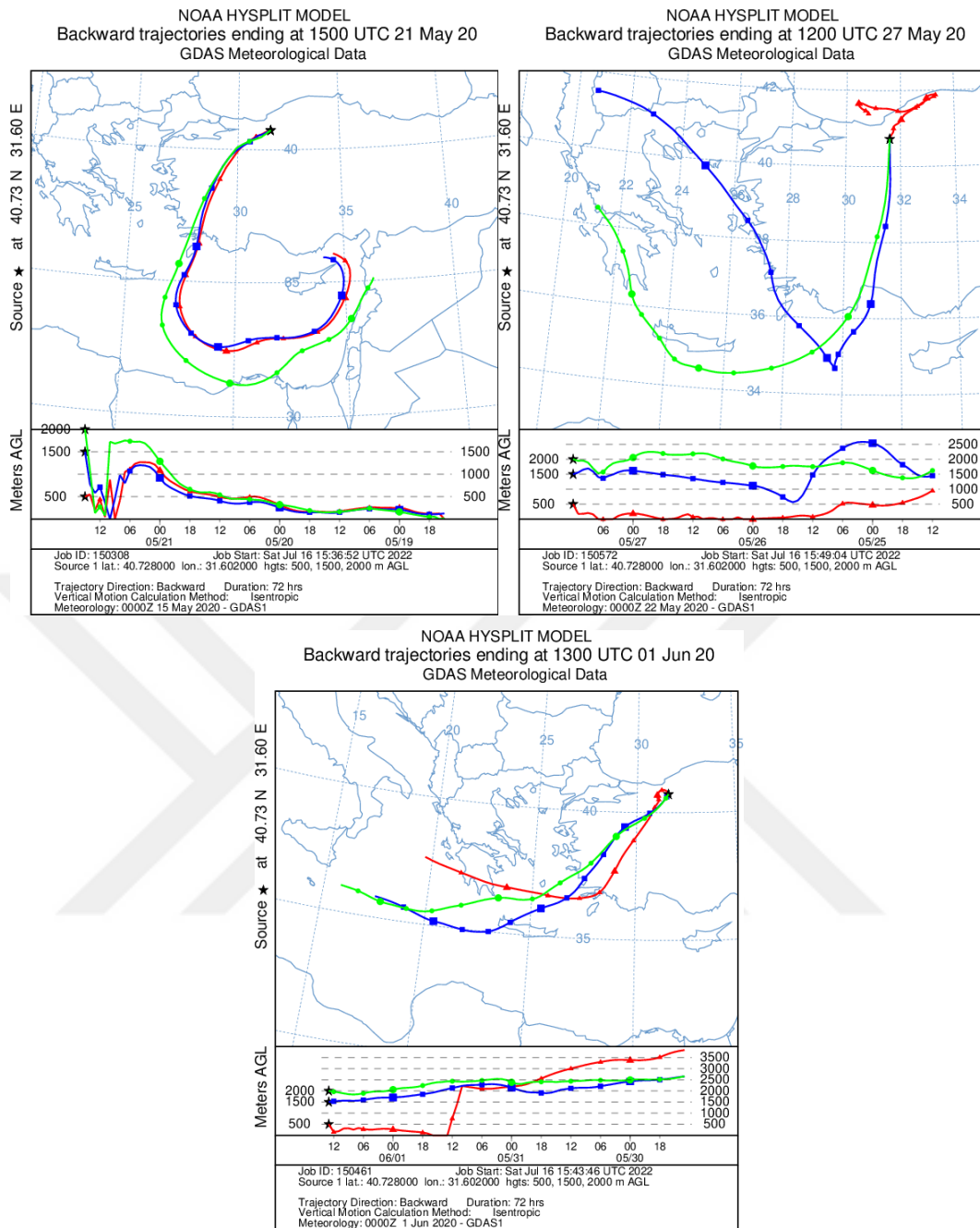


Figure 3.31. The back trajectories of the highest G scores for Factor 4

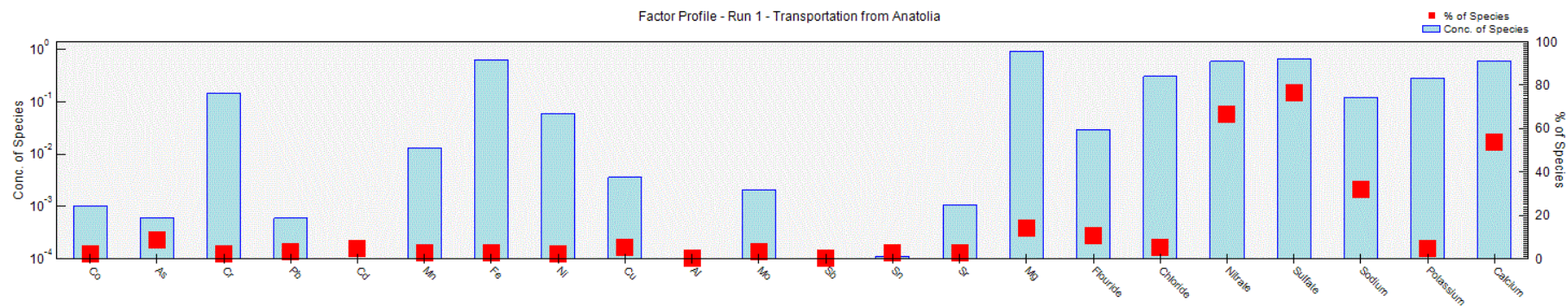


Figure 3.32. PMF results for Factor 4

Coal contains almost all elements in the Periodic Table, and coal combustion releases these elements into the atmosphere (29). The studies showed that as a tracer element, As comes from Turkish coal (120). Moreover, many elements, such as Cd, Pb, Sb, Sr, Sn, and Al, were found in coals belonging to different countries (119,121,122). Cadmium contributed mostly to Factor 5, with 77.9%, followed by Pb, Sb, Sr, Sn, As, and Al. Because of the high loadings of these elements, particularly As, Factor 1 was attributed to the coal burning. Also, according to the examination of G-score values, the back trajectory and wind rose were generated for the highest G-score date on 04/05/2020. The G-score values, back trajectory, and wind rose are illustrated in Figure 4.23, Figure 4.24, and Figure 4.25. Coal is used for residential heating in villages around Bolu. The results showed that it has many villages in the direction of the air mass from 500 m and in the prevailing wind directions of NNW and WNW. The PMF results belonging to the Factor 5 are shown in Figure 4.26.

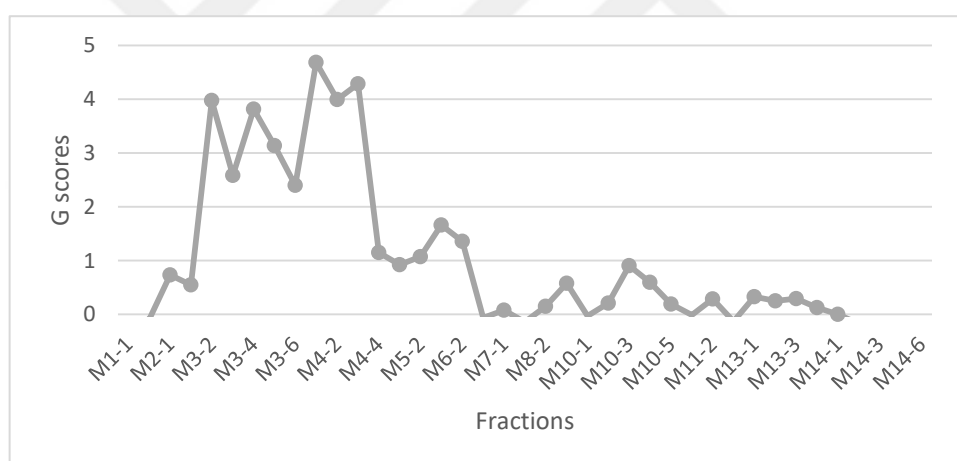


Figure 3.33. G score values of fractions for Factor 5

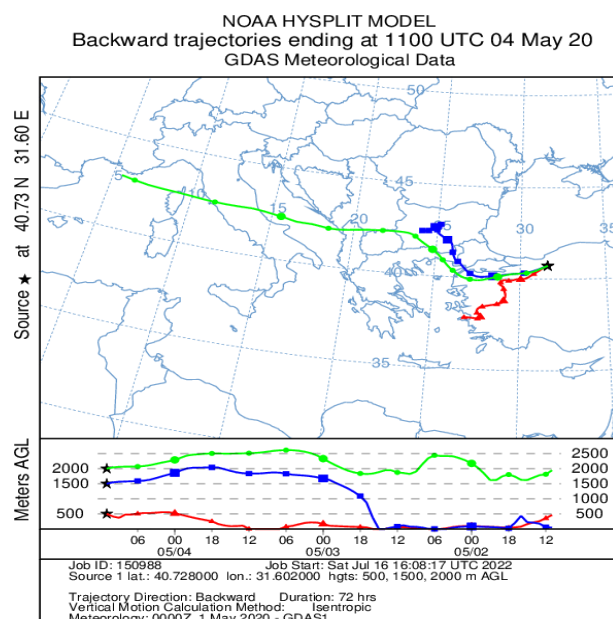


Figure 3.34. The back trajectory of the highest G score for Factor 5

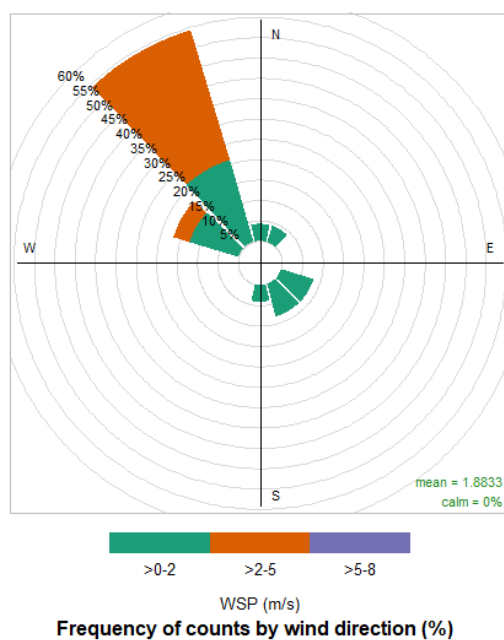


Figure 3.35. The windrose for the highest G score value

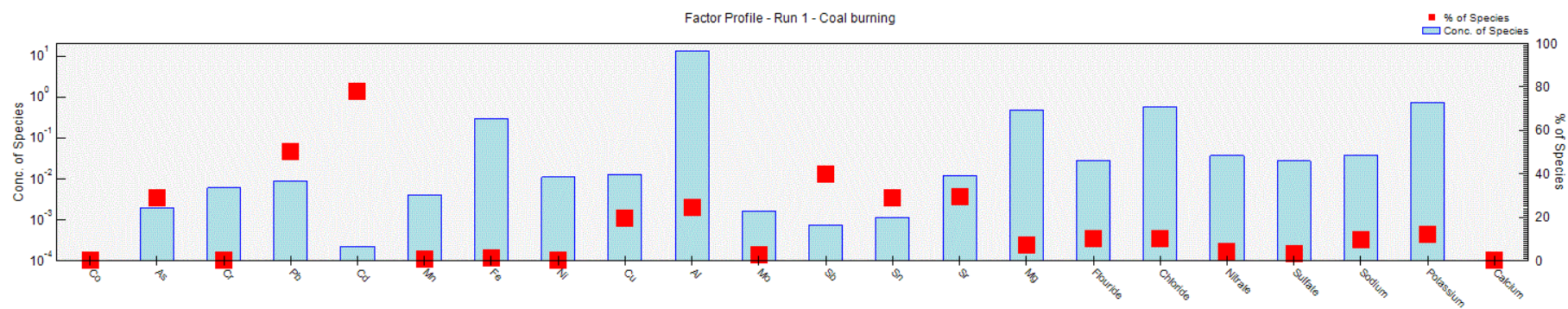


Figure 3.36. PMF results for Factor 5

The contributions of Mg, Al, Sb, Sr, and Pb were observed in Factor 6. Magnesium had a higher contribution to Factor 6, explained as 70%, followed by Al, Sb, Sr, and Pb in the descending order. Magnesium, Al, and Sr are highly found in the earth's crust, and sandstorms bring these elements to the atmosphere through the erosion of rocks and sediments (112,123). Further, one of the possible sources of Pb in the urban atmosphere is vehicular emissions. Antimony is a tracer element of waste incineration (124), and people living in Bolu burn their garbage in open atmosphere (125). Moreover, the back trajectory was generated from the fraction date with the highest G score. The higher G score value was determined on 02/06/2020. It has been observed that the air masses at 500 and 1500 m travel in the Bolu's urban atmosphere before coming to the sampling site. For that reason, Factor 6 was named the urban atmosphere. The G score values, the back trajectory, and PMF results are illustrated in Figures 4.27, 4.28, and 4.29, respectively.

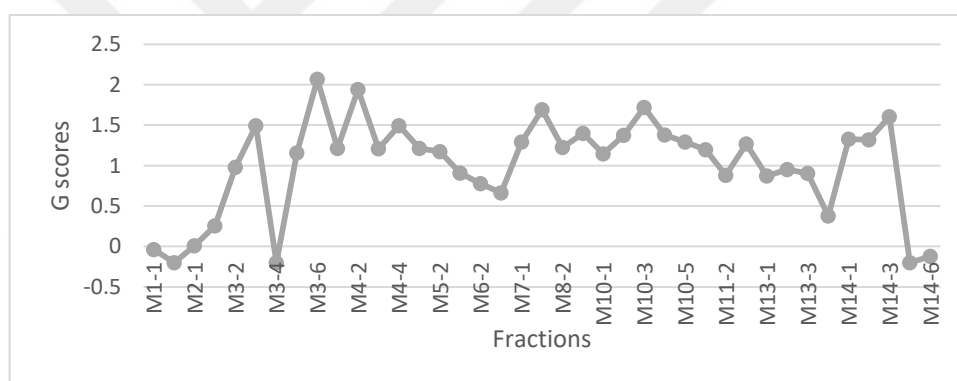


Figure 3.37. G score values of fractions for Factor 6

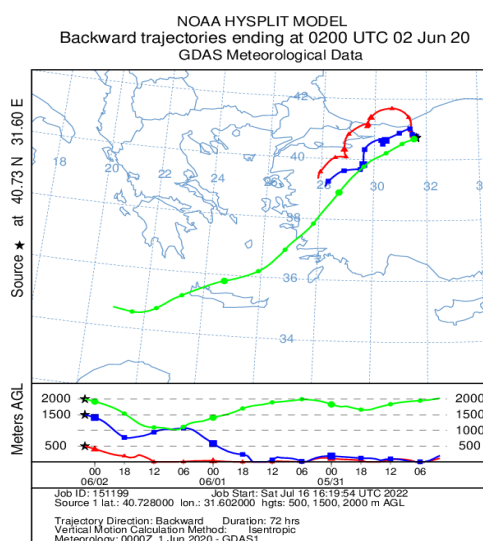


Figure 3.38. The back trajectory of the highest G score for Factor 6

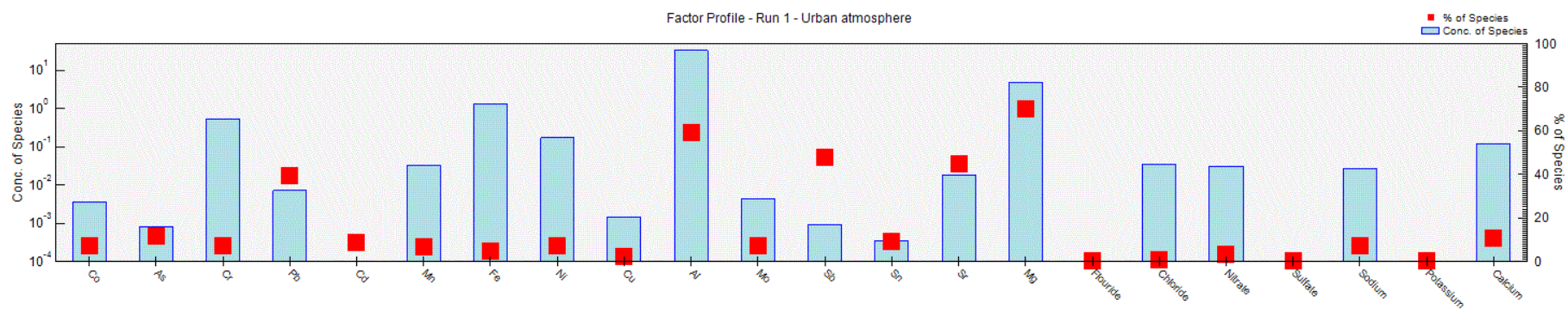


Figure 3.39. PMF result for Factor 6

4.8.2.2 The PMF Results for the Semi-urban Area

In Factor 1, the characteristic species were SO_4^{2-} , Ca^{2+} , Na^+ , and Sr with the contribution rates of 80%, 76%, 54%, and 21%. Previous studies have shown that SO_4^{2-} and Ca^{2+} could be considered markers of sulfur-rich minerals like gypsum (30). Also, analyses performed on minerals and stones revealed that Sr is frequently present in gypsum (126). Moreover, coal combustion is a primary source of SO_2 in our country. After SO_2 is released into the atmosphere, it may have been converted to SO_4^{2-} with atmospheric chemical reactions during transportation to the sampling point with rain clouds (127,128). These results demonstrated that this factor was affected by the long-range transportation, and back trajectory analysis was performed to support our estimation by the highest G-score values on 18.06.2020 and 04.05.2020, and according to the back trajectory analysis, the air mass at 1000 m was observed coming from the Europe and Mediterranean Sea-Anatolia regions to the sampling site. The G-score values, back trajectory analysis results, and PMF results are shown in Figures 4.30, 4.31, and 4.32.

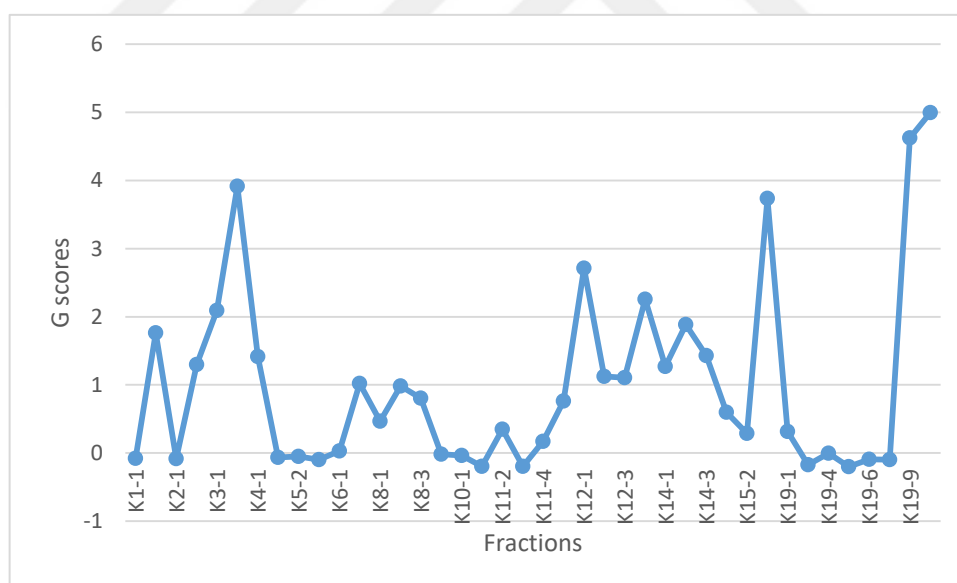


Figure 3.40. G score values of fractions for Factor 1

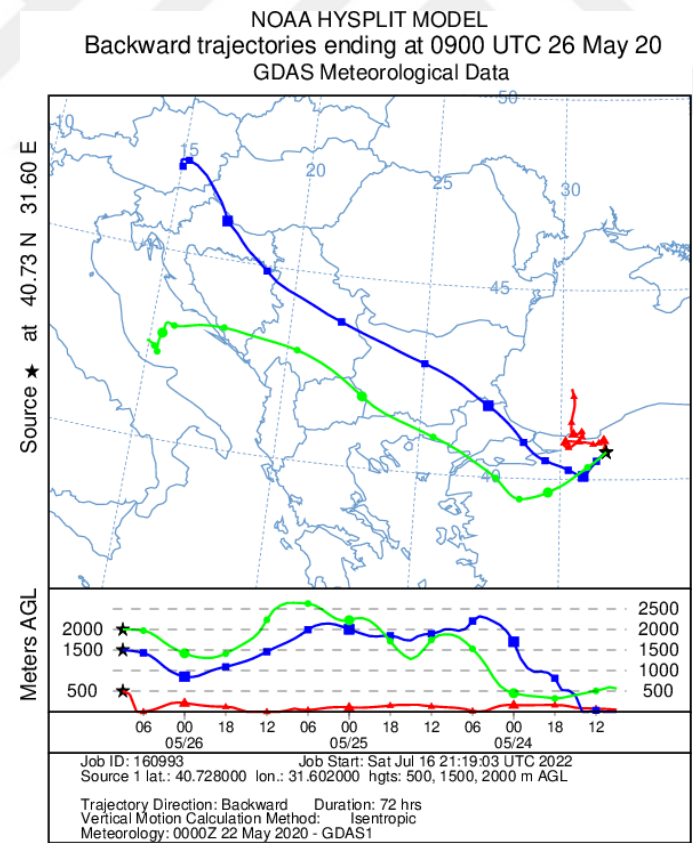
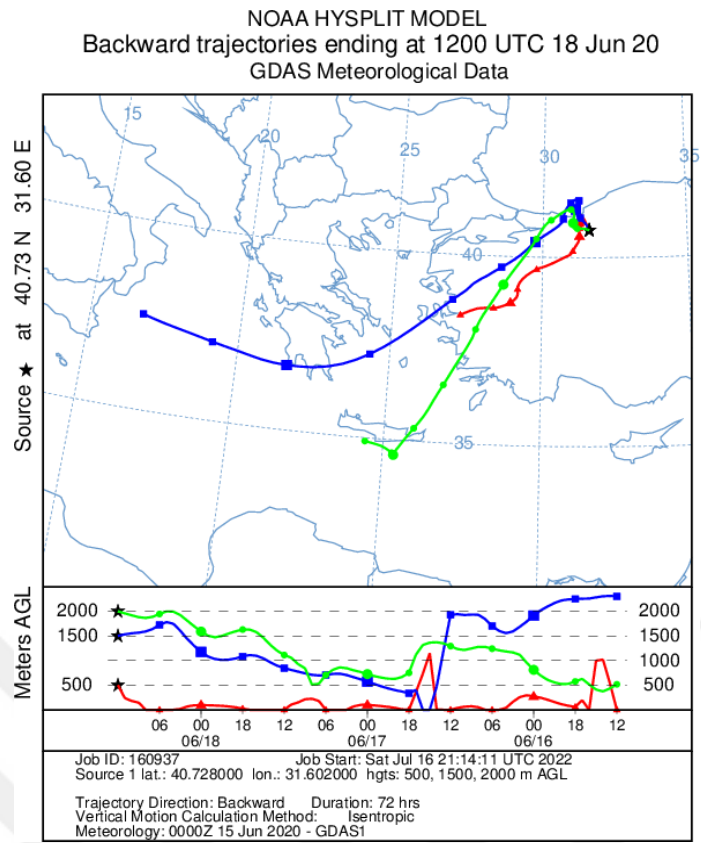


Figure 3.41. The back trajectories of the highest G scores for Factor 1

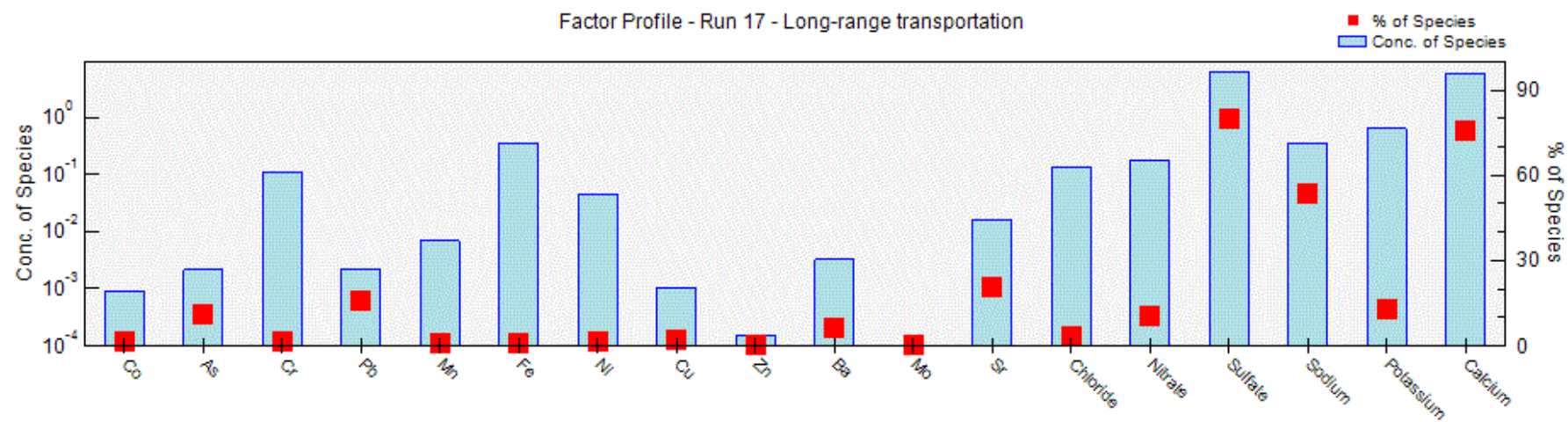


Figure 3.42. PMF results for Factor 1

Factor 2 was composed of the contribution of NO_3^- , with 79%. For that reason, this factor was attributed to the nitrate factor. In the atmosphere, NO_3^- might come from various sources, such as vehicles and biomass burning as anthropogenic sources and forest fires and soils as natural sources (32). Also, the windrose, created from the highest G-score values, showed that the prevailing wind direction was the NNW sector, which had TEM and D100 highways, and this sector might affect the emission of NO_3^- coming from the traffic. The G score values, the windrose, and the PMF results are shown in Figures 4.33, 4.34, and 4.35.

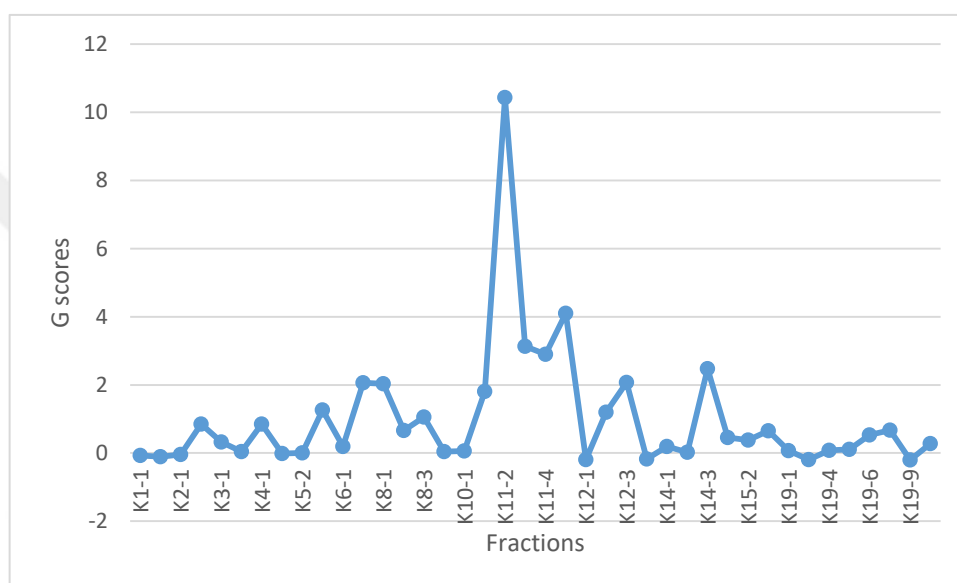


Figure 3.43. G score values of fractions for Factor 1

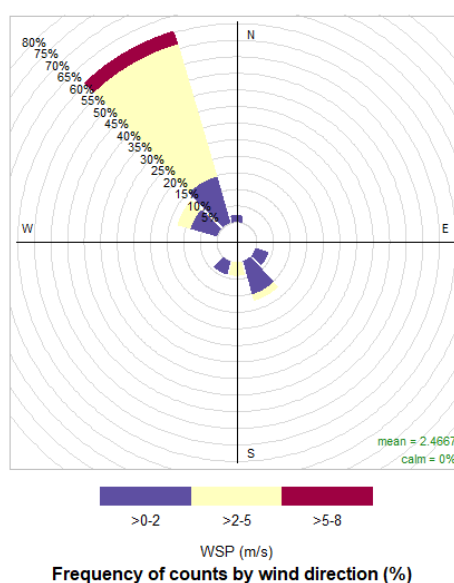


Figure 3.44. The windrose for the highest G score values

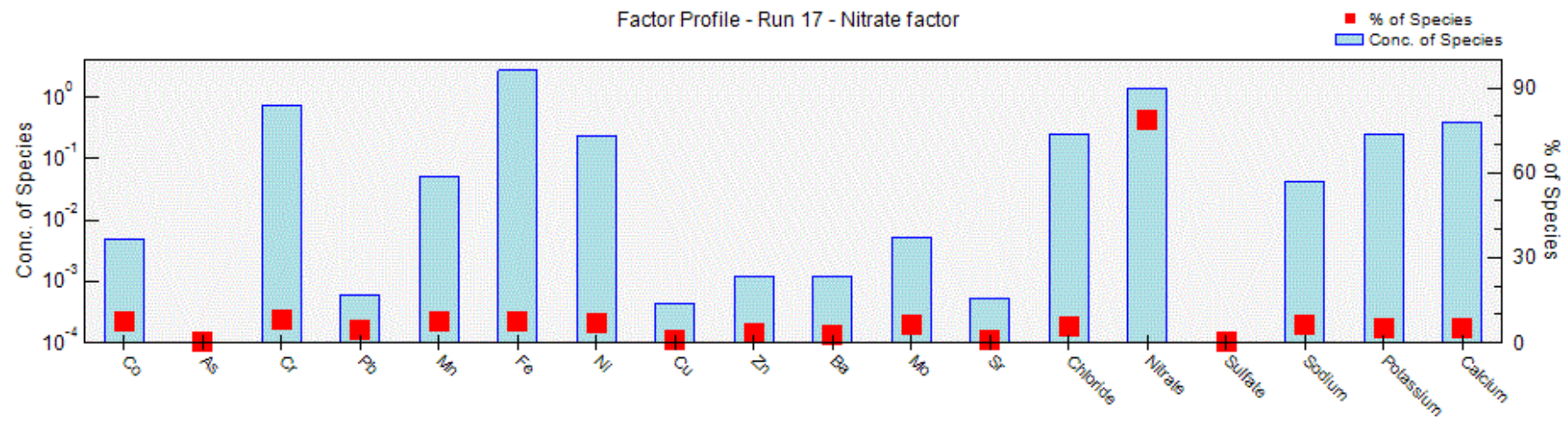


Figure 3.45. PMF results for Factor 2

In Factor 3, the characteristic elements were determined to be Mo, Co, Cr, Ni, Fe, Mn, and Cu. The back trajectory and pollution rose were generated from the highest G-score value on 26.06.2020 to support our prediction. From the back trajectory, the air mass at 500 m was close to Zonguldak, and the windrose showed that one of the prevailing wind sector was in the NNE direction. Zonguldak has many iron-steel factories known as ERDEMİR. For that reason, this factor was attributed to iron-steel industries. The G score, the back trajectory, the windrose, and the PMF results are illustrated in Figures 4.36, 4.37, 4.38, and 4.39.

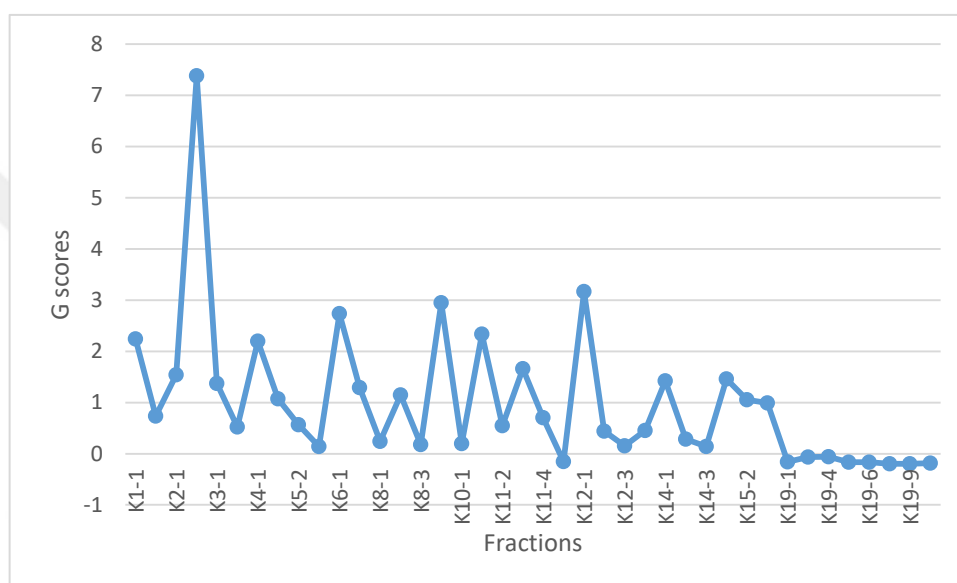


Figure 3.46. G score values of fractions for Factor 3

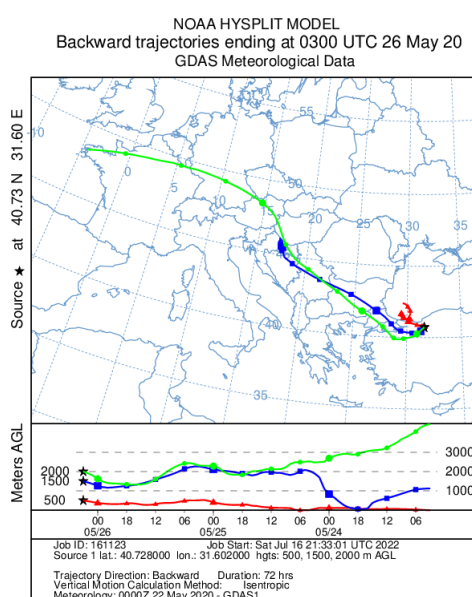


Figure 3.47. The back trajectory of the highest G score for Factor 3

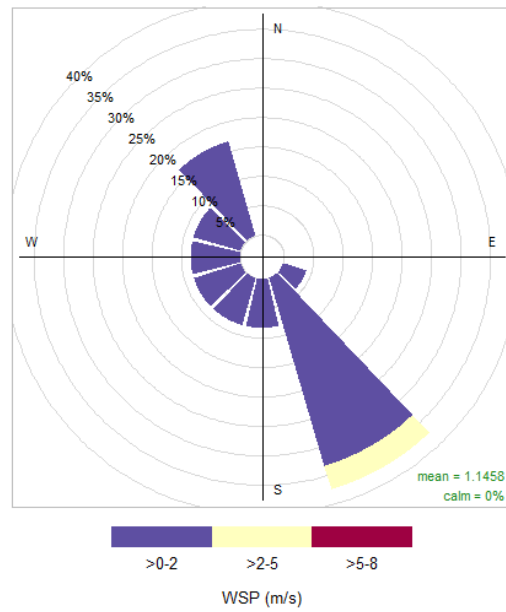


Figure 3.48. The windrose for the highest G-score value

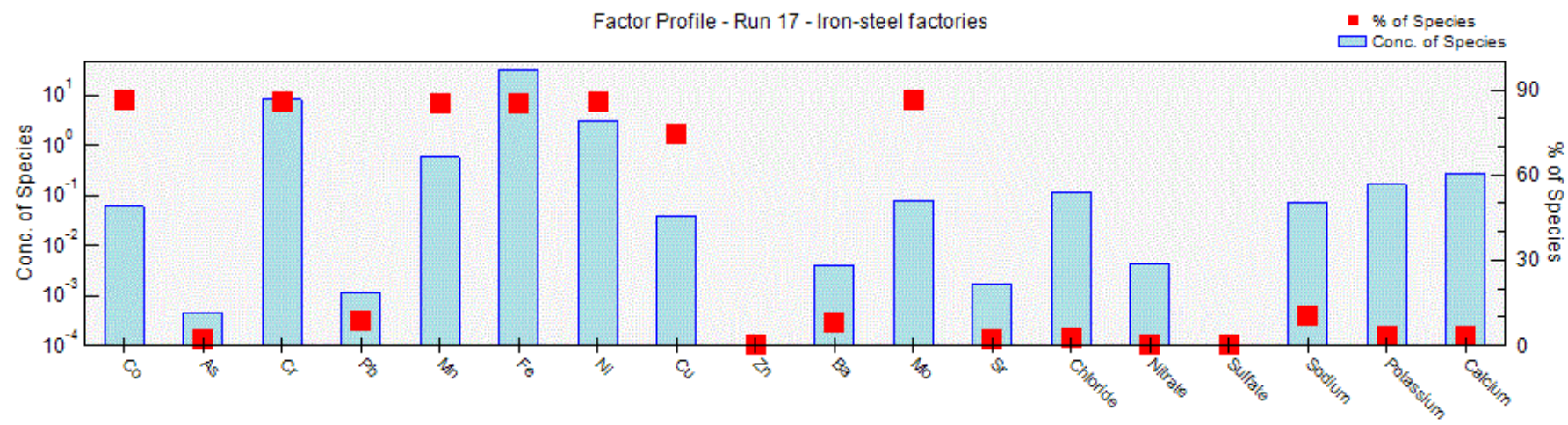


Figure 3.49. PMF results for Factor 3

Potassium mainly comes from biomass burning, such as the forest fire, domestic fuel, and crop burning, and Cl^- also may come from biomass burning (71,129). For that reason, factor 4 was identified as biomass burning, and windrose was generated from the highest G-score value on 03.05.2020 to support our prediction. The prevailing wind sectors were determined as SSE, NNW, and S, and some agricultural areas are located in these directions, where people use wood for domestic heating and people also burn their garbage in the stoves. The G score, the windrose, and the PMF results are shown in Figures 4.40, 4.41, and 4.42.

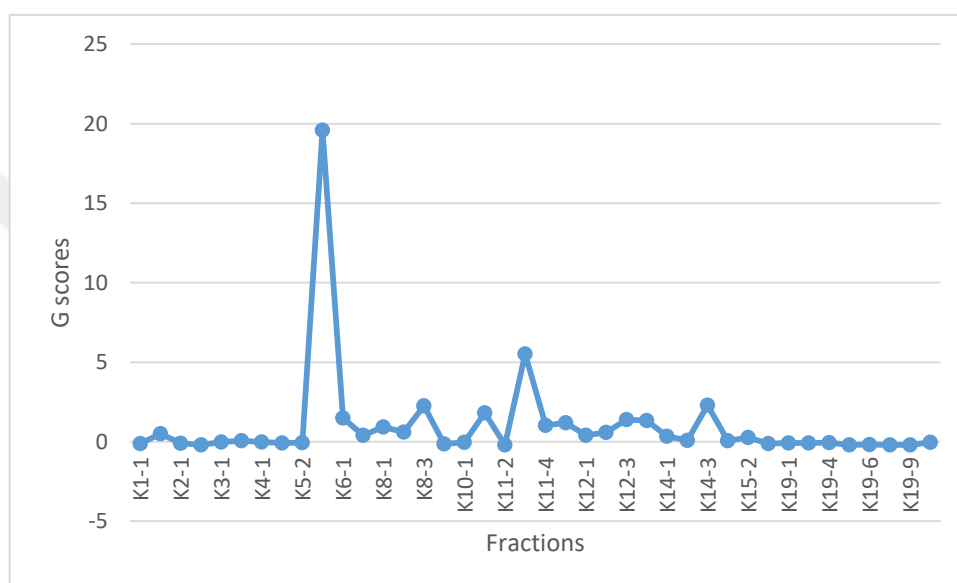


Figure 3.50. G score values of fractions for Factor 4

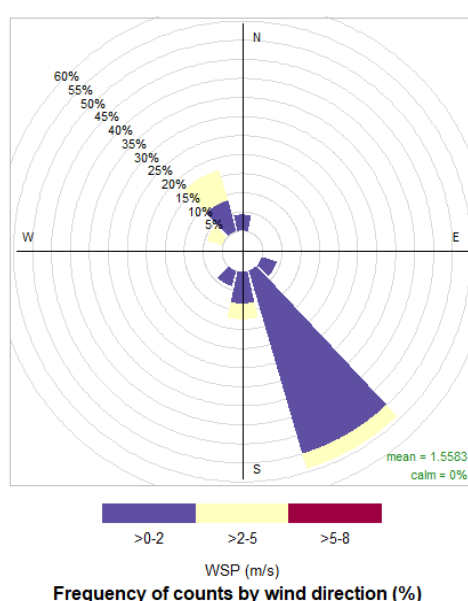


Figure 3.51. The windrose for the highest G score value

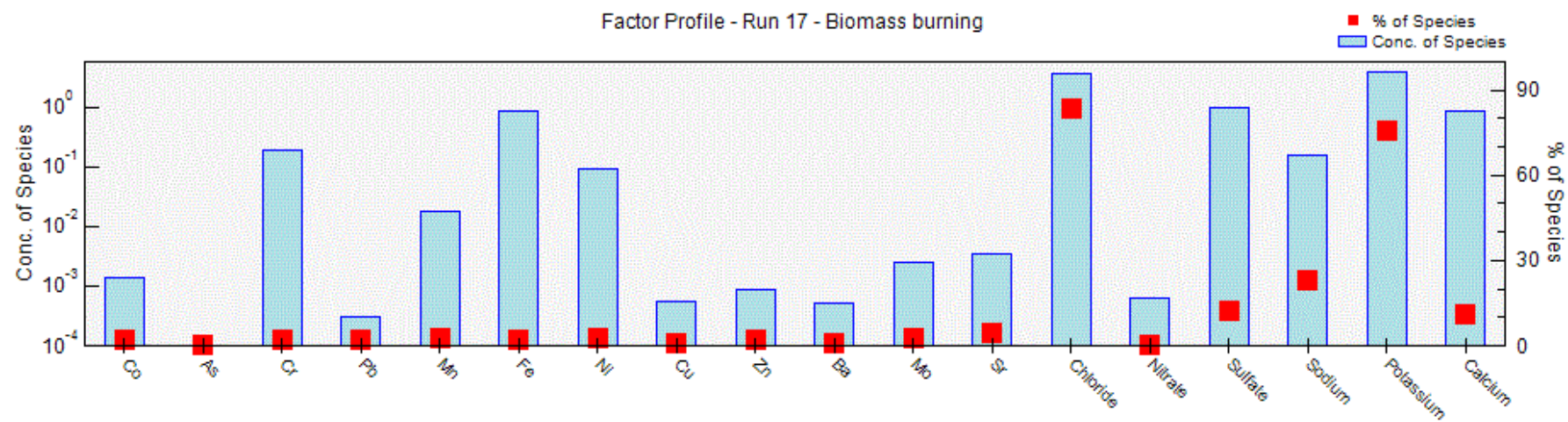


Figure 3.52. PMF results for Factor 4

The PMF results of Factor 5 are illustrated in Figure 4.46. This factor was comprised from high loadings of Zn, As, Ba, Se, Pb, and Cu. The percent contributions of Zn, As, Ba, Se, and Pb were higher than 60%, and Cu contributed 20%. The coal is still used for domestic heating in the sampling area, and As is known as a tracer element for Turkish coal (120). Also, Zn, Ba, Se, Pb, and Cu are probably related to vehicle emissions, which can contribute to the loading of metals into the atmosphere through different pathways, such as fuel combustion or mechanical abrasion of tires and brakes (117,130,131). The highest G-score value was observed on 16.06.2020 and is illustrated in Figure 4.43. The back trajectory (Figure 4.44) and windrose (Figure 4.45) were created for this date. After examination of the results, it has been observed that the air mass at 500 m and 1500 m sank to the ground when above TEM and D100 highways and then rose to the sampling area. On the other hand, the prevailing wind sectors were determined as NNW, WNW, and SSE, which might cause the coal emissions from the villages. For that reason, Factor 5 was named vehicular emissions and coal burning.

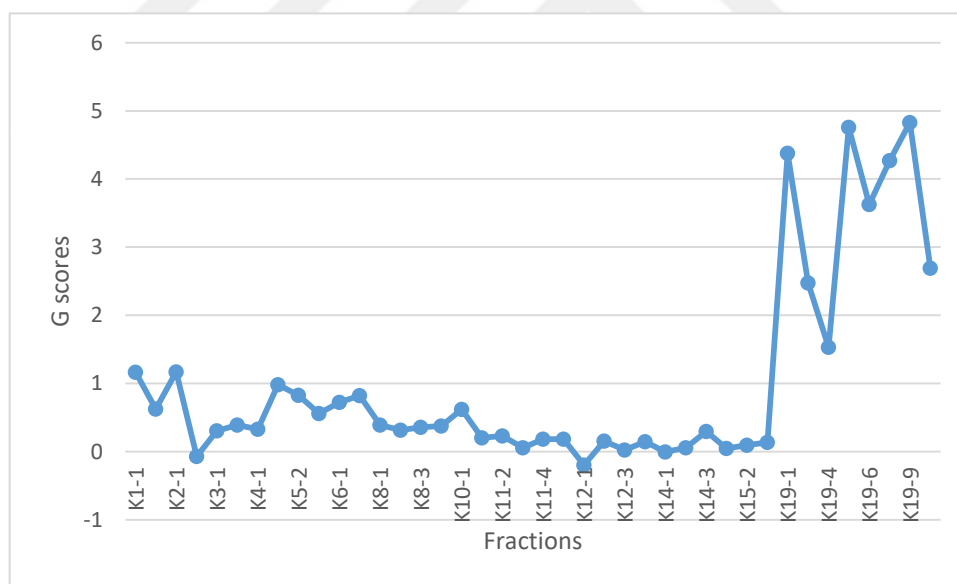


Figure 3.53. G score values of fractions for Factor 5

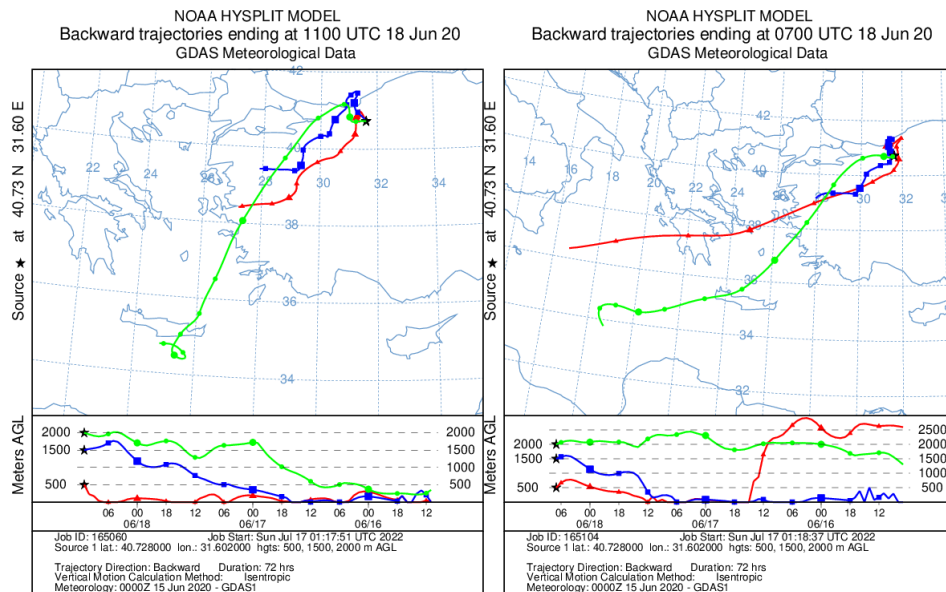


Figure 3.54. The back trajectories of highest G scores for Factor 5

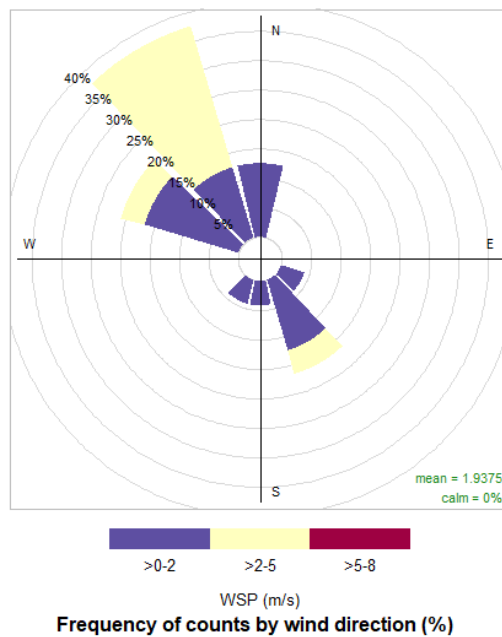


Figure 3.55. The windrose for the highest G-score value

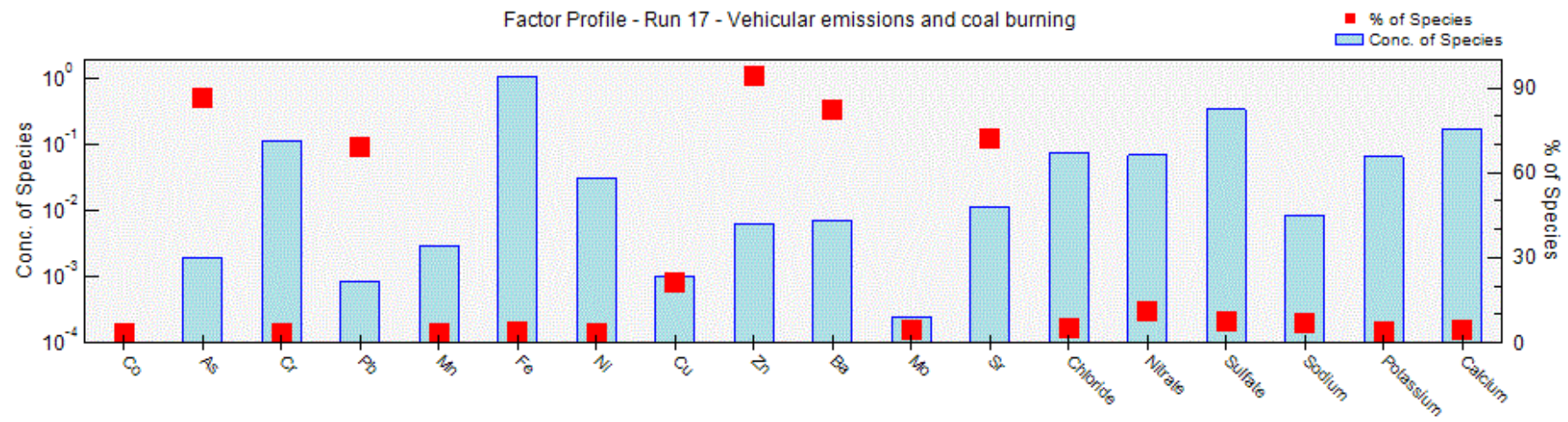


Figure 3.56. PMF results for Factor 5

The percent contribution of each factor in urban area is illustrated in Figure 4.47. Iron-steel factories had the highest contribution, while bolu-cement factory had the lowest contribution in the urban area.

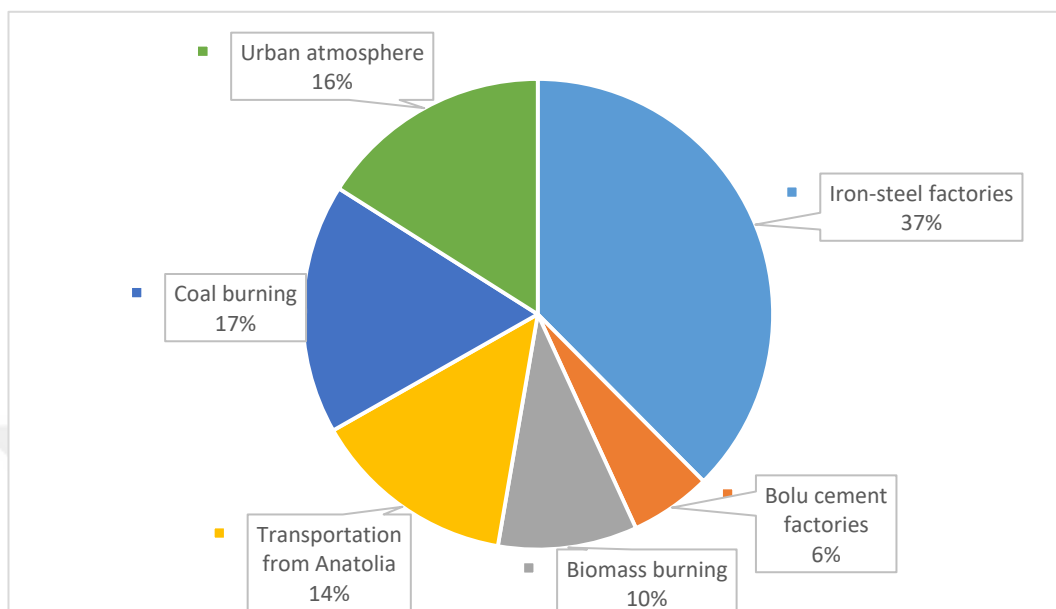


Figure 3.57. Percent contribution of each factor for urban area

The percent contribution of each factor in semi-urban area is illustrated in Figure 4.48. Iron-steel factories had the highest contribution, while nitrate factor had the lowest contribution in the semi-urban area.

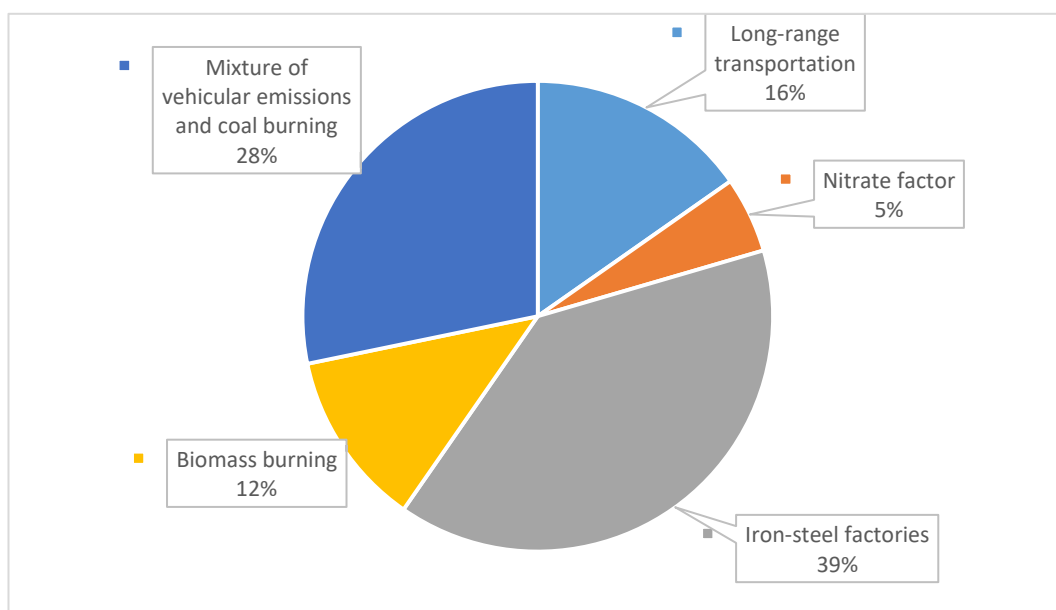


Figure 4.58. Percent contribution of each factor for semi-urban area

5. CONCLUSIONS AND RECOMMENDATIONS

1. One hundred sixty-seven volume-based fractional precipitation samples were collected to investigate the chemical characteristics of rainwater in two (urban and semi-urban) sites of Bolu from May to June 2020.
2. The major anions (F^- , Cl^- , NO_2^- , Br^- , NO_3^- , PO_4^{3-} , and SO_4^{2-}) and major cations (Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+}) and trace elements (Ag, Al, As, Ba, Bi, Cd, Co, Cr, Cs, Cu, Fe, Ga, Li, Mg, Mn, Mo, Ni, Pb, Sb, Sn, Sr, V, and Zn) were determined by using ion chromatography and ICP-MS in the collected samples, respectively.
3. The ion balance was calculated by adding bicarbonate and hydronium ions to the total concentration of anions and cations, and the results were in the range of quality criteria of the EPA.
4. The semi-urban area showed higher VWM concentrations for anions and cations than the urban area. The concentrations of anions and cations were found as 524 $\mu eq/L$ and 798 $\mu eq/L$ for the semi-urban area, while 176 $\mu eq/L$ and 202 $\mu eq/L$ for the urban area. The concentrations of anions in the urban area followed the order of $Cl^- > SO_4^{2-} > HCO_3^- > NO_3^- > F^- > PO_4^{3-} > NO_2^-$, while cations were in the order of $K^+ > Ca^{2+} > NH_4^+ > Na^+ > Mg^{2+}$. Also, the concentrations of anions in the semi-urban area followed the order of $SO_4^{2-} > Cl^- > HCO_3^- > NO_3^- > PO_4^{3-} > NO_2^- > F^-$, while cations were in the order of $Ca^{2+} > NH_4^+ > K^+ > Na^+ > Mg^{2+}$.
5. According to the calculated volume-weighted mean concentrations of trace elements, the semi-urban area (103 $\mu g/L$) higher than the urban area (70.2 $\mu g/L$). The order of trace elements for the urban area was in the sequence of $Al > Fe > Mg > Cr > Ni > Ba > Li > Mn > Ga > Zn > V > As > Sr > Mo > Pb > Cu > Co > Cs > Sn > Bi > Ag > Sb > Cd$. Also, the trace elements in the semi-urban area were in the order of $Fe > Al > Cr > Mg > Ni > Mn > Sr > Li > Mo > Zn > As > V > Co > Ga > Cu > Ba > Pb > Cs > Sn > Bi > Ag > Cd > Sb$.
6. The pH of the collected samples in the urban area varied from 4.66 to 7.74, with a median of 6.29, while from 5.37 to 8.37, with a median of 6.79 for the semi-urban area. Despite the alkaline character of rainwater in both

areas, 7.40% for the urban area and 4.30% for the semi-urban area, acid rain was observed.

7. The neutralization of acidity was predominantly carried out by K^+ (NF = 3.02) and Ca^{2+} (NF = 1.47) for the urban area, while Ca^{2+} (NF = 1.99) and NH_4^+ (NF = 1.12) for the semi-urban area.
8. The multiple linear regression analysis was used to investigate the correlation between the acidic and alkaline ions. The results showed that 82.9% of SO_4^{2-} and 87.1% of NO_3^- were explained by alkaline species for the urban area, while 82.0% of SO_4^{2-} and 3.76% of NO_3^- were explained for the semi-urban area. Calcium, with 80.1%, mostly contributed to the neutralization of SO_4^{2-} in the urban area, while Mg^{2+} , with 98.0%, contributed to the semi-urban area.
9. The fractional acidity ratios were calculated as 0.0244 for the urban area and 0.00135 for the semi-urban area, and it indicated that almost all of the acidity of precipitation was neutralized by alkaline species in both areas.
10. Because agricultural activities are common in the sampling points, the percent ratios of AAI were calculated for the urban and semi-urban areas as 43.0% and 46.3%. As a result of agricultural activities, it was found that nearly half of the acidity was neutralized by ammonia in both sampling points.
11. The high NP/AP for the urban (4.40 on average) and the semi-urban (3.70 on average) areas demonstrated that alkaline species in the rainwater of Bolu had great potential for stabilizing acidity.
12. It was observed that the acidity in the atmosphere of Bolu was mainly caused by sulfuric acid when the $[NO_3^-] / [SO_4^{2-}]$ ratio was examined. The results were found to be 0.62 for the urban area and 0.52 for the semi-urban area, and it also showed that point sources were dominant over mobile sources.
13. According to the Na^+ % (36.9 for the urban and 24.6 for the semi-urban) and SAR (0.655 for the urban and 0.719 for the semi-urban) values, it has been observed that the rainwater in Bolu is of good quality, had no pose a danger to the vegetation, and might also be used as irrigation water in agricultural activities.

14. In the urban area, the results of the crustal enrichment factor for elements stated that Cu, Fe, Al, Zn, Ba, Mn, and Mg originated from the crustal source, while Bi, Cr, Mo, and Ni originated from anthropogenic emissions. On the other hand, in the semi-urban area, Fe, Mn, Cu, Pb, Zn, V, Al, Mg, and Ba came from the crustal origin, while Bi, Cr, Mo, Ni, and Ag came from anthropogenic emissions. Moreover, the elements, which arose from a mix of anthropogenic and soil-derived, were determined as Sb, Ni, Ga, V, Co, Sn, Cd, and Pb in the urban area and as Sb, Ni, Ga, V, Co, Sn, Cd, and Pb in the semi-urban area.
15. Using the PMF model, six factors were identified for urban area. The high-loading elements in Factor 1 were Fe, Co, Mn, Cr, Ni, Mo, Cu, and Sn, and this factor was named iron-steel factories. Factor 2 was identified as a cement factory, and F^- , Na^+ , Ca^{2+} , and As contributed mostly to this factor. Factor 3 was attributed to biomass burning because of the high loadings of K^+ and Cl^- , tracers of biomass burning. Sulfate, NO_3^- , Ca^{2+} , and Na^+ greatly contributed to Factor 4, named as transportation from Anatolia. The contributions of Cd, Pb, Sb, Sr, Sn, and Al were observed in Factor 5, and because As is a tracer element for Turkish coal, this factor was attributed to coal burning. Factor 6 had the contribution of Mg, Al, Sb, Sr, and Pb, and because of the high local source potential of these elements, this factor was named the urban atmosphere.
16. Likewise, five factors were identified for the semi-urban area. Sulfate, Ca^{2+} , and Na^+ were observed in Factor 1, named as long-range transportation. Because the NO_3^- was the only ion in Factor 2, this factor was attributed to nitrate. Molybdenum, Co, Cr, Ni, Fe, Mn, and Cu were contributed to Factor 3, called iron-steel factories. Biomass burning affected Factor 4, and Cl^- , K^+ , and Na^+ were observed in this factor. Finally, due to the contribution of Zn, As, Ba, Sr, Pb, and Cu in Factor 5, this factor was named as the mixture of vehicular emission and coal burning.
17. The percent contribution of factors in the urban area was determined as iron-steel factories at 37%, coal burning at 17%, the urban atmosphere at 16%, transportation from Anatolia at 14%, the biomass burning at 10%, and the Bolu cement factories at 6%.

18. The percent contribution of factors in the semi-urban area was determined as iron-steel factories at 39%, mixture of vehicular emissions and coal burning at 28%, long-range transportation at 16%, biomass burning at 12%, nitrate factor at 5%.
19. In future works, the precipitation samples should be collected in rural, semi-urban and urban areas. Also, temporal, seasonal, and long-term variability should be evaluated by collecting long-term (2-5 years) fractional precipitation samples.
20. The collected samples should be analyzed to determine the concentrations of persistent organic compounds, EC-OC, and the amount of microplastics even viruses or bacteria.



6. REFERENCES

“Vancouver citation system was used in this thesis.”

1. Manahan S. Environmental chemistry, Tenth edition. Environmental Chemistry, Tenth Edition. CRC Press; 2017. 1–752 p.
2. Manisalidis I, Stavropoulou E, Stavropoulos A, Bezirtzoglou E. Environmental and Health Impacts of Air Pollution: A Review. Vol. 8, Frontiers in Public Health. Frontiers Media S.A.; 2020.
3. Kılıç Z. Su Kirliliği Nedenleri, Olumsuz Etkileri ve Önleme Yöntemleri. İstanbul Sabahattin Zaim Üniversitesi Fen Bilimleri Enstitüsü Dergisi. 2021 Mar 15;
4. Chen HY, Hsu LF, Huang SZ, Zheng L. Assessment of the components and sources of acid deposition in northeast asia: A case study of the coastal and metropolitan cities in Northern Taiwan. Atmosphere (Basel). 2020;11(9).
5. Environmental Pollution Centers [Internet]. What Is Soil Pollution? 2021 [cited 2021 Oct 20]. Available from: <https://www.environmentalpollutioncenters.org/soil/>
6. Hassan Al-Taai SH. Soil Pollution - Causes and Effects. In: IOP Conference Series: Earth and Environmental Science. IOP Publishing Ltd; 2021.
7. EPA [Internet]. Criteria Air Pollutants. 2021 [cited 2021 Oct 20]. Available from: <https://www.epa.gov/criteria-air-pollutants>
8. Meng Y, Zhao Y, Li R, Li J, Cui L, Kong L, et al. Characterization of inorganic ions in rainwater in the megacity of Shanghai: Spatiotemporal variations and source apportionment. Atmos Res. 2019 Jul 1;222:12–24.
9. Wang L, Shen Z, Lu D, Zhang Q, Zhang T, Lei Y, et al. Water-soluble components in rainwater over Xi'an in northwest China: Source apportionment and pollution controls effectiveness evaluation. Atmos Pollut Res. 2019 Mar 1;10(2):395–403.
10. Marlon JR, Bloodhart B, Ballew MT, Rolfe-Redding J, Roser-Renouf C, Leiserowitz A, et al. How Hope and Doubt Affect Climate Change Mobilization. Front Commun (Lausanne). 2019 May 21;4.
11. Suman HK, Bolia NB, Tiwari G. Comparing public bus transport service attributes in Delhi and Mumbai: Policy implications for improving bus services in Delhi. Transp Policy (Oxf). 2017 May 1;56:63–74.
12. Upadhyay A, Bolia NB. An optimization based decision support system for integrated planning and scheduling on dedicated freight corridors. Int J Prod Res. 2014 Dec 17;52(24):7416–35.
13. Gautam D, B. Bolia N. Air pollution: impact and interventions. Vol. 13, Air Quality, Atmosphere and Health. Springer; 2020. p. 209–23.
14. Keresztesi Á, Nita IA, Boga R, Birsan MV, Bodor Z, Szép R. Spatial and long-term analysis of rainwater chemistry over the conterminous United States. Environ Res. 2020;188.

15. State of Global Air [Internet]. Boston, MA; 2020 [cited 2021 Oct 20]. Available from: <https://www.stateofglobalair.org/>
16. Esworthy R. Air Quality: EPA's 2013 Changes to the Particulate Matter (PM) Standard [Internet]. 2015. Available from: www.crs.gov
17. Atkinson RW, Fuller GW, Anderson HR, Harrison RM, Armstrong B. Urban ambient particle metrics and health: A time-series analysis. *Epidemiology*. 2010 Jul;21(4):501–11.
18. Cheung K, Daher N, Kam W, Shafer MM, Ning Z, Schauer JJ, et al. Spatial and temporal variation of chemical composition and mass closure of ambient coarse particulate matter (PM_{10-2.5}) in the Los Angeles area. *Atmos Environ*. 2011 May;45(16):2651–62.
19. Srimuruganandam B, Shiva Nagendra SM. Source characterization of PM₁₀ and PM_{2.5} mass using a chemical mass balance model at urban roadside. *Science of the Total Environment*. 2012 Sep 1;433:8–19.
20. Kwon HS, Ryu MH, Carlsten C. Ultrafine particles: unique physicochemical properties relevant to health and disease. Vol. 52, *Experimental and Molecular Medicine*. Springer Nature; 2020. p. 318–28.
21. EPA [Internet]. Ground-level Ozone Basics. 2021 [cited 2021 Oct 21]. Available from: <https://www.epa.gov/ground-level-ozone-pollution/ground-level-ozone-basics#effects>
22. EPA [Internet]. Basic Information about Carbon Monoxide (CO) Outdoor Air Pollution. 2021 [cited 2021 Oct 21]. Available from: <https://www.epa.gov/co-pollution/basic-information-about-carbon-monoxide-co-outdoor-air-pollution#Effects>
23. Hill KA, Shepson PB, Galbavy ES, Anastasio C. Measurement of wet deposition of inorganic and organic nitrogen in a forest environment. *J Geophys Res Biogeosci*. 2005;110(G2):n/a-n/a.
24. Crutzen PJ, Lelieveld J. Human Impacts on Atmospheric Chemistry. *Annu Rev Earth Planet Sci* [Internet]. 2001 May 1;29(1):17–45. Available from: <https://doi.org/10.1146/annurev.earth.29.1.17>
25. Khan MF, Maulud KNA, Latif MT, Chung JX, Amil N, Alias A, et al. Physicochemical factors and their potential sources inferred from long-term rainfall measurements at an urban and a remote rural site in tropical areas. *Science of the Total Environment* [Internet]. 2018;613–614(October 2017):1401–16. Available from: <https://doi.org/10.1016/j.scitotenv.2017.08.025>
26. Jickells T, Knap A, Church T, Galloway J, Miller J. Acid rain on Bermuda. *Nature* [Internet]. 1982;297(5861):55–7. Available from: <https://doi.org/10.1038/297055a0>
27. Möller L, Schuetzle D, Autrup H. Future research needs associated with the assessment of potential human health risks from exposure to toxic ambient air pollutants. *Environ Health Perspect*. 1994 Oct;102(suppl 4).
28. Burt PJA. Book review: “Atmospheric pollution: History, science, and regulation” by Mark Z. Jacobson. *Weather*. 2003 Jun 1;58(6).

29. Martins EH, Nogarotto DC, Mortatti J, Pozza SA. Chemical composition of rainwater in an urban area of the southeast of Brazil. *Atmos Pollut Res* [Internet]. 2019;10(2):520–30. Available from: <https://doi.org/10.1016/j.apr.2018.10.003>
30. Tripathy GR, Mishra S, Danish M, Ram K. Elevated Barium concentrations in rain water from east-coast of India: role of regional lithology. *J Atmos Chem*. 2019;76(1):59–72.
31. Suzuki K, Shirohada M. Seasonal and temporal changes in the fluxes of major inorganic ions via wet and dry depositions, observed in Matsumoto, central Japan. *Geochem J*. 2006;40(6):609–23.
32. EPA [Internet]. Report on the Environment, Nitrogen Oxides Emissions. 2021 [cited 2021 Oct 21]. Available from: https://cfpub.epa.gov/roe/indicator_pdf.cfm?i=15
33. Ekmekyapar F, Bahadır EB, Meric S. Ecotoxicological and inorganic chemicals' characterization of rainwater in an urban residential area. *Desalination Water Treat*. 2015;56(5):1291–8.
34. Herawati N, Suzuki S, Hayashi K, Rivai IF, Koyama H. Cadmium, Copper, and Zinc Levels in Rice and Soil of Japan, Indonesia, and China by Soil Type. *Bull. Environ. Contam. Toxicol*. 2000.
35. He ZL, Yang XE, Stoffella PJ. Trace elements in agroecosystems and impacts on the environment. *Journal of Trace Elements in Medicine and Biology*. 2005 Dec;19(2–3).
36. Shallari S, Schwartz C, Hasko A, Morel JL. Heavy metals in soils and plants of serpentine and industrial sites of Albania. *Science of The Total Environment*. 1998 Jan;209(2–3).
37. Tchounwou PB, Yedjou CG, Patlolla AK, Sutton DJ. Heavy Metal Toxicity and the Environment. In 2012.
38. Gautam PK, Gautam RK, Banerjee S, Chattopadhyaya MC, Pandey JD. Heavy metals in the environment: fate, transport, toxicity and remediation technologies. Nova Sci Publishers. 2016;60:101–30.
39. Masindi V, Muedi KL. Environmental Contamination by Heavy Metals. In: Heavy Metals. InTech; 2018.
40. Walker CH, Sibly RM, Sibly RM, Peakall DB. Principles of Ecotoxicology. CRC Press; 2005.
41. Seinfeld JH, Pandis SN, Παηδής ΣΝ 1963. Atmospheric chemistry and physics : from air pollution to climate change. J. Wiley; 2006. 1203 p.
42. Preciado HF, Li LY. Evaluation of Metal Loadings and Bioavailability in Air, Water and Soil Along Two Highways of British Columbia, Canada. *Water Air Soil Pollut*. 2006 May 1;172(1–4).
43. Tanner PA, Wong AYS. Soluble trace metals and major ionic species in the bulk deposition and atmosphere of Hong Kong. *Water Air Soil Pollut*. 2000;122(3–4):261–79.

44. Al-Khashman OA, Jaradat AQ, Salameh E. Five-year monitoring study of chemical characteristics of Wet atmospheric precipitation in the southern region of Jordan. *Environ Monit Assess*. 2013;185(7):5715–27.
45. Kim JE, Han YJ, Kim PR, Holsen TM. Factors influencing atmospheric wet deposition of trace elements in rural Korea. *Atmos Res* [Internet]. 2012;116:185–94. Available from: <http://dx.doi.org/10.1016/j.atmosres.2012.04.013>
46. Molles MC, Borrell Brendan. *Environment : science, issues, solutions*. New York: W H Freeman; 2016.
47. Négrel P, Roy S. Chemistry of rainwater in the Massif Central (France): a strontium isotope and major element study. *Applied Geochemistry*. 1998 Nov;13(8).
48. Zhang L, Qiao B, Wang H, Tian M, Cui J, Fu C, et al. Chemical Characteristics of Precipitation in a Typical Urban Site of the Hinterland in Three Gorges Reservoir, China. *J Chem*. 2018;2018.
49. Polkowska Z, Górecki T, Namieśnik J. Determination of atmospheric pollutants in wet deposition. Vol. 19, *Environmental Reviews*. National Research Council of Canada; 2011. p. 185–213.
50. Oğuz K, Pekin MA. Yapay Sınır Ağları ile Esenboğa Havaalanı için Sis Görüş Mesafesinin Tahmin Edilebilirliği. *European Journal of Science and Technology*. 2019 Mar 31;542–51.
51. Calderón-Garcidueñas L, Mora-Tiscareño A, Francolira M, Torres-Jardón R, Peña-Cruz B, Palacios-López C, et al. Exposure to urban air pollution and bone health in clinically healthy six-year-old-children. *Arh Hig Rada Toksikol*. 2013;64(1):23–34.
52. Kumar R, Nagar JK, Kumar H, Kushwah AS, Meena M, Kumar P, et al. Indoor air pollution and respiratory function of children in Ashok Vihar, Delhi: an exposure-response study. *Asia-Pacific journal of public health / Asia-Pacific Academic Consortium for Public Health*. 2008;20(1):36–48.
53. Power MC, Adar SD, Yanosky JD, Weuve J. Exposure to air pollution as a potential contributor to cognitive function, cognitive decline, brain imaging, and dementia: A systematic review of epidemiologic research. *Neurotoxicology*. 2016 Sep 1;56:235–53.
54. Health Effects Institute. 2020. *State of Global Air 2020*. Special Report. Boston, MA:Health Effects Institute.e
55. Briffa J, Sinagra E, Blundell R. Heavy metal pollution in the environment and their toxicological effects on humans. Vol. 6, *Heliyon*. Elsevier Ltd; 2020.
56. Beasley VR, Levensgood JM. Principles of ecotoxicology. In: *Veterinary Toxicology*. Elsevier; 2012.
57. Masindi V, Muedi KL. Environmental Contamination by Heavy Metals. In: *Heavy Metals*. InTech; 2018.
58. Villanueva R, Bustamante P. Composition in essential and non-essential elements of early stages of cephalopods and dietary effects on the elemental profiles of *Octopus vulgaris* paralarvae. *Aquaculture*. 2006 Nov;261(1).

59. Tchounwou PB, Yedjou CG, Patlolla AK, Sutton DJ. Heavy Metal Toxicity and the Environment. In 2012.
60. Rice KC, Herman JS. Acidification of Earth: An assessment across mechanisms and scales. *Applied Geochemistry*. 2012 Jan;27(1).
61. RASTOGI N, SARIN M. Chemical characteristics of individual rain events from a semi-arid region in India: Three-year study. *Atmos Environ*. 2005 Jun;39(18).
62. Charlson RJ, Rodhe H. Factors controlling the acidity of natural rainwater. *Nature*. 1982 Feb;295(5851).
63. Langmuir D. *Aqueous environmental geochemistry*. Upper Saddle River, N.J.: Prentice Hall; 1997.
64. Schemenauer RS. Acidic deposition to forests: The 1985 chemistry of high elevation fog (CHEF) project. *Atmosphere-Ocean*. 1986 Dec;24(4).
65. Al-Khashman OA. Chemical characteristics of rainwater collected at a western site of Jordan. *Atmos Res* [Internet]. 2009;91(1):53–61. Available from: <http://dx.doi.org/10.1016/j.atmosres.2008.05.007>
66. MORTIMER CH. A treatise on limnology. Volume 1. Geography, physics and chemistry. *Limnol Oceanogr* [Internet]. 1959 Jan 1 [cited 2021 Sep 28];4(1):108–14. Available from: <https://onlinelibrary.wiley.com/doi/full/10.4319/lo.1959.4.1.0108>
67. Dong Z, Qin D, Qin X, Cui J, Kang S. Changes in precipitating snow chemistry with seasonality in the remote Laohugou glacier basin, western Qilian Mountains. *Environmental Science and Pollution Research*. 2017 Apr 18;24(12).
68. Guo J, Kang S, Huang J, Zhang Q, Tripathee L, Sillanpää M. Seasonal variations of trace elements in precipitation at the largest city in Tibet, Lhasa. *Atmos Res*. 2015 Feb;153.
69. Moreda-Piñeiro J, Alonso-Rodríguez E, Moscoso-Pérez C, Blanco-Heras G, Turnes-Carou I, López-Mahía P, et al. Influence of marine, terrestrial and anthropogenic sources on ionic and metallic composition of rainwater at a suburban site (northwest coast of Spain). *Atmos Environ*. 2014 May;88.
70. Adhikari S, Zhang F, Adhikari NP, Zeng C, Pant RR, Ram K, et al. Atmospheric wet deposition of major ionic constituents and inorganic nitrogen in Bangladesh: Implications for spatiotemporal variation and source apportionment. *Atmos Res* [Internet]. 2021;250(October 2020):105414. Available from: <https://doi.org/10.1016/j.atmosres.2020.105414>
71. Zhang Z, Cui Y, He Q, Guo L, Tian X, Zhang K, et al. Predominant effects of emission reduction by recording 8-year water-soluble ions in precipitation in Taiyuan, North China. *Atmos Pollut Res* [Internet]. 2020;11(11):1922–32. Available from: <https://doi.org/10.1016/j.apr.2020.08.004>
72. Liyandeniya AB, Deeyamulla MP, Priyantha N. Source apportionment of rainwater chemical composition in wet precipitation at Kelaniya in Sri Lanka. *Air Qual Atmos Health*. 2020;13(12):1497–504.

73. Pacyna JM. Atmospheric Deposition. Encyclopedia of Ecology, Five-Volume Set. 2008 Jan 1;275–85.
74. World Meteorological Organization [Internet]. Atmospheric Deposition. 2021 [cited 2021 Oct 22]. Available from: <https://public.wmo.int/en/our-mandate/focus-areas/environment/atmospheric-deposition>
75. Fowler D. Transfer to terrestrial surfaces. Philosophical Transactions of the Royal Society of London B, Biological Sciences. 1984 May;305(1124).
76. Montoya-Mayor R, Fernández-Espinosa AJ, Seijo-Delgado I, Ternero-Rodríguez M. Determination of soluble ultra-trace metals and metalloids in rainwater and atmospheric deposition fluxes: A 2-year survey and assessment. Chemosphere [Internet]. 2013;92(8):882–91. Available from: <http://dx.doi.org/10.1016/j.chemosphere.2013.02.044>
77. Povinec PP, Hirose K, Aoyama M. Fukushima Radioactivity Impact. In: Fukushima Accident. Elsevier; 2013. p. 131–275.
78. Skoog DA. Principles of instrumental analysis [Internet]. Fourth edition. Fort Worth : Saunders College Pub., [1992] ©1992; Available from: <https://search.library.wisc.edu/catalog/999674775302121>
79. Weiss, J. (2016). Handbook of ion chromatography. Wiley-VCH Verlag GmbH & Co. KGaA. <https://doi.org/10.1002/9783527651610>
80. Column properties that make an impact on ion chromatography | Spectroscopy Europe/World [Internet]. [cited 2021 Sep 29]. Available from: <https://www.spectroscopyeurope.com/article/column-properties-make-impact-ion-chromatography>
81. Thomas R. Practical guide to ICP-MS. New York, NY : Marcel Dekker,; 2004. 324 p.
82. The 30-Minute Guide to ICP-MS [Internet]. [cited 2021 Oct 22]. Available from: https://www.perkinelmer.com/CMSResources/Images/44-74849tch_icpmsthirtyminuteguide.pdf
83. Principle of ICP Mass Spectrometry (ICP-MS): Hitachi High-Tech GLOBAL [Internet]. [cited 2021 Oct 22]. Available from: <https://www.hitachi-hightech.com/global/products/science/tech/ana/icp/descriptions/icp-ms.html>
84. Brima EI, Jenkins RO, Haris PI. Understanding arsenic metabolism through spectroscopic determination of arsenic in human urine. Vol. 20, Spectroscopy. IOS Press; 2006.
85. Kuzet iç anadolu temiz hava merkez müdürlüğü. (2016). Bolu ili hava kalitesi analiz raporu. www.kiathm.csb.gov.tr
86. Nüfus [Internet]. [cited 2021 Oct 6]. Available from: <http://www.bolu.gov.tr/nufus-yapisi>
87. Erşahin, G., & Şerifeken, İ. (2002). Bolu ili raporu. <http://ekutup.dpt.gov.tr/iller/bolu/2002.pdf>

88. Belis CA, Favez Olivier, Harrison RM, Larsen BR (Bo R), Amato F (Fulvio), el Haddad Imad, et al. European guide on air pollution source apportionment with receptor models. Publications Office; 2014.
89. Stein AF, Draxler RR, Rolph GD, Stunder BJB, Cohen MD, Ngan F. NOAA's HYSPLIT Atmospheric Transport and Dispersion Modeling System. *Bull Am Meteorol Soc.* 2015 Dec 1;96(12):2059–77.
90. Norris G, Duvall R. EPA Positive Matrix Factorization 5.0 Fundamentals and User Guide [Internet]. 2014 [cited 2022 Dec 11]. Available from: <https://www.epa.gov/air-research/epa-positive-matrix-factorization-50-fundamentals-and-user-guide>
91. Brown SG, Eberly S, Paatero P, Norris GA. Methods for estimating uncertainty in PMF solutions: Examples with ambient air and water quality data and guidance on reporting PMF results. *Science of The Total Environment.* 2015 Jun;518–519:626–35.
92. Statgraphics® Centurion XVI User Manual. 2019 [cited 2022 Dec 22]; Available from: www.STATGRAPHICS.com
93. Gros N, Camões MF, Oliveira C, Silva MCR. Ionic composition of seawaters and derived saline solutions determined by ion chromatography and its relation to other water quality parameters. *J Chromatogr A* [Internet]. 2008 Nov 7 [cited 2022 Dec 3];1210(1):92–8. Available from: <https://pubmed.ncbi.nlm.nih.gov/18829032/>
94. Nieberding F, Breuer B, Braeckvelt E, Klemm O, Song Q, Zhang Y. Fog Water Chemical Composition on Ailaoshan Mountain, Yunnan Province, SW China. *Aerosol Air Qual Res* [Internet]. 2018 Jan 1 [cited 2022 Dec 3];18(1):37–48. Available from: <https://aaqr.org/articles/aaqr-17-01-fog-0060>
95. Rao PSP, Tiwari S, Matwale JL, Pervez S, Tunved P, Safai PD, et al. Sources of chemical species in rainwater during monsoon and non-monsoonal periods over two mega cities in India and dominant source region of secondary aerosols. *Atmos Environ.* 2016 Dec 1;146:90–9.
96. Bisht DS, Srivastava AK, Joshi H, Ram K, Singh N, Naja M, et al. Chemical characterization of rainwater at a high-altitude site “Nainital” in the central Himalayas, India. *Environ Sci Pollut Res Int* [Internet]. 2017 Feb 1 [cited 2022 Dec 3];24(4):3959–69. Available from: <https://pubmed.ncbi.nlm.nih.gov/27913957/>
97. Possanzini M, Buttini P, di Palo V. Characterization of a rural area in terms of dry and wet deposition. *Sci Total Environ* [Internet]. 1988 Aug 1 [cited 2022 Dec 3];74(C):111–20. Available from: <https://pubmed.ncbi.nlm.nih.gov/2851879/>
98. Wu Q, Han G, Tao F, Tang Y. Chemical composition of rainwater in a karstic agricultural area, Southwest China: The impact of urbanization. *Atmos Res.* 2012 Jul 1;111:71–8.
99. Balasubramanian R, Victor T, Chun N. Chemical and Statistical Analysis of Precipitation in Singapore. *Water, Air, and Soil Pollution* 2001 130:1 [Internet]. 2001 [cited 2022 Dec 3];130(1):451–6. Available from: <https://link.springer.com/article/10.1023/A:1013801805621>

100. Balasubramanian R, Victor T, Chun N. Chemical and Statistical Analysis of Precipitation in Singapore. *Water, Air, and Soil Pollution* 2001 130:1 [Internet]. 2001 [cited 2022 Dec 17];130(1):451–6. Available from: <https://link.springer.com/article/10.1023/A:1013801805621>
101. Behera SN, Sharma M. Investigating the potential role of ammonia in ion chemistry of fine particulate matter formation for an urban environment. *Sci Total Environ* [Internet]. 2010 Aug [cited 2022 Dec 3];408(17):3569–75. Available from: <https://pubmed.ncbi.nlm.nih.gov/20452648/>
102. Singh DK, Gupta T. Role of ammonium ion and transition metals in the formation of secondary organic aerosol and metallo-organic complex within fog processed ambient deliquescent submicron particles collected in central part of Indo-Gangetic Plain. *Chemosphere* [Internet]. 2017 [cited 2022 Dec 3];181:725–37. Available from: <https://pubmed.ncbi.nlm.nih.gov/28478233/>
103. Roy A, Chatterjee A, Tiwari S, Sarkar C, Das SK, Ghosh SK, et al. Precipitation chemistry over urban, rural and high altitude Himalayan stations in eastern India. *Atmos Res*. 2016 Nov 15;181:44–53.
104. Thomas J, Joseph S, Thiruvikramji KP, Manjusree TM, Arunkumar KS. Seasonal variation in major ion chemistry of a tropical mountain river, the southern Western Ghats, Kerala, India. *Environ Earth Sci* [Internet]. 2014 Mar 11 [cited 2022 Dec 3];71(5):2333–51. Available from: <https://link.springer.com/article/10.1007/s12665-013-2634-2>
105. Saleh A, Al-Ruwaih F, Shehata M. Hydrogeochemical processes operating within the main aquifers of Kuwait. *J Arid Environ*. 1999 Jul 1;42(3):195–209.
106. Collins R, Jenkins A. The impact of agricultural land use on stream chemistry in the Middle Hills of the Himalayas, Nepal. *J Hydrol (Amst)*. 1996 Nov 1;185(1–4):71–86.
107. Special communication with Yeniso-y-Karakas, Serpil.
108. Bayramoğlu Karşı MB, Yeniso-y-Karakaş S, Karakaş D. Investigation of washout and rainout processes in sequential rain samples. *Atmos Environ*. 2018;190(July):53–64.
109. Karadeniz H, Yeniso-y-Karakaş S. Evaluation of hourly-based precipitation chemistry in suburban site of Bolu. *Atmos Pollut Res*. 2020;11(12):2164–72.
110. Rao PSP, Tiwari S, Matwale JL, Pervez S, Tunved P, Safai PD, et al. Sources of chemical species in rainwater during monsoon and non-monsoonal periods over two mega cities in India and dominant source region of secondary aerosols. *Atmos Environ* [Internet]. 2016;146:90–9. Available from: <http://dx.doi.org/10.1016/j.atmosenv.2016.06.069>
111. Wu Y, Xu Z, Liu W, Zhao T, Zhang X, Jiang H, et al. Chemical compositions of precipitation at three non-urban sites of Hebei Province, North China: Influence of terrestrial sources on ionic composition. *Atmos Res* [Internet]. 2016;181:115–23. Available from: <http://dx.doi.org/10.1016/j.atmosres.2016.06.009>
112. Samayamanthula DR, Sabarathinam C, Alayyadhi NA. Trace Elements and Their Variation with pH in Rain Water in Arid Environment. *Arch Environ Contam*

- Toxicol [Internet]. 2021;80(2):331–49. Available from: <https://doi.org/10.1007/s00244-020-00787-y>
113. Cukurluoglu S. Sources of trace elements in wet deposition in Pamukkale, Denizli, western Turkey. *Environ Forensics* [Internet]. 2017;18(1):83–99. Available from: <http://dx.doi.org/10.1080/15275922.2016.1263899>
 114. Rivera-Rivera DM, Escobedo-Urías DC, Jonathan MP, Sujitha SB, Chidambaram S. Evidence of natural and anthropogenic impacts on rainwater trace metal geochemistry in central Mexico: A statistical approach. *Water (Switzerland)*. 2020;12(1).
 115. Xing J, Song J, Yuan H, Wang Q, Li X, Li N, et al. Atmospheric wet deposition of dissolved trace elements to Jiaozhou Bay, North China: Fluxes, sources and potential effects on aquatic environments. *Chemosphere* [Internet]. 2017;174:428–36. Available from: <http://dx.doi.org/10.1016/j.chemosphere.2017.02.004>
 116. Salmanighabeshi S, Palomo-Marín MR, Bernalte E, Rueda-Holgado F, Miró-Rodríguez C, Fadic-Ruiz X, et al. Long-term assessment of ecological risk from deposition of elemental pollutants in the vicinity of the industrial area of Puchuncaví-Ventanas, central Chile. *Science of The Total Environment*. 2015 Sep 15;527–528:335–43.
 117. Cereceda-Balic F, Gala-Morales M de la, Palomo-Marín R, Fadic X, Vidal V, Funes M, et al. Spatial distribution, sources, and risk assessment of major ions and trace elements in rainwater at Puchuncaví Valley, Chile: The impact of industrial activities. *Atmos Pollut Res* [Internet]. 2020;11(6):99–109. Available from: <https://doi.org/10.1016/j.apr.2020.03.003>
 118. Dordević D, Mihajlidi-Zelić A, Relić D. Differentiation of the contribution of local resuspension from that of regional and remote sources on trace elements content in the atmospheric aerosol in the Mediterranean area. *Atmos Environ*. 2005 Nov 1;39(34):6271–81.
 119. Xu M, Yan R, Zheng C, Qiao Y, Han J, Sheng C. Status of trace element emission in a coal combustion process: a review. *Fuel Processing Technology*. 2004 Feb 15;85(2–3):215–37.
 120. Yenisoy-Karakas S. Biomonitoring of the atmospheric pollutants at western Anatolia [PhD Thesis]. [Ankara]: METU Graduate School of Natural Applied Science; 2000.
 121. Duluiu OG, Culicov OA, Rădulescu I, Cristea C, Vasiu T. Major, trace, and natural radioactive elements in bituminous coal from Australia, Romania, Russia, South Africa and Ukraine: A comparative study. *Journal of Radioanalytical and Nuclear Chemistry* 2005 264:3 [Internet]. 2005 [cited 2022 Dec 3];264(3):525–34. Available from: <https://link.springer.com/article/10.1007/s10967-005-0748-z>
 122. Querol X, Fernandez Turiel JL, Lopez Soler A, Duran ME. Trace elements in high-S subbituminous coals from the teruel Mining District, northeast Spain. *Applied Geochemistry*. 1992;7(6):547–61.
 123. Başak B, Alagha O. Trace metals solubility in rainwater: evaluation of rainwater quality at a watershed area, Istanbul. *Environ Monit Assess* [Internet]. 2010 [cited

2022 Dec 3];167(1–4):493–503. Available from:
<https://pubmed.ncbi.nlm.nih.gov/19603281/>

124. Christian TJ, Yokelson RJ, Cárdenas B, Molina LT, Engling G, Hsu SC. Trace gas and particle emissions from domestic and industrial biofuel use and garbage burning in central Mexico. *Atmos Chem Phys*. 2010;10(2):565–84.
125. Karadeniz H. Composition and source apportionment of atmospheric particulate matter: Bolu case [PhD Thesis]. [Bolu]: Abant Izzet Baysal University Graduate School of Natural and Applied Sciences; 2017.
126. Franceschi E, Locardi F. Strontium, a new marker of the origin of gypsum in cultural heritage? *J Cult Herit*. 2014 Sep 1;15(5):522–7.
127. Kulshrestha UC, Kulshrestha MJ, Sekar R, Sastry GSR, Vairamani M. Chemical characteristics of rainwater at an urban site of south-central India. *Atmos Environ*. 2003 Jul 1;37(21):3019–26.
128. Hu GP, Balasubramanian R, Wu CD. Chemical characterization of rainwater at Singapore. *Chemosphere*. 2003 Jun 1;51(8):747–55.
129. Dordević D, Mihajlidi-Zelić A, Relić D. Differentiation of the contribution of local resuspension from that of regional and remote sources on trace elements content in the atmospheric aerosol in the Mediterranean area. *Atmos Environ*. 2005 Nov 1;39(34):6271–81.
130. Vallius M, Lanki T, Tiittanen P, Koistinen K, Ruuskanen J, Pekkanen J. Source apportionment of urban ambient PM_{2.5} in two successive measurement campaigns in Helsinki, Finland. *Atmos Environ*. 2003 Feb 1;37(5):615–23.
131. Sternbeck J, Sjödin Å, Andréasson K. Metal emissions from road traffic and the influence of resuspension—results from two tunnel studies. *Atmos Environ*. 2002 Oct 1;36(30):4735–44.

7. APPENDICES

Appendix 1 Sampling Information

Table 7.1. Sampling information for the city center of Bolu

Date (dd.mm.yyyy)	Code	Rain start time (UTC+3)	Rain start time (UTC+3)	Volume (mL)	pH
01.05.2020	M1-1	16:45	17:30	62.0	6.95
01.05.2020	M1-2	17:30	18:20	23.0	7.12
03.05.2020	M2-1	21:30	22:30	72.0	6.84
04.05.2020	M3-1	00:00	00:44	106	6.35
04.05.2020	M3-2	00:44	00:58	106	5.94
04.05.2020	M3-3	00:58	01:17	112	5.83
04.05.2020	M3-4	01:17	01:40	108	5.98
04.05.2020	M3-5	01:40	02:10	106	6.04
04.05.2020	M3-6	02:10	03:00	99.0	5.85
04.05.2020	M4-1	12:19	13:52	106	5.95
04.05.2020	M4-2	13:52	14:18	115	6.03
04.05.2020	M4-3	14:18	15:58	124	5.82
04.05.2020	M4-4	15:58	18:07	116	5.98
05.05.2020	M5-1	08:49	11:58	98.0	5.94
05.05.2020	M5-2	11:58	13:49	104	6.67
07.05.2020	M6-1	02:07	02:37	87.0	5.52
07.05.2020	M6-2	02:37	04:07	124	5.91
07.05.2020	M6-3	04:07	04:37	22.0	6.60
21.05.2020	M7-1	16:58	17:28	24.0	6.83
22.05.2020	M8-1	11:37	13:37	127	6.36
22.05.2020	M8-2	13:37	15:19	90.0	6.19
26.05.2020	M9-1	04:07	04:58	114	6.23
26.05.2020	M10-1	10:58	11:37	126	6.36
26.05.2020	M10-2	11:37	12:28	124	6.02
26.05.2020	M10-3	12:28	13:58	104	6.03
26.05.2020	M10-4	13:58	14:58	108	6.16
26.05.2020	M10-5	14:58	16:28	105	6.19
27.05.2020	M11-1	14:48	14:58	95.0	6.16
27.05.2020	M11-2	14:58	15:07	50.0	6.03
27.05.2020	M12-1	15:49	15:58	120	6.09
01.06.2020	M13-1	15:35	15:52	106	6.17
01.06.2020	M13-2	15:52	18:12	112	4.66
01.06.2020	M13-3	18:12	18:26	125	4.84
01.06.2020	M13-4	18:26	18:43	83.0	4.93
02.06.2020	M14-1	02:07	02:30	98.0	5.61

02.06.2020	M14-2	02:30	03:35	96.0	5.81
02.06.2020	M14-3	03:35	04:45	109	5.66
02.06.2020	M14-4	04:45	05:33	109	5.57
02.06.2020	M14-5	05:33	06:41	109	5.39
02.06.2020	M14-6	06:41	07:17	27.0	5.69
12.06.2020	M15-1	17:30	17:33	127	6.96
12.06.2020	M15-2	17:33	17:37	125	6.62
12.06.2020	M15-3	17:37	17:39	127	6.32
12.06.2020	M15-4	17:39	17:41	123	6.36
12.06.2020	M15-5	17:41	17:44	115	6.38
12.06.2020	M15-6	17:44	17:48	105	6.35
12.06.2020	M15-7	17:48	17:52	111	6.29
12.06.2020	M15-8	17:52	17:54	105	6.35
12.06.2020	M15-9	17:54	17:57	103	6.15
12.06.2020	M15-10	17:57	18:00	101	6.59
12.06.2020	M15-11	18:00	18:03	107	6.55
12.06.2020	M15-12	18:03	18:05	113	6.84
12.06.2020	M15-13	18:05	18:09	111	6.30
12.06.2020	M15-14	18:09	18:11	103	6.88
12.06.2020	M15-15	18:11	18:14	103	7.33
12.06.2020	M15-16	18:14	18:17	103	7.30
12.06.2020	M15-17	18:17	18:21	111	6.34
12.06.2020	M15-18	18:21	18:29	107	7.20
12.06.2020	M15-19	18:29	18:36	110	6.63
12.06.2020	M15-20	18:36	18:46	112	6.47
12.06.2020	M15-21	18:46	18:52	108	6.86
12.06.2020	M15-22	18:52	19:00	103	7.09
12.06.2020	M15-23	19:00	19:11	129	6.51
15.06.2020	M16-1	06:49	07:32	129	6.80
15.06.2020	M16-2	07:32	08:35	104	6.93
15.06.2020	M16-3	08:35	09:01	117	6.66
15.06.2020	M16-4	09:01	09:30	117	6.80
15.06.2020	M16-5	09:30	09:38	121	6.56
15.06.2020	M16-6	09:38	09:48	114	6.93
15.06.2020	M16-7	09:48	09:54	113	6.54
15.06.2020	M16-8	09:54	10:04	111	6.28
15.06.2020	M16-9	10:04	10:25	112	6.41
15.06.2020	M16-10	10:25	10:52	117	5.71
15.06.2020	M16-11	10:52	11:00	112	6.40
15.06.2020	M16-12	11:00	11:22	126	6.04
15.06.2020	M16-13	11:22	11:42	106	5.20
15.06.2020	M16-14	11:42	11:58	117	5.43
15.06.2020	M16-15	11:58	12:11	113	5.76

15.06.2020	M16-16	12:11	12:25	116	5.75
15.06.2020	M16-17	12:25	12:40	115	5.700
15.06.2020	M16-18	12:40	13:00	114	5.65
15.06.2020	M16-19	13:00	13:09	113	6.04
15.06.2020	M16-20	13:09	13:19	117	5.61
15.06.2020	M16-21	13:19	13:26	105	5.80
15.06.2020	M16-22	13:26	13:30	106	6.71
15.06.2020	M16-23	13:30	13:40	117	5.92
15.06.2020	M16-24	13:40	13:55	119	5.57
15.06.2020	M16-25	13:55	13:58	111	5.99
15.06.2020	M16-26	13:58	15:35	82.0	6.69
17.06.2020	M17-1	17:50	18:16	109	7.74
17.06.2020	M17-2	18:16	18:18	121	7.42
17.06.2020	M17-3	18:18	18:20	111	7.04
18.06.2020	M18-1	13:58	14:01	62.0	6.68
18.06.2020	M18-2	14:01	14:06	57.0	6.77
18.06.2020	M18-3	14:06	14:14	59.0	6.62
18.06.2020	M18-4	14:14	14:28	61.0	6.75
18.06.2020	M18-5	14:28	14:33	61.0	6.77
18.06.2020	M18-6	14:33	14:39	59.0	6.39
18.06.2020	M18-7	14:39	14:44	60.0	6.53
18.06.2020	M18-8	14:44	14:48	59.0	6.43
18.06.2020	M18-9	14:48	14:49	59.0	6.64
18.06.2020	M18-10	14:49	14:50	61.0	6.48
18.06.2020	M18-11	14:50	14:51	57.0	6.49
18.06.2020	M18-12	14:51	14:52	60.0	6.42
18.06.2020	M18-13	14:52	14:52	60.0	6.57
18.06.2020	M18-14	14:52	14:53	58.0	6.43
18.06.2020	M18-15	14:53	14:53	58.0	6.27
18.06.2020	M18-16	14:53	14:54	61.0	6.19
18.06.2020	M18-17	14:54	14:55	59.0	6.23
18.06.2020	M18-18	14:55	14:56	59.0	6.88
18.06.2020	M18-19	14:56	14:56	60.0	6.42
18.06.2020	M18-20	14:56	14:58	61.0	6.22
18.06.2020	M18-21	14:58	15:01	59.0	6.17
18.06.2020	M18-22	15:01	15:04	60.0	6.19
18.06.2020	M18-23	15:04	15:06	62.0	6.16
18.06.2020	M18-24	15:06	15:10	59.0	6.05
18.06.2020	M18-25	15:10	15:16	59.0	6.15
18.06.2020	M18-26	15:16	15:30	58.0	6.14
18.06.2020	M18-27	15:30	16:22	59.0	6.57
18.06.2020	M18-28	16:22	16:49	59.0	6.30
18.06.2020	M18-29	16:49	16:54	61.0	6.42

Table 7.2. Sampling information for the BAIBU Campus

Date (dd.mm.yyyy)	Sampling code	Rain start time (UTC+3)	Rain start time (UTC+3)	Volume (mL)	pH
01.05.2020	K1-1	15:00	15:29	130	6.56
01.05.2020	K1-2	15:29	16:01	126	6.80
03.05.2020	K2-1	21:20	21:30	125	6.68
03.05.2020	K2-2	21:30	22:00	112	6.80
04.05.2020	K3-1	00:00	00:54	126	7.10
04.05.2020	K3-2	00:54	03:00	54.0	7.15
04.05.2020	K4-1	09:00	12:51	44.0	7.12
04.05.2020	K5-1	12:51	13:18	132	6.92
04.05.2020	K5-2	13:18	13:50	132	6.72
04.05.2020	K5-3	13:50	14:15	51.0	7.08
04.05.2020	K6-1	16:50	17:43	48.0	6.79
05.05.2020	K7-1	03:00	07:00	135	6.53
05.05.2020	K8-1	09:00	12:48	78.0	6.45
05.05.2020	K8-2	12:48	13:18	130	7.03
05.05.2020	K8-3	13:18	17:00	22.0	6.98
06.05.2020	K9-1	19:10	19:40	135	6.22
07.05.2020	K10-1	02:38	02:46	135	6.57
07.05.2020	K11-1	12:58	17:15	106	6.43
21.05.2020	K11-2	16:42	17:30	134	5.70
21.05.2020	K11-3	17:30	18:00	38.0	6.60
22.05.2020	K11-4	11:32	13:28	56.0	6.56
22.05.2020	K11-5	13:28	17:00	80.0	6.84
26.05.2020	K12-1	04:00	06:12	134	6.89
26.05.2020	K12-2	06:12	08:42	77.0	6.85
26.05.2020	K12-3	08:42	10:00	41.0	7.43
26.05.2020	K13-1	11:00	12:07	119	6.37
26.05.2020	K14-1	12:07	13:05	82.0	7.02
26.05.2020	K14-2	13:05	13:20	134	6.60
26.05.2020	K14-3	13:20	15:00	27.0	7.39
27.05.2020	K15-1	14:48	15:12	133	6.63
27.05.2020	K15-2	15:12	15:34	34.0	6.79
01.06.2020	K16-1	15:35	18:26	134	6.75
17.06.2020	K17-1	18:03	18:20	15.0	8.37
18.06.2020	K18-1	12:02	12:46	31.0	7.74
18.06.2020	K19-1	14:07	14:16	129	6.84
18.06.2020	K19-2	14:16	14:27	129	6.90
18.06.2020	K19-3	14:27	14:42	128	7.06
18.06.2020	K19-4	14:42	14:58	121	6.47
18.06.2020	K19-5	14:58	15:10	133	5.53
18.06.2020	K19-6	15:10	15:24	117	5.37

18.06.2020	K19-7	15:24	15:46	15.0	7.45
18.06.2020	K19-8	15:46	16:01	115	6.56
18.06.2020	K19-9	16:01	16:12	109	7.12
18.06.2020	K19-10	16:12	16:27	63.0	7.19
18.06.2020	K19-11	16:27	16:41	122	6.98
18.06.2020	K19-12	16:41	16:58	85.0	6.59

