BOLU ABANT IZZET BAYSAL UNIVERSITY

THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

SPATIAL MONITORING OF GASEOUS POLLUTANTS IN THE CITY CENTER OF BOLU BY PASSIVE SAMPLING METHOD

MASTER OF SCIENCE

ESRA MAĞAT TÜRK

BOLU, MAY 2019

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APPROVAL OF THE THESIS

SPATIAL MONITORING OF GASEOUS POLLUTANTS IN THE CITY CENTER OF BOLU BY PASSIVE SAMPLING METHODsubmitted by **ESRA MAĞAT TÜRK** and defended before the below named jury in partial fulfillment of the requirements for the degree of **Master of Science** in **Department of Chemistry, The Graduate School of Natural and Applied Sciences of Bolu Abant Izzet Baysal University in 30.05.2019** by

Examining Committee Members	**Signature**
Supervisor Prof. Dr. Serpil YENİSOY KARAKAŞ Bolu Abant İzzet Baysal University	.....
Member Prof. Dr. Azra BOZCAARMUTLU Bolu Abant İzzet Baysal University	.....
Member Ass. Prof. Dr. Mihriban Civan Kocaeli University	.....

Prof. Dr. Ömer ÖZYURT .....

Director of Graduate School of Natural and Applied Sciences

To my family

DECLARATION

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Esra MAĞAT TÜRK

ABSTRACT

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MSC THESIS

ESRA MAĞAT TÜRK

BOLU ABANT IZZET BAYSAL UNIVERSITY GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

DEPARTMENT OF CHEMISTRY

(SUPERVISOR: PROF. DR. SERPİL YENİSOY KARAKAŞ)

BOLU, MAY 2019

In this study, spatial evaluation of inorganic gaseous pollutants (SO_2, NO_2, and O_3) and organic pollutants, BTEXs compounds were evaluated by passive sampling method at three different regions (high altitude villages, roadside and city center) in Bolu.

Nitrogen dioxide (NO_2), sulfur dioxide (SO_2) and ozone (O_3) are among important inorganic gaseous air pollutants and organic air pollutants benzene, toluene, ethylbenzene, xylene (BTEXs) are the most important VOCs because of their high potential to exert health effects. These compounds have negative effects on the human health and ecosystem.

The aim of this study is to observe the levels and distribution of these inorganic (NO_2, SO_2 and O_3) and organic (BTEXs) air pollutants in Bolu atmosphere and also to determine the ozone formation potentials and estimation of cancer risk assessment of BTEXs compounds.

Passive sampling which is the most convenient method for the determination of spatial distributions of the pollutant concentrations was performed in two seasons. The winter (January- February 2017) and summer (July 2017) sampling campaign were conducted in Bolu plateau including city center, high altitude forested areas, towns and villages.

NO_2-SO_2 passive sampler and O_3 passive sampler which were developed by Anadolu University Environmental Engineering Department Air Pollution Research Group were used. Tenax-TA tubes were used as BTEX passive sampler. Inorganic passive samples were analyzed by using ion chromatography method and organic (BTEX) samples were analyzed with thermal desorption-gas chromatography-mass spectroscopy system. Analysis results were converted into pollution maps by MapInfo Professional 7.5 SCP in order to interpret the spatial distribution.

High ozone concentrations were observed in rural-forested sites while low ozone concentrations were measured around the TEM and D-100 roads. Ozone is generally expected to be higher in summer season due to high intensity of solar radiation than in winter season but in the study ozone concentrations were observed higher in winter season than in summer season. High ozone formation rates in the

rural and forested areas were observed due to the presence of biogenic volatile organic compounds (BVOCs), NO_x and sunlight. It has been known that BVOCs, which are released from trees, are more reactive than their anthropogenic forms because of the double bond (pi bond) (Abelson, 1988). The spatial distribution of BTEX pollution maps had demonstrated that the highest concentrations were found at the major roads because of heavy traffic. NO_2 and SO_2 are the major determinants in the evaluation of the pollution sources such as traffic and domestic heating. NO_2 concentrations were observed to be higher around TEM, D-100 highways and in the city center. NO_2 concentrations had been found to be higher in summer season than in winter season. The widespread usage of natural gas in the city center made SO_2 concentrations to be low in the city center, while higher levels had been obtained in the semi-rural sites because of coal usage as domestic heating. It was seen that the summer values were higher than the winter values because the plateau settlement starts in summer season and due to low temperature in these areas, people use coal for residential heating.

Non-carcinogenic and carcinogenic air pollutants levels were detected using the exposure calculations assessment. It was observed that the values of lifetime cancer risk (LTCR) were the greater than 0.0001 for benzene for villages. Benzene compound had not the risk level because it was not at the definite risk level ($1x10^{-4}$) for the other regions (roadside and city center). On the other hand, it was found that the values of noncarcinogenic risk ratio, the hazard quotient (HQ) was lower than 1 for all BTEXs compounds. These risks were accepted as negligible because they were smaller than 1. As a result of this, non-carcinogenic risk values were at safe level.

KEYWORDS: Gaseous Inorganic Pollutants, BTEX, Passive Sampling, Spatial variations, Seasonal Variations, Pollution Maps, Ozone formation potential, Risk assessment

ÖZET

BOLU ŞEHİR MERKEZİNDE GAZ KİRLETİCİLERİNİN ALANSAL OLARAK PASİF ÖRNEKLEME YÖNTEMİYLE İZLENMESİ

YÜKSEK LISANS TEZI

ESRA MAĞAT TÜRK

BOLU ABANT İZZET BAYSAL ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ
KIMYA ANABILIM DALI
(TEZ DANIŞMANI: PROF. DR. SERPİL YENİSOY KARAKAŞ)

BOLU, MAYIS – 2019

Bu çalışmada, inorganik gaz fazı (NO_2, SO_2 ve O_3) ve organik kirleticilerin, BTEX (Benzene, toluene, ethylbenzene and xylene) mekansal değerlendirmeleri Bolu'daki üç farlı bölgede (yüksek rakımlı köyler, yol kenarı ve şehir merkezi) pasif örnekleme yöntemiyle değerlendirilmiştir.

Azot dioksit (NO_2), kükürt dioksit (SO_2) ve ozon (O_3) önemli inorganik gaz kirleticileri arasındadır ve diğer önemli organik hava kirleticileri ise benzene, toluene, etilbenzen ve ksilen (BTEX) dir. Bunlar sağlık etkisini ortaya koymada yüksek potansiyele sahip olmalarından dolayı en önemli uçucu organik bileşiklerdir. Bu bileşikler insan sağlığı ve ekosistem üzerinde negatif etkilere sahiptirler.

Bu çalışmanın amacı, inorganik (NO_2, SO_2 and O_3) ve organik (BTEX) hava kirleticilerinin dağılımını ve seviyelerini gözlemlemektir. Ayrıca benzene, toluene, etilbenzen ve ksilen bileşiklerinin kanser riski değerlendirme hesaplamalarını ve ozon oluşturma potensiyellerini belirlemektir.

Kirletici konsentrasyonlarının mekansal dağılımını belirlemek için en uygun metot olan pasif örnekleme metodu sırasıyla kış (Ocak-Şubat 2017) ve yazın (Temmuz 2017) olarak iki sezonda, şehir merkezini, yüksek ormanlık alanlarını, kasaba ve köylerini içinde barındıran Bolu platosunda gerçekleştirilmiştir.

Anadolu Üniversitesi Çevre Mühendisliği Bölümü Hava Kirliliği Araştırma Grubu tarafından geliştirilen NO_2-SO_2 ve O_3 pasif örnekleyiciler kullanılmıştır. Tenax-TA tüp ise BTEX pasif örnekleyicisi olarak kullanılmıştır. Inorganik pasif örnekler ion kromotografi metodu kullanılarak, organik pasif örnekler (BTEX) ise termal desorpsiyon-gas chromatografi- kütle spektroskopi sistemi kullanılarak analiz edilmiştir. Analiz sonuçları, mekansal dağılımın yorumlanması için MapInfo Professional 7.5 SCP programı ile çizilen kirlilik haritalarına dönüştürülmüştür.

Yüksek ozon derişimleri kırsal-ormanlık alanlarda gözlemlenmiştir. Düşük ozon derişimleri ise TEM ve D-100 yolları çevresinde gözlemlenmiştir. Ozon derişimi yaz sezonunda yüksek güneş radyasyonundan dolayı kış sezonundan daha fazla olması beklenilmesine ragmen, kış sezonunda daha fazla gözlemlenmiştir. Yüksek

ozon oluşturma oranı biyojenik uçucu organic bileşikler (BVOCs), NO_x ve güneş ışığı varlığından dolayı kırsal ve ormanlık alanlarda gözlemlendi. Ağaçlardan salınan biyojenik uçucu organic bileşikler çift bağlarından dolayı antropojenik formlarından daha reaktif olduğu bilinmektedir (Abelson, 1988). BTEX kirlilik haritalarının mekansal dağılımı, yüksek derişimlerinin yoğun trafiğin olmasından dolayı ana yollarda bulunduğunu göstermiştir. NO_2 ve SO_2, trafik ve evsel ısınma gibi kirlilik kaynaklarının değerlendirmesinde temel belirleyicilerdir. NO_2 derişimleri TEM, D-100 yolları çevresinde ve şehir merkezinde daha yüksek olduğu gözlemlenmiştir. NO_2 derişimleri yaz sezonunda kıştan daha yüksek olduğu bulunmuştur. Doğalgazın yaygın kullanımı, şehir merkezindeki SO_2 derişimlerini düşürmüşken, evsel ısınma olarak kömür kullanımından dolayı kırsal alanlarda yüksek seviyeleri gözlemlenmiştir. Yaz değerlerinin kış değerlerinden daha yüksek çıktığı görülmüştür. Yaz sezonunda yayla yerleşimi başladığından ve bu bölgelerde sıcaklığın az oluşundan dolayı konutsal ısınma olarak kömür kullanılmaktadır.

Kanserojenik ve kanserojenik olmayan hava kirleticilerinin seviyeleri kanser riskine maruz kalma hesaplamaları kullanılarak belirlenmiştir. Benzen için 0,0001 ‘den büyük olan yaşam boyu kanser riski değerlerinin (LTCR) köyler için kanser riski taşıdığı gözlemlenmiştir. Diğer bölgeler için (yol kenarı ve şehir merkezi) muhtemel risk değeri olan $1x10^{-4}$ değerinde olmadığından kanser riskine sahip değildir. Diğer yandan, tüm BTEX bileşikleri için kanserojen olmayan risk oranı, tehlike katsayısının (HQ) 1’den küçük olduğu bulunmuştur. Bu risk 1 ‘den küçük olduğundan dolayı ihmal edilebilir olarak sayılmıştır. Bunun sonucu olarak, kanserojen olmayan risk değerleri güvenli seviyededir.

ANAHTAR KELİMELER: Gaz fazı İnorganic Kirleticiler, BTEX, Pasif Örnekleme, Mekansal Değişimler, Mevsimsel Değişimler, Kirlilik Haritaları, Ozon Oluşum Potensiyeli, Risk Değerlendirmesi

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations

EPC : Environmental Pollution Center

VOCs : Volatile Organic Compounds

BTEX : Benzene, Toluene, Ethylbenzene, Xylene

PAN : Peroxyacetyl Nitrate

ROC : Reactive Organic Carbon

NMHC : Non-Methane Hydrocarbon

WHO : World Health Organization

UV-B : Ultraviolet-B radiation

BVOCs : Biogenic Volatile Organic Compounds

EPA : Environmental Pollution Center

UV :Ultra violet

AOT40 : Accumulated Ozone Exposure over a threshold of 40 Parts Per Billion

SOA : Secondary Organic Aerosol

ppm : Parts Per Million

ppb : Parts Per Billion

NCDs : Non-communicable Diseases

T/B : The ratio of Toluene to Benzene

X/B : The ratio of Xylene to Benzene

OFP : Ozone Formation Potential

IARCH : International Agency for Research on Cancer

IC : Ion Chromatography

GC-MS : Gas Chromatography- Mass Spectrometry

GC-FID : Gas Chromatography- Flame Ionization Detector

TD : Thermal Desorber

TD-GC-MS: Thermal Desorption - Gas Chromatography- Mass Spectrometry

TEA : Triethanolamine

HR : Hazard Ratio

C_i : Average Concentration

R_fC **:** Reference Concentration

USEPA **:** United States Environmental Protection Agency

ELCR **:** Excess Lifetime Cancer Risk

LCR **:** Lifetime Cancer Risk

UR **:** Unit Risk Factor

IRIS **:** Integrated Risk İnformation System

RAIS **:** Risk Assessment Information System

CDI **:** Chronic Daily Intake

CA **:** Contaminant Concentration in Air

IR **:** Inhalation Rate

BW **:** Body Weight

ET **:** Exposure Time

EF **:** Exposure Frequency

ED **:** Exposure Duration

AT **:** Averaging Time

Symbols

NO_2 **:** Nitrogen dioxide

SO_2 **:** Sulfur dioxide

O_3 **:** Ozone

NO_x **:** Oxides of nitrogen

NO **:** Nitric oxide

CO_2 **:** Carbon dioxide

SO_x **:** Oxides of sulfur

N_2 **:** Nitrogen gas

NH_3 **:** Ammonia

NH_4^+ **:** Ammonium ion

N_2O **:** Nitrous oxide

HNO_2 **:** Nitrous acid

HNO_3 **:** Nitric acid

NO_3 **:** Nitrate

N_2O_3 **:** Dinitrogen trioxide

N_2O_4 **:** Dinitrogen tetroxide

N_2O_5 : Dinitrogen pentoxide

NH_4NO_3 : Ammonium nitrate

O_2 : Oxigen gas

O : Oxigen atom

$NaNO_2$: Sodium nitrite

Na_2CO_3 : Sodium carbonate

H_2O_2 : Hydrogen peroxide

HCHO : Formaldehyde

NO_3^- : Nitrate ion

SO_4^{2-} : Sulphate ion

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1. INTRODUCTION

1.1 Air pollution and sources of air pollutions

Urbanization, industrialization, and rapid economic growth in both developed and developing countries have caused to the extreme deterioration in air quality because of the emission of various air pollutants to the environment. It is known that air pollution is generated by the consumption of a variety of resources (Shahadin et al., 2018). A variety of air pollutants have known or suspected harmful effects on human health and the environment. In both developed and rapidly industrializing countries, the major threat to clean air is now posed by traffic emissions. Vehicles with petrol- and diesel-engines emit a wide variety of air pollutants, for instance: Oxides of nitrogen (NO_x) (Bea et al., 2004; Gilbert et al., 2007; Stranger et al., 2008), SO_2 (Mensink et al., 2006; Zou et al., 2007; Stranger et al., 2008), volatile organic compounds (VOCs) (Bea et al., 2004; Stranger et al., 2008), which have an increasing impact on urban air quality.

In addition, photochemical reactions resulting from the action of sunlight on NO_2 and VOCs causes the formation of O_3, a secondary long-range pollutant, which impacts in rural areas often far from the original emission site (Duenas et al., 2002; Stranger et al., 2008). Acidic rain is another long-range pollutant influenced by vehicle NOx and SO_2 emissions (Khoder, 2002; Stranger et al., 2008). In all, except for the worst case situations, industrial and domestic pollutant sources, together with their impact on air quality, tend to be steady-state or decrease over time. However, traffic pollution problems are worsening world-wide (Han et al., 2006; Stranger et al., 2008).

Air pollution can be defined as the presence of toxic chemicals or compounds which include those of antropogenic and natural origin in the air, at levels that pose a health risk. In an even broader sense, air pollution infers the presence of chemicals or compounds in the air which are usually not present, and which lower the quality of the air or cause detrimental changes to the life quality such as the damaging of the ozone layer or causing global warming. Air pollution which affects people, plants and

ecosystem badly is probably one of the most serious environmental problems all over the world (EPC, 2017). Air pollution may be caused by various processes, either natural or anthropogenic (man-made). It is frequently caused by human activities such as mining, transportation, construction, industrial work, smelting, agriculture, etc. However, natural processes such as volcanic eruptions and wildfires may also pollute the air, but their occurrence is rare, and they usually have a local effect, unlike human activities that are ubiquitous causes of air pollution and contribute to the global pollution of the air every single day (EPC, 2017). Human activities such as combustion of fossil fuels used for regeneration of energy and transportation are the major cause of environmental pollution compared to geographical influences such as volcanoes and fires (Shahadin et al., 2018).

The four major groups of gaseous air pollutants by historical importance, concentration, and overall effects on plants and animals (including people), are sulphur dioxide (SO_2), oxides of nitrogen (NOx: NO, NO_2), carbon dioxide (CO_2) and ozone (O_3). Sulphur dioxide and nitric oxide (NO) are primary pollutants they are emitted directly from sources. Volatile Organic Compounds (VOCs) are also significant atmospheric, and indoor and outdoor ambient air pollutants. At room temperature, VOCs vaporize readily. And also, all living beings are exposed to benzene, toluene, ethylbenzene and xylene known as BTEX, are environmentally VOCs with inhalation pathway which is the most important route of exposure (Hazrati et al., 2015).

1.2 General information of NO_x, SO_2, O_3 and BTEXs pollutants

Transport-related emissions have become prominent as a dominant component of air pollution during the recent years (Marc et al., 2016). Industrial and traffic activities together with natural emissions are the major air pollution sources in urban areas. Large number of pollutants such as nitrogen oxides (NO_x), sulfur oxides (SO_x), ozone (O_3), volatile organic compounds (VOCs), metals, ions, PAHs and radioactive pollutants are released by these sources into the ambient air (Miri et al., 2016). Vehicles with petrol- and diesel-engines emit a wide variety of air pollutants, such as NO_2, SO_2 and VOCs, which have an accelerating impact on urban air quality. As the vehicular traffic increases, air pollution rises evenly in the future (Marc et al., 2016).

VOCs are an important class of air pollutants found in any industrial and urban region. Some VOCs are toxic like benzene while many participate in complex photochemical reactions in the presence of sunlight. The photo-chemical reactions lead to an increase in the formation of airborne toxic chemicals, to production of tropospheric ozone (Shao et al., 2009; Derwent et al., 2003; Finlayson-Pitts and Pitts, 1997). Benzene has been defined as a Group-I human carcinogen by the International Agency for Research on Cancer. VOCs are emitted from various outdoor sources such as transportation, industrial processes, fossil fuel combustion and solvent use (Adgate et al., 2004; Dodson et al., 2007; Sexton et al., 2007; D'Souza et al., 2009; Pandey and Kim,2010; Demirel et al., 2014).

Nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) are two of the most omnipresent pollutants found in the ambient air which exhibit documented adverse effects on health and welfare (Santis et al., 1997). In addition, photochemical reactions resulting from the action of the sunlight on NO_2 and VOCs from vehicles causes the formation of O_3. Acidic-rain is the long-range pollutant influenced by vehicle NO_x and SO_2 emissions (Duenas et al., 2002; Khoder, 2002; Stranger et al., 2008). Nitrogen dioxide is a pollutant gas (NO_2) involved in many different chemical processes in the atmosphere. In the troposphere, it acts as a photocatalyst in a serious of oxidation reactions of VOCs, generating O_3. Furthermore, NO_2 is a precursor in the formation of nitric acid (Hallquist et al., 2009; Marc et al., 2016).

Sulfur dioxide (SO_2) is a very poisonous gas that can occur both anthropogenically or naturally. Some of them are naturally forms like volcanic eruptions, and relatively harmless. Some, can be man-made as a byproduct of industrial processing, and are extremely toxic (http-1, 2017). Sulphur dioxide is distributed in the atmosphere from both natural sources such as grassland, volcanoes and also forest fires and many anthropogenic sources involving the use of fossil fuels such as coal transformation processes and crude oil, metal smelting, fossil fuel combustion and other industrial processes.

SO_2 may oxidize to S (VI) species and it acts as a sulphate precursor in the aerosol system in this form by altering the direct and indirect radiative forcing and upsizing the acid deposition. Coal-fired power plants are the biggest source of world

of sulphur dioxide air pollution which contributes to acid rain, smog, and the health problems that involve lung disease.

Ozone is a colorless gas at ambient temperature and pressure, and unstable especially at higher concentration. The production of ozone is based on photochemical reactions of air pollutants such as hydrocarbon and nitrogen oxides. When these pollutants build up to sufficiently high level, a chain reaction occurs from their interaction with sunlight in which nitrogen oxide is converted to nitrogen dioxide, and later, it can absorb sunlight and breaks down oxygen atoms that assembling with the air-oxygen to produce ozone. Ozone is also emitted from germicide lamps, copy machine, printers, welding and other industrial process (Helaleh et al., 2002).

The presence of ozone (O_3) in the troposphere is understood to arise from two basic processes: tropospheric/stratospheric exchange that brings about the transport of stratospheric air which is rich in ozone into the troposphere; and production of ozone from photochemical reactions occurring within the troposphere. Ozone is produced in the troposphere due to interaction of meteorological conditions, sunlight, nitrogen oxides (NOx), O_2 and volatile organic compounds (VOCs) (Alejo et al., 2011).

1.2.1 Sulphur oxides (SO_x)

Sulfur dioxide (SO_2) is a prevalent pollutant in most civilized countries, from industrial processing plants such as oil, coal, metal, cement, copper, wood, electric power plants etc (http-1, 2017). When sulfur burns with oxygen from the air, sulfur dioxide (SO_2) is produced.

The basic sources of sulfur dioxide are coal-fired power stations, and other metals, and exhaust from diesel vehicles (EPA, 1992). SO_2 can also be showed up due to kerosene heaters and coal combustion (Godish et al., 2015; Yurdakul et al., 2017). In addition, SO_2 levels are also likely to increase with the growth of various industrial area (Appalasamy et al., 2017). Besides that, the ‘acid rain’ debate focused on the ecological impact of sulfur dioxide emissions (Cape et al., 2003).

Sulfur dioxide (SO_2) is released into the atmosphere through natural and anthropogenic emissions. Natural emissions include intentional biomass burnings and

volcanic eruptions. Anthropogenic emissions are mainly due to combustion of coal and oil fuel, which accounts for more than 75% of global emissions (Chin et al., 2000; Zhang et al., 2017). Convention on Long-Range Transboundary Air Pollution realized the reason of SO_2 in the formation of acid rain and resultant acidification problems in the environment (http-2, 2017; Zhang et al., 2017).

1.2.1.1 The effects of sulphur dioxide (SO_2) on human health and ecosystem

Adverse effects of sulphur dioxides on human health and environment have been seen for a long time (Demirel et al., 2014). They cause some problems such as smog, acid rain, and health problems that include lung disease. SO_2 can affect both health and the environment. Short-term exposures to SO_2 can harm the human respiratory system and make breathing difficult. Children, the elderly, and those who suffer from asthma are particularly sensitive to effects of SO_2 (EPA, 1992). Sulfur dioxide irritates the respiratory tract and increases the risk of tract infections. It causes coughing, mucus secretion and aggravates conditions such as asthma and chronic bronchitis. SO_2 may cause bronchoconstriction in healthy adults and adults who have respiratory problems (Bernstein et al., 2008; Yurdakul et al., 2017).

Besides its health effects, environmental effects are also seen. At high concentrations, gaseous SO_x can harm trees and plants by damaging foliage and decreasing growth. SO_2 and other sulfur oxides can contribute to acid rain which can harm sensitive ecosystems (EPA, 1992). When sulfur dioxide combines with water and air, it forms sulfuric acid, which is the main component of acid rain. It can cause deforestation, corroding paints and building materials (http-3, 2017). Sources of the sulfur dioxides and their health and environmental effect are given in Table 1.1

Table 1.1 Sources of the Sulfur Dioxides and their health and environmental Effect

Pollutant	Anthropogenic sources	Health effects	Environmental effects
Sulphur Dioxide (SO_2)	Burning of coal and oil, especially high-sulfur coal; industrial processes like paper manufacturing, metal smelting.	Respiratory illness, breathing problems, may cause permanent damage to lungs.	Precursor of acid rain, which can damage trees, lakes, and soil; aerosols can reduce visibility. Acid rain also causes buildings, statues, and monuments to deteriorate.

1.2.2 Nitrogen oxide (NO_x)

1.2.2.1 Nitrogen compounds in the atmosphere

Nitrogen is an important element because some of the compounds which are formed by nitrogen cause the environmental problems such as urban smog, acid rain and global warming as well as it plays a part between the elements that found most in atmosphere and plays a role in development of animal and plants.

Although molecular nitrogen (N_2) is found to a large extent in atmosphere, Nitrogen compounds in reduced form also play a part to a lesser extent in the atmosphere. Reduced compounds are ammonia (NH_3) and ammonium ion (NH_4^+) and oxidized compounds can be categorized as nitrous oxide (N_2O), nitrogen monoxide (NO), nitrous acid (HNO_2), nitric acid (HNO_3), peroxyacetylnitrate (PAN) and nitrate (NO_3) (Löublod et al., 1997).

Physical and chemical properties of various nitrogen compounds taking part in the global nitrogen cycle and found in the open atmosphere is given in Table 1.2.

- **Nitrogen oxides (NO_x = NO + NO_2):**

Although there are more N_2O, NO and NO_2 in the atmosphere, NO and NO_2 are two important components of air pollutant and the mixture of these two gases as shown as the symbol of NO_x. The main component of waste gases coming from the anthropogenic sources is NO gases. The formation reaction of these gases during the process is given. (http-4, 1993).

$$N_2 + O_2 \rightleftharpoons 2NO \qquad (\Delta G^o = 86.596 \text{ kJ/mol}, \ \Delta H^o = 90.291 \text{ kJ/mol})$$

Table 1.2. Physical and chemical properties of Nitrogen Oxides (http-5, 1997)

Oxide	**Molecular Weight (g mol^{-1})**	**Melting Point (°C)**	**Boiling Point (°C)**	**Solubility in water (0°C, cm^3/100g)**	**Enthalpy of Formation (kcal mol^{-1})**	**Entropy (cal mol^{-1}-°C)**
NO	30.01	-163.6	-151.8	7.34	21.58	50.35
NO_2	46.01	-11.2	21.2	It occurs HNO_2 and HNO_3 by reacting H_2O	7.91	57.34
N_2O	44.01	-90.8	-88.5	130.52	19.61	52.55
N_2O_3	76.01	-102	47	It occurs HNO_2 by reacting H_2O	19.80	73.91
N_2O_4	92.02	-11.3	21.2	It occurs HNO_2 and HNO_3 by reacting H_2O	2.17	72.72
N_2O_5	108.1	30	3.24	It occurs HNO_2 by reacting H_2O	2.7	82.8

Table 1.2. Continued

HNO_2	47.01	-	-	-	-	-
HNO_3	63.01	-42	83	-	-32.1	63.7
PAN ($CH_3COOONO_2$)	121.06	-	-	-	-	-
NH_4NO_3	80.04	169.6	210	118.3 g (100 $cm^3)^{-1}$	-87.37	36.11

NO_2 is a gas which has color of red-brown, odorous and corrodent. Conversions between NO and NO_2 underlie the formation of photochemical smog. NO and O atom occurred as a result of the photolysis of NO_2 with sunlight (http-5, 1997).

Nitrogen dioxide (NO_2) is one of the most common air pollutants in ambient and indoor air (Lai et al., 2006; Hanninen et al., 2004; Kornartit et al., 2010). It is also the basic gaseous compound that affect both indoor and outdoor quality (WHO, 2003; Kornartit et al., 2010; Han et al., 2011; Demirel et al., 2014). Nitrogen dioxide (NO_2) is released from both stationary (combustion of fuel) and mobile sources (Gauderman et al., 2005; Zhang et al., 2017). The major outdoor sources of NO_2 concentrations are mobile and stationary combustion sources (Kampa and Castanas, 2008; Kaushik et al., 2006; Lewne et al., 2004; Kornartit et al., 2010), and also transportation and industrial activities (Demirel et al., 2014), whereas indoor sources include gas cookers, wood stoves, fireplaces, and environmental tobacco smoke (Kornartit et al., 2010), space and water heaters, unflued kerosene heaters (Levy, 1998; Willers et al., 2006; Can et al., 2015) and also tobacco smoke (Cyrys et al., 2000; Can et al., 2015). Additionally, outdoor air is known as an important source for indoor NO_2 pollution (Can et al., 2015).

NO_2 is formed from the combination of nitrogen and oxygen (O_2) during high temperature combustion processes (Brunekreef, 2001). NO_2 and associated compounds can also produce secondary aerosol by photochemical oxidation (Bencs et al., 2008). NO_2 is significantly associated with the traffic count on highways or motorways and with distance from roadways. Concentrations decreased drastically with increasing distance from traffic (Stranger et al., 2008). NO_x is generally emitted

in combustion processes in the form of NO that, after interaction with other species such as O_3 and volatile organic compounds (VOCs), is transformed to NO_2 (Escuredo et al., 2016). Sources of the Nitrogen Oxides and their health and environmental effect are given in Table 1.3 below.

Table 1.3. Sources of the Nitrogen Oxides and their health and environmental Effect

Pollutant	**Anthropogenic sources**	**Health effects**	**Environmental effects**
Nitrogen oxides (NO_x)	Burning of gasoline, natural gas, coal, oil (Cars are a major source of NO_x)	Lung damage, respiratory illnesses	Ozone (smog) effects; precursor of acid rain which damages trees, lakes, and soil; aerosols can reduce visibility. Acid rain also causes buildings, statues, and monuments to deteriorate

1.2.2.2 Conversion reaction of nitrogen oxides in the atmosphere and photochemical smog formation

Combustion of fossil fuels in motor vehicles is one of the major sources of anthropogenic NO_x in most large cities. Therefore, NO_2 is the main traffic-related air pollution and has been used as an indicator of motor vehicle exhaust (Stranger et al., 2008). Nitrogen oxides (NO_x) in urban environments are principally emitted from

fossil fuel combustion as NO (Masiol et al., 2014). In other words, the primary emission of NO_x from vehicles is largely NO, but it is rapidly oxidized to NO_2 by reaction with O_3 (Stranger et al., 2008)

$$2NO + O_2 \longrightarrow 2NO_2 \quad (1)$$

Some of the amount of NO so formed then reacts with oxygen and NO_2 is formed.

$$NO_2 + h\nu \longrightarrow NO + O \quad (2)$$

In the presence of sunlight, nitrogen dioxide molecule present in high concentration breaks up and gives oxygen atom.

$$O + O_2 \longrightarrow O_3 \quad (3)$$

This free oxygen (O) reacts with oxygen molecules present in the atmosphere and ozone (O_3) is formed.

$$NO + O_3 \longrightarrow NO_2 + O_2 \quad (4)$$

Ozone so formed then reacts with NO to form NO_2 and O_2.

Oxidation of NO to NO_2 takes place in two different ways. Reactions with number 3 and 4 show that the mechanism of the oxidation of NO to NO_2.

Ozon occurred because of photolysis of NO_2 in the presence of sunlight according to the reactions with number 2 and 3.

The other reactions which are oxidized NO to NO_2 are organic compounds. Organic compounds in the atmosphere can be categorized as the VOCs (Volatile Organic Carbon), ROC (Reactive Organic Carbon) and NMHC (Non-methane hydrocarbon). Urban region is characterized as the origin of nitrogen oxides and ROC. The photochemical smog formation is formed in the suitable atmospheric conditions with these compounds. Reactions providing to smog formation starts with the photolytic reactions causing the formation of free radicals. Amount of NO_x given to

the atmosphere determines the amount of O_3 that can form in the reactions leading to photochemical smog formation.

1.2.2.3 The effect of nitrogen oxides (NO_x) on human health and ecosystem

Nitrogen dioxide (NO_2) can cause many health problems including eye mucosa, irritation of nose, throat and respiratory system (Berglund, 1993; Kattan et al., 2007; Kornartit et al., 2010; WHO, 2010; Can et al., 2015). NO_2 is an irritant gas and can increase susceptibility to airway infections and impair lung function in exposed populations (Kattan et al., 2007; Curtis et al., 2006; Kraft et al., 2005; Kornartit et al., 2010). The toxicity of NO_2 depends on its oxidative and free radical properties, as well as its ability to form nitric and nitrous acids in aqueous solution on the moist surfaces (Utell et al., 1991). Its main effect, therefore, on human health is to damage respiratory tract cells such as mucous membranes of the lung (Blomberg et al., 1999; Kornartit 2010).

The two most important ones which are found in the atmosphere and nitrogen oxides are NO and NO_2. NO gas has not an irritating property and also effects on health (< 5 ppm) are quite a little. NO which is found at low concentrations in the atmosphere are quickly oxidized to NO_2 having toxic effect. NO_2 gases have a big importance among the NO_x in terms of human and environmental health. The negative effects of NO_2 on human health and air quality are given in Table 1.4 (Löublod et al., 1997; Ozden, 2005).

Table 1.4. Air quality of NO_2 and negative effects on human health (Löublod et al., 1997; Ozden, 2005).

NO_2 ($\mu g/m^3$)	**Time**	**Effects**
1	Annual Average	Air guality standard
24	-	Odor detection limit
2	15 minutes	Reduction of bronchial respiratory tract resistance

Table 1.4. Continued

5	**2 hours**	**Reduction of respiratory tract resistance in healthy infants**
1	15 minutes	Inhibition of gas exchange in the lungs
2	-	Inhibition of odor perception
1	-	recycled bronchiolitis
3	-	Death at the end of the bronchiolitis fibrosa obliterans within 2-3 weeks

Besides, nitrogen oxides create nitric acid and some particles by reacting ammonia and other components. Those components affect negatively human respiratory systems and also damaging lung tissue and causing the premature death Small particles cause to show up the respiratory diseases such as bronchitis by inserting the sensitive area of lungs (http-6, 2017).

The effect of NO_2 on many animals look like the effect on humans due to physiological, metabolic and structural similarities of mammalian, but concentration of NO_x and its exposure times show the differences. Shedding of eyelashes, alveolar tissue deterioration, blockage of respiratory bronchi and sensitivity increase that may occur in the lungs against the bacterial infection are observed in the animals which expose to concentration of NO_2 in the level of 94 $\mu g\ m^{-3}$ Nitrogen oxides and mainly NO_2 cause the effect of health problems such as making defense mechanisms slow, damaging the lung structure, metabolism and functions (http-5, 1997).

Nitrogen oxides are indirectly effective through the products resulting from the photochemical reactions on plants and they are directly affected when taken and stored by plant leaves and soil. The effect of nitrogen oxides on plants occur in the form of

increasing sensitivity against external factors such as whitening of plant tissue (chlorosis) or death, spillage of leaves, decrease of growth rate and production yield. It has been identified in the case of exposure to nitrogen oxides for a short time (average 24 hours) the determined critical value is 75 μg m^{-3} and the annual critical value is 3 μg m^{-3} (http-5, 1997). If the critical values are exceeded, nitrogen oxides cause a phytotoxic effect on the plants. At the same time, that nitrogen oxides are inherent in the formation of other phytotoxic substances such as ozone and organic nitrate causes to agricultural product losses.

Acid rains have harmful effects on plants due to their influence on the chemical and biological structure of the soil. They transport the elements such as calcium, magnesium found in the structure of soil to the ground water and causes to soil weakening and reduction of agricultural yield. Otherwise, acid rains slow down or stop the ability of assimilation damaging the chlorophyll in the tree leaves and breaking down the cell wall. Consequently, the growth of the trees is interrupted (Nielsen et al., 1999).

Nitrogen oxides cause to formation of ozone which is a serious problem in troposphere. It is expressed that 95 percent of the plant damage originates from the ozone in the North America (Ozden, 2005; http-14). When meteorological and climatic conditions are effective in the formation of ozone, it causes to decrease the production yield due to the adverse effects on plants especially during planting season.

1.2.3 Ozone (O_3)

Ozone is a reactive and oxidant gas that has some positive and negative properties and occurring in a trace amount in the atmosphere and playing a key role in the photochemical air pollution and atmospheric oxidation processes (Curci et al., 2009; Masiol et al., 2014). Ozone is a special form of oxygen. While normal oxygen (O_2) contains two oxygen atoms, ozone (O_3) contains three oxygen atoms. Ozone is less stable and more reactive than oxygen. Besides, ozone has a property of breaking of organic substances and it can damage the organisms and plant because of that property. Ozone forms and their properties are introduced in Table 1.5 (http-7, 2000).

Table 1.5. Ozone forms and their properties in the atmosphere.

Oxygen form	Number of atom	Chemical stability	Amount in the atmosphere
Atomic Oxygen	1	Unstable/ more reactive	Trace amount
Normal Oxygen	2	Stable	21 percent of the air
Ozone	3	Quite stable/ Reactive	10- 100 ppb (20- 200 $\mu g/m^3$)

Stratospheric ozone plays a vital role in the atmosphere. The only important aspect about stratospheric O_3 has been its protective role for harmful ultra-violet rays from sun (Hunova et al., 2004). However, tropospheric ozone is an undesirable compound due to adverse effects on human health. Furthermore, although it acts as a barrier for ultraviolet rays in the upper atmosphere, it is a secondary air pollutant generated through a series of complex photochemical reactions involving solar radiation and ozone-precursors, i.e. NO_2 and reactive hydrocarbons (Curci et al., 2009). Therefore, stratospheric ozone is defined as 'good' and tropospheric ozone is defined as 'bad'.

1.2.3.1 Stratospheric ozone

The distance of stratosphere layer from the tropopause which is a boundary separating the troposphere and stratosphere layers rise about 50 km altitude. Strong winds reaching to the speed of 200-350 km per hour may occur in the stratosphere. The most concentrated layer of ozone is located at a height of 35 km. The uppermost boundary of the stratosphere is called stratopause. It is seen that the temperature is reached to value of earth at this level (Ozden, 2005).

About 90 percent of the atmospheric ozone in the world is in the stratosphere. Ozone has a critical importance such as absorbing of the ultraviolet light emitted by sun. The 1 percent reduction in the stratospheric ozone concentration cause that UV-

B levels reaching to earth increase at the rate of 2 percent. This phenomenon results in becoming widespread of skin cancer (Seinfeld and Pandis, 1998). Stratospheric chemistry contains some chemical processes determining ozone amounts in stratosphere. Ozone formation and depletion in stratosphere occur within the cycle of 'Chapman'. The Chapman cycle reveals the chemical description of the ozone balance in the atmosphere. According to this cycle, oxygen (O_2) is a critical component in the atmosphere and the oxygen atoms are broken down by high energy ultraviolet photons in the presence of sunlight according to reactions with the number of 1.2.

$$O_2 \xrightarrow{hc/\lambda} O + O \qquad (1.2)$$

h is the Planck constant, c is the light velocity and the λ is the wavelength of photon. Oxygen atoms cause to formation of ozone by reacting oxygen molecules according to reaction of 1.3 because of the oxygen atoms formed are too reactive.

$$O_2 + O \xrightarrow{M} O_3 \qquad (1.3)$$

M in the reaction shows the other molecules which helps to take place the reactions. Ozone gives free oxygen by absorbing the ultraviolet light according to reaction of 1.4.

$$O_3 \xrightarrow{hc/\lambda} O_2 + O \qquad (1.4)$$

Reactions given above take place immediately due to the fact that duration time of atomic oxygen in the atmosphere is shorter than one second and absorbing the sunlight having a wave length of 150-300 nm. (http-12, 2019). Consumption of ozone takes place as a result of the catalytic reactions with the hydrogen atoms, hydroxyl radicals, NO, chlorine and compounds of bromine. A mole of catalyst reacts until the source chemical is depleted in the catalytic reaction. All ozone molecules in the stratosphere are not scattered throughout the stratosphere. They are found in the form of a thick and thin film layer. The thickness of this layer which is called ozone layer is 300 Dobson (http-7, 2000; Ozden, 2005).

1.2.3.2 Tropospheric ozone

1.2.3.2.1 General properties of tropospheric ozone

Troposphere which is the lowest layer of atmosphere reaches out approximately 10 km up from the earth. This region is the site of widespread meteorological events such as clouds, rain, storm and temperature decrease with altitude. This is because the surface of the earth absorbs the solar radiation and radiation disperse from the ground again. All events related with climate occurs between ground surface and lower stratosphere. This active region has 80 percent of atmospheric mass. For this reason, it is known as the most important layer of the atmosphere regarding to meteorological events (Ozden, 2005).

Tropospheric ozone forms the 10-15 percent of atmospheric ozone. While stratospheric ozone gets thinner, ozone amounts in the troposphere increases. There are many studies related with ground-level ozone measurement across America and Europe. They show that the daily changes with respect to reaching minimum values with ozone levels in rural regions reactions with NO during the night in the morning or minimum as a result of the dry deposition and photo-chemical formation in the afternoon or reaching the maximum values as a result of the transportation of ozone-rich-air down in the upper layer. As well as ozone concentrations depend on the hours of the day, they show the alteration between days as well.

Tropospheric O_3 is a main secondary air pollutant that plays a crucial role in atmospheric chemistry produced from photochemical reactions involving nitrogen oxides (NO_x) and volatile organic carbons (VOCs) in the presence of sunlight and some anthropogenic processes (Zhang and Rao, 1999). It is a colorless gas at ambient pressure and temperature and unstable especially at higher concentrations (Özer et al., 1997; Grigorieva and Mihalev, 1998; Helaleh, 2002; Sanz, 2007).

A principal constituent of the stratosphere, O_3 is an undesired pollutant in the troposphere resulting in photochemical smog. On the other hand, O_3 is also a significant substance to control the chemical composition of troposphere (Duenas et al., 2002). Ozone is highly reactive and an irritating gas (Markovic and Markovic, 2005) that has unfavorable effects on biosphere (Duenas et al., 2002), vegetation (Latif

et al., 2012; Zhang, 2011; Barrero et al., 2006; Kovac-Andric et al., 2009) and human health (Shanhueza et al., 2002; Tu et al., 2007).

The first tropospheric O_3 measurements were conducted between 1876 and 1910 at Montsouris near Paris showed background levels of ~20 μg m^{-3} (Bytnerowicz et al., 2002; Hunova I., 2003). Ozone is an exclusive pollutant that there are no compounds other than O_3 in the troposphere that has a small range between the natural and toxic levels. That means effects of O_3 can occur at lower levels than current ambient concentrations (Hunova et al., 2003; WHO, 2000).

1.2.3.2.2 Sources of tropospheric ozone

Tropospheric ozone is not a component given directly to the atmosphere. Tropospheric ozone is a secondary component as a result of the reactions which occur between nitrogen oxides, VOCs as firstly, CO, water and hydroxyl radicals which cause to ozone formation. The formation of tropospheric ozone can be sequenced as below; (http-13, 2019).

* Transition to troposphere of stratospheric ozone in some times especially in the period of thunderstorm.

* Lightning

* Urban air pollution

High energy occurring as a result of the lightning causes to dissociate the oxygen and water vapor. The resulting radicals ($\cdot O$ and $\cdot OH$) cause to ozone formation by combining immediately with oxygen.

Air pollution originated ozone which is called ‘bad ozone’ occurs as a result of some chemical reactions taking place between especially NO_x and VOCs in the presence of sunlihgt which are given to the atmosphere from automobiles, gas vapor, energy facilities which use fossil fuel, refinery and some industrial resources.

Ozone can stay in the atmosphere during several days after formation of ozone. For this reason, ozone measured in any region results from the emissions of VOCs or nitrogen oxide hundreds or thousands of kilometers away. The much more ozone occur with the transportation of primary air pollutants of air movements to far away and therefore, the maximum ozone concentrations are seen in the region far away from the pollutant emission sources on the dominant direction of wind (EC, 1999).

The basic sources of tropospheric ozone are due to the production of photochemical reactions with NO_x, VOCs and CO (Tuncel et al., 1996; Grigorieva and Mihalev, 1998; Tang et al., 1998; Bernard et al., 1999; Harrison, 2001; Helaleh et al., 2002; Godish, 2004; Sanz et al., 2007; Shan et al., 2008; Kovac-Andric, 2009; Gerosa et al., 2009; Sicard et al., 2011), transport of vertical from stratosphere (Alloway and Ayres, 1997; Kovac-Andric et al., 2009), transport of horizontal (dispersion) from local sources by winds (Tuncel et al., 1996; Duenas et al., 2002).

1.2.3.2.3 Chemistry of tropospheric ozone

Tropospheric O_3 is susceptible to climate change due to its dependence on sunlight and temperature for the formation (Bell et al., 2007) and also it is a precursor to the hydroxyl radical's formation which affects the oxidizing capacity of the troposphere (Tang et al., 1998; Satsangi et al., 2004; Oltmans et al., 2006; Wallace and Hobbs, 2006). Ozone is one of the atmospheric trace gases (NO_2, H_2O_2, HCHO, HNO_3, etc.) whose photolytic products; O, NO, OH, H, HCO, HO_2 and organic peroxyl radicals are very reactive.

The non-methane hydrocarbons oxidation in the presence of NO_x are the responsible for photochemical processes. Furthermore, ultraviolet-B radiation (UV-B, 290-320 nm) is very energetic that can be the other parameter for the processes. The detection of the effects of UV-B on tropospheric constituents will be difficult due to the fact that the concentrations of the species can be also influenced by many factors especially anthropogenic emissions (Solomon et al., 2003).

O_3 residence time is 1 to 2 weeks in summer and 1 to 2 months in winter. This can give rise to O_3 concentration levels in urban sides where traffic is much denser

than in rural sides are low (Bayındır, 2008; Paoletti, 2009; Tuncel et al., 1996; Akimoto et al., 2003). The main reasons could be determined as follow. First of all, ozone is a secondary pollutant which means it is not emitted directly then, it can be formed at a certain distance from the precursor sources. Moreover, biogenic hydrocarbons (BVOCs) are reactive than anthropogenic hydrocarbons then, in remote or green areas the contribution of BVOCs are proper in the formation of ozone. Finally, ozone can be consumed by NO_x in polluted areas. (Akimoto et al., 2003).

1.2.3.2.4 Formation and removal mechanism of ozone in the troposphere

Generally, two processes are declared for the formation of tropospheric ozone; one of them is the photochemical production from the oxidation of hydrocarbons or carbon monoxide in the presence of nitrogen oxides and UV radiation and the other one is the downward transport from the stratosphere in literature (Tang et al., 1998).

Besides, there are two sink processes for the tropospheric ozone; photolysis of ozone and deposition at the Earth's surface (Tang et al, 1998; Harrison, 2001). Surface deposition involves the reaction with plants, ice and snow, bare land and man-made structures. However, the primary sink for tropospheric O_3 is its photo-dissociation on absorption of UV radiation and subsequent formation of radicals, especially OH.

The potential for tropospheric O_3 formation can be related both local sources and non-local origin that means the transported air masses in large scale. Non-local sources involve anthropogenic and natural O_3 as well as the precursor compounds needed for photochemical reactions (Williams et al., 2009). The removal of tropospheric O_3 at daytime is given in Figure 1.1 (Jenkin and Clemitshaw, 2000).

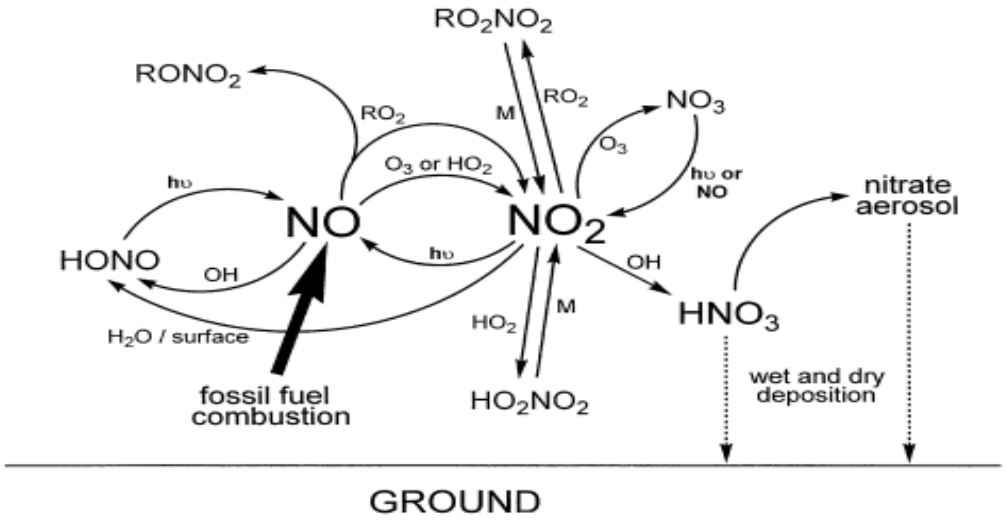


Figure 1.1. Removal mechanisms of tropospheric O_3 in daytime (Jenkin and Clemitshaw, 2000).

In the absence of sunlight during night time, O_3 reacts with NO and NO_2 to produce HNO_3 (R.1-R.4) which remains in the gas phase until it reacts with NH_3 to form ammonium salt (R9). The ammonium nitrate removal is achieved by dry or wet deposition processes. In Figure 1.2 the removal of tropospheric O_3 at nighttime is given (Jenkin and Clemitshaw, 2000; Notario et al, 2012).

$$O_3 + NO \longrightarrow NO_2 + O_2 \quad \text{(R.1)}$$

$$NO_2 + O_3 \longrightarrow NO_3\cdot + O_2 \quad \text{(R.2)}$$

$$NO_2 + NO_3\cdot \longrightarrow N_2O_5 \quad \text{(R.3)}$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_3 \quad \text{(R.4)}$$

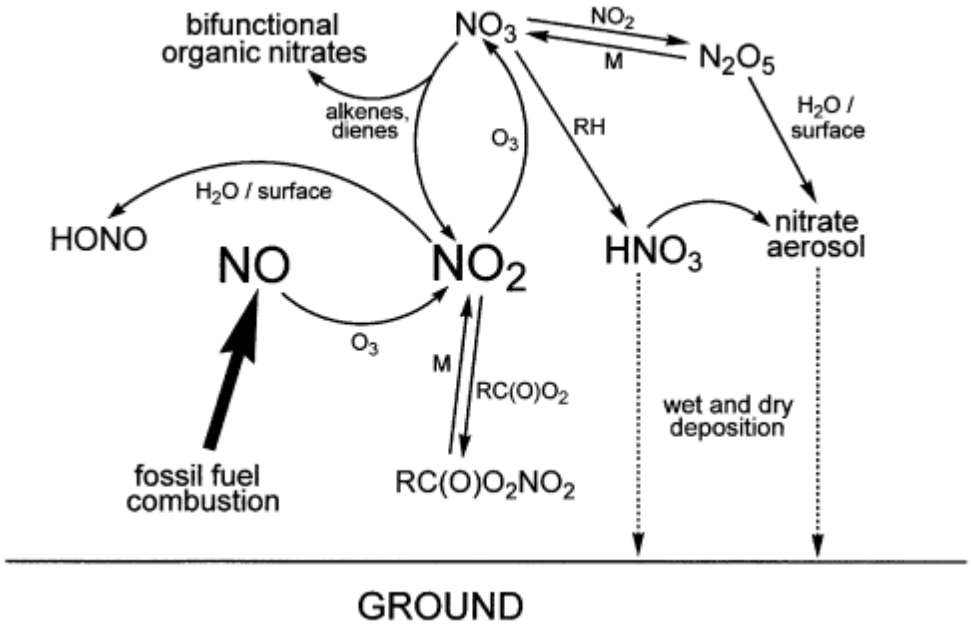


Figure 1.2. Removal mechanisms of tropospheric O_3 in night time (Jenkin and Clemitshaw, 2000).

Reactions between NO_2 and O_3 produce nitrate radical ($NO_3\cdot$) that reacts with NO_2 to produce N_2O_5. Then, dinitrogen pentoxide reacts rapidly and produce HNO_3. Nitric acid is also produced by reaction between $NO_3\cdot$ and formaldehyde (HCHO) or hydrocarbon radicals (R.5 and R.6).

$$NO_3\cdot + HCHO \longrightarrow HNO_3 + CHO\cdot \qquad (R.5)$$

$$NO_3\cdot + RH\cdot \longrightarrow HNO_3 + R\cdot \qquad (R.6)$$

Nitrate radical is a key component in tropospheric O_3 chemistry because of the fact that it is placed in the production of biogenic VOCs in nighttime (Godish, 2004).

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3 \qquad (R.7)$$

1.2.3.2.5 Meteorological parameters

Meteorology plays an important role in the formation of air pollutants, transport, dispersion and dilution (Duenas et al., 2002; Tu et al., 2007). Tropospheric ozone evaluation is generally related with meteorological parameters in literature

however, there is a difficulty in the detection of changes in O_3 concentration due to change in emissions in the presence of meteorological fluctuations (Rao and Zurbenko, 1994). Brönnimann and Neu (1997) found that some meteorological conditions like high temperature and intense solar radiation are the favorable ones for production of ozone in urban and rural areas in Switzerland.

In addition, high ozone levels are also related with stationary air and zero rainfall, which are suitable for photochemical accumulation and production of ozone (Thompson et al., 2001; Vukovich and Sherwell, 2003; Duenas et al., 2002, Shan et al., 2009). Also, it is represented that meteorological parameters affect the ozone circulation in a short time interval (Kovac-Andric et al., 2009). However, O_3 chemistry and the effects of meteorological conditions could vary depending on the characteristics of the climate and air pollutants emissions in the place of interest (Tu et al., 2007).

1.2.3.2.6 The effect of tropospheric ozone on human health and ecosystem

Tropospheric O_3 can be a principal environmental problem when it exceeds the threshold value. It is well known that higher concentrations of O_3 have harmful impacts on human health, animal populations, agriculture productivity, biosphere and forest ecosystem (Sillman, 1999; Duenas et al., 2002; Latif et al., 2012; Zhang et al., 2011). The trouble of tropospheric ozone to human, animal and plant health at molecular and cellular level arises from oxidative damage to lipids, proteins and nucleic acid depending on the dose (Kovac-Andric et al., 2009).

Even though EPA determined the value of 80 ppb (160 μg m^{-3}) as a threshold for significant health effects, the standards in other developed countries have adopted more drastic levels as 65 ppb (130 μg m^{-3}) in Canada and 50 ppb (100 μg m^{-3}) in U.K (Sanhueza et al., 2002). Then, forecasting atmospheric O_3 concentration has great importance, especially in populated areas, so that the population may be warned in advance and preventive measures can be taken (Barrero et al., 2006).

Ozone is one of the most high-powered oxidizing agent in the atmosphere which releases free oxygen radicals during the photochemical reactions. These radicals protect the body from the harmful bacteria by inflammatory reactions. Oxygen radicals are toxic to bacteria however they also damage normal tissues if the dose of them are higher (Sanhueza et al., 2002). Besides, it is the third most important greenhouse gas that contributes the climate change (Sicard et al., 2011).

In studies on animals and human about repeated exposure to O_3 have been shown that most of the diseases are related with respiratory systems (Kovac-Andric et al., 2009). Shanhueza et al. (2002) listed the diseases as chronic obstructive pulmonary diseases (asthma, bronchitis, and emphysema), cough and chest pain, lung inflammation, allergic airway diseases (Kovac-Andric et al., 2009).

Helaleh et al., 2002 and WHO (2005) detailed the adverse health effects with exposure dose. Ozone concentration in ambient air in short term exposure to 0.11 ppm cause irritation to noise and throat, swelling within the nasal passages and nasal congestion, itchy and watery ices. The exposure to 0.1-0.3 ppm results in lung damage, asthma and bronchitis and 2-hour exposure to concentration of 1.5 ppm of O_3 is regarded as very dangerous (Alloway and Ayres, 1997).

Tropospheric ozone is identified as one of the most poisoned compounds for plants in the atmosphere (Fuhrer et al., 1997; Grünhage et al., 1999; Kovac-Andric et al., 2009). Like other atmospheric gases, O_3 is taken up by plants through transpiration and stomatal diffusion (Hunova et al., 2003; Gerosa et al., 2009; Sicard et al., 2011; Grünhage et al., 1999). Penetration through stomata depends on hydric condition of air (Sicard et al., 2011; Hunova et al., 2003; Gerosa et al., 2009), air temperature, photosynthetic active radiation; indirectly, to wind velocity (Gerosa et al., 2009), pH of the wetted surface, the surface temperature and the water solubility of O_3 (Grüngahe et al., 1999). One of the basic factor to determine the sensitivity of plant to O_3 is the identification of stomatal conductance genetically and environmentally (Hunova et al., 2003).

O_3 exposure reduces the photosynthetic activity rate, affect the cultures productivity and at sites with high O_3 concentration severe defoliation and foliar symptoms have been observed (Sicard et al., 2011). Although O_3 exposure affects

trees, trees also affect O_3 in the air (Paoletti, 2009). Trees reduce air temperature through shading and evapotranspiration thus they reduce emissions of O_3 precursors. Decrease in temperature also affects the emissions of hydrocarbons from biogenic and anthropogenic sources, which change the reaction rate of O_3 formation (Nowak et al., 2000).

Inside the leaf, O_3 diffuses into the intercellular spaces and dissolves in water content to form toxic reactive oxygen species. Generally, deposition of gaseous pollutants is greater in woodlands than in shorter vegetation. In addition, in greater leaf areas turbulent mixing of the air passing over land gets higher. The effect of ozone on plants can be ordered in regard to preventing the growth by decreasing the food storage capacity, increasing sensitivity against the effects of diseases, insects and environmental especially in sensitive plants and damaging to plants leaves or causing to death (Ozden, 2005).

Ozone reacts with water found in leaf immediately by passing from stoma on the leaf surface. The types of oxygen that are formed can influence the natural protective mechanism of plant because of being quite reactive. Necrotic and chlorotic regions in the leaf surface and plant cells may be damaged. Physiological changes like decreasing of photosynthesis are observed in longer exposures. For example, the damage occurred in cherry leaf as a result of the chronic ozone exposure are shown as percent in Figure 1.3.

% 0 %4.4 %7.8 %12.3 %24.5

Figure 1.3. Affected percentages of plant leaves from ozone chronically (Ozden, 2005).

The term of AOT40 is used in determination of ozone effects on plants. AOT40 is defined as total hourly ozone concentration over the 40 ppb (80 $\mu g/m^3$) between the morning at 8 a.m. and evening at 8 p.m. during the months of May to

September (Ozden, 2005). It is calculated by subtracting the 40 ppb which is threshold value from every hourly concentration over the 40 ppb and then to sum up the value as a result of these subtraction.

1.2.4 Benzene, toluene, ethylbenzene and xylenes (BTEXs)

Volatile organic compounds are a class of air pollutants sharing the same characteristic of high volatility in the ambient environment. The concentration of VOCs in the air is determined by processes such as emissions, evaporation, deposition, and photochemical reactions under the sunlight. Among traffic related VOCs, aromatic compounds, including benzene, toluene, ethylbenzene, and isomers of xylene (BTEXs), namely m-, o-, and p-xylene, have public health importance (Han and Naeher, 2006).

Benzene, toluene, ethylbenzene, and xylene, known as BTEX, are environmentally important VOCs. They are released to the atmosphere from both artificial and natural sources (Caselli et al., 2010; Davil et al., 2013; Fazlzadeh et al., 2012; Liu et al.,2009; Sturaro et al., 2010; Hazrati et al., 2015). BTEX compounds are known to have important impact on human health including cancer and may induce neurological disorders and symptoms such as weakness, loss of appetite, fatigue, confusion, and nausea (Hoskins, 2011; Hazrati et al., 2015). BTEXs also act as sensitizers and cause irritation in upper respiratory tract (Masih et al., 2017; Amini et al., 2017). Benzene has been identified as a Group-I human carcinogen by the International Agency for Research on Cancer (IARC, 1982; Caselli et al., 2010; Demirel et al., 2014; Hazrati et al., 2015).

Besides, benzene, toluene, ethyl benzene, and xylenes (BTEXs) are derived from crude oil and can be found near natural gas and petroleum deposits. BTEX aromatics are important petrochemical compounds that are generated during the processing of petroleum products and production of consumer goods such as adhesives, cosmetics, inks, paints, pharmaceuticals, rubbers, and thinners, making BTEX compounds part of the most abundantly produced chemicals worldwide (Lecompte et al., 2018).

Benzene is the most toxic chemical within the BTEX family and long-term exposure to benzene may increase incidence of leukemia and a plastic anemia in human (Baker et al., 1985; Mehlman, 1990; Wong, 1995; Niri et al., 2009; Hazrati et al., 2015). Toluene is a potent human teratogen (Hersh J.H., 1989; Donald et al., 1991). Ethylbenzene has been categorized as a possible human carcinogen and has been placed in group 2B by IARC (IARC, 2000; Masih et al., 2017). Among BTEX, benzene and toluene have the highest toxicity (Masih et al., 2017).

VOCs not only cause pollution problem on local scale, but also play an important role on regional scale like photochemical ozone formation introduced by the reaction with OH radicals in the troposphere in the presence of nitrogen oxides and sunlight. Moreover, it also increases the risk of cancer (Finlayson-Pitts and Pitts, 2000; Masih et al., 2016). Several VOCs are also precursors of ground level ozone formation and they are mainly emitted in areas of intense transport and industrial activity (Warneck, 1988; Singh et al., 2014; Masih et al., 2016). Physical parameters of BTEXs are given in Table 1.6.

Table 1.6. Physical parameters of BTEXs

Compound	Mole weight g $mole^{-1}$	Density g ml^{-1}	Boiling point °C	Water solubility mg l^{-1}	Vapor pressure mmHg	Log K_{ow}
Benzene	78	0.88	80.1	1780	76	2.13
Toluene	92	0.87	110.8	535	22	2.69

Table 1.6. Continued

o-Xylene	106	0.88	144.4	175	5	2.77
m-Xylene	106	0.86	139	135	6	3.20
p-Xylene	106	0.86	138.4	198	6.5	3.15
Ethylbenzene	106	0.87	136.2	152	7	3.15

Source: Data from EUGRIS database (http-8, 2017) (Maish et al., 2016)

1.2.4.1 Sources of BTEXs

Highly reactive volatile organic compounds (VOC) which are reported to be toxic and also may participate in numerous reactions in the atmosphere to form

secondary air pollutants including ground level ozone and secondary organic fine particles (Griffin et al., 1997; Rappengluck et al., 1998). Volatile Organic Compounds are emitted from various outdoor sources such as industrial processes, solvent use, fossil fuel combustion and transportation. Environmental tobacco smoke (ETS), personal care products, cleaning products, perfumes, glues, paints, solvent based products, and some building and construction materials are major indoor sources of VOCs (Adgate et al., 2004; Dodson et al., 2007; Sexton et al., 2007; D'Souza et al., 2009; Pandey and Kim, 2010; Demirel et al., 2014).

VOC sources are both anthropogenic and natural ones; the most important sources of VOCs in Europe are (ESIG, 1997, European Solvents Industry Group, Brussels, Fernandez-Villarrenaga et al., 2004): transportation (35%), solvent usage (24%), vegetation (22%), production processes (7%) and combustion (6%).

Major sources of BTEXs include vehicle exhaust, automobile service stations and industrial emissions. The vehicular emissions come from different contributions: exhaust emissions (cold and hot), evaporative emissions, and emissions from brake and tyre wear. Transport-related emissions are important factors in determining air quality in many urban regions, depending on the altitude and thus the dispersion pattern of emissions. In addition to these, another main source of BTEXs in urban areas is gasoline evaporation and vehicle emission (Lan and Minh 2013). In most urban areas, air pollution is now badly affecting the quality of life and the improvement of air quality has become a priority for most cities in developed countries (Snyder and Kalf, 1994; Zhang et al., 1996; Lovern et al., 1997; Wiwanitkik, 2008; Pilidis et al., 2009).

At outdoors, pollutants are diluted in air due to dispersion. However, in indoor environment, due to lack of proper ventilation and high humidity, the concentration of pollutants increases exceedingly. Amongst the wide variety of organic and inorganic air pollutants which have been recognized, volatile organic compounds (VOCs) deserve special consideration, because of their ability to affect human health as well as the environment. Contamination of indoor air by BTEXs can be attributed to various emission sources. The major sources include the combustion processes like cooking, heating and burning. In most of the religious rituals, burning of scented candles and incense is quite common (Masih et al., 2017).

Similarly, some of the occupant activities such as smoking, use of air fresheners, deodorants and insect repellants may also release BTEX in indoor air. It can be easily noticed that even a single house contains numerous synthetic chemical products such as cleansers, stain removers, paints, adhesives, solvents, oils and various plastic products. These products continuously emit many harmful VOCs including BTEXs in air and hence deteriorate the quality of indoor air. In addition to these, BTEXs from outdoor air may also enter indoor air through various vents present in the building (Batterman et al., 2007; Masih et al., 2017).

1.2.4.2 Diagnostic ratio (T/B and X/B)

Toluene to benzene (T/B) ratio has been used as an indicator of traffic emissions in a widespread manner. Toluene and benzene are constituents of gasoline and are emitted into the atmosphere by car exhausts (Hoque et al., 2008). The research of toluene to benzene (T/B) and xylene to benzene (X/B) concentration ratios are useful in identifying the distance of vehicle emission sources and photochemical age of air mass (Monod et al., 2001; Khoder et al., 2007).

A value approaching in the range of 1.5-4.3 for T/B ratio indicates the traffic originated emission sources while the ratio reaching the value of 10 or higher concludes the strong industrial sources nearby (Niu et al., 2012; Kumar et al., 2017). T/B ratio can also be used as an indicator for age of air mass having fresh air mass values between 3 and 5 decreasing values for the older air mass (de Blas et al., 2016; Navazo et al., 2008). Besides, lower reactivity of benzene than xylene leading to higher atmospheric lifetime of benzene where the ratio of X/B indicates the evidence of transport and the photochemical age of air parcel. Higher and lower values of X/B ratios indicate fresh air mass, which means “local sources”, and old air mass which means “transported”, respectively.

1.2.4.3 Ozone formation potential (OFP)

BTEXs are photo-chemically active materials and are considered as important precursor of ozone formation in the atmosphere (Tan et al.,2012; Alghamdi et al.,

2014) introduced by the reaction with OH radicals in the presence of nitrogen oxides and sunlight (Masih et al., 2016; Atkinson, 2000).

The reaction of BTEXs with hydroxyl radicals (OH) and or nitrate (NO_3) radicals function as the dominant degradation processes for aromatic VOCs in the atmosphere and then the resulting products contribute to secondary organic aerosol (SOA) formation by nucleation and condensation (Brocco et al., 1997). It was informed by Odum et al., (1997) that the toluene reaction with NO_x in the presence of light source formed SOA with a significant aerosol yield. Consequently, aromatic VOCs affect gas phase pollutants directly and particle-phase pollutants indirectly (Odum et al., 1997). There are two conditions in the atmosphere, which are usually referred to as the low and high NO_x regimes. Under lower NO_x conditions it is availability of NO_x, which must be present so ozone can be formed, that limits ozone formation. Under high NO_x conditions, the amount of ozone formed is designated by the levels of radicals formed from the reactions of the VOCs (Carter, 1994).

Photochemical ozone formation reactivities of volatile organic compounds as a result of the photochemical mechanisms for the atmospheric reactions of VOCs were used to measure their effects on ozone formation under various NOx conditions in model scenarios. The effects of BTEXs on ozone were used to obtain from different ozone reactivity scales. Maximum Incremental Reactivity (MIR) scale is one of the ozone reactivity scale which is used to calculate BTEX effects on ozone formation. In Maximum Incremental Reactivity (MIR) scenarios the NOx inputs are adjusted so that the base reactive organic gas (ROG, VOCs other tan CO, methane and chlorofluorocarbons) mixture had the highest incremental reactivity. The NOx adjustment was done by varying both the initial NOx and emitted NOx by the same factor. These MIR scenarios represent NOx conditions where emissions of ROGs have the greatest effect on ozone formation, and where NOx has the strongest ozone inhibiting effect. Thus they represent conditions where ROG control has the greatest effect on ozone (Carter, 1994).

1.2.4.4 The effect of BTEX on human health and ecosystem

Among traffic-related VOCs, aromatic compounds, including benzene, toluene, ethylbenzene, and isomers of xylene (BTEX), namely m-, o-, and p-xylene, have public health importance. Among the BTEX compounds, benzene has been widely recognized as a human carcinogen (IARC, 2002) and the others also possess high toxicity, especially to central nervous system in humans. Therefore, this group of VOCs has received much attention in exposure assessment studies (Han and Naeher, 2006).

The group of alkylbenzenes includes benzene, toluene, ethylbenzene, p-xylene, m-xylene, and o-xylene (BTEX), which are toxic aromatic VOCs (Bolden et al., 2015). The International Agency for Research on Cancer has classified benzene as carcinogenic to humans (Group 1) (International Agency for Research on Cancer, 2016), and the other BTEX species have a range of adverse health effects, even at low concentrations. These effects mainly include non-communicable diseases (NCDs), such as reproductive and developmental outcomes (Donald et al., 1991) sperm abnormalities and reduced fetal growthdand effects on cardiovascular disease, respiratory dysfunction, asthma, sensitization to common antigens (Aguilera et al., 2009; Bolden et al., 2015; Delfino et al., 2003; Amini et al., 2017).

Inhalation is the major route for VOCs because of their relatively high vapor pressures. Potential health effects of VOCs on human health extend from throat and eye irritation to chronic asthma and even carcinogenic effects (Kim et al., 2011a, 2011b; Wu et al., 2012). VOC exposure may lead to fatigue, headache, dizziness, and vertigo (Guo et al., 2003; Hinwood et al., 2007). The relationship between NO_2 and health effects includes respiratory symptoms, episodes of respiratory illness, and mortality (D'amato et al., 2001; WHO, 2006; Demirel et al., 2014).

Benzene is recognized to be the most toxic among all BTEX compounds because it can be rapidly and efficiently absorbed as well as widely distributed throughout the body after exposure. As a result, benzene ingestion may cause dizziness, stomach irritation, vomiting, increased heart rate, convulsions, hematological effects which may lead to aplastic anemia and acute myelogenous

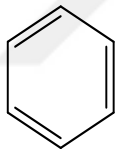
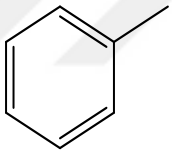
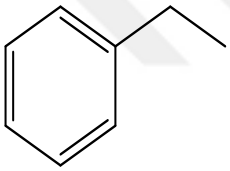
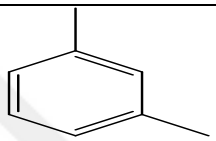
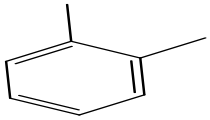
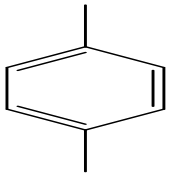
leukemia (carcinogenetic effects), coma, and even death (Leusch and Bartkow, 2010; Lecompte et al., 2018).

Toluene, ethylbenzene, and xylenes are readily absorbed from the gastrointestinal tract after its ingestion or after inhalation, and distribute in adipose tissue, kidneys, liver, and brain, where its main effect arises affecting the nerve system, with various symptoms including drowsiness and fatigue, as well as neurological effects including affectation of attention, memory, and psychomotor functions (Health Canada, 2017; Lecompte et al., 2018). The potential health effects of exposure to BTEX are presented in Table 1.7.

Table 1.7. Health effects of BTEXs

Parameter	**Benzene**	**Toluene**	**Ethylbenzene**	**Meta, ortho, and para-Xylene**
Short-Term Exposure	⁕ nervous system disorder ⁕ immune system depression ⁕ anemia	⁕ minor nervous system disorders ⁕ fatigue ⁕ nausea ⁕ weakness ⁕ confusion	⁕ drowsiness ⁕ fatigue ⁕ headache ⁕ mild eye and respiratory irritation	⁕ disturbances of cognitive abilities, balance, and coordination.

Table 1.7. Continued

Long-Term Exposure (lifetime)	* chromosome aberration * cancer	* pronounced nervous disorders * spasms * tremors * impairment of speech hearing vision memory coordination * liver * kidney damage	* liver * kidneys * central nervous system * eyes	* damage to the central nervous system, liver and kidneys
Chemical Structure				 m-xylene  o-xylene  para-xylene

1.2.4.5 Health risk evaluation of BTEXs

Several health problems may arise from acute and chronic exposure to pollutants. The risk assessment study plays an important role for the determination of chronic exposure to chemicals that may cause cancer or other toxic effects. The International Agency for Research on Cancer (IARC) that is part of the World Health Organization (WHO) categorizes benzene as "carcinogenic to humans". Besides, US Environmental Protection Agency categorizes benzene as a known human carcinogen. Therefore, cancer risks associated with inhalation of benzene were estimated. Other VOCs such as toluene, ethylbenzene and xylene have some non-carcinogenic risks. Risk evaluations for these compounds were performed by determining hazard ratio (HR) values for each compound (Bozkurt et al., 2018).

For non-carcinogenic compounds, risk evaluation is explained by hazard ratio (HR) of each compound represented as the ratio of daily average, (Ci in μg m^{-3}) to corresponding reference concentrations (RfC in μg m^{-3}) (Kumar et al., 2018), which is given by equation (1). The total non-carcinogenic risk is defined by the sum of individual hazard ratios of pollutants. If hazard ratio was equal to or smaller than "1", risk was regarded as negligible (USEPA, 2011). RfC is taken from USEPA-Integrated Risk Information System (IRIS) (http-1) and Risk Assessment Information System (RAIS) (http-2).

$$HR = Ci/RfC \quad (1)$$

Reference concentrations (RfC) were used to define toxicity of non-carcinogenic compounds. The RfC demonstrates the level of daily intake that does not constitute a negative health effect of a particular substance. (Lagrega et al., 1994; Artun et al., 2017; Kumar et al., 2018).

The life time cancer risk (LCR) associated to benzene exposure was also calculated by multiplying the chronic daily intake (CDI) by the IRIS potency factor (IRIS-Integrated Risk Information System) (Lerner et al., 2012). The inhalation exposure estimate was generally obtained from the point of chronic daily intake (mg kg^{-1} day^{-1}) using Equation (2) within the Superfund program of USEPA (U.S EPA,

2009). This treatment has been used by many researchers for the calculation of health risk (Guo et al., 2004; Payne-Sturges et al., 2004; Massolo et al., 2010)

$$CDI = \frac{CA\ x\ IR\ x\ ET\ x\ EF\ x\ ED}{BW\ x\ AT} \quad (2)$$

In Equation 3, CA is contaminant concentration in air (mg/m^3), IR is inhalation rate ($m^3\ h^{-1}$), BW is body weight (kg), ET is exposure time (hours day^{-1}), EF is exposure frequency (days $year^{-1}$), ED is exposure duration (years) and AT is the averaging time (period over which exposure is averaged) (days).

Cancer risk is defined as the possibility of cancer during the life-time of a person as a result of exposure to a potential carcinogenic compound. Risk margin for CDI has been classified as, CDI > 1.0 x 10^{-4} considered as "definite risks", 1.0 x 10^{-4} > CDI > 1.0 x 10^{-5} as "probable risks" and 1.0 x 10^{-5} > CDI > 1.0 X 10^{-6} as "possible risk" (USEPA, 2013; Romanazzi et al., 2014; Kumar et al., 2018).

1.2.4.5.1 Monte Carlo simulation

USEPA gives advise in risk assessment of the usage of probabilistic analysis in order to adequately characterize variability and uncertainty in exposure and dose-response assessments for human health (USEPA, 2009). The computer-based model, Monte Carlo method is one of the probabilistic analysis techniques. It was developed in the 1940's. It is probably the most commonly used technique for spreading the uncertainties in model inputs to arrange the uncertainties in model outputs (Fjeld, 2007). Statistical sampling techniques is used in Monte Carlo method uses in obtaining a probabilistic approximation to the solution of a mathematical equation or model (USEPA, 1997). Information about the importance of various assumptions is given by the model in the model inputs and their effects on the final model output distribution.

The probability distribution function for each input variable is inserted into the model for exposure of model parameters. A large number of data sets of input parameters (e.g. 10,000) are produced by sampling randomly from their respective probability distribution. Random number generation is used by the model to combine

distribution. Hence, its analysis produces a final output distribution of exposure or risk values, rather than a single point estimate (Robson and Toscana, 2007).

The main purpose of a Monte Carlo analysis is to quantitatively characterize the variability in estimates of exposure or risk. The next purpose is to define the key sources of variability and to measure the relative contribution of these sources to the overall variance and range of model results (USEPA, 1997).

1.3 Passive and active sampling method

Passive sampling is based on free flow of analyte molecules from the sampled medium to a collecting medium as a result of a difference in chemical potentials. Passive sampling can be used in the determination of both organic and inorganic compounds in a variety of matrices, water, soil and including air. The devices used for passive sampling are usually based on diffusion through a well-defined diffusion barrier or permeation through a membrane. Living organisms can also be used as passive samplers. In many cases, passive sampling vastly simplifies sampling and sample preparation, eliminates power requirements, and significantly reduces the costs of analysis. The technique is particularly suited to the determination of time-weighted average concentrations (Gorecki and Namiesnik, 2002).

Passive sampling technology has been developing very quickly since it was first published by Palmes and Gunnison in 1973 (Palmes and Gunnison, 1973) and now is widely used as a sampling technique for monitoring pollutants in different environments, such as air, soil and water (Kot et al., 2000; Marc et al., 2015). Not to overestimate the advantage of passive sampling techniques is its potential to create, on a wide scale, a monitoring network that also makes it possible to install samplers in hard-toreach and remote areas. However, each sampling technique has some limitations, and there are no perfect solutions.

iSome of the most important drawbacks of the passive sampling technique include: the need to calibrate the samplers for individual analytes, sensitivity to environmental conditions, such as temperature fluctuations, air velocity and humidity. In addition, passive samplers seem to have relatively low sampling rates, which require

long sampling times in environments with low pollutant concentrations. However, long sampling times at low concentrations can also be viewed as an advantage of passive sampling, as it makes it easy to determine time-weighted average (TWA) concentrations of analytes.

Active samplers are also used for determination of atmospheric concentrations of pollutant gases in order to detect the quality of the air. Sampling of pollutant components found in the atmosphere with active sampling method carry out with that the air in known volume are passed with the help of pump from a trapping medium such as filter or chemical solution for a lenght of time.

1.3.1 Comparison of passive and active sampling method

Passive samplers are relatively simple, portable and, as previously stated, inexpensive to deploy in the field. They do not require electrical power to operate. All these features make passive samplers very attractive for use in regional-scale relative air quality measurements. Table 1.8 provides a summary of the comparative characteristics of passive samplers and active monitors for quantifying ambient air pollutants.

Table 1.8. Comparative characteristics of passive samplers and active (continuous) monitors for quantifying ambient air pollutant concentrations[a] (Krupa and Legge, 2000).

	Feature	**Passive**	**Active**
1	Usage history	Since late 1800s	Mostly since the 1950s
2	Complexity of field deployment	Low (+)	High (-)
3	Construction/deployment cost	Low (+)	High (-)
4	Field labor requirement	Low (+)	High (-)
5	Field maintenance costs	Low (+)	High (-)
6	Laboratory analysis costs	Moderate to high (-)	None to moderate (+/-)

Table 1.8. Continued

7	**Time resolution of pollutant levels**	**Low (-)**	**High (+)**
8	Electricity requirement for field deployment	None (+)	Needed (-)
9	Measurement specificity (other pollutants)	Interference possible (+/-)	Interference none (+)
10	Meteorology interference	Can be high (-)	Low (+)
11	Minimum detection limit (in fine-time resolution)	Relatively high (-)	Relatively low (+)
12	Integrated measurement value intercomparison	Differs from active (-)	(+)
13	Regional (spatial) scale usage cost	Low (+)	High (-)
14	Relevance to vegetation effects relationships	Low (-)	High (+)
15	Detection of short-term (e.g. 1 or 2 h) episodes and regulatory noncompliance, where appropriate	Low (-)	High (+)

1.4 Instruments

1.4.1 Ion chromatography

Ion chromatography (IC) is an efficient method to identify ions qualitatively and quantitatively through columns. The main principle is the ion-exchange capacity in the column. Although ion-exchange separations have been applied since ion-exchange resins were developed (mid-1930s), ion change chromatography was first developed in the mid-1970s (Skoog et al., 2007). During that time, detection was performed by conductivity measurements however, they were not met the need due to the high electrolyte concentrations in both sample and mobile phases (eluents). Then low-exchange capacity columns were used to allow high sensitivity of conductivity (Skoog et al., 2007).

Generally, ion analysis in IC has six main stages as indicated in Figure 1.4. Eluent delivery systems are the first stage. Mobile phase or eluent contains a liquid that helps to separate the ions in sample and go through the system without any decomposition. Isocratic mobile phase delivery systems are more common in IC analysis in which the composition and the concentration of mobile phases are constant. An eluent introduced to the system by pumps and reached to the injection valves. A liquid sample is loaded to the system with these valves manually or automatically. Separation is achieved by a guard column and an analytical column. The guard column removes the impurities that might plug the analytical (separator) column. Ions in the sample are separated in the analytical column according to the ion-exchange principle. This means different ions migrate through the column at different rates depending on their interaction with the stationary phase in the column. Then, the eluent and the sample ions leave the column and reached the suppression system. The suppressor reduces the eluent conductivity and enhances the conductivity of the sample ions, thereby increase the detection sensitivity. Conductivity cell is used for detection. It measures the electrical conductance of sample ions and produces a signal based on chemical and physical properties of the analyte. Finally, these signals are transmitted to the data collection system. Data is quantified by comparing the sample peaks in chromatogram that produced from standard solutions. Sample ion analysis process was given in Figure 1.4. (Skoog et al., 2007

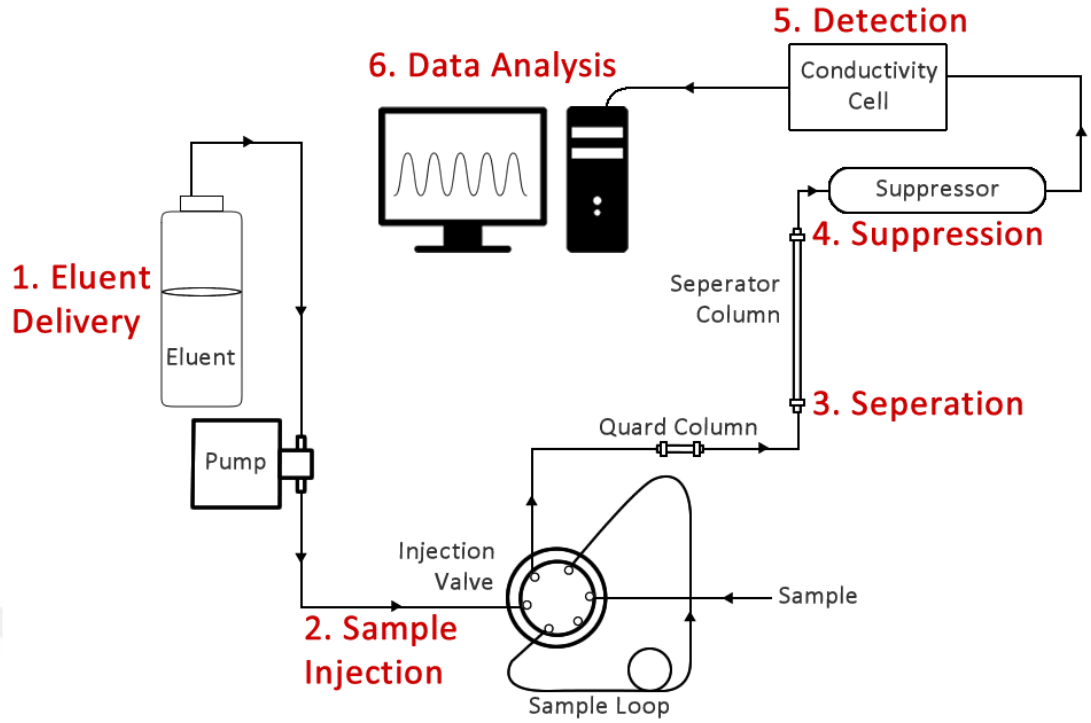


Figure 1.4. Sample ion analysis process (Skoog et al., 2007)

Anions (NO_3^-, SO_4^{2-}) were determined by Dionex ICS 1100 Series Ion Chromatography in this study. It is shown in Figure 1.5. Optimum operation conditions are given in Table 1.10 for Dionex ICS 1100 Ion Chromatography.

Table 1.9. Optimum operation conditions for Dionex ICS 1100 Ion Chromatography.

Parameters	Anion
Mobile phase	10 mM Na_2CO_3
Column	Ionpac AS9-HC (250 x 4 mm)
Guard column	Ionpac AG9-HC (50 x 4 mm)
Suppressor	ASRS-4 mm
Suppressor current	45 mA
Detector	Conductance detector
Pressure (psi)	2000-3000
Oven temperature	30 ºC
Background conductance	< 30 µS
Flow rate	1.00 mL min^{-1}
Injection volume	500 µL
Rate of data transfer	5.0 Hz
Duration	30 min

1.4.2 Gas chromatography-mass spectrometry (GC-MS)

The most commonly used techniques in quantitative and qualitative analysis of VOCs are gas chromatography (GC)–based techniques such as gas chromatography–mass spectrometry (GC-MS), GC with flame ionization detector (GC-FID), and thermal desorption–gas chromatography–mass spectrometry (TD-GC-MS). GC is suitable for qualitative and quantitative analysis of VOCs and has a well-structured technique. In general, there are two types of columns which are packed and capillary. Although packed columns are used for some applications, capillary columns are more commonly used in VOC research. The most important property of the column is its stationary phase. Nowadays, capillary columns are covered with various stationary phases from nonpolar to polar, depending upon the functionality of the target compounds.

The GC instrument is composed of a temperature-controlled oven, capable of being rapidly ramped up reproducibly from room temperature to over 300 ° C. The device also has a series of pressure control systems and derives the interfaces for the introduction of samples and the analytical detectors. Inside the oven there is an open tubular column which has 30–60 m, including a stationary-phase film capable of separating compounds according to their chemical and physical properties. The end of the gas chromatograph column is attached to the inlet which is usually an injector, and the other end which is outlet is attached to the detector. Samples are sent by way of a heated inlet and then transported by the carrier gas flow which is usually helium through the column. Each of the VOCs is in interaction by differently with the stationary phase of the column and is partitioned differentially between the mobile phase which is helium and stationary phase. A rising in temperature changes the partition coefficient, eventually resulting in the compound being exactly moved into the mobile phase and being swept into the detector, by the way of a heated transfer line. Hence, different VOCs come out of the column at different times which is known as retention time, and after exiting the column, they may be described and measured by a mass spectrometer or other detector (Materic et al., 2015)

The interface of a commercial TD system with a gas chromatograph and mass spectrometer as a detector (TD-GC-MS) is shown in Fig. 1.5 (Materic et al., 2015)

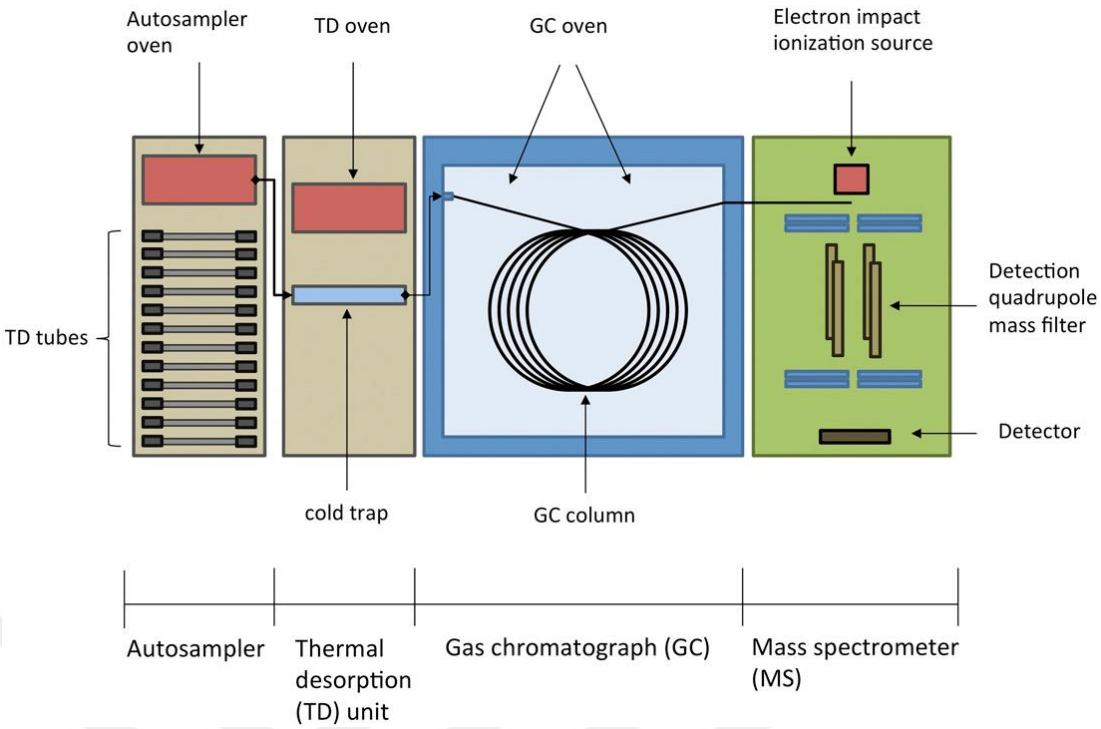


Figure 1.5. Thermal desorption–gas chromatograph–mass spectrometer (TD-GC-MS) (http-9, 2017).

The samples trapped on TD tubes are desorbed thermally, over several minutes, and retrapped on a cold trap in the thermal desorption instrument (Fig.1 5). The cold trap is a tube which is containing packing material, is then rapidly heated and the VOCs are delivered and bring in through a heated transfer line to the GC. From the cold trap, the sample can be split and a portion of the sample may be saved in a TD tube for later use, which is particularly useful if the sample is rare and precious. The cold trap have to ensure that the compounds are carried to the column adequately. Optimized injection parameters are required to ensure optimal peak resolution and good chromatographic peak shapes (Materic et al., 2015).

TD-GC-MS system is used for extraction and analysis of VOCs and shown in Figure 1.6. The VOCs adsorbed to the Tenax-TA were desorbed thermally by the thermal desorption (TD) system and sent to the Gas Chromatography Mass Spectrometer (GC-MS) system.

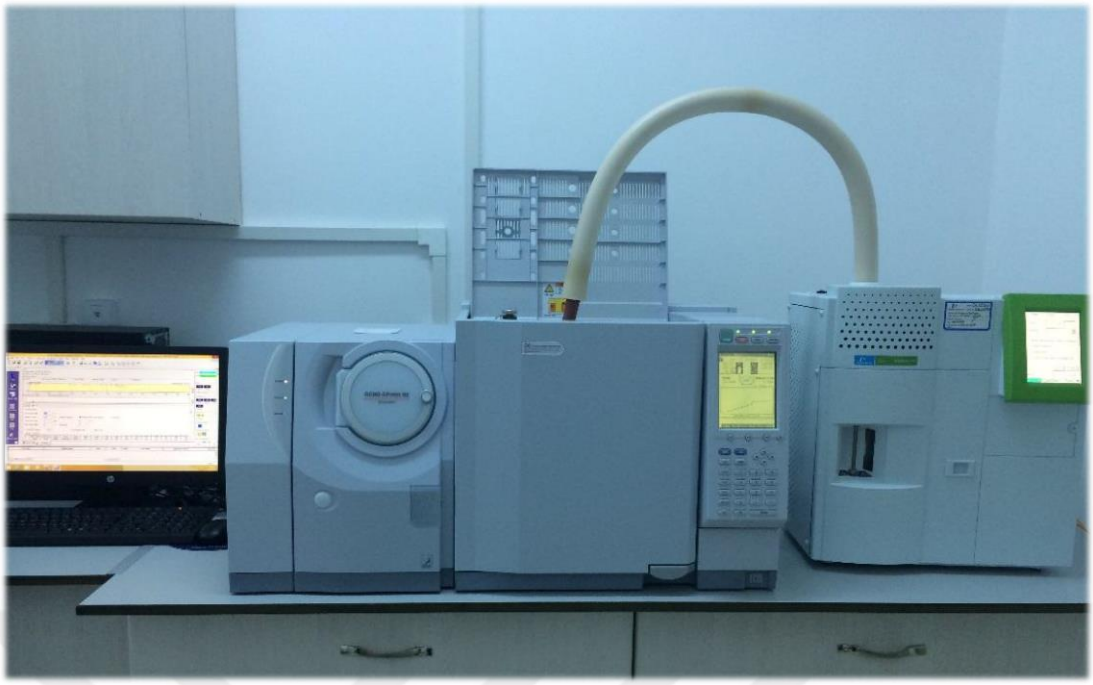


Figure 1.6. TD-GC-MS System using in the analyses of VOCs (Photo from our research laboratory)

The GC-MS method program is shared in Table 1.10.

Table 1.10. GC-MS method program

GC	
GC column	RTX-624 60.0 m x 0.25 mm x 1.40 µm
Column oven temperature	40°C
Injection port temperature	100°C
Injection type	spitless
Sampling time	1 min.
Carrier gas	Ultra-pure Helium, 99.999%
Pressure	155.9 kPa
Total flow	50 mL / min
Column flow	1.4 mL / min
Linear speed	30.2 cm / s
Purge flow	3 mL / min

Table. 1.10. Continued

Split ratio	-1
Oven temperature program	40 ° C (5 min), 7,5 ° C / min to 180 ° C, 28 ° C / min to 240 ° C (15 min)
Injection volume	1 μL
MS	
Mass spectrometry	Electron impact, 70 eV
Ion source temperature	230 ° C
Interface temperature	240 ° C
Solvent cutting time	1 min
Detector voltage	0 kV
GC program duration	40.81 min
TD	
Valve temperature	230 ° C
Tube temperature	250 ° C
Transfer temperature	250 ° C
Rate	40 C s^{-1}
High temperature	250 ° C
Low temperature	-30 ° C
Purge time	2 min
Desorb time	10 min
Cycle time	20 min
Mode	2-stage desorb
Split	Flow
Outlet Split flow	30 mL min^{-1}
Column flow	1.4 mL min^{-1}
Desorb flow	20 mL min^{-1}
Inlet split flow	30 mL min^{-1}

2. AIM AND SCOPE OF THE STUDY

Air pollution is generated by the consumption of a variety of resources. Human activities such as combustion of fossil fuels used for regeneration of energy and transportation are the major cause of environmental pollution compared to geographical influences such as volcanoes and fires (Kampa and Castamas, 2008; Shahadin et al., 2018). These activities lead to the emission of ambient (outdoor) air pollutants to the environment such as sulphur dioxide (SO_2), nitrogen oxides (NO_x), carbon monoxide (CO), and ozone (O_3) (Kampa and Castamas, 2008; Shahadin et al., 2018), thus contributing to the adverse effect on human health. BTEXs are also traffic related air pollutants which cause to serious health proplems. Besides serious health problems, these air pollutants have a critical and significant impacts on ecosystem as well. As a result, it is required to bring those pollutants under control. This phenomenon can be managed to detect the sources of pollutants, and the amount of pollutants.

The following purposes must be achieved in the context of this thesis.

- To examine the spatial distribution of NO_2, SO_2, and O_3 gases and BTEXs with passive sampling method,
- To find the source areas of the pollutants,
- To compare the results seasonally,
- To compare the results of passive and active sampling,
- To determine the correlation of BTEXs with inorganic gaseous pollutants (NO_2, SO_2 and O_3),
- To find the ozone formation potential of BTEXs,
- To examine the health risk estimation of BTEXs.

3. LITERATURE REVIEW

3.1 Comparison of NO_2, SO_2 and O_3 data with literature values

Nitrogen dioxide is one of the basic traffic-related air pollutants and precursors occuring photochemical smog (together with VOCs) and ground-level ozone. Sharing the same seasonal pattern with several other air pollutants, NO_2 level is usually lower in the summer than in the winter. Many studies demonstrated that NO_2 concentration decreased drastically with increasing distance downwind from traffic (Gilbert et al., 2003; Singer et al., 2004). Investigation handled at schools near Northern California freeways (Singer et al., 2004) found highest NO_2 levels (24–30 ppb) in schools downwind and close to freeways. In developing countries, exposure studies on NO_2 usually show higher exposure levels than in the developed world. In Tartu, Estonia, ambient level of NO_2 rised by 50% to 100% in several monitoring stations, according to the yearly monitoring data from 1994 to 1999. This rise may have been primarly caused by increasing number of vehicles, poor maintenance of many of these vehicles, and narrow streets in the city (Kimmel and Kaasik, 2003).

In Korean study brought about in two cities (Son et al., 2004), 31 taxi drivers were monitored for their in-vehicle personal exposures to NO_2. One-year monitoring data from several intersections in Calcutta, India (Mondal et al., 2000) demonstrated that NO_x levels were the highest in the winter (120 ppb) and the lowest in the summer monsoon season (30 ppb).

Besides other UK studies outdoor NO_2 levels in Hertfordshire decrease towards a lower range. For example, outdoor levels reported involve Ashford: 12.4 ppb; Birmingham: 10 ppb; Oxford: 12.4 ppb (Garcia Algar et al., 2004; Harrison et al., 2002; Lai et al., 2004). Asian cities seem to have highest outdoor NO_2 concentrations like Hong Kong (38±8 ppb), where vehicular emission seems to be a main contributor (Chao and Law, 2000). The NO_2 concentrations of this study in Bolu is the lowest one. The results of studies are summarized in Table 3.1

Table 3.1. A comparative summary of NO_x levels in various studies

Study	Location	Exposure Type	Subject/Location	Pollutant	Level (ppb)
This Study	Bolu, Turkey	Ambient (14-day (passive sampling)	Urban / Rural	NO_2	7.33
Son et al., (2004)	Asan and Seoul, Korea	Personal and microenvironments (varies)	Outdoor home	NO_2	23.3
Mondal et al., (2000)	Calcutta, India	Ambient (14-day passive sampling)	Intersection (Winter)	NO_x	120
			Intersection (Summer)		30
Singer et al., (2004)	Northern California, US	Ambient (1-week passive sampling)	Schools (downwind)	NO_2	24–30
			near a highway		
Lai et al. (2004)	Oxford, UK		Outdoor	NO_2	12.4
Garcıa Algar et al. (2004)	Ashford		Outdoor	NO_2	12.4
Harrison et al. (2002)	Birmingham		Outdoor	NO_2	10
Chao and Law (2000)	Hong Kong		Outdoor	NO_2	38.2

A study (Adon et al., 2016) on 15-days SO_2 measurements were carried out by using passive sampling method at five sites during the dates from 19 January to 2 February in 2009 in Bamako and six sites during the dates from 30 November to 13 December in 2009 in Dakar. In addition, biomass burning and domestic fires sources and meteorological factors affect the air quality in these cities. Results show that the pollution levels of SO_2 are higher in Dakar than in Bamako. In Singapore, China, He et al. (2014) reported average SO_2 concentrations ranging from 12.5 to 14.9 ppb that are comparable to the average value found in Dakar (15.9 ppb). Lower values of SO_2 were found in Kampala and Accra, as well in Bamako. The results of SO_2 concentrations of our study in Bolu were lower than the other studies in the world as given in Table 3.2.

Table 3.2. Avarage SO_2 concentration observed in the study sites in the world (Adon et al., 2016).

Sites	Type	Period	SO_2 (ppb)	References
Bolu, Turkey	Urban /Rural	28 January- 11 February 2017 / 7- 22 July 2017	3.03	This study
Dakar, Senegal, West Africa	Traffic	Jan. 2008 - Dec. 2009	15.9	Adon et al., 2016
Bamako, Mali, West Africa	Traffic	Jun. 2008 - Dec. 2009	3.6	Adon et al., 2016
Cairo, Egypt	Suburban	Summer of 2009 and Winter of 2009 - 2010	13.0	Hassan et al., 2013
Kampala, Uganda	Urban	Jul. 2014	0.29 - 3.13	Kirenga et al., 2015
Accra, Ghana	Urban	Jul. 2016	1.11 - 1.23	Arku et al., 2008
Al-Ain city, UAE[a]	Traffic	Feb. 2005 - Feb. 2006	5.8	Salem et al., 2009
Singapore, China	Urban	Sep. 2007 - Aug. 2008	12.5 - 14.9	He et al., 2014
Lahore, Pakistan	Urban	Dec. 2005 - Feb. 2006	7.4	Biswas et al., 2008
Kolkata, India	Urban	Nov. 2003 - Nov. 2004	4.7	Gupta et al., 2008
Nan-Ji-Do, Seoul, South Korea	Landfill	22 March–4 April 2000 / 20 September–4 October 2000	5.42	Ki-Hyun Kim and Min Young Kim, 2002

A study (Kim and Kim, 2002) on 2 weeks O_3 and BTEX measurements were carried out at the Nan-Ji-Do (NJD) landfill site in Seoul during the date from 22 March–4 April 2000 / 20 September –4 October 2000. A study (Burley and Bytnerowicz, 2011) on day to day and week to week O_3 and BTEX measurements were carried out at two sites, White Mountain Summit (4342 m elevation) and Barcroft Station (3783 m), that are believed to be higher in elevation than any previously investigated sampling locations in North America. O_3 concentrations had the lowest one of all sites. These two sites in North America showed that average ozone

concentration increased with elevation. Our study in Bolu was lower than the studies of North America and comparable with other studies given in Table 3.3.

Table 3.3. Avarage O_3 concentration observed in the study sites.

Site	Type	Period	O_3 (ppb)	References
Bolu, Turkey	Urban / Rural	28 January- 11 February 2017 / 7- 22 July 2017	27.7	This study
Barcroft Station, North America	Mountain region (3783 m in elevation)	July 15 - Aug. 15	50.98	Burley and Bytnerowicz, 2011
White Mtn. Summit, North America	Mountain region (4342 m in elevation)	July 15 - Aug. 15	52.68	Burley and Bytnerowicz, 2011
Nan-Ji-Do, Seoul, South Korea	Landfill	22 March–4 April 2000 / 20 September –4 October 2000	15.1	Ki-Hyun Kim and Min Young Kim, 2002
Delhi, India		Jan.- Dec. 2014	37.5	Tyagi et al., 2016
Delhi, India		Jan. 2013 - Dec.2014	29.1	Kumar et al., 2015.
Kannur, India		Nov. 2009 - Oct. 2010	18.4	Nishanth et al., 2012.

3.2 Comparison of BTEX data with literature values

Among traffic-related VOCs, aromatic compounds, involving benzene, toluene, ethylbenzene, and isomers of xylene (BTEX), namely m-, o-, and p-xylene, have public health importance. In urban regions, these aromatic VOCs are mainly emitted from traffic vehicles. Thus, this group of VOCs has received much attention in exposure assessment studies. The influence of industrial sources on VOC levels along traffic road seemed negligible (Batterman et al., 2002).

The comparisons of the studies conducted in Turkey are summarized in Table 3.4. BTEX concentrations measured in this study were lower than those measured in İzmir which are industrial and urbanised city in Turkey. Similar study was done in

Kocaeli. Volatile organiz compounds (VOCs) were measured using passive sampling technique at 49 sampling points in Kocaeli which is an important industrial city in Turkey (Pekey and Yılmaz, 2011). Our average summer-winter BTEX concentrations were lower than found in Kocaeli. The other study was done around the gas station in Ankara was considerably higher than our study.

Table 3.4 Comparison of outdoor BTEX concentrations (μg m^{-3}) with some literature.

Location	Sampling Site	Pollutants	Level (μg m^{-3})	Study
Kocaeli, Turkey)	Industrial foundations, highways, coast	Benzene Toluene Ethylbenzene m-p Xylene o-Xylene	2.26 35.51 9.72 36.87 12.46	Pekey and Yılmaz (2011
Ankara, Turkey	Gas station	Benzene Toluene Ethylbenzene m-p Xylene o-Xylene	27.52 52.28 11.47 43.11 15.43	Kuntasal et al. (2005
İzmir, Turkey	Urban, suburban	Benzene Toluene Ethylbenzene m-p Xylene o-Xylene	3.31 15.39 3.65 7.5 5.74	Elbir et al. (2007
Bolu, Turkey	Urban / Rural	Benzene Toluene Ethylbenzene Xylene	1.019 1.406 0.242 0.7	This study

Other studies are shown in Table 3.5. Our results were also generally lower than those found in UK (Derwent et al., 2000), Brazil (Colon et al., 2001), Germany (Monod et al., 2001), South Korea (Na and Kim, 2001), Spain (Fernandez-Martinez et al., 2001), China (Wang et al., 2002), Hong-Hong (Ho et al., 2004), Italy (Fabio, 2007), Thailand (Thi and Thi, 2007), Japan (Twari et al., 2010) and Vietnam (Lan and Minh, 2013) whereas at the same levels conducted study in Poland (Marc et al., 2014).

Table 3.5. Comparison of BTEX levels in ambient air worldwide (μg m^{-3}).

Location	Sampling Site	Pollutants	Level (μg m^{-3})	Study
UK / London	Urban	Benzene	3.7	Derwent et al., 2000
		Toluene	8.1	
		Ethylbenzene	2.3	
		Xylene	10.0	
Brazil / Sau Paulo	Urban	Benzene	4.6	Colon et al., 2001
		Toluene	44.8	
		Ethylbenzene	13.3	
		Xylene	16.5	
Germany / Berlin	Urban	Benzene	6.9	Monod et al., 2001
		Toluene	13.8	
		Ethylbenzene	2.8	
		Xylene	5.2	
South Korea / Seoul	Urban	Benzene	3.2	Na and Kim, 2001
		Toluene	24.5	
		Ethylbenzene	3.0	
		Xylene	6.7	
Spain / La Coruna	Urban	Benzene	3.4	Fernandez-Martinez et al., 2001
		Toluene	23.6	
		Ethylbenzene	3.3	
		Xylene	3.9	
China / Pearl River Delta	Urban Roadside	Benzene	35.7	Wang et al., 2002
		Toluene	62.5	
		Ethylbenzene	13.55	
		Xylene	54.9	
USA / California	Semi-rural and Urban	Benzene	2.2	Pankow et al., 2003
		Toluene	6.0	
		Ethylbenzene	1.5	
		Xylene	4.7	
France / Taulouse	Urban	Benzene	2.0	Simon et al., 2004
		Toluene	6.6	
		Ethylbenzene	0.1	
		Xylene	2.4	
Hong-Hong / Hok Tsui	Urban, Rural Roadside	Benzene	30.5	Ho et al., 2004
		Toluene	200.8	
		Ethylbenzene	15.1	
		Xylene	45.6	

Table 3.5. Continued

Italy / Naples	Urban	Benzene	14.2	Fabio, 2007
		Toluene	180.6	
		Ethylbenzene	58.3	
		Xylene	280.8	
Thailand	Industrial (The site in different traffic volume)	Benzene	65	Thi and Thi, 2007
		Toluene	62.0	
		Ethylbenzene	15.0	
		Xylene	32.5	
Japan / Yokohama	Industrial	Benzene	25.5	Twari et al., 2010
		Toluene	27.8	
		Ethylbenzene	31.4	
		Xylene	31.8	
Algeria/ Algiers	Urban and Semi-rural	Benzene	14.5	Kerchich and Kerbachi, 2012
		Toluene	31.15	
		Ethylbenzene	8.0	
		Xylene	23.7	
Poland / Tczew	Suburban	Benzene	0.9	Marc et al., 2014
		Toluene	1.11	
		Ethylbenzene	0.38	
		Xylene	0.5	
Vietnam / HoChiMinh	Urban (Roadside)	Benzene	56.0	Lan and Minh, 2013
		Toluene	121.0	
		Ethylbenzene	21.0	
		Xylene	43.5	
Turkey / Eskişehir	Urban, Suburban	Benzene	1.7	Demirel et al., 2014
		Toluene	26.2	
		Ethylbenzene	0.73	
		Xylene	6.0	

Table 3.5. Continued

India / Terai Zone	Urban, Rural	Benzene	15.91	Masih et al., 2016
		Toluene	28.21	
		Ethylbenzene	3.38	
		Xylene	2.84	
Mexico/Mexico City	Gas Station	Benzene	82.4	Bravo et al., 2002
		Toluene	319.8	
Karachi, Pakistan	Traffic Street	Benzene	16.6	Barletta et al., 2002
		Toluene	26.8	
		Xylene	8.2	
Turkey / Bolu	Urban, Rural	Benzene	1.02	This Study
		Toluene	1.41	
		Ethylbenzene	0.24	
		Xylene	0.34	

4. MATERIAL AND METHODS

4.1 Sampling area (The city center of Bolu)

Bolu is the city which is located in the North Eastern Part of Black Sea Region between 30º 32' and 32º 36' east longitudes and 40º 06' and 41º 01' north latitudes. The city has an 8458 km² area, and 56 percent of the area is covered by mountains. Köroğlu volcanic mountain which is among the mountains surrounding the city in three sides is the highest one with an altitude of 2.499 m. Moreover, forests form the main part (65%) of the city area (http-10, 2016).

The altitude of the campus and the city center from sea level are 874 m and, 726 respectively. The total population of Bolu was 303.184 at the end of 2017 according to the Turkish Statistical Institute (http-11, 2017). Despite the population of Bolu is not much, the significant air pollution problems are arising of traffic, agricultural-industrial activities and common usage of coal and wood for domestic heating and then topographical position of the city.

Bolu is located between two metropolitan cities, Istanbul and Ankara, and two international highways TEM and D-100. Consequently, the density of traffic on these roads affects the air quality of the city. Coal, wood and diesel oil have been used for domestic heating in Bolu. However, utilization of natural gas was started in Bolu Abant İzzet Baysal University and industrial zone in 2010. Since 2009 allocation of natural gas to residence has been performed. It is expected that whole city would be using natural gas by the end of 2014. Howerever, in 2017, there was a still usage of coal for domesting heating both in the city center and in villages.

Mountains surrounding the city center of Bolu, does not permit dispersion of pollutants which is emitted in the city center especially during stagnant conditions, and causes high concentration of pollutants in the city atmosphere.

4.2 Sampling schedule

Components which are determined by passive sampling method consist of nitrogen dioxide (NO_2), sulfur dioxide (SO_2), ozone (O_3) and BTEXs which are the important members of VOCs. Passive samplings to be performed in the sampling site have done two times in winter and in summer period. In winter period, passive samplers are inserted to the 47 points indicated the map in Figure 4.1 in the dates of January 28-30. The samplers which were kept in the field for two weeks, they were brought into the laboratory by collecting from the points in the dates of February 11-12. Passive sampling points were shown in Figure 4.1. Due to hard winter conditions, it was not possible to go high altitude places in the north of the city center.

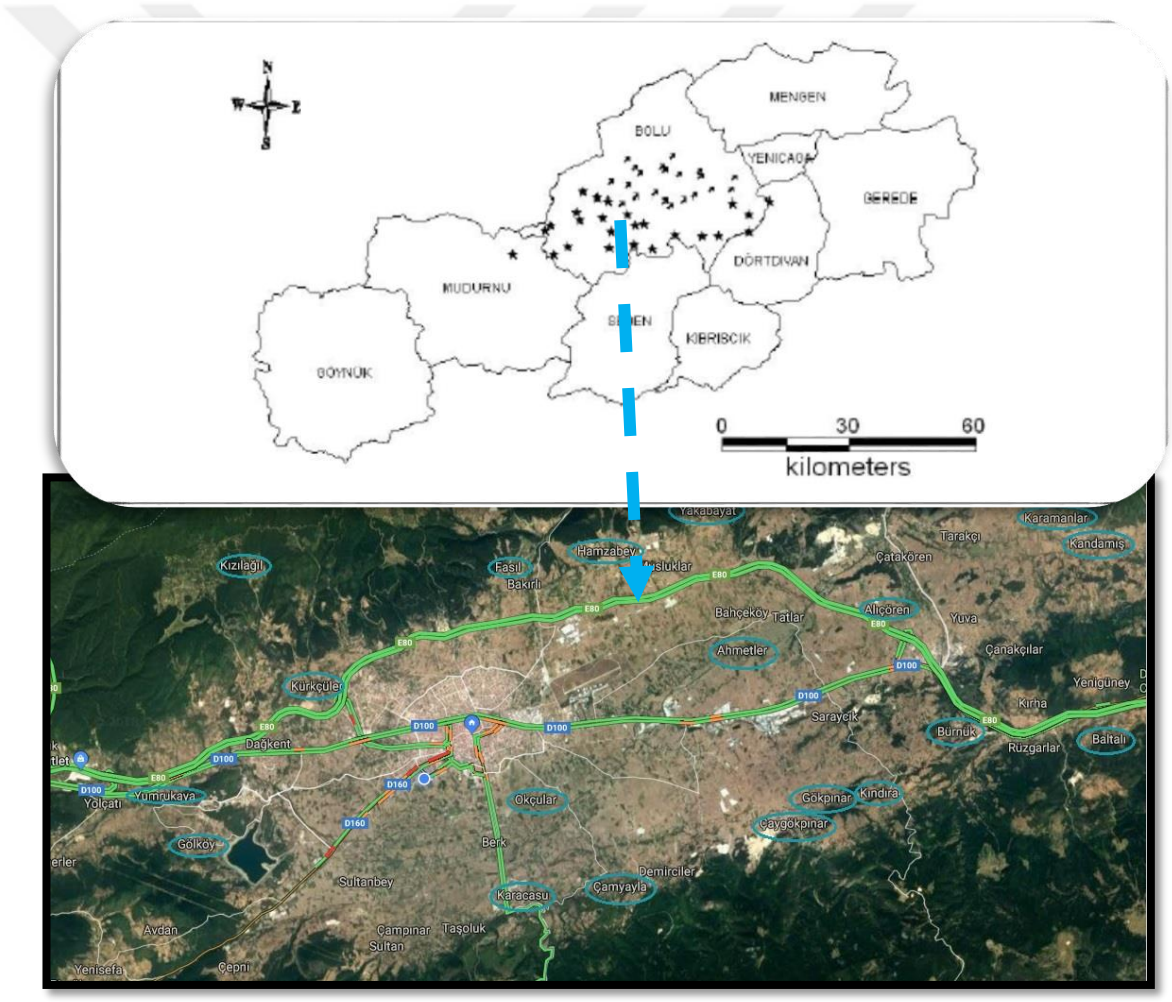


Figure 4.1. The satellite images of passive sampling points

In summer period, passive samplers are inserted to the 62 points indicated the map in red flag in Figure 4.2 in the dates of July 7-8. The samplers which were kept in

the field for two weeks were brought into the laboratory by collecting from the points in the dates of July 22-23. Passive sampling points of winter and summer period were given in Figure 4.2.

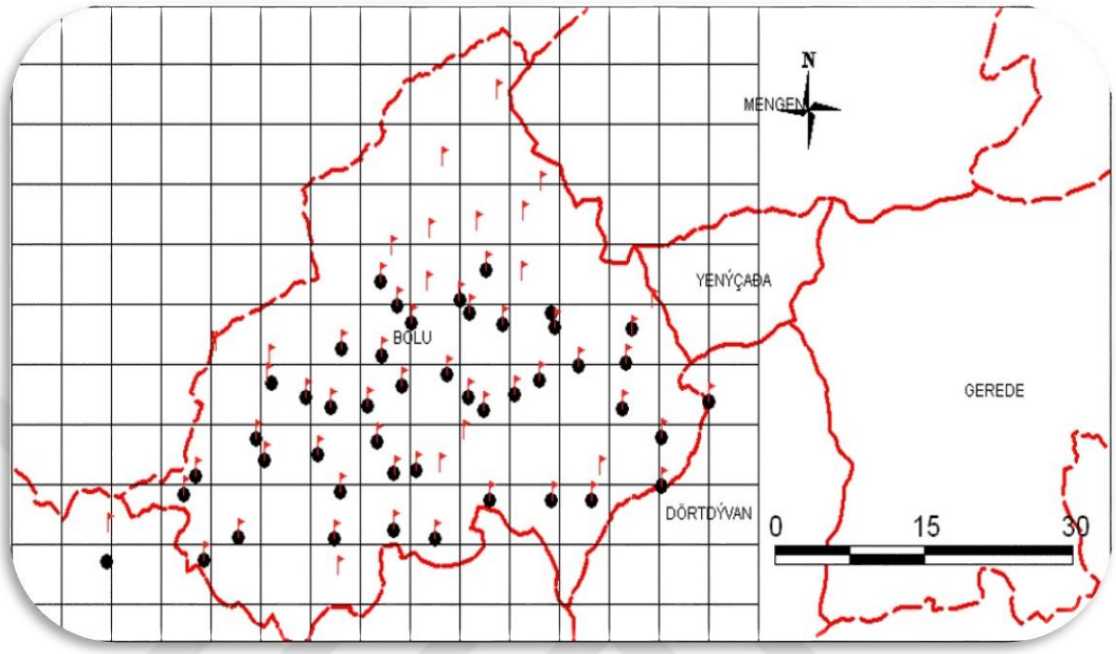


Figure 4.2. The points of passive sampling in winter and summer

The details of sampling points in winter and summer season were given in Appendix A and B.

4.3 Passive samplers for NO_2, SO_2, O_3 and BTEXs

4.3.1 NO_2, SO_2 and O_3

Inorganic passive samplers developed by air pollution research group of Environmental Engineering Department in Eskişehir Technical University are used. An inorganic passive sampler is shown in Figure 4.3. BTEXs were sampled by using Tenax passive samplers.

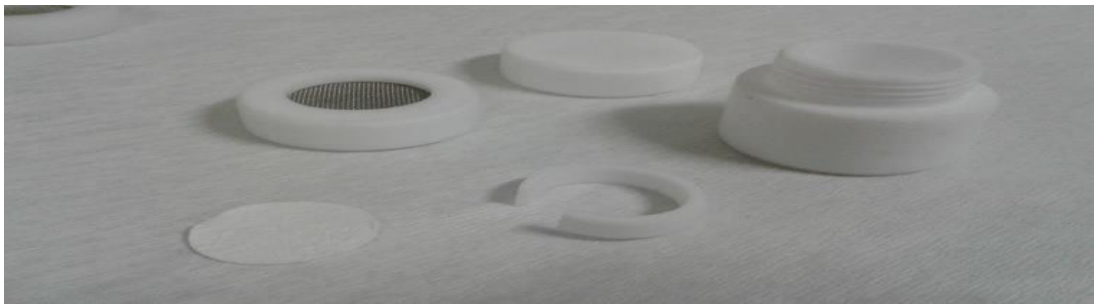


Figure 4.3. Inorganic passive sampler tube (Photo from our laboratory)

NO_2-SO_2 tubes are made of teflon mate material and O_3 tubes are made of bright delrin material. The samplers have the same dimensions, and they have 2.5 cm in length and 2 cm in internal diameter. Pre-sampling studies of NO_2, SO_2 and ozone passive samplers were carried out at Eskişehir Technical University, Department of Environmental Engineering. The samplers were placed in shelters and left at sampling points. Photograph belonging to samplers in the shelters are introduced in Figure 4.4.

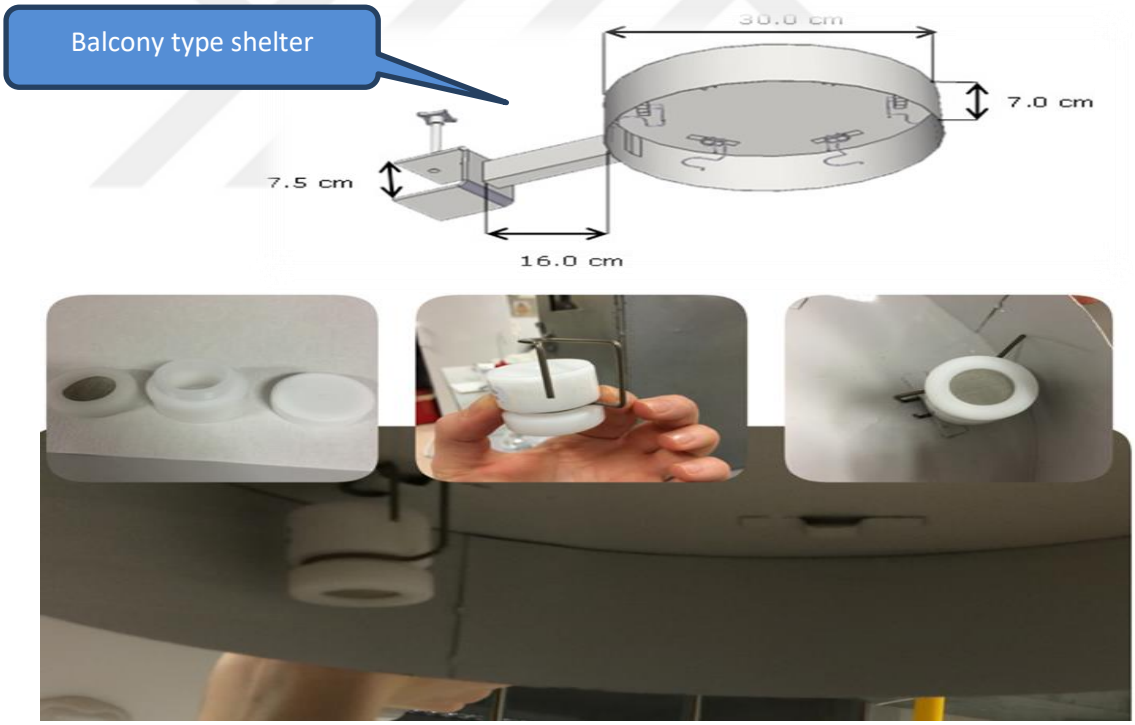


Figure 4.4. Passive samplers of NO_2, SO_2 and O_3 in the shelter (Photo from our laboratory)

4.3.2 BTEXs

Tenax-TA tube was used in passive sampling of volatile organic compounds. The tenax tube has a length of 89 mm, an outer diameter of 6.4 mm, an inner diameter of 5 mm and a diffusion path length of 15 mm. There is a Tenax-TA sorbent in the size of 35/60 sieve. This type of sorbent is the most suitable type of hydrophobic sorbent for thermal desorption applications. The flow direction of the tube is towards the way, which is shown with arrow.

Figure 4.5. Tenax-TA tube used in passive sampling of Volatile Organic Compounds (Photo from our laboratory)

4.4 Reagents and materials

For preparation of the trapping medium for NO_2-SO_2 passive samplers, Whatman glass fiber filter papers are coated with 5 mL of 25% TEA (triethanolamine) aqueous solution (Merck, Germany) in the laboratory medium. 25% TEA (triethanolamine) (Merck, Germany) was used to trap the atmospheric NO_2-SO_2. In other words, TEA (triethanolamine) (Merck, Germany) was used as chemical absorbent. In the process of extraction of components which are collected in GF/A fiber glass filter paper (Whatman, USA) covered with TEA (Triethanolamine) solution was carried out by adding 10 mL ultra pure water and 20 µL H_2O_2.

For preparation of the trapping medium for O_3 passive samplers, Whatman GF / A fiber glass filter papers (Whatman, USA) are coated with 1 % $NaNO_2$ (Merck, Germany), 2 % Na_2CO_3 (Merck, Germany), 2 % glycerol (lab kim) aqueous solution in the laboratory medium. Glycerol was used to keep the humidity stable and Na_2CO_3 was used to supply alkaline medium. $NaNO_2$ was used to capture the atmospheric O_3.

Na_2CO_3 was also used as mobile phase for anion determination in the course of analysis in Ion Chromatography.

In the determination of gaseous inorganic pollutants with Ion Chromatography, seven anion standard Dionex mixture was used as a calibration standard for anion determination. ERM-CA408 (simulated rain water) was used to determine the accuracy of results of anion analyses. In the analysis of BTEXs, mixture with 69 components (LGC Standards, Great Britain) was used as a standard in GC-MS. Whatman Puradisc Syringe Filters- Cellulose Acetate shown in Figure 4.6 were also used in order to filter the extraction solution in order not to clog the analytical column.

Figure 4.6. Whatman puradisc syringe filters- cellulose acetate (Photo from our laboratory)

Analyses of extracted solutions were performed by 1 mL of insulin injector. Reagent and chemicals used in ion determination are given in Table 4.1.

Table 4.1. Reagent and chemicals used in ion determination

Name	Trademark	Properties	Purpose
Sodium carbonate	Dionex	The concentration of stock solution is 0.5 M and it includes 94.7% (w/v) water and 5.3% (w/v) Na_2CO_3.	Used as the mobile phase for anion determination

Table 4.1. Continued

Standard Anion Mixture	Absolute Standards,USA	It contains NaBr, NaCl, NaF, $NaNO_2$, $NaNO_3$, K_3PO_4, K_2SO_4. The concentration of each component is 1000 µg mL^{-1} and the purity of each one is above 99 %.	Used as calibration standards for anion determination
ERM-CA408 (simulated rain water)	JRC, EC	It consists of artificial rainwater with a relatively low level of electrolytes (Cl^-, Ca^{2+}, H_3O^+, K^+, Mg^{2+}, Na^+, NH_4^+, NO^{3-}, SO_4^{2-}).	Used to determination of accuracy of results
BCR 409 Simulated Rainwater	IRMM, Belgium	It consists of artificial rainwater with a relatively high level of electrolytes (Cl^-, Ca^{2+}, $H3O^+$, K^+, Mg^{2+}, Na^+, NH_4^+, NO^{3-}, SO_4^{2-}).	Used to determination of accuracy of results
69 components VOC	LGC, Great Britain	BTEX compounds and other VOCs	Used as a calibration standard in GC-MS

4.5 Preparation of the samples for the analyses

The sampling period was planned in summer and in winter seasons. Samplers are left to the sampling area. The samplers were marked before sampling. An example for the labelled passive samplers is shown in Figure 4.7.

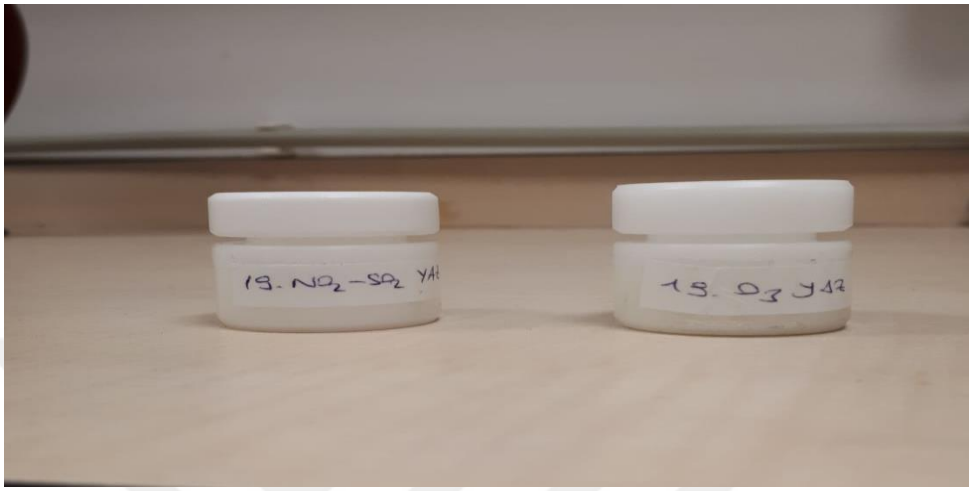


Figure 4.7. Labelled passive samplers (Photo from our laboratory)

4.5.1 Impregnation for NO_2, SO_2 and O_3

The order of experimental process is firstly impregnation then extraction and finally analyses. Our experimental process is given in Figure 4.8.

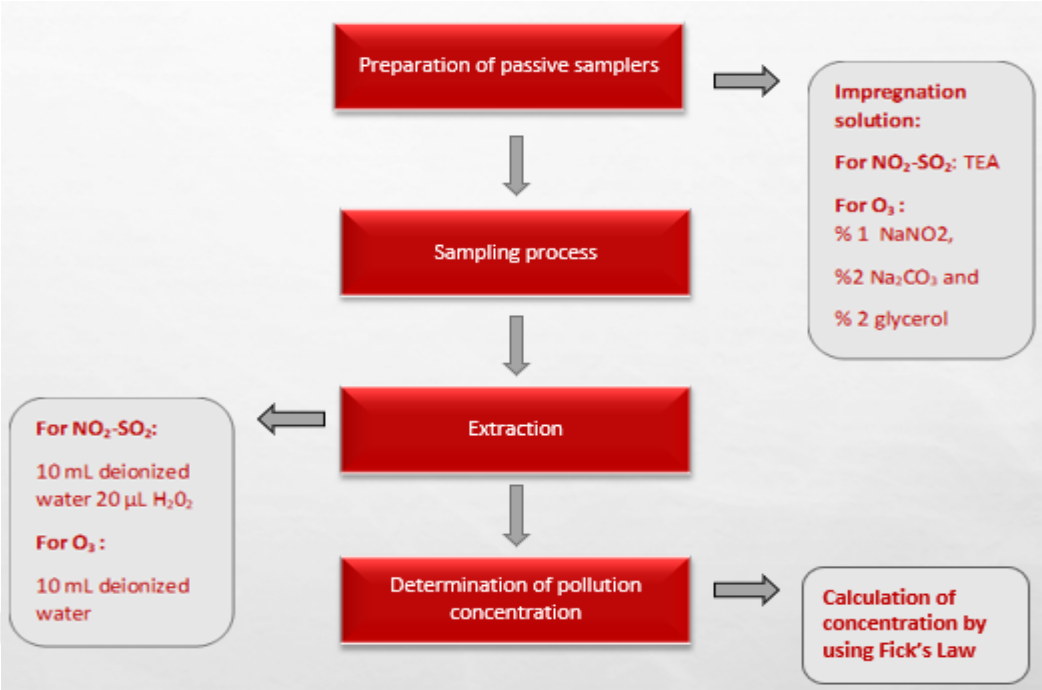


Figure 4.8. Experimental flow chart

In the impregnation process, for preparation of the trapping medium for NO_2-SO_2 passive samplers, Whatman GF / A fiber glass filter papers are coated with 25% TEA (triethanolamine) aqueous solution in the laboratory medium. 5 mL of TEA solution is taken and diluted to 25 mL of total volume of ultrapure water for preparation of coating solution. GF / A Whatman filters are cut with a cutting tool that has a 20 mm in a diameter to fit into the passive samplers. These 20 mm diameter filter papers are immersed in to TEA solution. Atmospheric NO_2 is converted into the nitrite ions (NO_2) on the surface of these impregnated filter papers. Triethanolamine N-oxide is another product that is formed as a result of the below reaction (Vardaulakis et al., 2011).

$$2NO_2 + N(CH_2CH_2OH)_3 + 2OH^- \rightarrow 2NO_2^- + {}^-O^+N(CH_2CH_2OH)_3 + H_2O$$

They are dried for 20 minutes in the infrared light dryer. Finally, they are placed at the bottom of the sampler tube. Impregnation process is shown in Figure 4.9.

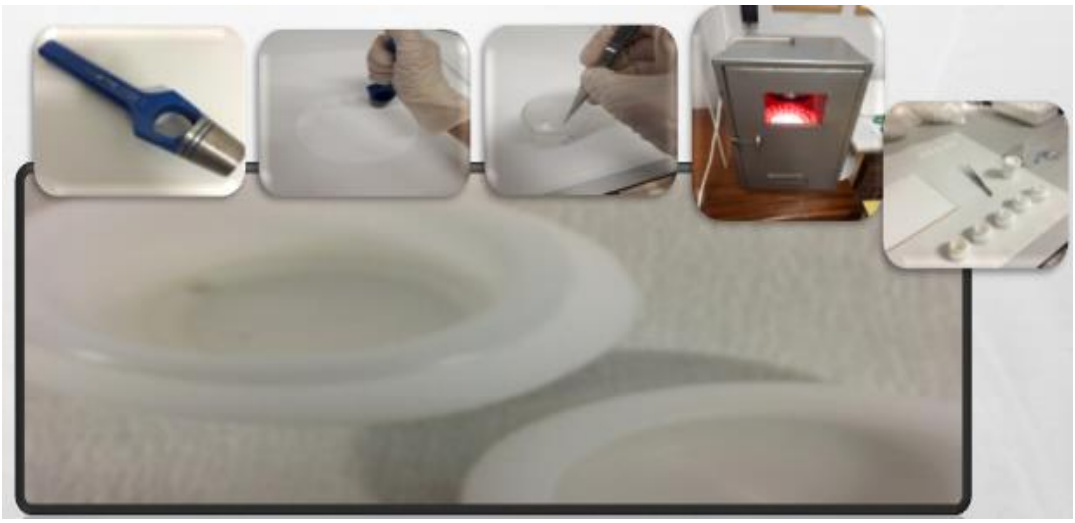


Figure 4.9. NO_2-SO_2 impregnation (Photo from our laboratory)

For preparation of the trapping medium for O_3 passive samplers, Whatman GF / A fiber glass filter papers are coated with 1 % $NaNO_2$, 2 % Na_2CO_3, 2 % glycerol aqueous solution in the laboratory medium. 1 g $NaNO_2$, 2 g Na_2CO_3, 1.6 mL glycerol are taken and diluted to 100 mL with deionized water. The rest of other parts are the same as the NO_2-SO_2 impregnation process. In ozone passive samplers NO_2^- ions in trapping solution converted into NO_3^- ions by being oxidized with O_3 during the sampling period according to the reaction below.

$$NO_2^- + O_3 \rightarrow NO_3^- + O_2$$

Impregnation process for O_3 is given in Figure 4.10.

Figure 4.10. O_3 impregnation (Photo from our laboratory)

The next process is the sampling. In this process samplers stayed at the sampling area for 2 weeks between the dates of January 28-29 and February 10-11. In summer period, they were also waited in the sampling area for two weeks between the dates of July 7-8 and July 22-23.

The samplers were placed in the shelters and left at sampling points. Photograph belonging to samplers in the shelters in sampling point is presented in Figure 4.11.

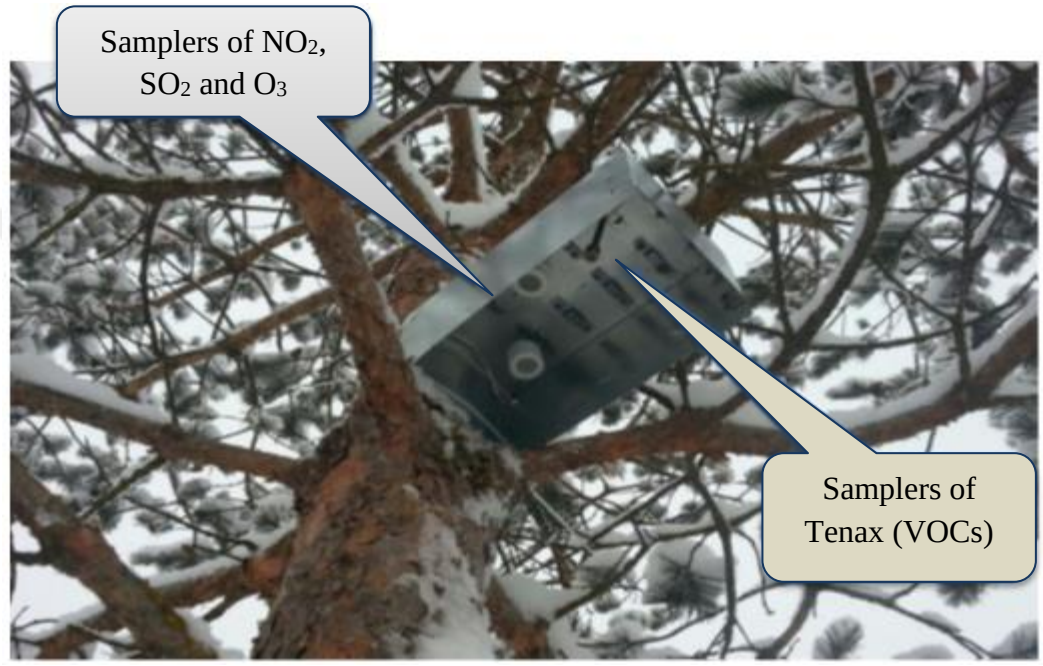


Figure 4.11. Passive Samplers of NO_2, SO_2 and VOCs into the shelters used in our study in the sampling point (Photo from our laboratory)

4.5.2 Extraction for NO_2, SO_2 and O_3

The last stage of the experimental prosess is the extraction. In this process, after the samplers were collected from the area, the following steps were applied for NO_2-SO_2 and O_3.

For NO_2-SO_2:

► 10 mL deionized water is added

► 20 µL H_2O_2 is added

► wait 15 minutes

For O_3:

► 10 mL deionized water is added

► wait 15 minutes

Figure 4.12. Extraction process (Photo from our laboratuary)

4.5.3 Preparation of BTEXs sampler

Tenax-TA tube was used in the passive sampling of volatile organic compounds. Tenax-TA tube used in the passive sampling is shown in Figure 4.13.

Before the sampling, Tenax-TA tubes were cleaned and conditioned with the help of thermal desorber. The conditioning was carried out at 320 ºC for 60 minutes under high purity helium gas. The conditioned Tenax-TA tubes were stored in stand-up Falkon tubes made of polypropylene material, screw-capped. Silica gel and activated carbon folded in the coarse filter papers were placed in Falkon tubes in order to prevent the humidity and VOCs that will cause contamination problem, respectively. The sample name was labeled and moved to the sampling points as shown in Figure 4.13.

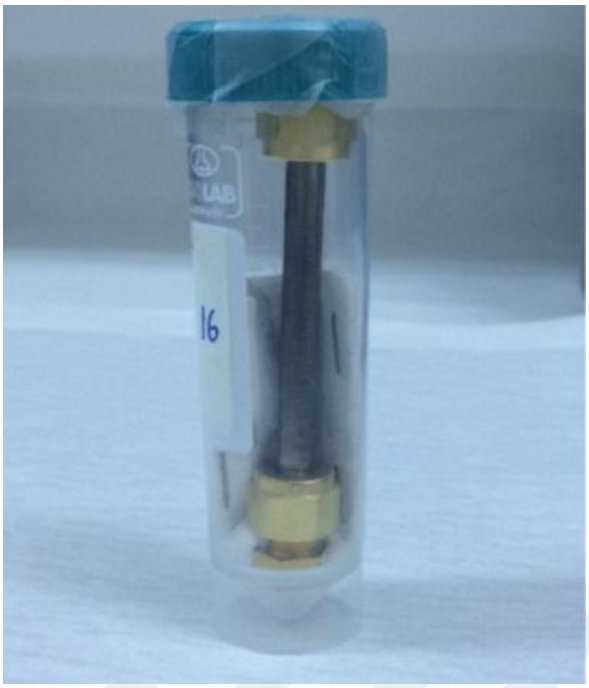


Figure 4.13. The mode of transport to sampling points of tenax tubes (Photo from our laboratory)

During the sampling, the diffusion headers were used to protect the sorbent bed found in tube from the effects of excessive wind, dust, and insects (Figure 4.14). At the end of the sampling, the diffusion caps were removed and the covers of the tubes are attached. Likewise, specimens were carried in the laboratory with Falcon tubes and stored in the deep freezing at -18 ° C until analysis.

Figure 4.14. The diffusion head of Tenax-TA passive sampling tube (Photo from our laboratory)

4.6 Analyses

4.6.1 Analysis of NO_2, SO_2 and O_3

Analysis of the inorganic components was carried out with a Dionex ICS 1100 Series Ion Chromatograph. Samplings were analyzed by using manual injecting part, which is shown in the figure (Figure 4.15).

Figure 4.15. Ion Chromatography used in the analyses of inorganic components and injection part (Photo from our laboratory)

The operating parameters of the ion chromatograph are given in Table 4.2.

Table 4.2. Operating parameters of Ion Chromatography

Column	AS9-HC (4x250 mm)
Suppressor	AERS 500 (4 mm)
Eluent	10 mM Na_2CO_3
Flow rate	1.0 mL/min
Suppressor current	45 mA
Suppressor type	ASRS 4mm
Pre-column	AG9-HC (4x50 mm)

Optimum operation conditions are given in Table 4.3 for Dionex ICS 1100 Ion Chromatography.

Table 4.3. Optimum operation conditions for Dionex ICS 1100 Ion Chromatography.

Parameters	Anion
Mobile phase	10 mM Na_2CO_3
Column	Ionpac AS9-HC (250 x 4 mm)
Guard column	Ionpac AG9-HC (50 x 4 mm)
Suppressor	ASRS-4 mm
Suppressor current	45 mA
Detector	Conductance detector
Pressure (psi)	2000-3000
Oven temperature	30 ^oC
Background conductance	< 30 μS
Flow rate	1.00 mL/min
Injection volume	500 μL
Rate of data transfer	5.0 Hz
Duration	30 min

Standards with 0.25 ppm, 0.5 ppm, 1 ppm, 2.5 ppm, 5 ppm and 10 ppm are prepared by taking from 10.0 ppm anion standard as 12.5 μL, 25 μL, 50 μL, 125 μL, 250 μL and 500 μL and diluted to 5 mL with deionized water. Regression coefficient belonging to ions are shared in Table 4.4.

Table 4.4. Regression coefficients of ions in Ion Chromatography system

Ion	**NO_2^-**	**NO_3^-**	**SO_4^{2-}**
R^2	0.9984	0.9995	0.9996

Chromatograms of the standard and samples are shown in Figure 4.16, Figure 4.17 and Figure 4.20.

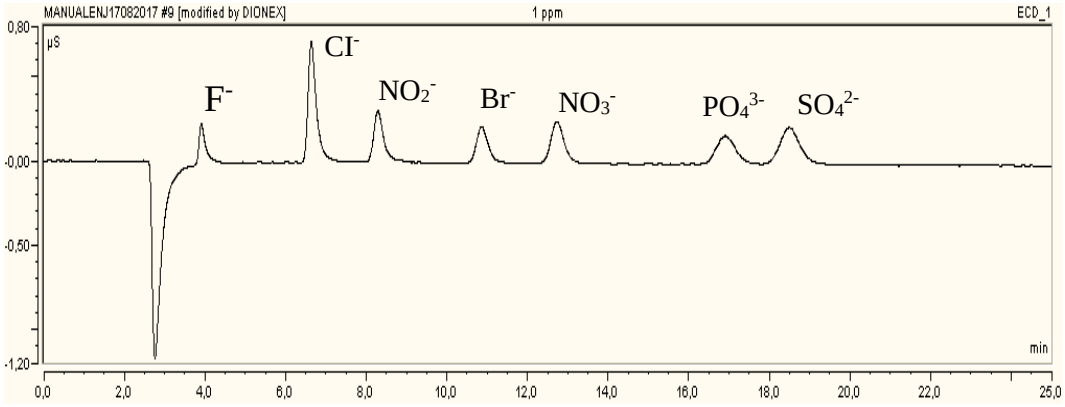


Figure 4.16. Chromatogram of standard of 1 ppm

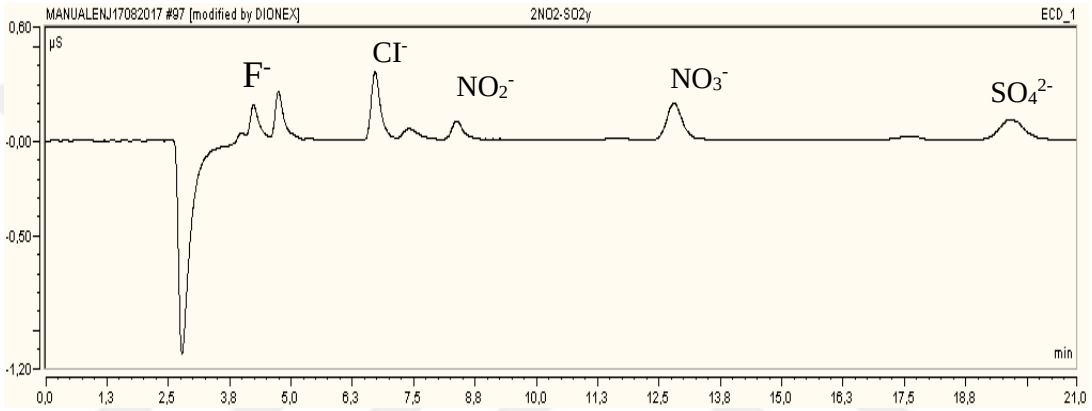


Figure 4.17. Chromatogram of NO_2-SO_2 passive sampler

After the standards were analyzed, the calibration curve was drawn. NO_2 was determined as NO_2^- ions and SO_2 was converted to SO_4^{2-} ions. NO_2^- concentration was determined from the calibration curves (Figure 4.18 and Figure 4.19).

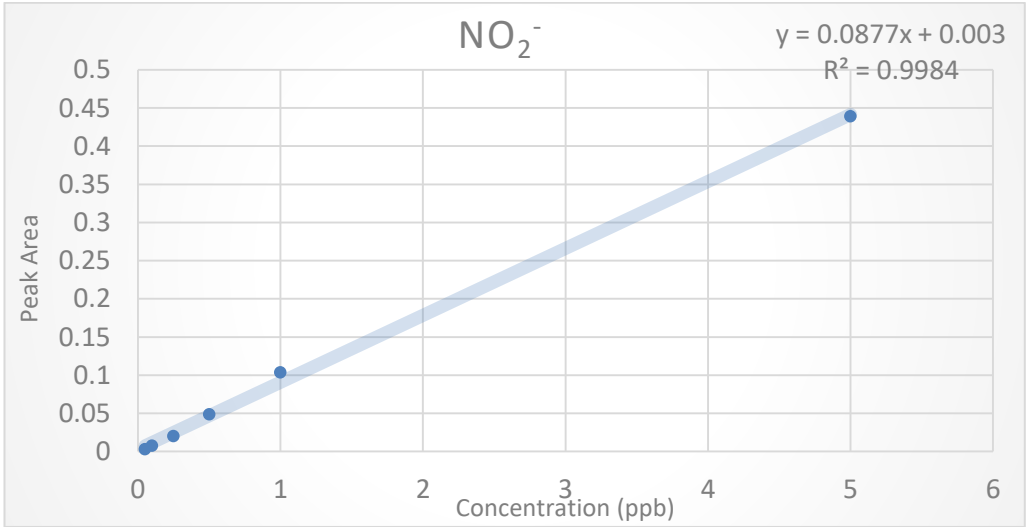


Figure 4.18. NO_2 calibration curve

SO_2 was determined as SO_4^{2-} ions. The concentrations of sulphate ion was also determined from the calibration curve (Figure 4.19).

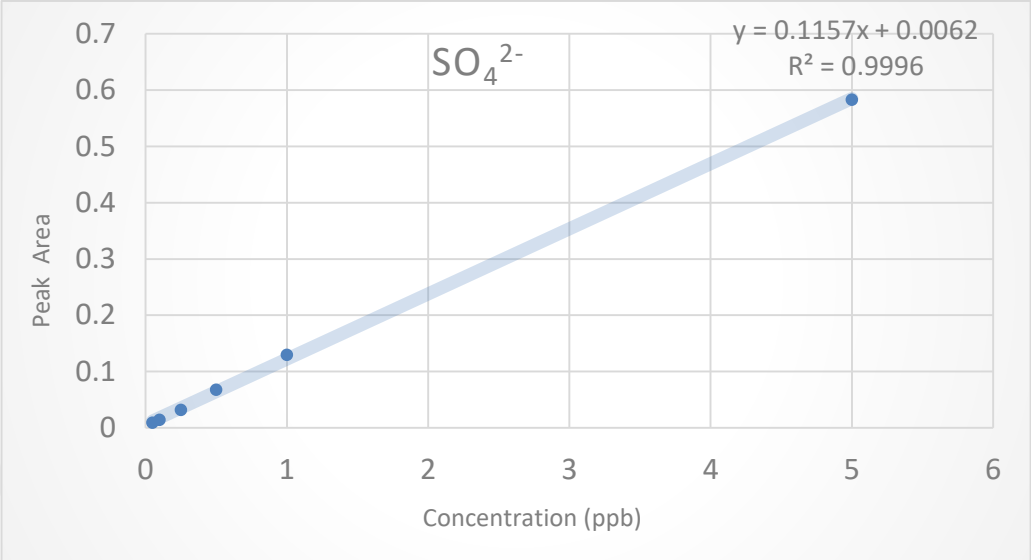


Figure 4.19. SO_2 calibration curve

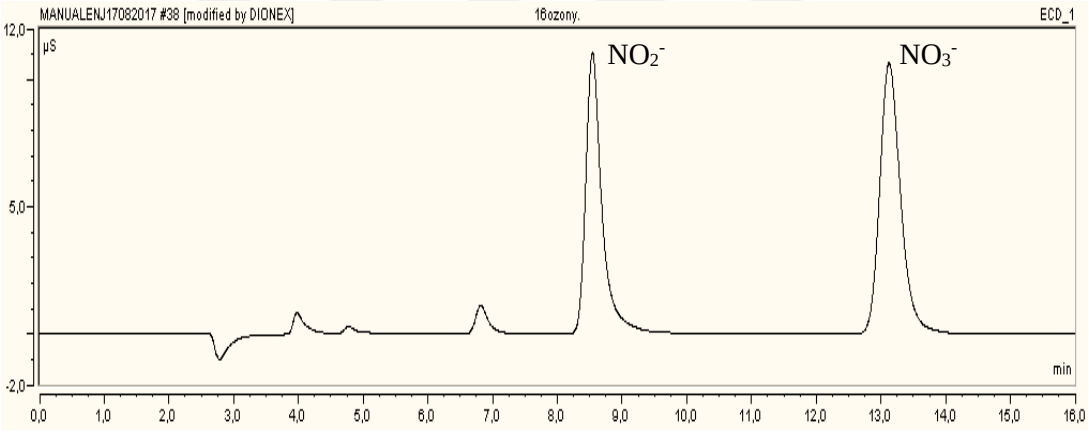


Figure 4.20. Chromatogram of O_3 passive sampler

O_3 was determined as NO_3^- ions (Figure 4.21). NO_3^- concentration was also determined from the calibration curve (Figure 4.21).

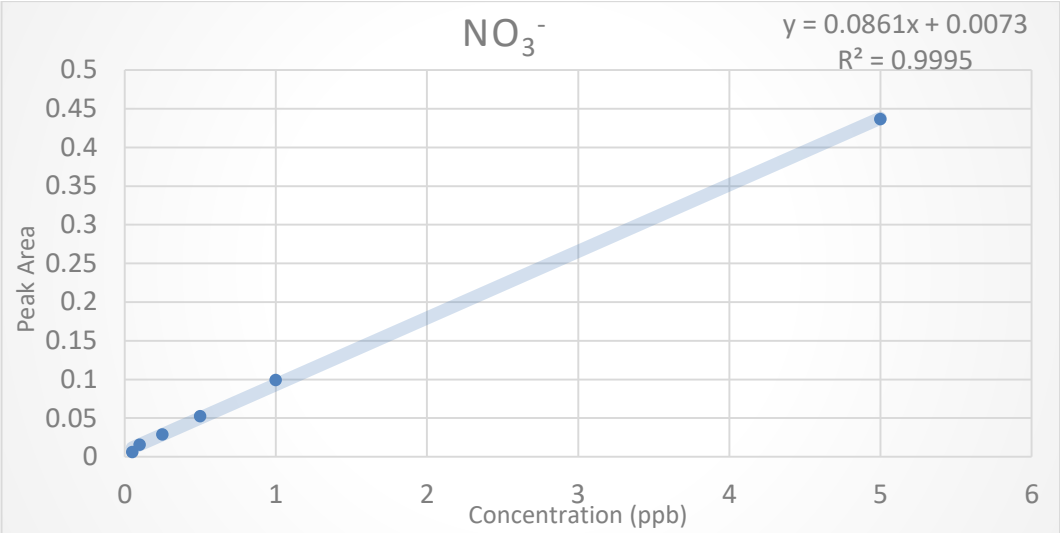


Figure 4.21. O_3 calibration curve

4.6.2 Calculations of NO_2, SO_2 and O_3

The amounts (µg) of NO_2^-, SO_4^{2-} and NO_3^- are determined by multiplying the concentrations (mg L^{-1}) determined by Ion Chromatography with extraction volumes (mL).

When the concentration of O_3 was calculated, O_3 concentration was found multiplying by (48/62) coefficient owing to passing from the NO_3^- ions concentration to O_3 concentration in the air (O_3/NO_3^-).

When the SO_2 concentration was calculated, it was found multiplying by (64/96) coefficient because of passing from SO_4^{2-} ions concentration to SO_2 concentration in the air. Fick first law of diffusion equation was used to determine the pollutants concentration in the atmosphere.

Fick first law of diffusion;

$$C = \frac{Q * L}{D * A * t}$$

L : Path length (m)

D : Diffusion coefficient ($m^2 s^{-1}$)

Q : Amount of pollutant (microgram)

$D_T = D_{298.15} * (T)^{1.75} * (298.15)^{-1.75}$ A : Crossectional area of diffusion (m^2)

t : Sampling time (s)

C : Concentration of pollutant component ($\mu g\ m^{-3}$)

Diffusion coefficient;

For NO_2 ; $D_{298} = 0.154\ m^2\ s^{-1}$ (T in Kelvin) $D_T = D_{298} * (T)^{1.75} * (298.15)^{-1.75}$

For O_3 ; $D_{298} = 0.155\ m^2\ s^{-1}$ $D_T = D_{298} * (T)^{1.75} * (298.15)^{-1.75}$

For SO_2 ; $D_{298} = 0.127\ m^2\ s^{-1}$ $D_T = D_{298} * (T)^{1.75} * (298.15)^{-1.75}$

After that, NO_2 was divided into (46*41), O_3 was divided into (48*41) and SO_2 was divided into (64*41) to convert from $\mu g\ m^{-3}$ to ppm. Equation is given as below.

Concentration ($\mu g\ m^{-3}$) = Concentration (ppm)*41* molecular weight

Finally, it was multiplied by 1000 in order to convert from ppm to ppb.

4.6.3 Analysis of BTEXs

TD-GC-MS system was used for extraction and analysis of BTEXs. The VOCs adsorbed to the Tenax-TA were desorbed thermally by the thermal desorption (TD) system and sent to the Gas Chromatography Mass Spectrometer (GC-MS) system. Operating parameters of TD-GC-MS System are given in Table 8.

The selected ıon monitoring (SIM) mode was used in order to be able to perform more sensitive analyses in GC-MS and to increase resolution. Compounds were divided into 6 different SIM evaluation groups. Main and auxiliary ions belonging to the compounds reaching the detector for the selected time intervals are entered into the device while the groups are being created.

In order to prepare the standards, firstly 100 µL was taken from the 100-ppm main stock and diluted to 1 mL. Thus 10 ppm intermediate stock, solution was prepared by this way. Analysis was performed for 10 ng, 20 ng, and 50 ng standards by injecting 1 µL, 2 µL, and 5 µL to Tenax tubes, respectively, from a 10-ppm intermediate stock. 100 ng and 200 ng standards were also generated by injecting 1 µL and 2 µL into the Tenax tube from 100 ppm stock solution. So, the calibration curve was drawn with 5 points (10 ng, 20 ng, 50 ng, 100 ng and 200 ng). The calibration curve for the Benzene compound is given in Figure 4.22.

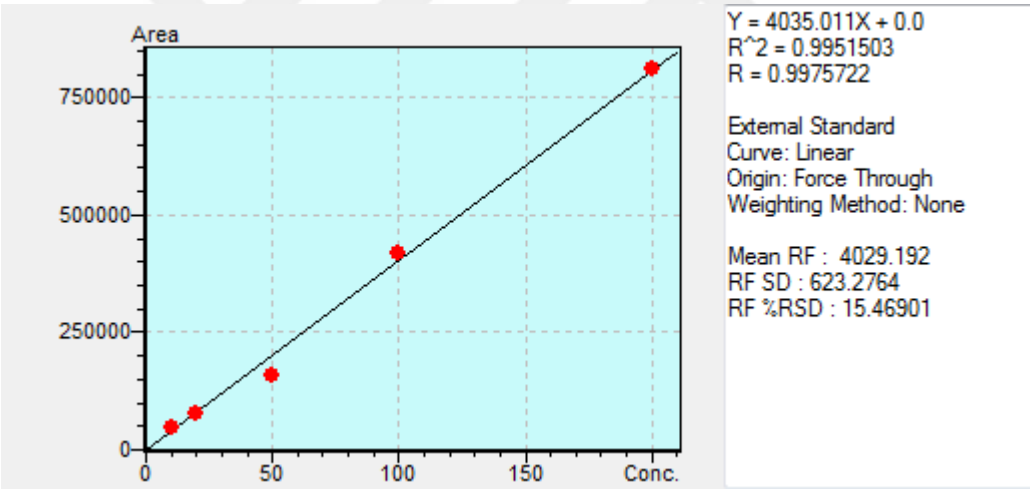


Figure 4.22. Example of the calibration curve of benzene obtained from the TD-GC-MS system

Regression coefficients belonging to the calibration curves and retention times are presented in Table 4.5.

Table 4.5. Retention time and regression coefficient belonging to BTEXs in TD-GC-MS

VOCs	Retention Time (min.)	R^2
Benzene	13.915	0.995
Toluene	17.395	0.988
Ethylbenzene	20.21	0.996
o-Xylene	21.227	0.988
m+p Xylene	20.431	0.997

Analysis of the samples was carried out with the TD-GC-MS system. Chromatograms belonging to the 10 ng standard and passive sample (number 1) are shown in Figure 4.23 and Figure 4.24.

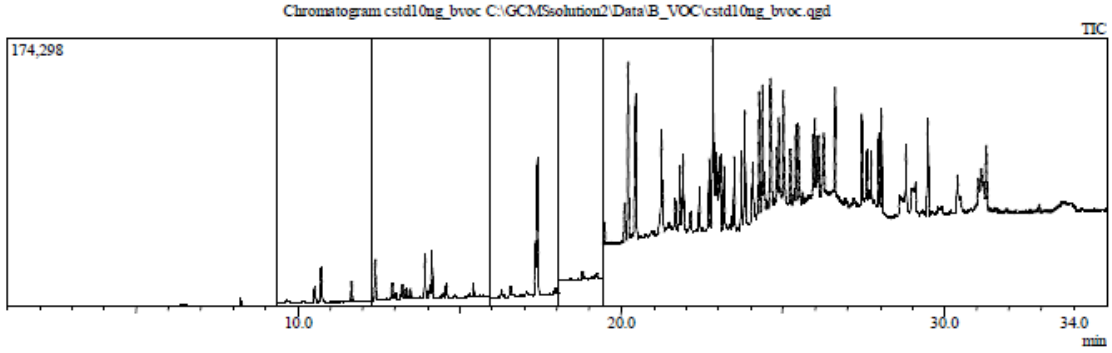


Figure 4.23. Chromatograms of the VOC standard (10 ng)

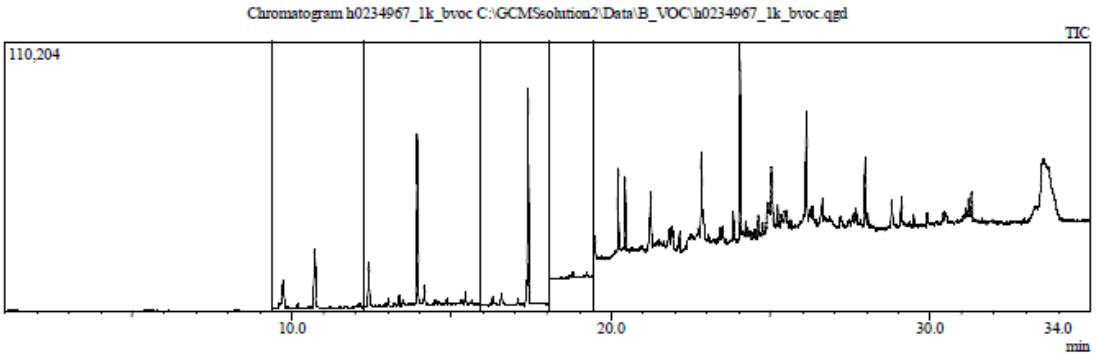


Figure 4.24. Chromatograms belonging to passive sample (number 1)

Atmospheric concentrations of BTEXs collected by passive sampling method were calculated using Fick's 1st Law.

$$Q= \{[(C1-C0) \times L]/ (D \times A \times t) \} \times 10^3 \quad (1)$$

Q: The amount of absorbed pollutant ($\mu g\ m^{-3}$)

L: Diffusion path (cm)

A: Sampler surface area (cm^2)

D: Diffusion coefficient ($cm^2\ sn^{-1}$)

C_1: Pollutant concentration at the open end of the sampler (ng)

C_0: Pollutant concentration initially (ng)

t: Sampling time (sn)

Equation 2 is used to adjust the diffusion coefficient to the mean temperature during the sampling period.

$$D_T = D_{298} \text{ x } (T)^{1.75} \text{ x } (298.15)^{-1.75} \quad (2)$$

4.7 Data quality and assurance

Within the scope of quality control (QC) and quality assurance (QA), the maximum care has been shown for the preparation of the samples before sampling, before they come to the laboratory and after they arrived in the laboratory in order not to contaminate the samples. In winter period, the accuracy of the results of ion analyzes performed in ion chromatography was tested using the certified reference material (BCR 409). The results are given in Table 4.6.

Table 4.6. Analysis results of BCR-409 standard reference material

	Certificate value (ppm)	**Uncertainity (k=2) (ppm)**	**Found value (n=2) average ± standard deviation**	**Error %**
Nitrate	1.61	0.062	2.19 ± 0.50	36
Sulphate	1.7	0.067	1.68 ± 1.29	0.86

In summer period, the accuracy of the results of ion analyzes performed in ion chromatography was tested using the certified reference material ERM-CA408 (simulated rain water). The results are presented in Table 4.7.

Table 4.7. Analysis results of ERM-CA408 (simulated rain water) standard reference material

	Certificate value (ppm)	**Uncertainity (k=2) (ppm)**	**Found value (n=2) average ± standard deviation**	**Error %**
Nitrate	1.01	0.09	1.002 ± 0.026	0.79
Sulphate	0.73	0.04	0.746 ± 0.034	2.18

In addition, 12 blank samples were collected in the study period. The mean of the ratios of the samples to blank was 5.66 ± 5.31 for O_3, 7.04 ± 5.78 for NO_2 and 1.00 ± 0.50 for SO_2. These ratios were calculated after the blank substraction.

In addition, totally 12 blank samples for BTEX samples were collected in the study period. The mean of the ratios of the sample to blank values is given in Table 4.8. The ratio values ranged between 3.6 to 95 for benzene, 2.4 to 108 for toluene, 6 to 500 for ethylbenzene, 3.8 to 563 for o-xylene and 3.2 to 257 for m+p xylene.

Table 4.8. The average values of the sample/blank ratios of BTEXs

BTEX	**Sample to blank ratio** **Average ± standard deviation**
Benzene	21 ± 22
Toluene	23 ± 21
Ethylbenzene	97 ± 98
o-Xylene	91 ± 107
m+p Xylene	52 ± 52

To calculate the repeatability of samples for BTEXs, NO_2, SO_2 and O_3, three parallel samplers at 6 sampling points were used. Percent relative standard deviation values (% RSD) of repeated samples are given in Table 4.9 and Table 4.10.

Table 4.9. Relative standard deviation values (RSD%) of BTEXs compounds (N=6)

VOCs	RSD% ± standard deviation
Benzene	6.7 ± 6.0
Toluene	5.2 ± 3.4
Ethylbenzene	7.4 ± 4.8
o-Xylene	5.4 ± 4.4
m+p Xylene	5.2 ± 4.4

Table 4.10. Relative standard deviation values (RSD%) for NO_2, SO_2 and O_3 (N=6).

	NO_2	SO_2	O_3
RSD% standard deviation	12.4 ± 8.1	16.9 ± 9.9	9.2 ± 7.2

After that, to determine the method detection limit (MDL), three times the standard deviation of 10 replicates of the standard of the lowest concentration in the calibration curve for each component were taken. The MDL values of nitrite, nitrate and sulfate are 1.97, 2.47 and 1.75 μg m^{-3}, respectively. These results were also given in Table 4.11. The method limit of quantification value (MLOQ) was determined by taking ten times the standard deviation of the repeated standard concentrations. The values presented in Table 4.11 for nitrite, nitrate and sulfate are 6.58, 8.23 and 5.82 μg m^{-3}, respectively.

Table 4.11. The MDL and MLOQ values (μg m^{-3}) of 10 replicates of standard for nitrite, nitrate and sulphate.

	NO_2	NO_3^- (O_3)	SO_4^{2-} (SO_2)
Standard (ppm)	0.05	0.05	0.05
Mean	4.16	2.83	1.84
Standard Deviation	0.59	0.51	0.39
MDL (μg m^{-3})	1.77	1.58	1.17
MLOQ (μg m^{-3})	5.89	5.02	3.89

The MDL and the MLOQ values of BTEXs were given in Table 4.12.

Table 4.12. The MDL and MLOQ values (μg m^{-3}) of BTEXs.

	Benzene	**Toluene**	**Ethylbenzene**	**m+p Xylene**	**o Xylene**
MDL	0.03	0.02	0.0008	0.002	0.005
MLOQ	0.12	0.05	0.003	0.007	0.016

To calculate the MDL and MLOQ values of BTEXs, three times and the ten times the standard deviation of 10 replicates of the standard of the lowest concentration in the calibration curve was taken, respectively.

5. RESULTS AND DISCUSSION

5.1 Spatial and seasonal evaluation of passive sampling results

In this thesis, the components determined with the passive sampling method were nitrogen dioxide (NO_2), sulfur dioxide (SO_2), ozone (O_3) and BTEXs which is a member of volatile organic compounds (VOCs). This study was carried out in two periods. In winter period, passive samplers of gaseous inorganic pollutants (NO_2, SO_2 and O_3) and BTEX were placed at 49 sampling points. In winter period due to hard winter conditions it was not possible to reach to the some of the high alttitude sampling places. The samplers were held from January 28 to February 12, 2017. In summer period, the passive samplers of gaseous inorganic pollutants (NO_2, SO_2 and O_3) and BTEX were placed at 62 sampling points. The samplers were held 7 to July 23, 2017. Statistical values in summer and winter seasons are shown in Table 5.1 Table and 5.2.

Table 5.1. Descriptive statistics for NO_2, SO_2 and O_3 in summer season (ppb) (N=64)

SUMMER			
	NO_2	**SO_2**	**O_3**
N	64	64	64
Mean	6.69	3.14	23.2
Standard deviation	4.45	3.96	15.9
Coefficient of variation	66.5	1.26	0.69
Minimum	2.31	0.52	0.42
Maximum	26.2	13.9	87.6
Range	23.9	13.4	87.2

The amount of NO_2 in the atmosphere in summer and winter seasons was in the range of 2.31 - 26.2 and 0.19 - 22.4, respectively. The amount of SO_2 in the atmosphere in summer and winter seasons was in the range of 0.52 - 13.9 and 0.14 - 8.92, respectively. The concentration range of O_3 in the atmosphere in summer and in winter seasons was 0.42 - 87.6 and 8.52 - 71.4, respectively. The concentrations levels of pollutants were not showing significant changes seasonally.

Table 5.2. Descriptive statistics for NO_2, SO_2 and O_3 in winter season (ppb) (N=47)

WINTER			
	NO_2	**SO_2**	**O_3**
N	47	47	47
Mean	7.88	3.09	32.1
Standard deviation	6.44	2.29	11.3
Coefficient of variation	81.6	74.1	35.2
Minimum	0.19	0.14	8.52
Maximum	22.4	8.92	71.4
Range	22.4	8.78	62.9

Benzene, toluene, ethylbenzene and xylenes (BTEXs) are important anthropogenic VOCs that have been the subject of many studies. According to the regulation on the protection of air quality, the average annual benzene concentration in the atmosphere should not exceed 5 μg m^{-3}. As a result of the winter passive sampling campaign data, it was determined that this limit value was not exceeded, but a value of 4.55 μg m^{-3} in the city center was obtained.

Descriptive statistics for BTEXs determined by passive sampling in winter season (μg m^{-3}) (N = 59) are given in Table 5.3.

Table 5.3. Descriptive statistics for BTEX in winter season (μg m^{-3}) (N = 59)

Component	**N**	**Mean**	**Median**	**Geometric mean**	**Standard deviation**	**Min.- Max.**
Benzene	59	1.75	1.36	1.48	1.06	0.20 - 4.55
Toluene	59	2.37	2.08	2.12	1.26	1.13 - 6.63
Ethylbenzene	59	0.42	0.34	0.37	0.23	0.22 - 1.22
m+p Xylene	59	0.43	0.33	0.37	0.28	0.19 - 1.31
o-Xylene	59	0.77	0.58	0.68	0.49	0.46 - 2.56

Descriptive statistics for BTEX determined by passive sampling in summer season (μg m^{-3}) (N = 63) are presented in Table 5.4.

Table 5.4. Descriptive statistics for BTEX in summer season (μg m^{-3}) (N = 63)

Component	N	Mean	Median	Geometric mean	Standard deviation	Min.-Max.
Benzene	63	0.20	0.25	0.27	0.15	0.17-1.28
Toluene	63	0.45	0.36	0.37	0.33	0.11-1.68
Ethylbenzene	63	0.07	0.05	0.05	0.6	0.01-0.28
m+p Xylene	63	0.12	0.06	0.07	0.13	0.02-0.50
o-Xylene	63	0.09	0.05	0.06	0.09	0.02-0.36

The concentrations of BTEXs compounds in winter season were generally 5-10 times higher than that of in summer season. That might have been due to the low mixing height in winter and also less photochemical reactions.

5.1.1 Spatial and Seasonal Evaluation of NO_2 (Nitrogen dioxide) and its pollution map

The values obtained from calculations were converted into pollution maps with the help of mapInfo Professional 7.5 SCP Program. NO_2 pollution map in winter season is shown in Figure 5.1.

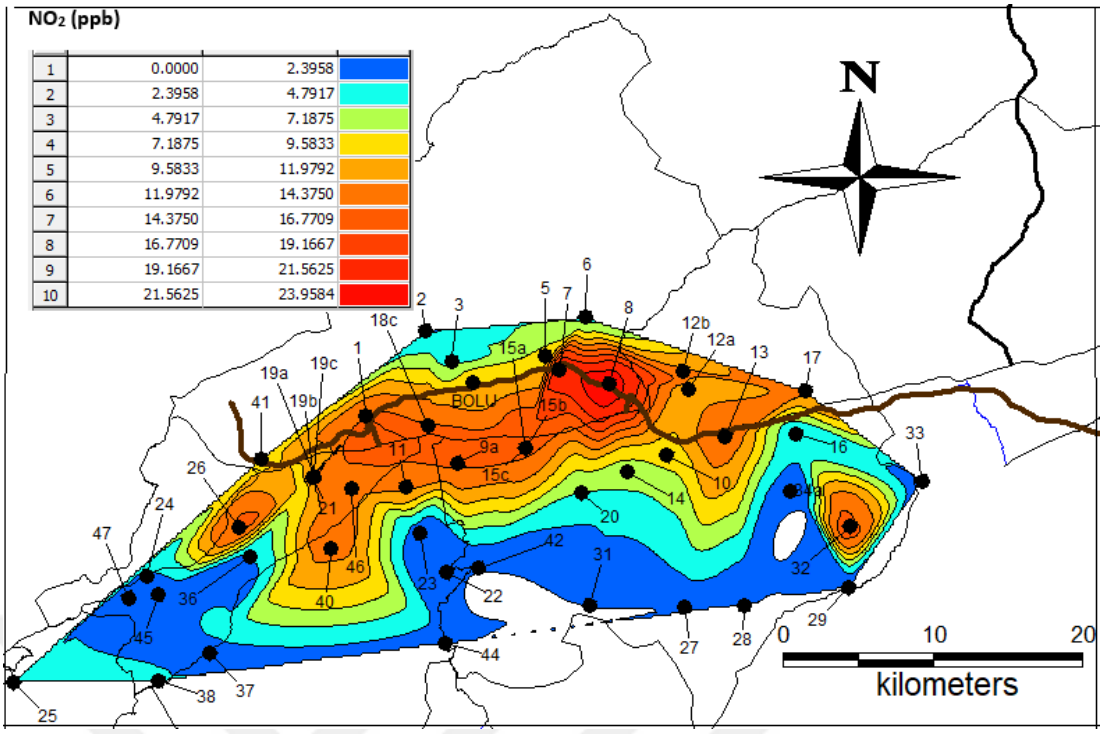


Figure 5.1. NO_2 pollution map in winter season

It has been observed that the NO_2 values were high near to TEM Highway, D-100 Highway (1, 5, 7, 8, 9a, 13 and 15a) and in the city center (18). Low amounts of NO_2 were seen in the mountainous areas (27, 28, 29, 36, 37, and 38). This could have explained by the fact that this pollutant was mostly traffic-originated.

NO_2 concentrations were decreased as O_3 was increased. This situation was seen in the maps of NO_2 and O_3 in summer period. This is because NO reacts with O_3 in order to form NO_2. In other words, while NO_2 is formed, O_3 is consumed (Caballero et al., 2012). As a result of this, as it was also seen in the NO_2 pollution maps, there was a negative relation between O_3 and NO_2 by reacting with NO and O_3.

$$O(g) + O_2(g) \longrightarrow O_3(g)$$

$$NO(g) + O_3(g) \longrightarrow NO_2(g)$$

NO_2 values were high in the city center which was close to TEM highway and D-100 and in the region with heavy traffic. This situation could have explained that this pollutant was again traffic originated. NO_2 values were low in high altitude areas

and areas with less dense traffic. NO_2 pollution map in summer season is shown in Figure 5.2.

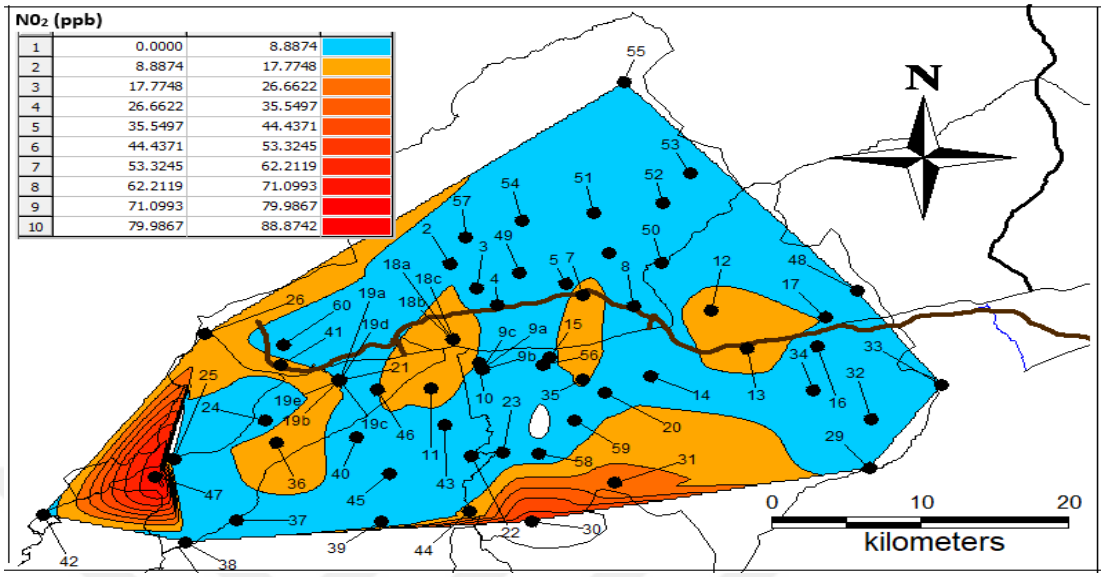


Figure 5.2. NO_2 pollution map in summer period

When comparing NO_2 values seasonally, it was seen that summer concentrations were lower than winter concentrations. The Box and Whisker plot of summer-winter concentrations of NO_2, SO_2 and O_3 is shown as graphically in Figure 5.3. The plots show maximum, 75th percentile, median 25th percentile and minimum concentrations.

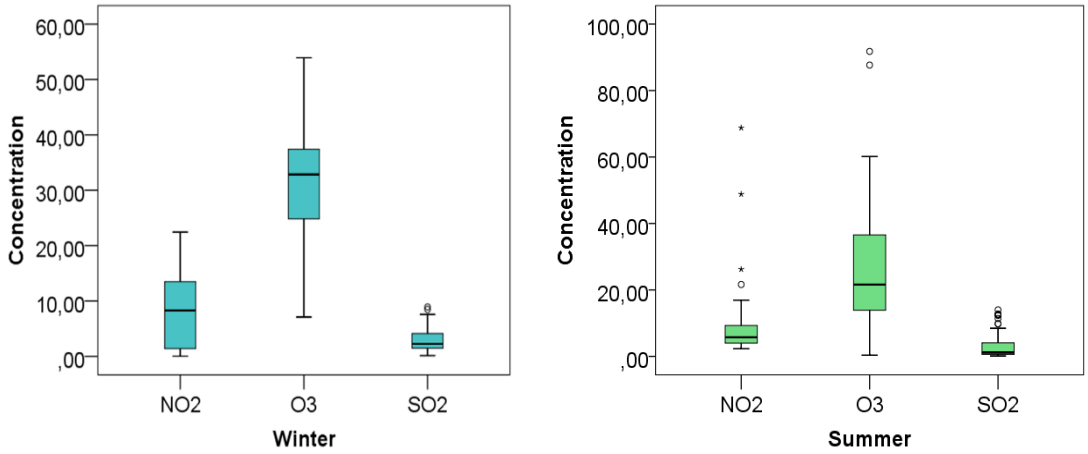


Figure 5.3. Plot of NO_2, SO_2 and O_3 concentrations in summer and in winter period

5.1.2 Spatial and seasonal evaluation of SO_2 (Sulfur Dioxide) and its pollution maps

SO_2 pollution distribution maps of winter and summer period were drawn in order to examine the spatial and seasonal evaluation. SO_2 pollution map in winter season is shown in Figure 5.4.

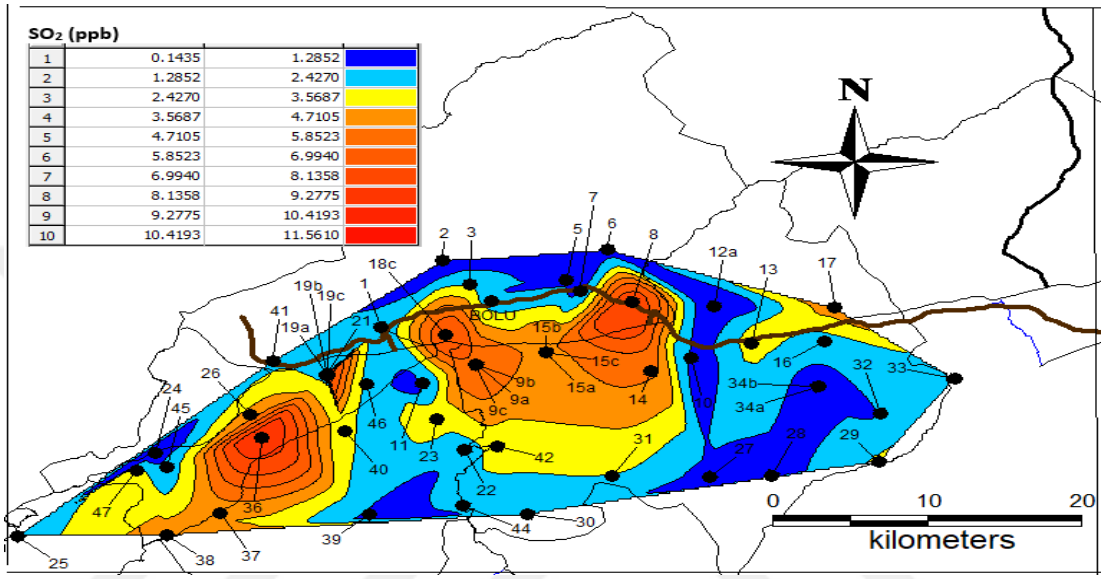


Figure 5.4. SO_2 pollution map in winter season

The concentrations of SO_2 concentartions were low in the city center (3) because of the usage of natural gas and in high altitude areas where people are not living in winters. The SO_2 concentrations were high in villages because coal had been still used for domestic heating.

In summer period, it was observed that SO_2 values were high in high altitude areas and high altitude villages especially in summer season because of the usage of coal as a domestic heating. SO_2 pollution map in summer season is shown in Figure 5.5.

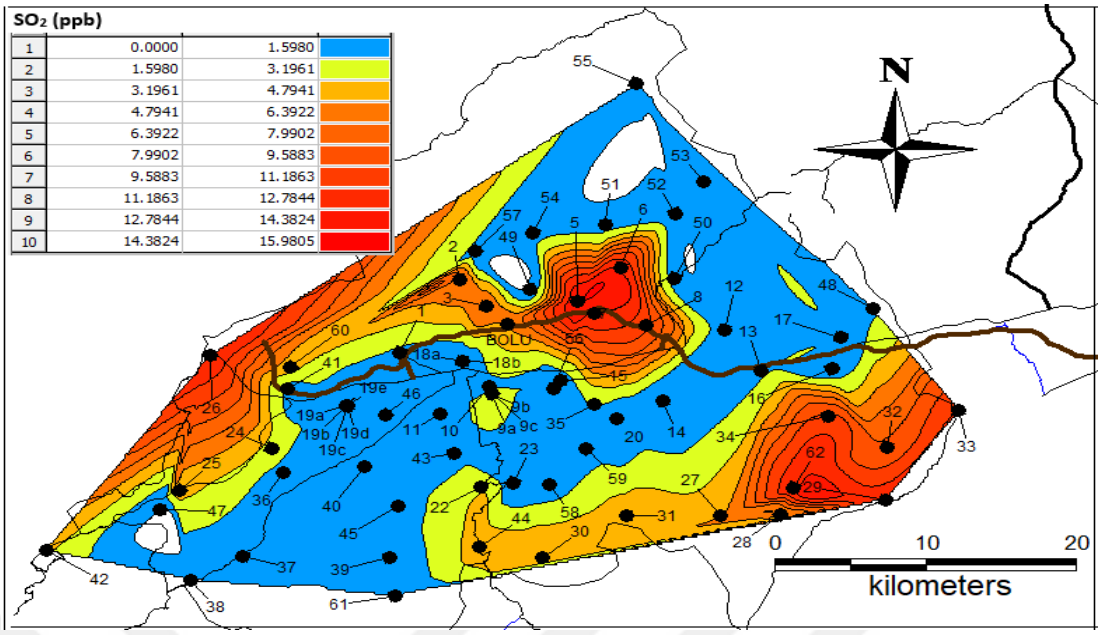


Figure 5.5. SO_2 pollution map in summer period

When comparing SO_2 values seasonally, it was seen that the summer values in some places were higher than the winter values. Because the plateau settlement starts in summer season and due to low temperature (Kartalkaya; min: 9.4 (ºC), max: 19.9 (ºC), Aladağlar; min.: 7.24 (ºC), max.: 24.9 (ºC)) in these areas, people use coal for residential heating. However, on the average summer-winter concentrations of SO_2 were the same as shown in Figure 5.3.

5.1.3 Spatial and seasonal evaluation of O_3 (Ozone) and its pollution maps

O_3 pollution distribution maps of winter and summer period were also drawn in order to evaluate the spatial and seasonal evaluation. O_3 pollution map in winter season is presented in Figure 5.6.

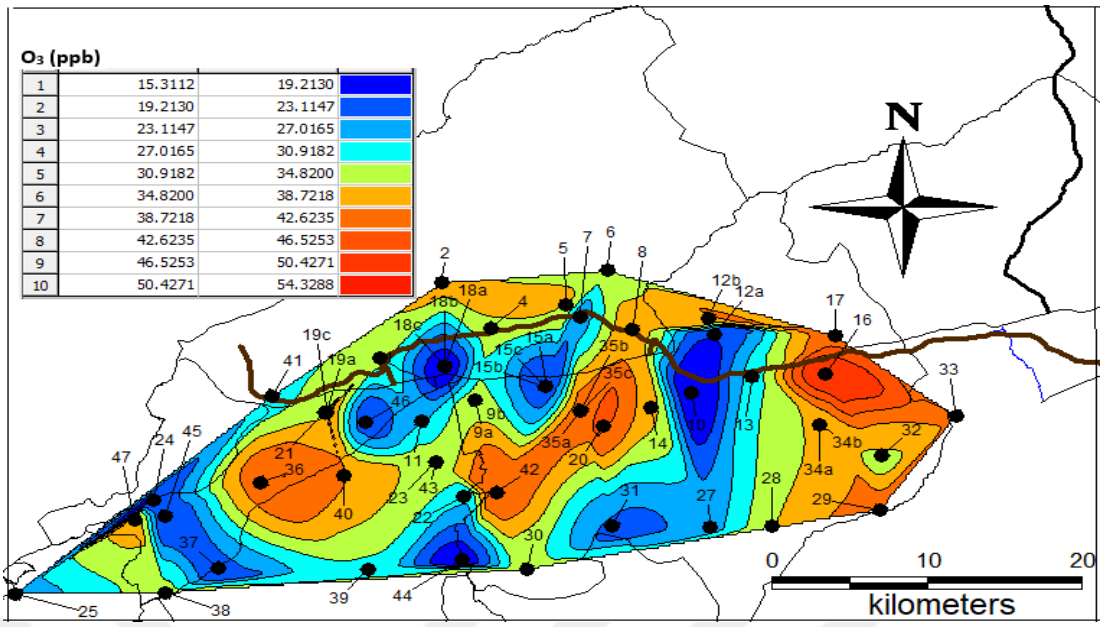


Figure 5.6. O_3 pollution map in winter season

Ozone values were high in rural areas (20, 35a, 35b, 35c, 36) and low around TEM and D-100 roads (5, 7, 10, 11, 12 and 13). Ozone reacts with NO around the roadside and central regions, and the quantity of ozone decreases. On the contrary, there are no pollutants that could lead to a decrease in the amount of ozone in rural areas, and high levels of ozone are detected.

That the biogenic volatile organic compounds released from trees cause the formation of O_3 in the presence of sunlight and NO_x in forests and rural areas (Calfapietra et al., 2009; Evtyugina et al., 2009). This might be a significant contributor to the high ozone concentration measured in forest areas.

In summer period, the pollution map of ozone is shown in Figure 5.7, ozone values were high in places far from the city center at high altitude areas and in forest sides. In contrast, ozone values were low around the TEM Highway and D-100 road. Ozone concentrations were decreased by reacting NO.

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

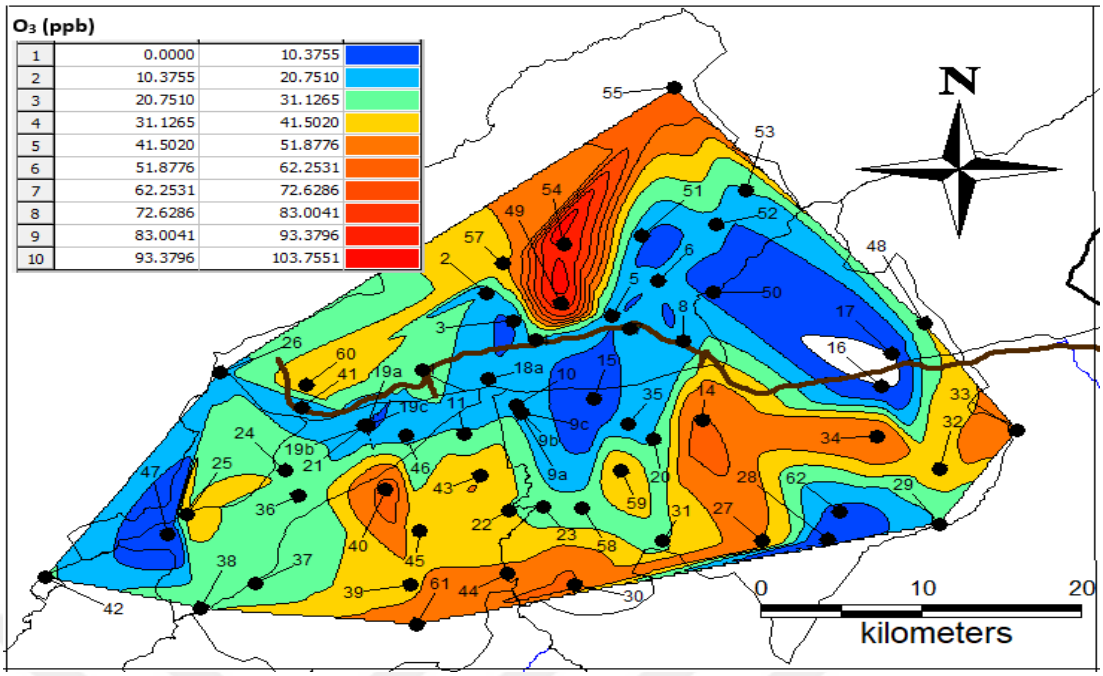


Figure 5.7. O_3 pollution map in summer season

Ozone values were expected to be high in summer season, and to be less in winter because of photochemical reactions (Lozano, et al., 2009). However, It was observed that winter concentrations were higher than summer concentrations. In our study, very low mixing height (150 m) is observed in winter season in Bolu. So, high concentrations of pollutants were obtained (Bayındır, 2009).

5.1.4 Spatial and seasonal evaluation of BTEXs (Benzene, toluene, ethlybenzene, xylenes) and their pollution maps

The distribution maps of BTEXs reveal that the components show spatial variation within the city. The spatial and seasonal effect of BTEX pollutants were shown in their pollution maps in Figure 5.8, 5.9, 5.10, 5.11, 5.12. In winter season, common sources have been found to be effective for BTEX components. The highest BTEXs levels were obtained in the city center (18a, 18b, 18c) e.g. 4.53 µg m^{-3} for benzene, 5.25 µg m^{-3} for toluene, 0.88 µg m^{-3} for ethylbenzene, 1.30 µg m^{-3} for m-p Xylene and 1.32 µg m^{-3} for o-Xylene.

In addition to this point, high BTEXs concentrations have been obtained in highly populated settlements, and in other areas which are close to highways such

30 at the south of the map have a small population, they had high BTEXs concentrations due to the fact that area is close to marble and chalk operating works. The heavy vehicles are carrying the marbles and chalk and giving high emission of diesel. The point 28 had high BTEXs concentrations which is close to Kartalkaya, an important part of the winter tourism of the region. Samples were affected by the emissions of the vehicles traffic and snow shoveling vehicles.

Emissions of anthropogenic origin and low mixing height cause high pollution in the center of Bolu province in winter.

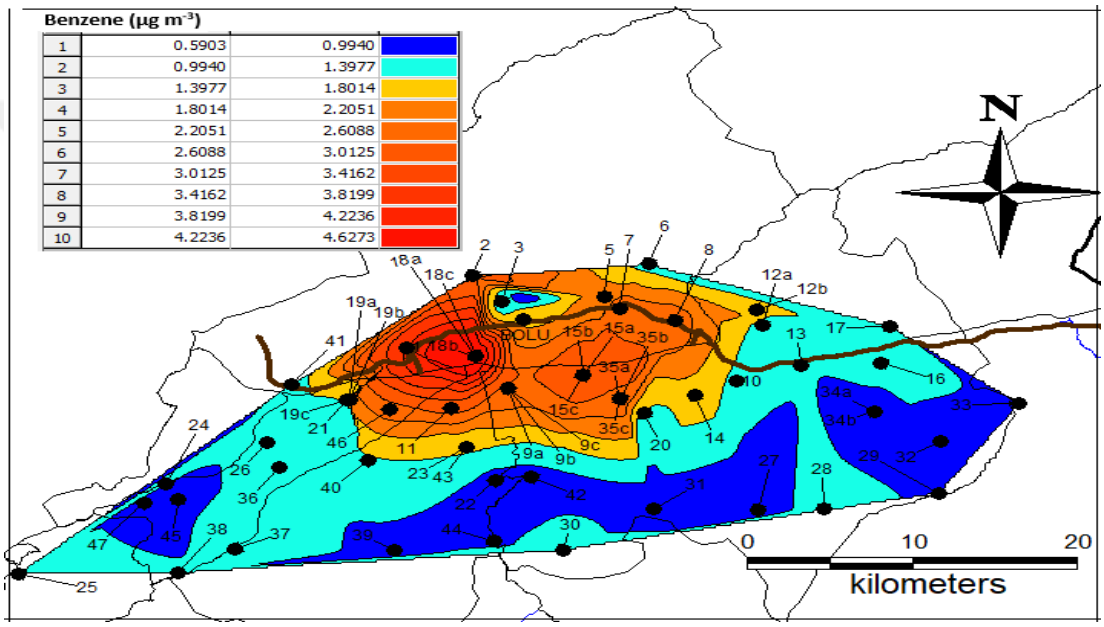


Figure 5.8. Benzene pollution map in winter season

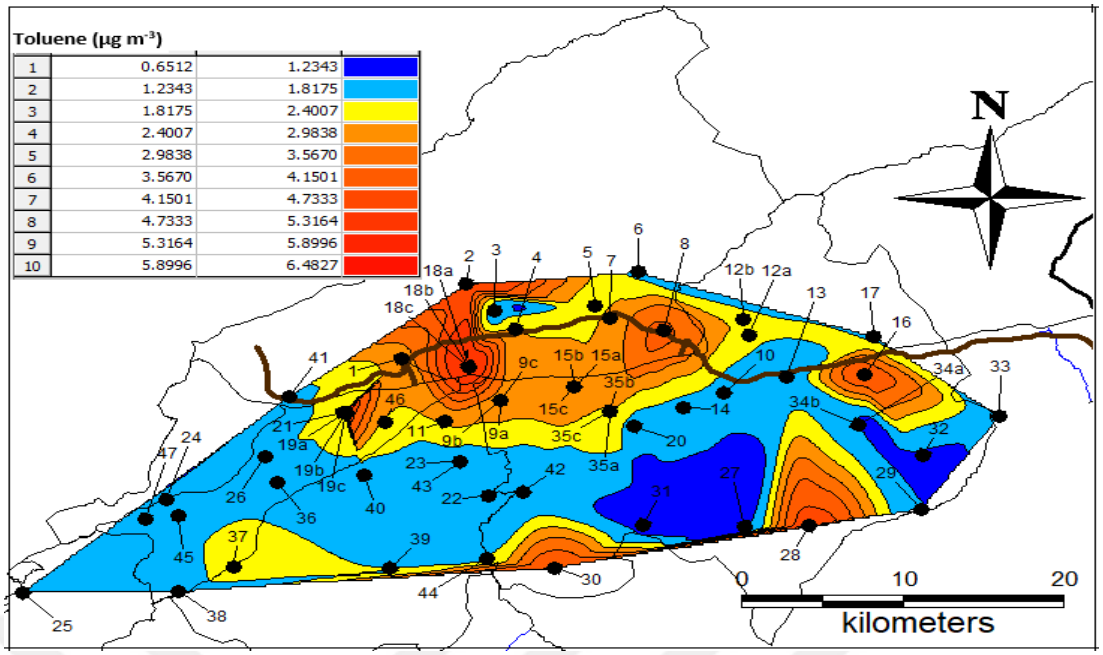


Figure 5.9. Toluene pollution map in winter season

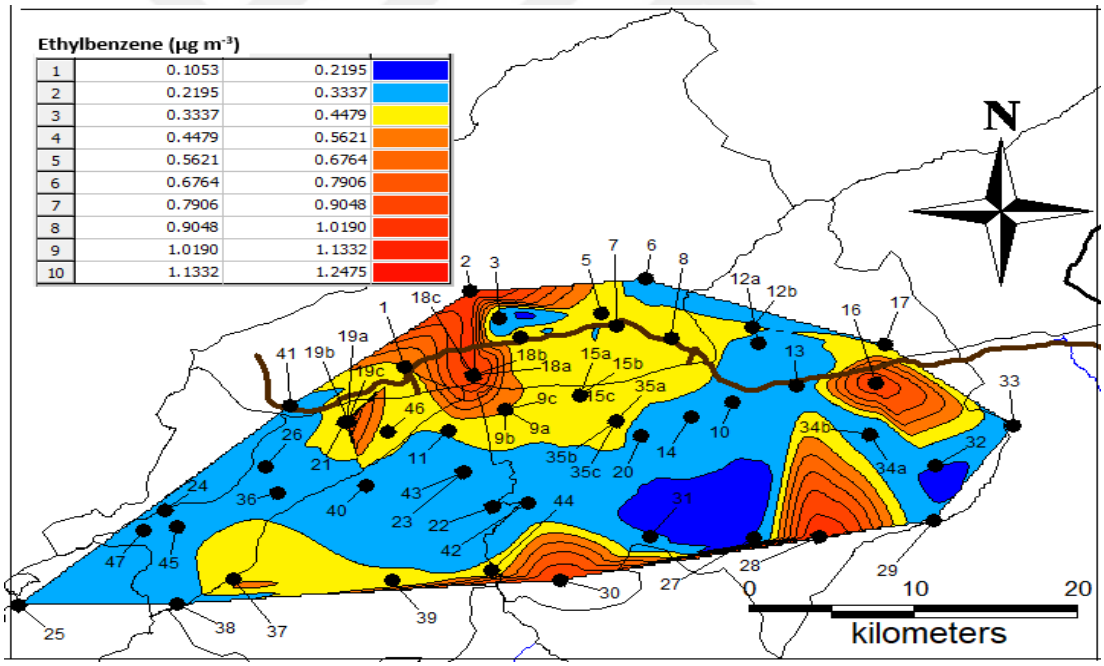


Figure 5.10. Ethylbenzene pollution map in winter season

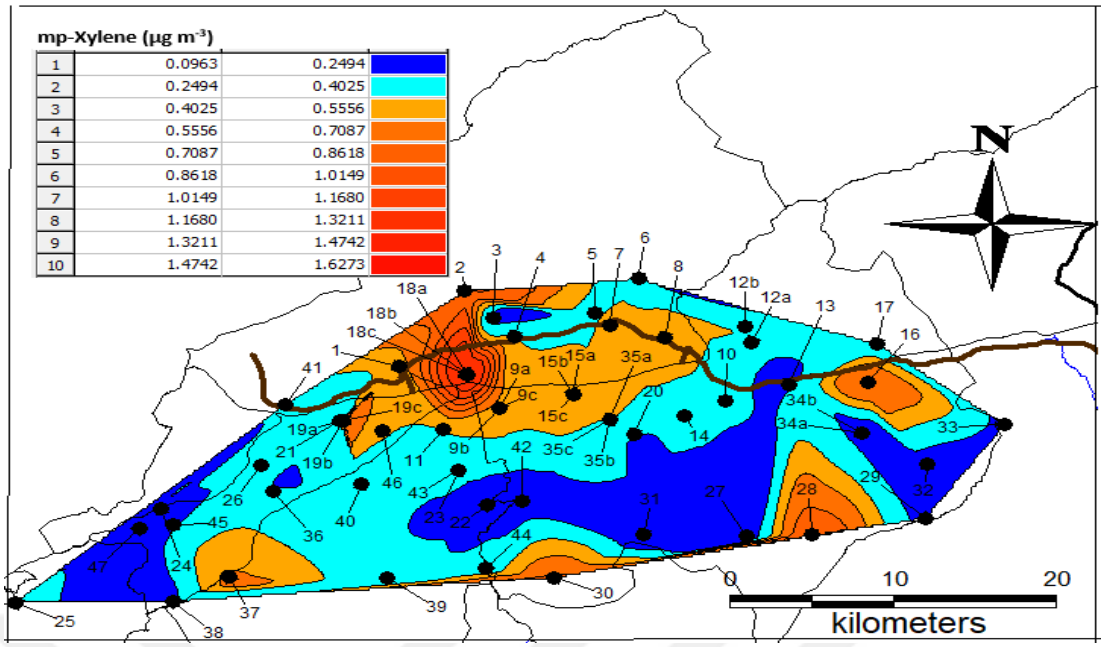


Figure 5.11. m+p-Xylene pollution map in winter season

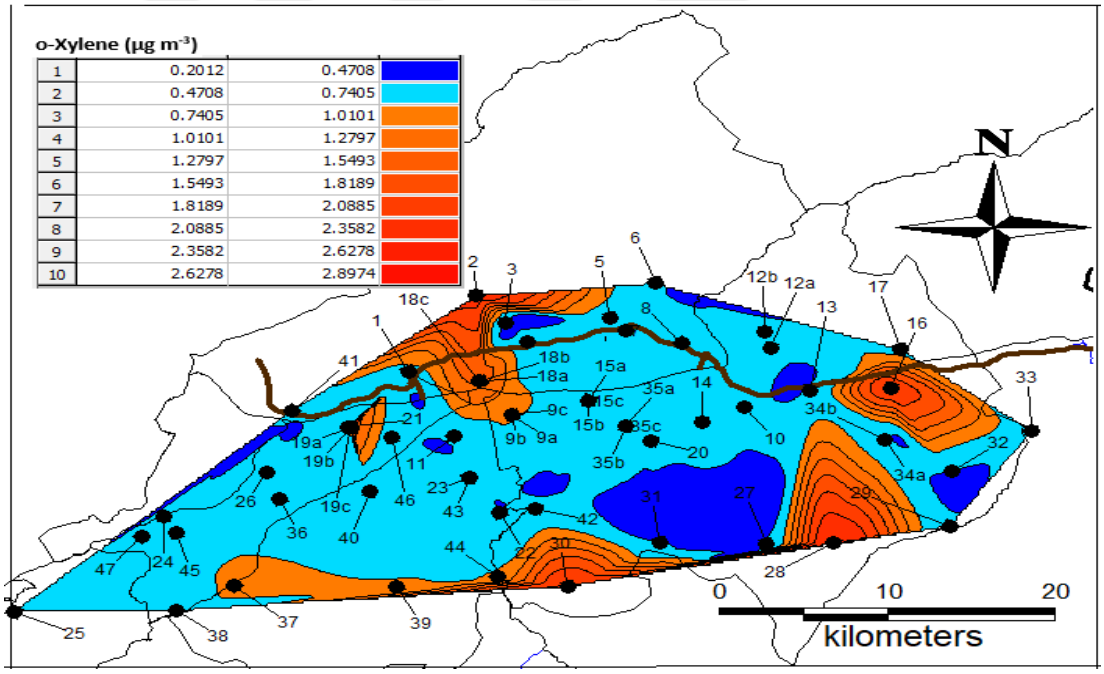


Figure 5.12. o-Xylene pollution map in winter season

In summer season, the spatial distribution maps of BTEXs are shown in Figures 5.13, 5.15, 5.16, 5.17, 5.18. Xylene, ethylbenzene, toluene which are sources of traffic emissions showed a similar tendency and high concentrations were found around the city center and the TEM and D-100 highways points: (7, 4, 1, 41, 26:Bolu Mountain).

It was seen that benzene had a high concentration in the point of number 18 (city center).

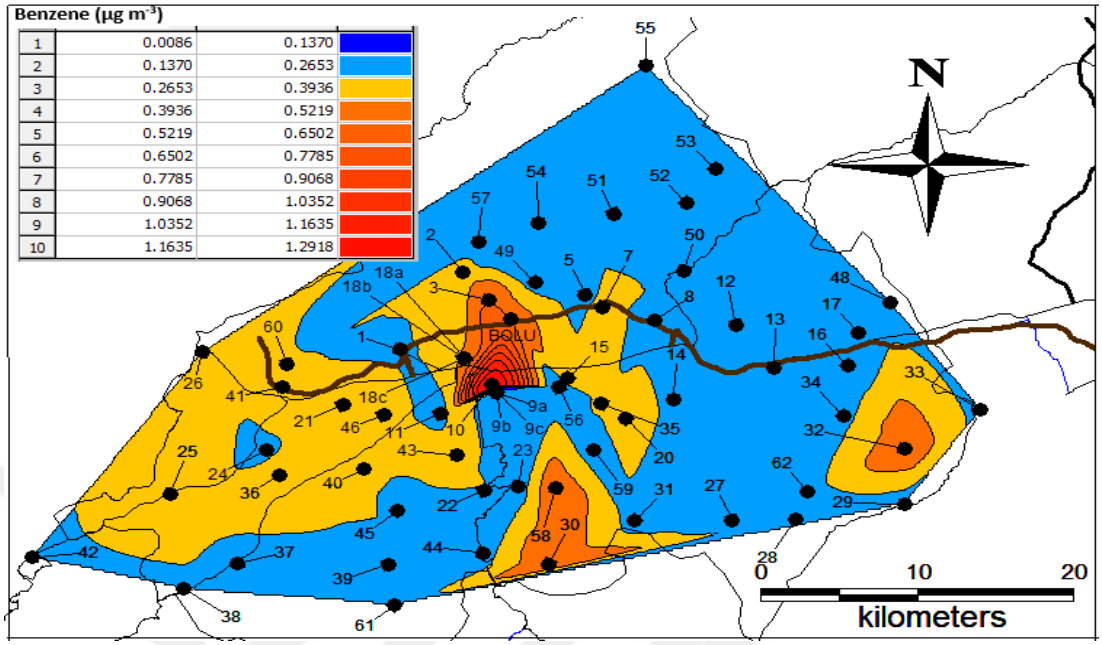


Figure 5.13. Benzene pollution map in summer season

The concentration of BTEXs were observed to be low in summer season. BTEXs are one of the ozon precursors. So, BTEXs concentrations decreased while ozon was formed. Since ozon was formed more in summer season in the presence of sunlight, VOCs and other ozon precursor like NO_2. The Box and Whisker plot of summer-winter concentrations of BTEXs is shown in Figure 5.14. BTEXs concentrations were higher in winter season than in summer season. Box plot shows maximum, 75th percentile, median 25th percentile and minimum concentrations (µg m^{-3}). The upper and lower bars show the maximum and minimum values. The lower and upper horizontal lines of the box demonstrate first and third quartile values. Horizontal lines inside the boxes show median values, and then circle and star indicate the outliers. Because source is only traffic emissions in summer but domesting heating source is also added to traffic emissions in winter. In addition, pollutants were trapped in the atmosphere due to low mixing height in winter.

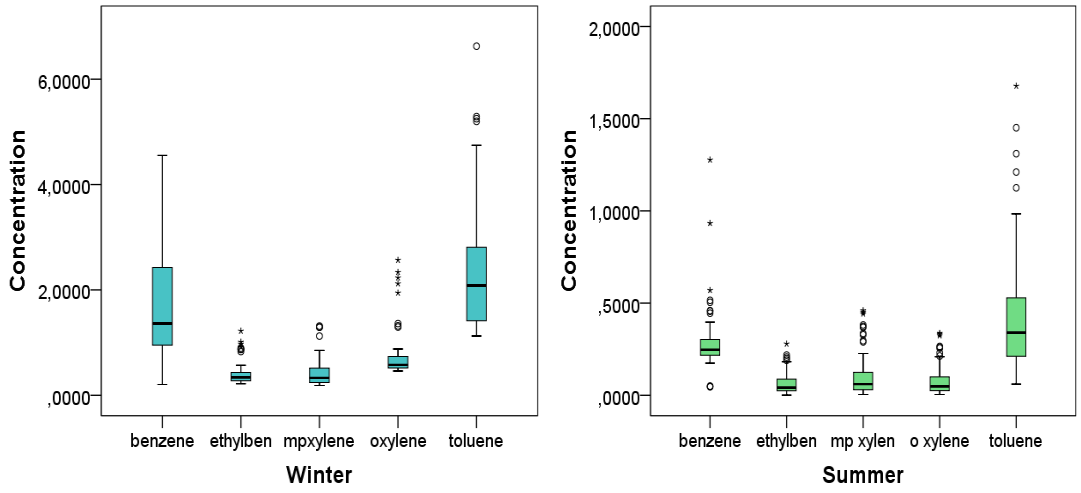


Figure 5.14. Plots of BTEXs concentrations in summer and in winter periods

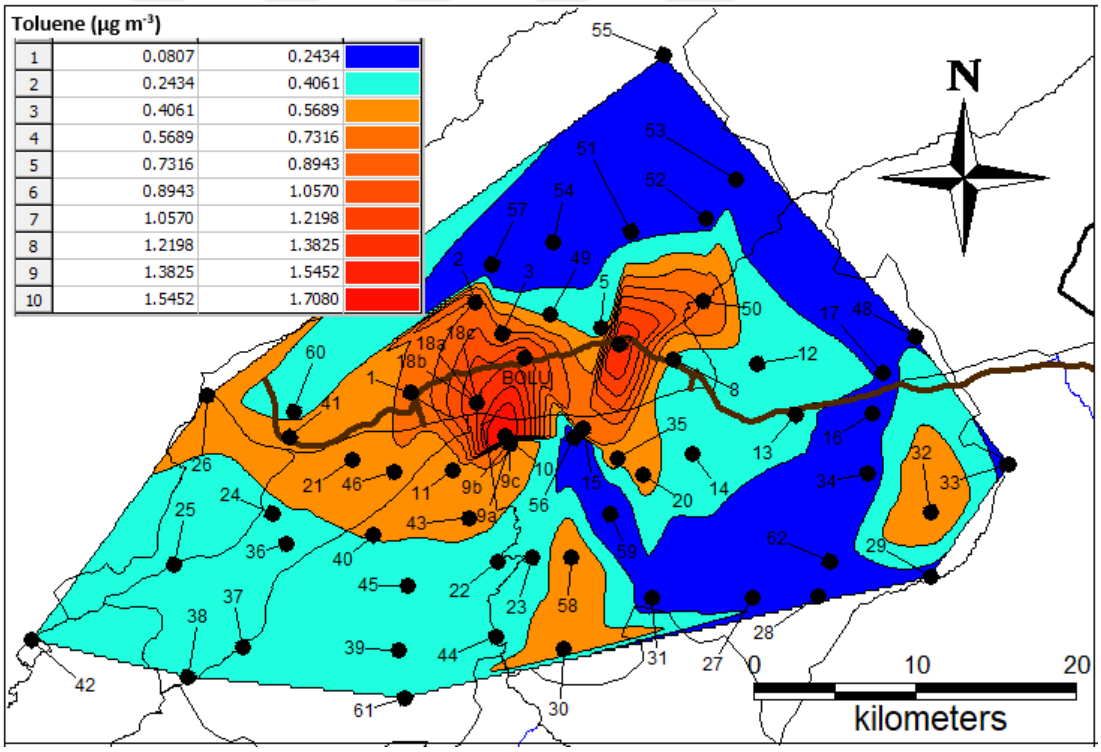


Figure 5.15. Toluene pollution map in summer season

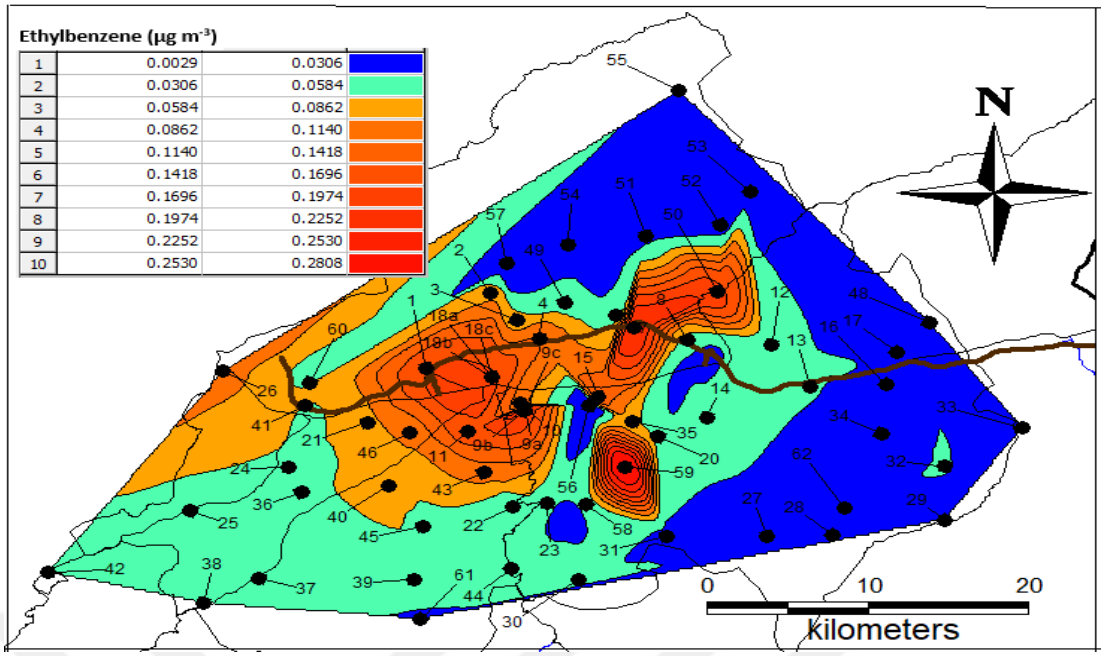


Figure 5.16. Ethylbenzene pollution map in summer season

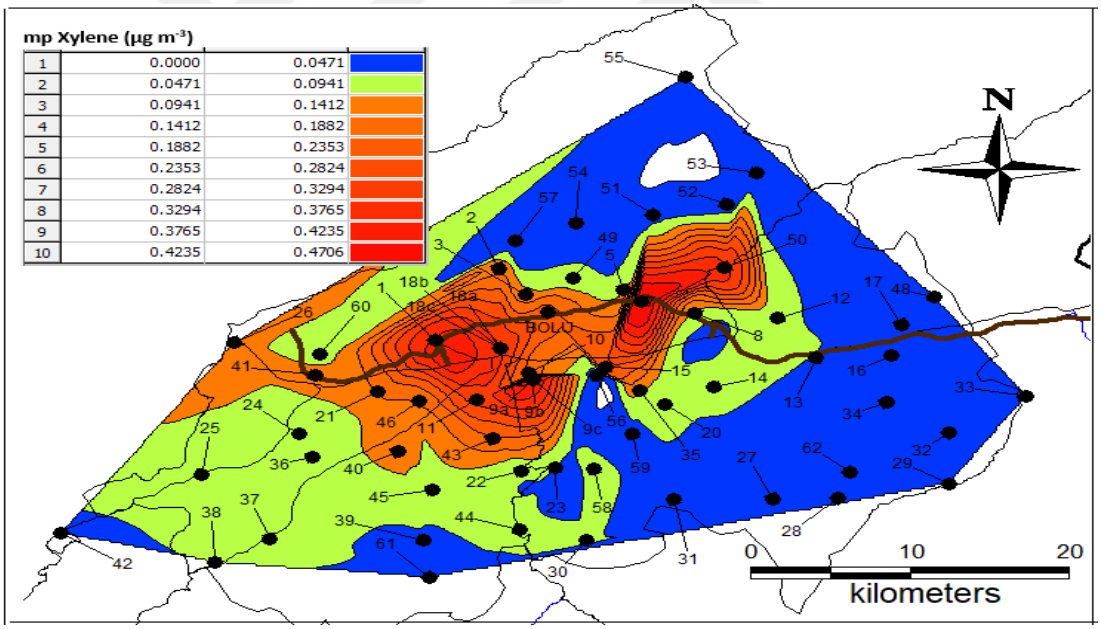


Figure 5.17. m+p-Xylene pollution map in summer season

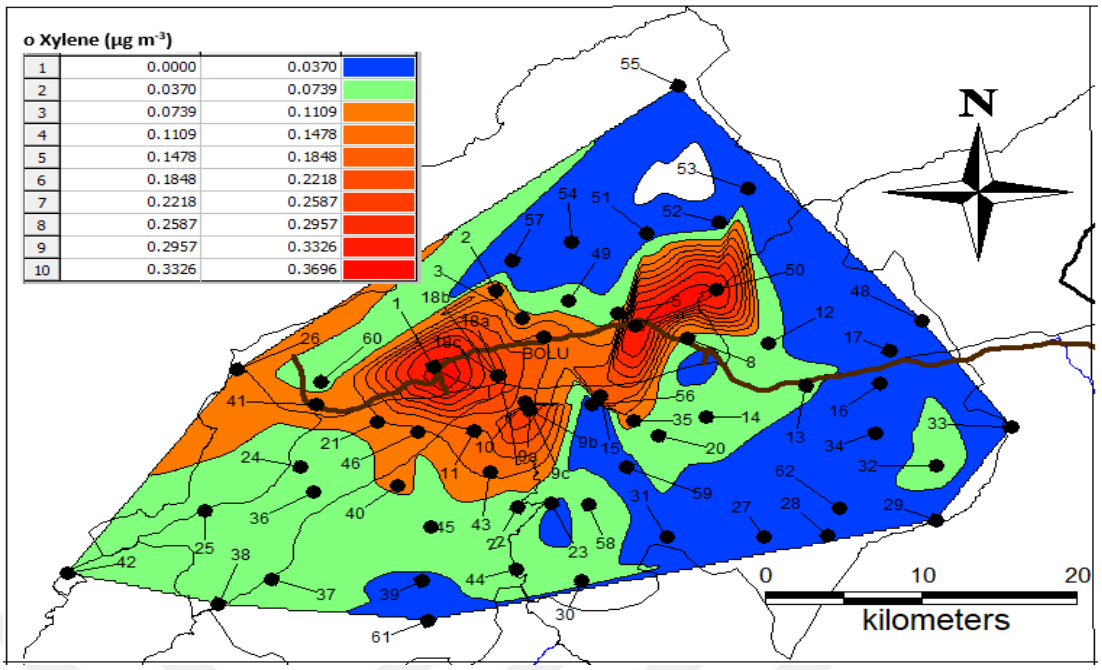


Figure 5.18. o-Xylene pollution map in summer season

5.2 Comparison of NO_2, SO_2 and O_3 data

5.2.1 Comparison of passive sampling data (NO_2, SO_2 and O_3) with active sampling data at BAIBU Campus

At the station shown in Figure 48 in the BAIBU Gölköy campus, real-time monitoring was done with O_3, NO_x and SO_2 analyzers. Regular data was obtained from three devices (Environnement AC31M NO_x, Environnement AF22M SO_2, Environnement 42M O_3) shown in Figure 5.19.

Figure 5.19. Outer view of active sampling station

Figure 5.20. Interior view of active sampling station-analyzers.

Passive and active sampling results and their ratios are given in Table 5.5.

Table 5.5. Passive and active sampling results and their ratios at BAIBU campus (N=5)

	WINTER			SUMMER		
ppb	**Passive**	**Active**	**Passive/Active**	**Passive**	**Active**	**Passive/Active**
NO_2	12.6	12.7	0.98	7.36	8.01	0.92
SO_2	6.10	9.91	0.62	0.91	1.54	0.59
O_3	39.9	22.3	1.79	17.4	29.9	0.58

When the results were examined, passive samplers show similar trends with automatic gas measurements in the stationary station seasonally for NO_2 and SO_2. However, there was a difference between passive and active sampling results of O_3 in winter and summer periods. Passive sampling O_3 results in summer period were lower than the results in winter period. Ozone might be consumed photochemically during 15 days sampling period.

5.3 Correlations and evaluations of gas phase pollutants (NO_2, SO_2 and O_3) with each other

There is a significant relationship between tropospheric O_3 concentrations and NO_2 concentrations. Ozone is formed as a result of the photolysis of NO_2. Relationship between concentrations of NO_2, SO_2 and O_3 at 47 different sampling point in winter are shown in Figure 5.21. It was seen that there was a negative correlation between O_3 and NO_2.

When the relationship between SO_2 and NO_2 components were examined, it was seen that there was a similar trends between these two components. The most important source of SO_2 in the atmosphere is the processes based on coal consumption. It was also seen that these two gas phase pollutants were combustion-originated as a result of the domestic heating.

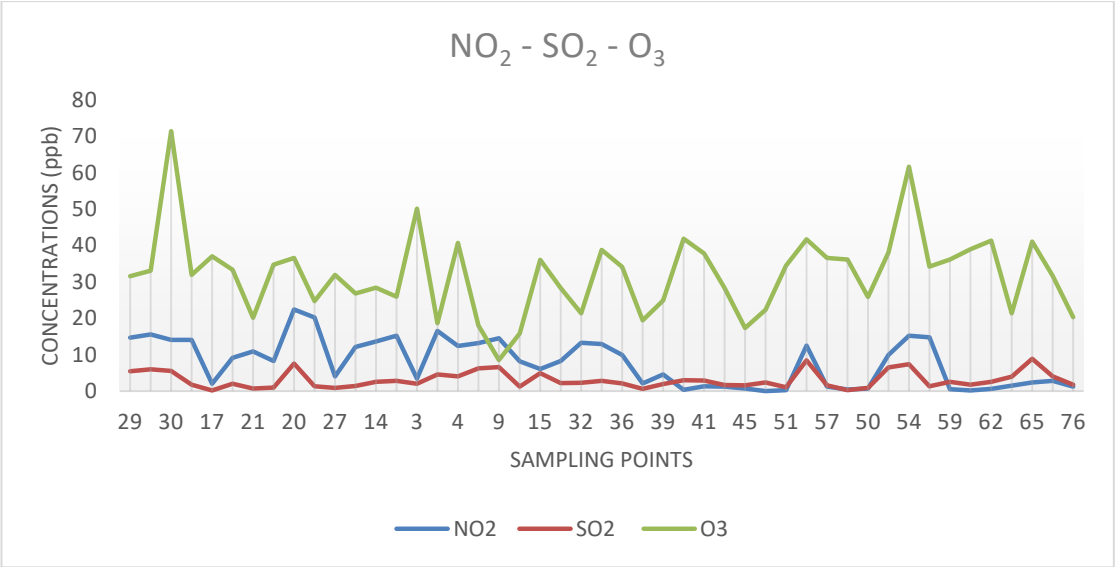


Figure 5.21. Point relationships of NO_2 - SO_2 - O_3 in winter

Correlation constants of the inorganic gaseous pollutants are given in Table 5.6. In winter season, NO_2 and SO_2 had a moderate correlation (0.421). They were emitted from common sources such as coal combustion and traffic emission. Ozone and NO_2 had a weak positive correlation. In summer season, as shown in Figure 5.22, ıt was seen a weak correlation among inorganic gaseous pollutants. Ozone was correlated negatively with NO_2 as it was expected due to photochemical reaction between them.

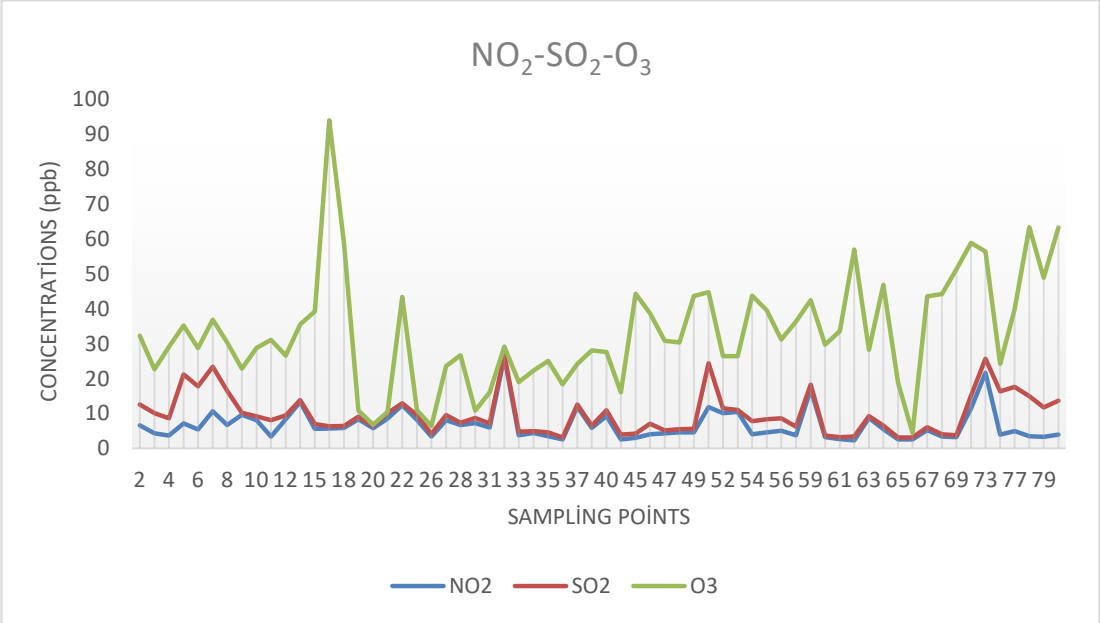


Figure 5.22. Point relationships of NO_2 - SO_2 - O_3 in summer

Table 5.6. Pearson correlation matrix of NO_2, SO_2 and O_3 in winter and in summer season ($p<0.05$)

		NO_2	SO_2	O_3
WINTER	NO_2	1		
	SO_2	0.421	1	
	O_3	0.014	0.284	1
SUMMER	NO_2	1		
	SO_2	-0.04	1	
	O_3	-0.21	-0.01	1

5.4 Diagnostic Ratios (T/B)

The ratio of some VOC concentrations with each other are able to give information about the sources in the atmosphere. The ratio commonly used in the atmosphere is toluene / benzene (T/B) ratio. Toluene and benzene can be released into the atmosphere from different sources (Masih et al., 2016; Hoque at al., 2008). The most important atmospheric sources of toluene are vehicle emissions, industrial activities and sources showing properties of evaporation (Lan and Binh, 2012; Hoque at al., 2008; Ho et al., 2004). The most important atmospheric source of benzene is vehicle emissions (Lan and Binh, 2012; Kumar et al., 2018; Hoque at al., 2008). It is also known that emissions originating from domestic heating are also important sources for benzene (Lan and Binh, 2012; Masih et al., 2016; Ho et al., 2004). The seasonal toluene to benzene concentration ratios (T / B) obtained at each sampling point were calculated and drawn in maps as winter and summer in Figures 5.23 and 5.24.

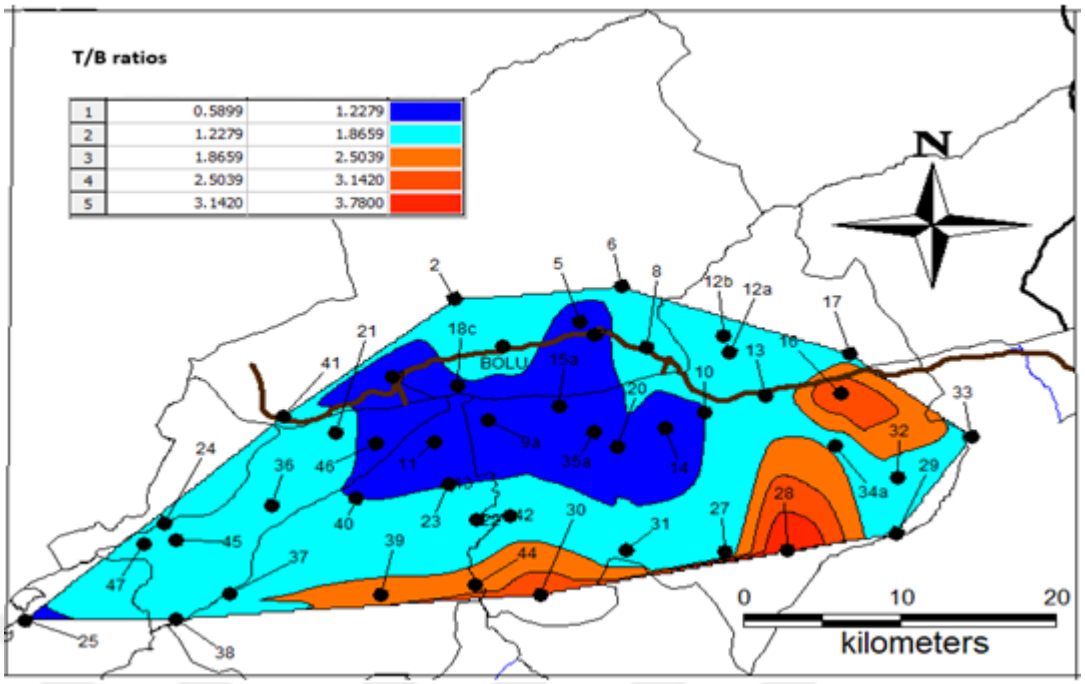


Figure 5.23. Toluene to benzene concentration ratios (T / B) in winter season

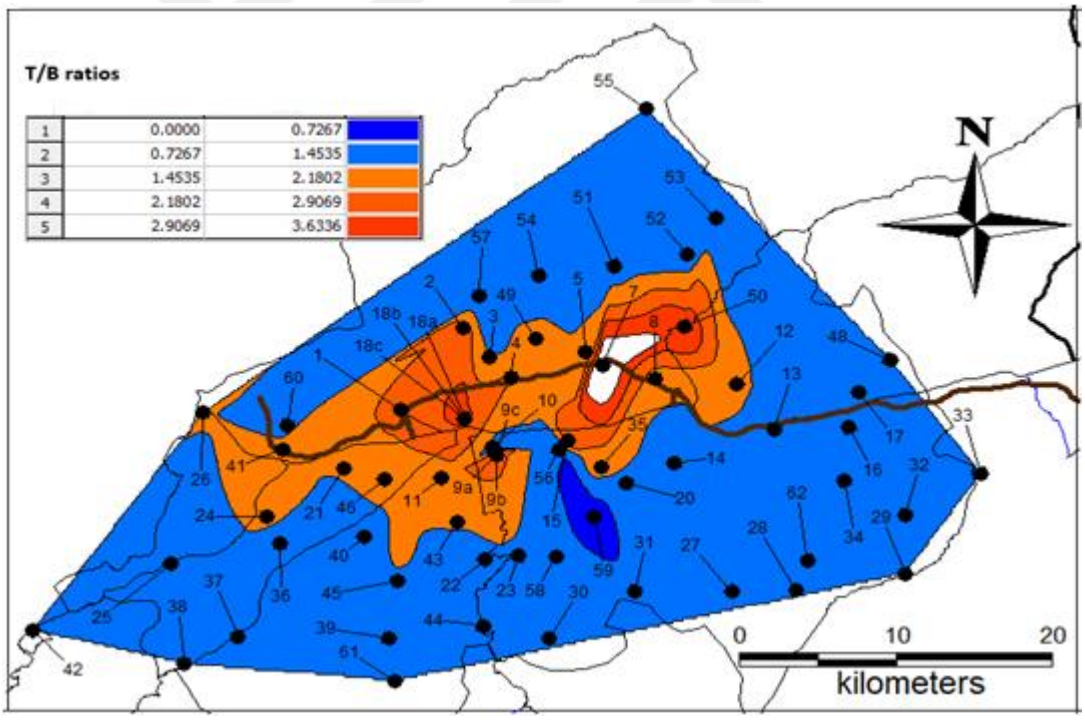


Figure 5.24. Toluene to benzene concentration ratios (T / B) in summer season

The T / B ratio is used as a marker of traffic-related emissions in general (Hsieh et al., 2011; Masih et al., 2016). Benzene and toluene compounds are found in gasoline used in motor vehicles. Toluene content in gasoline is 3-4 times more than benzene content (Pekey and Yilmaz, 2011). In winter season, in populated areas and areas

where traffic is intense (16, 9c, 39, 44, 30, 28, 19a, 19c), the T / B ratio was usually around 2-3. Similarly, in summer season, in the region with heavy traffic and in the city center (1, 2, 4, 7, 9a, 9b, 9c, 15, 18a ,50, 18b, 18c), the T / B ratio was usually around 2-5.

When the ratios of toluene to benzene were examined, it was observed that the points which have a greater than 2 T/B ratios found in summer season more than in winter season. Average values of T/B ratios in summer season were less than in the winter season. The average T / B ratio in winter was found to be 1.56 and the average T / B ratio in summer was also found to be 1.48. The calculated mean T / B ratios for both seasons were lower than the rates calculated in other studies in the literature (Bravo et al., 2002; Ho et al., 2004; Miller et al., 2012). The difference of (T/B) ratio among these is due to differences in vehicle types, fuel composition, and industrial activities (Masih et al., 2016).

A value approaching in the range of 1.5-4.3 for T/B ratio indicates the traffic originated emission sources (Niu et al., 2012; Kumar et al., 2017). Our T/B ratios have observed in this range. And also, T/B ratio can be used as an indicator for age of air mass having fresh air mass values between 3 and 5 decreasing values for the older air mass (de Blas et al., 2016; Navazo et al., 2008). Our T/B ratios showed that air mass were old.

5.5 Ozone formation potential (OFP)

In the assessment of ozone formation potential of various VOC compounds, the calculation of Maximum Incremental Reactivities (MIR) is popular in general. Carter's MIR is the amount (in grams) of ozone formed per gram of VOC added to an initial VOC-NO_x mixture specifying how much a compound may contribute to the ozone formation in the air mass (Carter, 1994). Ozone formation potential of BTEXs species in winter and summer period are given in Table 5.10. Depending on the MIR scale, toluene has the most dominant contributor to ozone formation among BTEX in the regions of villages, roadside and in the city center both in summer and winter season. Xylenes (m-/p-xylene plus o-xylene) are the second largest contributor to ozone formation. These phonemena has been shown the similarities with the

observation of Na et al. (2005) at Soeul and Grosjean et al. (1998) at Porte Alegre. It was observed that xylenes and toluene were the highest in these studies. In summer and in winter season, toluene had the greatest capacity in ozon formation at the city center followed by villages and roadside. Ozone formation potential of benzene is the minimum although it is the most hazardous species among BTEXs. Besides the reactivity of VOCs, the photochemical formation is also influenced by NOx concentrations, solar intensity and meteorological factors. MIR is considered as a good indicator in order to compare OFP of individual VOC.

Table 5.7. Ozone formation potential of BTEXs species

			WINTER		**SUMMER**	
	VOC	MIR Coefficient[a]	Mean values (μg m^{-3})	OFP[b]	Mean values (μg m^{-3})	OFP[b]
	B	0.69	2.00	1.38	0.31	0.21
Villages	T	3.88	2.44	9.48	0.51	1.96
	E	2.93	0.40	1.18	0.07	0.19
	X	7.5	0.56	4.22	0.10	0.77
	B	0.69	1.58	1.09	0.26	0.18
Roadside	T	3.88	2.21	8.58	0.35	1.37
	E	2.93	0.39	1.15	0.07	0.19
	X	7.5	0.56	4.23	0.09	0.64
	B	0.69	4.53	3.13	0.42	0.29
City Center	T	3.88	5.25	20.4	1.22	4.71
	E	2.93	0.89	2.60	0.17	0.51
	X	7.5	1.31	9.84	0.28	2.12

[a] MIR : Maximum Incremental Reactivity (Source: Carter,2009)

[b] OFP : Ozon Formation Potential (VOC x MIR)

5.6 Correlation of BTEXs Compounds

5.6.1 Correlation of BTEXs with each other

Correlations between compounds provide information about transport mechanism of the pollutants to the receptor sites and their sources. Strong correlations between compounds indicate that they generate with the same way and/or came from same source region (Hoque et al., 2008). There is a specific relationships between BTEXs components. Relationships among concentrations of BTEXs at 47 different sampling point are shown in Figure 5.25. There was a strong relationship among BTEXs.

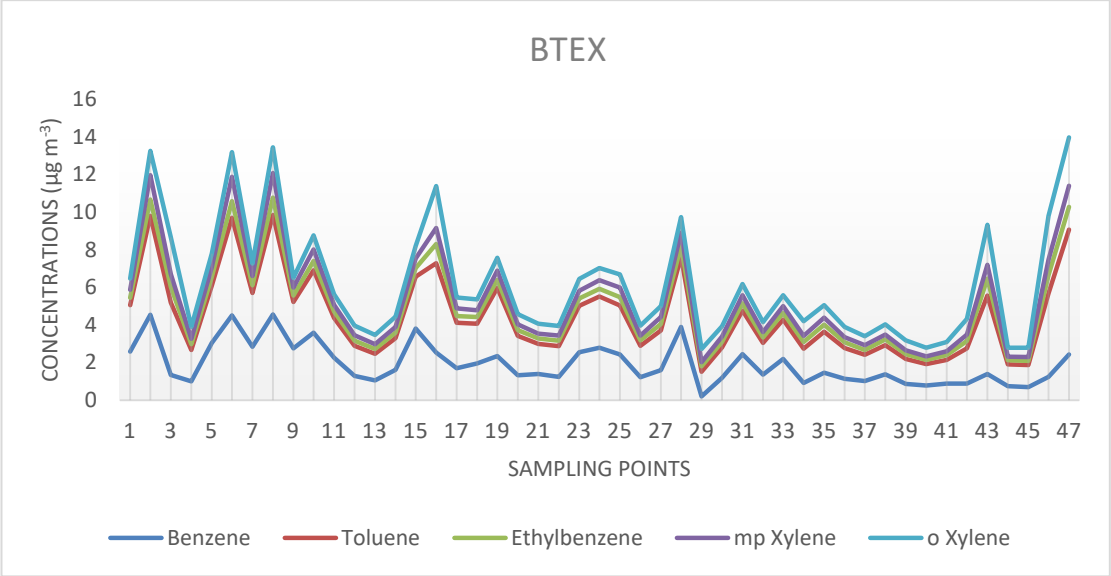


Figure 5.25. Point relationships of BTEXs in winter

Correlations constants among BTEXs are given in Table 5.8 in winter season. As it was expected, It was observed a strong correlation among BTEXs. They generally related with traffic emissions. Benzene showed correlation with toluene (0.75). Toluene also indicated a strong correlation with mp-xylene (0.70) and o-xylene (0.75). Besides, strong correlations were seen among ethylbenzene and mp-xylene (0.86), o-xylene (0.84). And also, mp- xylene and o-xylene had high correlation. High correlation of BTEXs components with each other can be explained by having common sources such as emissions resulting from traffic. Similar correlations were seen in summer season given in Table 5.9.

Table 5.8. Pearson correlation constants of BTEXs in winter season (p<0.5)

WINTER					
BTEX	Benzene	Toluene	Ethylbenzene	mp-Xylene	o-Xylene
Benzene	1				
Toluene	0.73	1			
Ethylbenzene	0.57	0.95	1		
mp-Xylene	0.78	0.96	0.92	1	
o-Xylene	0.30	0.82	0.95	0.75	1

Table 5.9. Pearson correlation constants of BTEXs in summer season (p<0.5)

SUMMER					
BTEX	Benzene	Toluene	Ethylbenzene	mp-Xylene	o-Xylene
Benzene	1				
Toluene	0.75	1			
Ethylbenzene	0.22	0.61	1		
mp-Xylene	0.23	0.70	0.86	1	
o-Xylene	0.29	0.75	0.84	0.97	1

5.6.2 Correlation of BTEX with NO_2, SO_2 and O_3

Ozone can be transported from the stratosphere to the troposphere by diffusion and also it can be produced in the presence of sunlight in the troposphere volatile organic compounds (biogenic and anthropogenic) and nitrogen oxides ($NO + NO_2 = NO_x$) result of photochemical reactions (Roelofs and Lelieveld, 1997). The statistical relationship between BTEX and ozone and NO_2 was examined to investigate the contribution of volatile organic compounds to ozone formation.

The correlation constants of BTEXs with NO_2, SO_2 and O_3 in winter period were not statistically significant but as given as in Table 5.10.

Table 5.10. Pearson correlation constants of BTEXs with NO_2, SO_2 and O_3 in winter ($p<0.5$)

WINTER								
BTEX	Benzene	Toluene	Ethylbenzene	mp-Xylene	o-Xylene	NO_2	SO_2	O_3
Benzene	1							
Toluene	0.73	1						
Ethylbenzene	0.57	0.95	1					
mp-Xylene	0.78	0.96	0.92	1				
o-Xylene	0.30	0.82	0.95	0.75	1			
NO_2	0.24	0.11	0.04	0.11	-0.03	1		
SO_2	-0.11	-0.02	0.00	-0.04	0.05	0.42	1	
O_3	-0.07	-0.03	0.06	0.02	0.11	0.01	0.28	1

The statistically significant correlations between BTEXs and O_3 were obtained in summer period given as in Table 5.11.

Table 5.11. Pearson correlation constants of BTEX with NO_2, SO_2 and O_3 in summer ($p<0.5$)

SUMMER								
BTEX	Benzene	Toluene	Ethylbenzene	mp-Xylene	o-Xylene	NO_2	SO_2	O_3
Benzene	1							
Toluene	0.75	1						
Ethylbenzene	0.22	0.61	1					
mp-Xylene	0.23	0.70	0.86	1				
o-Xylene	0.29	0.75	0.84	0.97	1			
NO_2	0.06	0.07	0.12	0.04	0.05	1		
SO_2	0.03	0.07	0.17	0.03	0.04	-0.04	1	
O_3	-0.14	-0.23	-0.15	-0.17	-0.18	-0.21	-0.01	1

It is thought that the negative correlations between BTEX and O_3 are seen as a result of the consumption of BTEXs in the O_3 formation mechanism. VOC oxidation starts with OH radicals found in the troposphere in O_3 formation mechanism (Figure 5.26).

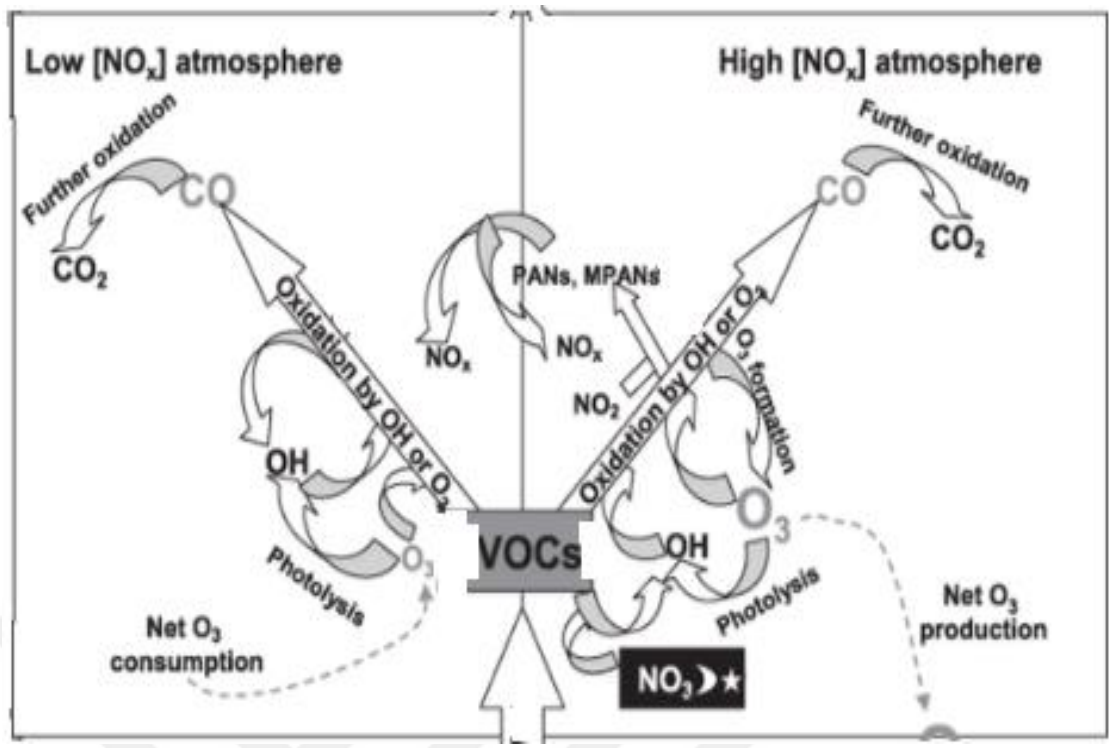


Figure 5.26. VOC, NO_x and ozone interaction mechanism in troposphere (Fuentes et al., 2000; Laothawornkitkul et al., 2009)

When the spatial relationship between O_3 and BTEXs are evaluated by analyzing with the distribution maps, it had been seen that lower ozon concantrations were observed close to the city center which had high BTEXs concentrations. This trend is also observed in other studies, and it is explained by the consumption of ozon as a result of the rapid reaction between O_3 and NO in the regions that the emission occured in the presence of low NO_x concentrations (Melkonyan and Kuttler, 2012; Hagenbjörk et al., 2017).

5.7 Health risk assessment of BTEXs

The risk assessment is related to chronic exposure to chemicals that may cause cancer or other toxic effects rather than on acute toxicity owing to sudden exposure to chemicals. The inhalation exposure estimate is generally obtained from the point of a chronic, daily "air intake" (mg kg^{-1} day^{-1}). The USEPA advises some values for some parameters such as average body weight and amount of air breathed per day for adults and children (U.S. EPA, 2009) to be used in risk calculations. Inhalation rate was taken as 20 m^3 day^{-1} and average body weight was 70 kg for the adults, and inhalation rate

was taken as 15.1 m^3 day^{-1} and average body weight was 39 kg for the children (EPA, 2019). In our study, exposure time (ET) was taken as 24 h day^{-1}, exposure frequency (EF) is 365 days $year^{-1}$ because there is 365 days in a year, exposure duration (ED) is 70 because of average lifetime of people and averaging time (AT) is 25550 days because there is 25550 days in 70 years.

LCR values were calculated for adults, children and different outdoor environments such as in villages, on roadside and in the city center. The lifetime cancer risk (LCR) was calculated for benzene due to its higher carginogenic properties in three different regions and two seasons for adults and children. LCR value for benzene in villages was 0.00013 which was greater than the value of 0.0001. So, this risk was definite risk because it is greater than 0.0001. On roadside, LCR value was 0.00001 which was in the interval of 0.0001 and 0.00001. So, that risk was probable risk because it was in interval of 0.0001 and 0.00001. In the city center, LCR value was 0.0003 which was greater than the value of 0.0001. So, it is definite risk. LCR values for each compound and each sampling regions (villages, roadside and city center) are given in Table 5.12. For children, LCR values for benzene in the region of villages and the city center were 0.0001 and 0.0002, respectively which were greater than the value of 0.0001. Thus these risks were accepted as definite risk. LCR value on roadside was 1.4×10^{-5}. That risk was probable risk because it was in the interval of 0.0001 and 0.00001.

In summer period, LCR value for benzene in villages was 0.00002 which was in the interval of 0.0001 and 0.00001. So, that risk was probable risk. On roadside, LCR value was 0.00002 which was in the interval of 0.0001 and 0.00001. So, that risk was also probable risk. In the city center, LCR value was 0.000028 which was in the interval of 0.0001 and 0.00001. So, that risk was again probable. It was observed that at all three sampling sites, the life time cancer risk for benzene did not exceed the threshold value of 1×10^{-4} indicating that there was no cancer risk for benzene. LCR values for each compound and each sampling regions (villages, roadside and city center) in winter and summer periods are given in Table 5.12 and in Table 5.13. For children, LCR values for benzene in the region of villages, on roadside and the city center were 2.7×10^{-5}, 2.0×10^{-5} an 3.8×10^{-6}, respectively. The first two values were in the interval of 0.0001 and 0.00001 and the last one is the acceptable risk because

the value was smaller than the 1 x 10^{-5}. So, these risks were probable risks. It was observed that at all three sampling sites, the lifetime cancer risk for benzene did not exceed the threshold value of 1 x 10^{-4} indicating that there was no cancer risk for benzene.

Table 5.12. Lifetime cancer risk values for benzene in winter season

WINTER			**CA (mg m^{-3})**	**IR (m^3 day^{-1})**	**ET (hours day^{-1})**	**EF (days $year^{-1}$)**	**ED (years)**	**BW (kg)**	**AT (days)**	**CDI (mg kg^{-1} day^{-1})**	**Potency factor**	**LCR**
Villages	Adults	Benzene	0.002	20	8	365	70	70	25550	0.0015	0.029	0.00013
	Children	Benzene	0.002	15.1	8	365	70	39	25550	0.0021	0.029	0.0002
Roadside	Adults	Benzene	0.002	20	8	365	70	70	25550	0.0012	0.029	1.0E-05
	Children	Benzene	0.002	15.1	8	365	70	39	25550	0.0016	0.029	1.5E-05
City center	Adults	Benzene	0.005	20	8	365	70	70	25550	0.0035	0.029	0.0003
	Children	Benzene	0.005	15.1	8	365	70	39	25550	0.0047	0.029	0.0001

Table 5.13. Lifetime cancer risk values for benzene in summer season

SUMMER			CA (mg m^{-3})	IR (m^3 day^{-1})	ET (hours day^{-1})	EF (days $year^{-1}$)	ED (years)	BW (kg)	AT (days)	CDI (mg kg^{-1} day^{-1})	Potency factor	LCR
Villages	Adults	Benzene	0.0003	20	8	365	70	70	25550	0.0002	0.029	2.0E-05
	Children	Benzene	0.0003	15.1	8	365	70	39	25550	0.0003	0.029	2.7E-05
Roadside	Adults	Benzene	0.00026	20	8	365	70	70	25550	0.0002	0.029	2.0E-05
	Children	Benzene	0.00026	15.1	8	365	70	39	25550	0.0003	0.029	2.0E-05
City center	Adults	Benzene	0.0004	20	8	365	70	70	25550	0.0003	0.029	2.8E-05
	Children	Benzene	0.0004	15.1	8	365	70	39	25550	0.0004	0.029	3.8E-06

5.7.1 Monte Carlo simulation

In order to calculate the health risk, probabilistic approach was used. This method relies on data accumulated from the selected population. The commercially available software package Crystal Ball Risk-analysis software application 11.1 was used for this purpose. The variability of the parameters throughout the calculation of the risk are distributed in the Crystal Ball software (Schuhmacher et al., 2001).

The Monte Carlo simulation calculates the risk several thousand times by drawing parameter values randomly from the distribution function of the input variables (Thompson et al., 1992). The final result was obtained as distribution of the risk with corresponding probabilities. Finally, the distributions can be plotted and various statistical features of the results were generated to help the interpretation of data. 10 000 iterations were used in this study.

5.7.2 Probabilistic exposure assessment

Probabilistic approaches can characterize variability in risk as they use different points on each input distribution for exposure. The probabilistic assessment was conducted using Monte Carlo analysis to describe by a probability distribution instead of a point estimate. The result was obtained as distribution of the risk with corresponding probabilities. The mean, median, standard deviation of distribution, minimum and maximum value are presented in Table 5.14 in order to analyze the results. The results of the simulation are illustrated in Figure 5.27 for benzene exposure as an example. The best fitting distributions for other compounds were determined to be used as an input probability distribution for cancer and hazard ratio calculation.

Table 5.14 Descriptive statistics for probabilistic exposure (μg day^{-1} kg^{-1}) for all points

	Mean	Median	Std. Dev.	Min.	Max.
Benzene	0.29	0.16	0.46	0.01	7.12
Toluene	0.08	0.04	0.14	0.00	3.51
Ethylbenzene	0.43	0.23	0.76	0.01	26.33
mp Xylene	0.08	0.04	0.14	0.00	3.86
o Xylene	0.12	0.04	0.29	0.01	7.12

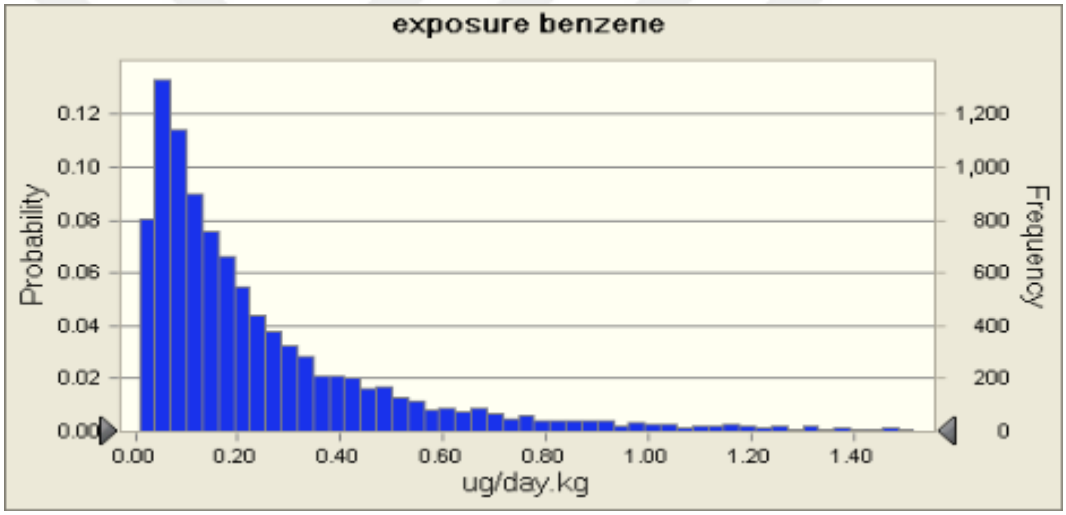


Figure 5. 27 Probability distribution of benzene exposure

5.8 Carcinogenic risk

5.8.1 Probabilistic estimation of cancer risk

The cancer risk was calculated ten thousands iterations by drawing a value of the parameter randomly from the distribution function. Final result obtained from Monte Carlo simulation was distribution of the risk with corresponding probabilities. Mean, median, standard deviation, minimum and maximum values were extracted from the model and presented in Table 5.15.

Table 5.15. Descriptive statistics for probabilistic carcinogenic risk assessment

Compound	Mean	Median	Std. Dev.	Min.	Max.
Benzene	4.41×10^{-6}	2.47×10^{-6}	6.54×10^{-6}	1.22×10^{-7}	1.07×10^{-4}

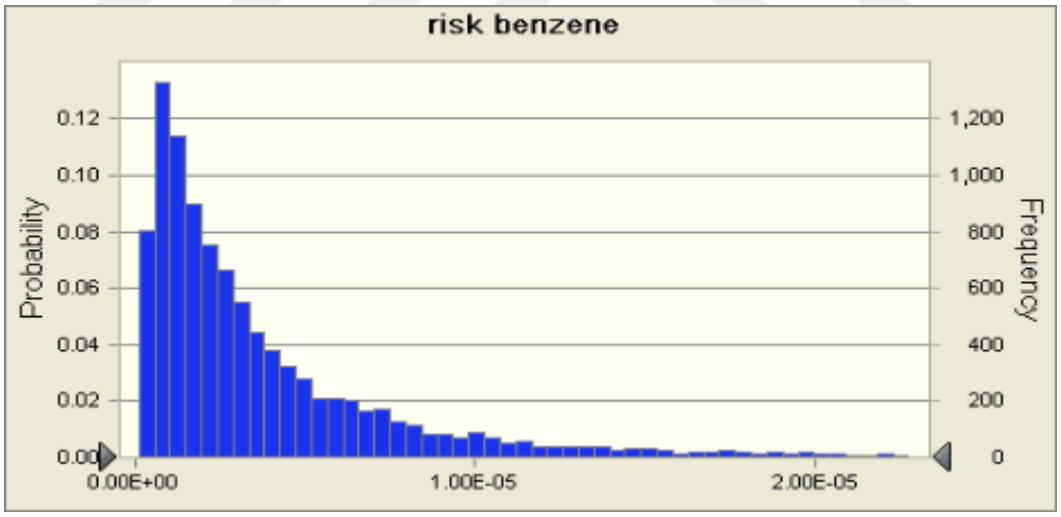


Figure 5.28. Carcinogenic benzene risk obtained from Monte Carlo simulation ($x10^{-6}$)

Figure 5.28 demonstrates the probability distribution graphs obtained from Monte Carlo simulation. The probability distributions achieved from the probabilistic approach were similar to those plotted for exposure plot given previously in Figure 5.27. Cancer risk is extrapolated by multiplying the slope factor for each compound by exposure; thus both cancer risk and exposure probability distribution graphs fit the same distribution.

These results have shown that all the statistical parameters demonstrated the cancer risk for benzene compound did not exceed the definite risk level ($1x10^{-4}$) according to USEPA (2009). Lifetime cancer risk and regional evaluation demonstrated that industrial activities and vehicles emissions were not intense in Bolu.

5.9 Noncarcinogenic risk

5.9.1 Probabilistic estimation of HQ

The probabilistic estimation of hazard ratios (HQ) for BTEXs were evaluated with Monte Carlo simulation. For non-carcinogenic assessment Monte Carlo simulation results were much more less than 1.

The results also showed that the concentration of the BTEXs compound was within the acceptable level because the hazard ratio was much more less than one. These results showed similarities with calculated hazard ratios (HQ). None of the BTEXs compounds exceeded the thresold value of 1.

For non-carcinogenic compounds, non-cancer hazard ratios (HR) for adults and children and each outdoor sampling region were also calculated by using HR formula in two seasons. HR ratio was also calculated for benzene which is carcinogenic compound. In winter season, HR values were determined for benzene, toluene, ethylbenzene and xylene as 0.07, 0.0005, 0.0004 and 0.006, respectively in the village region. In this region, non-carcinogenic risk values were within the safety limits. These risks were accepted as negligible because they were smaller than 1. HR values were determined for benzene, toluene, ethylbenzene and xylene as 0.05, 0.0004, 0.0004 and 0.005, respectively on the roadside region. In this region, non-carcinogenic risk values were safe again. These risks were negligible because they were smaller than 1. In city the center, HR values were determined for benzene, toluene, ethylbenzene and xylene as 0.15, 0.01, 0.0009 and 0.02, respectively. HR values for winter and summer seasons are given respectively in Table 5.16 and in Table 5.17.

Table 5.16. HR values in winter season

	WINTER								
	VILLAGES			ROADSIDE			CITY CENTER		
	Ci (µg m^{-3})	**RfC[a] (µg m^{-3})**	**HR**	**Ci (µg m^{-3})**	**RfC[a] (µg m^{-3})**	**HR**	**Ci (µg m^{-3})**	**RfC[a] (µg m^{-3})**	**HR**
Benzene	2.00	30	0.0665	1.58	30	0.0526	4.53	30	0.1511
Toluene	2.44	5000	0.0005	2.21	5000	0.0004	5.25	5000	0.0010
Ethylbenzene	0.40	1000	0.0004	0.39	1000	0.0004	0.89	1000	0.0009
mp-Xylene	0.41	100	0.0041	0.39	100	0.0039	3.55	100	0.0355
o-Xylene	0.71	100	0.0071	0.74	100	0.0074	1.32	100	0.0132

[a] **IRIS** The Integrated Risk Information System

Table 5.17. HR values in summer season

	SUMMER								
	VILLAGES			ROADSIDE			CITY CENTER		
	Ci (µg m^{-3})	**RfC[a] (µg m^{-3})**	**HR**	**Ci (µg m^{-3})**	**RfC[a] (µg m^{-3})**	**HR**	**Ci (µg m^{-3})**	**RfC[a] (µg m^{-3})**	**HR**
Benzene	0.31	30	0.0102	0.26	30	0.00879	0.42	30	0.0141
Toluene	0.51	5000	0.0001	0.35	5000	0.00007	1.22	5000	0.0002
Ethylbenzene	0.07	1000	0.0001	0.07	1000	0.00007	0.17	1000	0.0002
mp-Xylene	0.11	100	0.0011	0.10	100	0.00099	0.33	100	0.0033
o-Xylene	0.09	100	0.0009	0.07	100	0.00073	0.23	100	0.0023

[a] **IRIS** The Integrated Risk Information System

6. CONCLUSIONS AND RECOMMENDATIONS

In this study, the concentrations of inorganic gaseous pollutants SO_2, NO_2, and O_3 were determined by passive samplers which were developed and produced by Eskişehir Technical University Environmental Engineering Department (Air Pollution Research Group). The concentrations of BTEXs which are members of VOCs were determined by using Tenax passive samplers. The sampling was performed in urban, semi-urban and rural sites and carried out in two seasons namely in winter season and in summer season. The total area (1500 m^2) in the Bolu platau was divided into 5 km x 5 km grids.

Pollution maps were drawn in order to examine the spatial distribution of NO_2, SO_2, O_3 inorganic gaseous pollutants and BTEXs. Besides, seasonal evaluations and health risk assessments were also performed.

In winter season, Ozone levels were high in rural areas and forest side and low in TEM and D-100 roads. The reason for this is that ozone reacts with traffic pollutants such as NO in the roadside and central regions, and the quantity decreases. Highest concentrations of ozone were determined in the forest side and rural areas as 61.6 ppb and 71.5 ppb. It is revealed that ozon is a secondary air pollutants formed as a result of the photochemical reactions between NOx and VOCs in the presence of sunlight.

In summer season, it has been observed that the ozone values were high in the areas far from the city center, forest side and the region with high altitude and they were found to be low around the TEM and D-100 routes. Ozone amounts decreases with reacting NO. The highest concentration of ozone was also determined in the forest side as 91.8. Lowest concentrations of ozone were also determined around TEM and D-100 roads as 0.35 ppb, 0.42 ppb, 1.40 ppb and 2.22 ppb. 1.40 and 2.22 values belong to the areas of AIBU Campus. Ozon values were found to be low because of the heavy traffic from university service vehicles. In forests and rural areas, the biogenic volatile organic compounds released from trees were reacting with NO_x in the presence of sunlight cause to ozon formation. This is thought to be a significant contributor to the high ozone concentration measured in forest areas.

In winter season, it has been observed that the NO_2 values were high in the city center and close to TEM and D-100 roads. Significant declines were seen in remote mountainous areas and the areas which are far from the traffic. This can be explained by the fact that this pollutant is traffic-originated.

In summer season, it was seen that NO_2 concentrations were high in the city center and in the heavy traffic areas and found to be low in high altitude and less traffic areas. The highest NO_2 concentrations were detected in places close to roads and the city center as the value of 26.2 ppb and 12.6 ppb, respectively. The lowest concentration of NO_2 were found in high altitude region (Yedigöller) with the value of 2.56 ppb. It is revealed that there was a negative correlation between O_3 and NO_2 due to the reaction between NO and O_3. The summer concentrations of NO_2 were higher than the winter concentrations of NO_2.

In winter season, it was detected that SO_2 concentrations were low in the city center because of usage of natural gas and in the mountainous areas because there were few settlements in here. However, it was found to be high in the villages (especially in summer season) because coal has been still in usage for domestic heating.

In summer season, it was seen that SO_2 values were high in the villages especially in this season because of the usage of coal as a domestic heating at high altitude areas where even in summer season the temperature is low enough so that residential heating is necessary. The values SO_2 concentrations in summer were higher than the values of winter. Because the plateau settlement starts in summer season and due to low temperature in these areas, people use coal for residential heating.

In winter season, according to the their pollution maps, It was observed that common sources have been found to be effective for BTEXs components. In addition to this point, high BTEX concentrations have been obtained in the highly-populated settlements, and close to highways such as TEM and D100. The point near to Kartalkaya ski resort area had high BTEXs concentrations due to the contribution from vehicle emissions.

In summer season, the concentrations of toluene, ethylbenzene and xylene compounds were found to be high around the city center and around TEM Highway and Bolu Mountain. It was observed that benzene had also high concentrations around the point of the city center. Moreover, as it was expected, unlike the winter period, the lower concentrations were found in the summer season in Kartalkaya region.

When BTEXs values were compared seasonally, the lowest concentrations of BTEXs were found in summer season and the highest concentrations were found in winter season. Our study results were consistent with some of the literature values.

The Statgraphics version 15.2 statistical software was used in the detection of pearson correlation matrix in order to find the pollutant sources. Significant positive correlations between BTEX concentrations were found in summer and in winter seasons. The observed correlations between BTEX compounds demonstrated that the emission sources of these compounds couldd be probably similar.

It was seen that there was a weak correlation between O_3 and SO_2. While SO_2 is occuring as a result of the combustion events, O_3 is formed by the consequence of photochemical reactions in the atmosphere and ozon is a secondary air pollutant. NO_2 correlated moderately pozitively with SO_2. There was a negative correlation between O_3 and NO_2 compounds.

Carcinogenic and non-carcinogenic air pollutants levels were determined using the exposure calculations of health risk assessment. Health risk assessment study results demonstrated that cancer risk levels for benzene calculated for the people living in the villages, roadside and city center were found higher than USEPA acceptable risk value (1×10^{-6}). Although Bolu is a small city which has limited industrial activities, it can be said that pollutant concentrations affect people health especially in winter time. On the other hand, hazard ratios of non-cancer risk for each compound of BTEXs and each sampling region (villages, roadside and city center) were lower than 1 which indicated that risk was negligible.

In order to calculate the health risk, probabilistic approach was used. This method relies on data accumulated from the selected population. The second step of the study, VOC concentrations generated in the field measurement campaigns and the data accumulated from the questionnaire were extrapolated to the entire population using Monte Carlo simulation. The cancer risk was calculated ten thousands each time by drawing a value of the parameter randomly from the distribution function. These results demonstrate the cancer risk for benzene compound did not exceed the definite risk level ($1x10^{-4}$) according to USEPA (2009) calculation with the mean cancer risk $1x10^{-4}$. These results indicated that the Bolu was not the carginogenic city.

The study could be expanded by the increasing the number of VOC components. Then the sources of the pollutants can be investigated with respect to technique like factor analysis. The study can be repeated many times in a year in order to calculate ozone exposure to the vegetation and forest (such as AOT40 calculation). The study can be repeated within two-three years in order to compare the pollution loadings in the city.

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APPENDICES

8. APPENDICES

Appendix A.1

Table A.1 Details of the passive sampling points in Winter

Sample No	Sample Location	Coordinates	Height	Sample No	Sample Location	Coordinates	Height
1	Ağaççılar Village	N 40 45 05.02 E 31 33 28.0	862 m	21	Gölköy Campus at AİBÜ	N 40 42 51.7 E 031 30 55	872 m
2	Kozlu Village	N 40 48 05.2 E 31 36 17	1228 m	26	Bolu Mountain	N 40 44 58.6 E 031 24 32.1	1018 m
3	Fasıl Facility	N 40 47 01.4 E 31 37 30.08	989 m	24	Abant Way	N 40 41 03.3 E 031 27 25.7	941 m
4	Yeniköy	N 40 46 14.8 E 31 38 29.5	844 m	25	Abant Gökdere	N 40 39 20.1 E 031 23 04.7	915 m
5	Yakabayat Village (chicken coop)	N 40 47 13.6 E 31 41 50.8	891 m	42	Abant Lake Mudurnu Hill	N 40 35 32 E 031 16 45.3	1411 m
6	Banaz Village	N 40 48 35.7 E 31 43 51.6	926 m	41	Tokat-ı Hayrettin Way (close to D-100 and TEM)	N 40 43 31.2 E 31 28 30	1447 m

Table A.1 Continued

7	Bahçeköy	N 40 46 41.8 E 31 42 36.5	747 m	46	Near the Gölköy	N 40 42 27.6 E 031 32 45.3	1414 m
8	Aliçören Village	N 40 46 11.2 E 31 45 00.8	719 m	39	Sebebardı Way	40 36 32.6 K 031 32 56.8 D	1450 m
12a	Sazakşeyhler Village	N 40 46 02.0 E 31 48 42.7	816 m	40	Akkayalar Facility	N 40 40 19.6 E 031 31 49.8	1432 m
12b	Karamanlar Village-Sazakşeyhler	40 46 39.5 K 31 48 29.2 D	776 m	43	Hıdırşeyhler Village	N 40 40 53.1 E 031 36 02.1	1438 m
13	Baltalı Village (close to E5)	N 40 44 19.5 E 31 50 25	908 m		Blank Hıdırşeyhler Village	N 40 40 53.1 E 031 36 02.1	1438 m
10	Close to Bürrük (sand quarry)	N 40 43 39.2 E 31 47 39.0	870 m		Blank Hıdırşeyhler Village	N 40 40 53.1 E 031 36 02.1	1438 m
11	Çayırköy	N 40 42 29.5 E 31 35 20.4	718 m	22	Gölcük Way	N 40 39 28.2 E 031 37 15.5	1504 m
9a	The road of Narven	N 40 43 22.9 E 31 37 48.4	713 m	23	Close to Gölcük	N 40 39 38.1 E 031 38 47.6	1290 m

Table A.1 Continued

9b	The road of Narven	N 40 43 22.9 E 31 37 48.4	713 m	45	Sebanardı Way	N 40 38 40.4 E 031 33 22.1	1459 m
9c	The road of Narven	N 40 43 22.9 E 31 37 48.4	713 m	44	Between Gölcük and Sebenardı	N 40 36 56.7 E 031 37 13.1	1302 m
35a	Gökpınar	40 42 54.8 K 31 42 36.1 D	767 m	30	Close to Göksu Naturel Park	N 40 36 31.3 E 031 40 10.7	1353 m
35b	Gökpınar	40 42 54.8 K 31 42 36.1 D	767 m		Blank Yellow field	N 40 38 16.0 E 031 44 02.6	1411 m
35c	Gökpınar	40 42 54.8 K 31 42 36.1 D	767 m	31	Yellow field	N 40 38 16.0 E 031 44 02.6	1411 m
16	The way of Kuzörendağlı Village	40 44 24.4 K 31 53 48.5 D	1171 m		Blank Yellow field	N 40 38 16.0 E 031 44 02.6	1411 m
17	Ericek Village	40 45 57.8 K 31 54 14.4 D	1046 m	50	Kartalkaya Way	N 40 38 14.5 E 031 48 31.7	1482 m
18a	Environment and Urbanism Ministry	N 40 44 44.2 E 31 36 23.7	744 m	27	Kartalkaya Way	N 40 38 17.7 E 031 51 23.7	1489 m
18b	Environment and Urbanism Ministry	N 40 44 44.2 E 31 36 23.7	744 m	28	Continue to Kartalkaya Way	N 40 38 55.8 E 031 56 20.2	1271 m

Table A.1 Continued

18c	Environment and Urbanism Ministry	N 40 44 44.2 E 31 36 23.7	744 m	33	Çalköy	N 40 42 42.6 E 031 59 46.6	1299 m
15a	Yenigeçitveren	40 43 53.6 K 31 41 02.2 D	730 m	32	Aydıncık	N 40 41 06.3 E 031 56 22.8	1417 m
15b	Yenigeçitveren	40 43 53.6 K 31 41 02.2 D	730 m	34a	Continue to Aydıncık way	N 40 42 23.4 E 031 53 34.4	1555 m
15c	Yenigeçitveren	40 43 53.6 K 31 41 02.2 D	730 m	34b	Continue to Aydıncık way	N 40 42 23.4 E 031 53 34.4	1555 m
20	Çaygökpınar	40 42 19.1 K 31 43 41.4 D	838 m	47	Dereceneören Way	N 40 38 32.6 E 031 22 12.7	1945 m
14	Kartalkaya Way	40 43 02.6 K 31 45 50.5 D	1058 m	36	Piroğluna Way	N 40 40 02.0 E 031 28 00.0	1548 m
	Sumer Street	40 42 52.0 K 31 31 02.4 D	864 m		Blank Belkaraağaç Village	N 40 36 35.7 E 031 26 05.2	1563 m
	Sumer Street	40 42 52.0 K 31 31 02.4 D	864 m	38	Over the Belkaraağaç Village	N 40 35 34.5 E 031 23 38.4	1575 m
19a	Gölköy Campus at AIBU	N 40 42 51.8 E 031 31 02.2	874 m		Blank roof of rectory building	N 40 42 51.8 E 031 31 02.2	874 m

Table A.1. Continued

19b	Gölköy Campus at AIBU	N 40 42 51.8 E 031 31 02.2	874 m		Blank roof of rectory building	N 40 42 51.8 E 031 31 02.2	874 m
19c	Gölköy Campus at AIBU	N 40 42 51.8 E 031 31 02.2	874 m		Blank roof of rectory building	N 40 42 51.8 E 031 31 02.2	874 m

Appendix A.2

Table A.2 Details of the passive sampling points in summer season

Sample No	Sample Location	Coordinates	Height	Sample No	Sample Location	Coordinates	Height
1	Ağaççılar Village	N 40 45 05.02 E 31 33 28.0	862 m	51	Yeşilçele	N 40 45 25.0 E 31 43 09	1099 m
2	Kozlu Village	N 40 48 05.2 E 31 36 17	1228 m	52	Between the way of Bağışlar and Merkeşler	N 40 50 52.6 E 31 46 26.4	937 m
3	Fasıl Facility	N 40 47 01.4 E 31 37 30.08	989 m	53	Merkeşler Village	N 40 52 11.2 E 31 47 45.7	1000 m
4	Yeniköy	N 40 46 14.8 E 31 38 29.5	844 m		Blank Mengen Way	N 40 48 08.6 E 31 46 20.9	682 m
5	Yakabayat Village (chicken coop)	N 40 47 13.6 E 31 41 50.8	891 m	20	Çayköypınar	N 40 42 19.1 E 31 43 41.4	838 m

Table A.2. Continued

6	Banaz Village	N 40 48 35.7 E 31 43 51.6	796 m	35	Gökpınar	N 40 42 54.8 E 31 42 36.1	767 m
7	Bahçeköy	N 40 46 41.8 E 31 42 36.5	747 m	54	Yedigöller Way	N 40 50 03.6 E 31 39 43.9	1157 m
8	Aliçören Village	N 40 46 11.2 E 31 45 00.8	719 m	55	Yedigöller	N 40 46 13.5 E 31 44 36.4	869 m
9a	The road of Narven	N 40 43 22.9 E 31 37 48.4	713 m		Blank Yeniköy	N 40 46 14.8 E 31 38 29.5	844 m
9b	The road of Narven	N 40 43 22.9 E 31 37 48.4	713 m	56	Yedigöller Way	N 40 53 19. E 31 40 40.5	1664 m
9c	The road of Narven	N 40 43 22.9 E 31 37 48.4	713 m	57	Yukarı Soku Highland	N 40 49 18.8 E 31 37 01.7	1635 m
10	Close to Bürrük (sand quarry)	N 40 43 39.2 E 31 47 39.0	870 m	**22**	Going up the Gölcük	N 40 39 26.9 E 31 37 17	1774 m
11	Çayırköy	N 40 42 29.5 E 31 35 20.4	718 m	23	Gölcük fountain	N 40 39 37.1 E 31 38 48.6	2012 m
12	Sazakşeyhler Village	N 40 46 02.0 E 31 48 42.7	816 m	48	Gölcük	N 40 39 34.6 E 31 40 30.5	2237 m
58	Ericek Village	N 40 46 55.0 E 31 55 41.7	1184 m	59	Continue to Gölcük way	N 40 41 2.9 E 31 42 13.6	2237 m
13	Baltalı Village (close to E5)	N 40 44 19.5 E 31 50 25	908 m	26	Bolu Mountain	N 40 44 58.5 E 31 24 32.2	935 m
49	Hamzabey	N 40 47 41.3 E 31 39 35.5	1084 m	41	Highway	N 40 43 34 E 31 28 10.1	887 m
14	Going up to Kartalkaya	N 40 43 02.6 E 31 45 50.5	1058 m	21	AIBU Campus	N 40 42 51.7 E 31 30 55	844 m
15	Yenigeçitveren	N 40 43 53.6 E 31 41 02.2	730 m	62	Continue to Highway of upper way	N 40 44 26.5 E 31 28 19.1	1049 m
16	Kuzörendağlı Village	N 40 44 24.4 E 31 53 48.5	1171 m	25	Kartal Yuvası	N 40 39 20.1 E 31 23 4.7	916 m

Table A.2. Continued

17	Ericek Village	N 40 45 43.8 E 31 54 13.7	1046 m	42	Cottage entrance of Abant	N 40 36 49.8 E 31 16 48.9	1218 m
18a	Ministry of Environment and Urbanization	N 40 44 44.2 E 31 36 23.7	744 m	47	Way back of Abant	N 40 38 32.2 E 31 22 12.2	1140 m
18b	Ministry of Environment and Urbanization	N 40 44 44.2 E 31 36 23.7	744 m	24	Abant Way	N 40 41 3.1 E 31 27 25.3	866 m
18c	Ministry of Environment and Urbanization	N 40 44 44.2 E 31 36 23.7	744 m	36	Yenisefa Piroğlu lowland	N 40 40 3.2 E 31 27 59.9	1032 m
19a	roof of rectory building	N 40 42 51.8 E 31 31 2.2	897 m	37	Mudurnu Way	N 40 36 35.7 E 31 26 5.2	1097 m
19b	roof of rectory building	N 40 42 51.8 E 31 31 2.2	897 m	38	Continue to Mudurnu Way	N 40 35 36 E 31 23 38.5	1097m
19c	roof of rectory building	N 40 42 51.8 E 31 31 2.2	897 m	40	Opposite to pond	N 40 42 20.2 E 31 31 48.9	837 m
19d	roof of rectory building	N 40 42 51.8 E 31 31 2.2	897 m	46	Opposite to Emsan	N 40 42 27.4 E 31 32 45.7	678 m
19e	roof of rectory building	N 40 42 51.8 E 31 31 2.2	897 m	43	Son mekan fountain	N 40 40 53.2 E 31 32 45.7	770 m
31	Mengen Way	N 40 48 08.6 E 31 46 20.9	682 m		Blank Son mekan fountain	N 40 40 53.2 E 31 32 45.7	780 m
	Blank Son mekan fountain	N 40 40 53.2 E 31 32 45.7	780 m	27	Kartalkaya Way	N 40 38 15.8 E 31 48 32.2	1524 m
45	Sarmaşıklı Ağaç	N 40 38 40.3 E 31 33 22.3	971 m	28	Calışkan alabalık	N 40 38 17.9 E 31 51 23.8	1476 m
39	Entrance of çeşmi forest	N 40 36 30.4 E 31 32 57.2	1404 m	62	Calışkan alabalık	N 40 39 26.7 E 31 51 57.5	1563 m

Table A.2. Continued

61	Sebenardı Village	N 40 34 55 E 31 33 13.9	1446 m	29	Barrage way	N 40 38 56 E 31 56 20.1	1320 m
44	Gölcük Fountain	N 40 36 57.2 E 31 37 13.8	1617 m	33	Aydıncık way	N 49 42 40.5 E 31 59 46	1330 m
72	Aladağ scout camp	N 40 36 32.4 E 31 40 10.9	1422 m	32	Continue to Aydıncık way	N 40 41 6.4 E 31 56 21.7	1410 m
30	Sarıalan signboard	N 40 38 15.6 E 31 44 5.4	1422 m	34	Continue to Aydıncık way	N 40 42 23.8 E 31 53 34.8	1571 m

Appendix B.1

Table B.1. Toluene to benzene concentration ratios (T / B) in winter season

Sampling Points	T/B ratios	Sampling Points	T/B ratios	Sampling Points	T/B ratios
1	0.96	21	1.57	40	1.54
2	1.16	22	1.15	41	1.47
3	2.88	23	1.34	44	1.41
4	1.68	24	0.96	45	2.13
5	1.00	25	0.98	47	2.99
6	1.16	26	1.08	48	1.56
7	1.01	27	1.37	50	1.71
9	1.16	28	1.31	51	3.61
10	0.90	29	0.96	53	2.73
11	0.92	30	6.35	54	1.84
12	0.94	31	1.37	55	2.04
13	1.23	32	0.95	56	1.62
14	1.36	33	1.23	57	1.79
15	1.04	34	0.95	58	1.65
16	0.73	35	2.00	59	1.64
17	1.87	36	1.50	61	1.65
18	1.43	37	1.45	62	1.44
19	1.08	38	1.38	63	1.76
20	1.55	39	1.14	65	1.38
74	1.34	76	1.58		

Table B.2. Toluene to benzene concentration ratios (T / B) in summer season

Sampling Points	T/B ratios	Sampling Points	T/B ratios	Sampling Points	T/B ratios
1	2.41	31	3.22	54	1.41
2	2.22	32	3.21	55	1.16
3	1.55	33	1.14	56	1.01
4	2.18	34	1.14	58	1.52
5	1.75	35	1.06	59	1.21
7	4.10	36	1.34	60	1.35
8	1.96	37	3.05	61	1.07
9	2.43	38	1.32	62	1.36
10	2.20	40	1.69	63	1.58
11	2.44	41	1.03	64	1.51
12	1.31	42	0.79	65	0.88
13	1.88	43	1.26	66	1.24
14	1.54	44	0.83	67	1.42
15	1.02	45	0.97	68	1.17
16	1.20	46	1.20	69	1.05
17	1.68	47	1.33	71	1.17
18	1.23	48	1.15	72	1.15
19	2.20	49	0.48	73	0.85
20	1.06	51	1.47	74	0.83
21	1.26	52	1.49	75	0.93
22	2.55	53	1.52	76	0.79
77	0.88	78	0.83	79	1.24
80	0.81				

9. CURRICULUM VITAE

Name SURNAME **:** Esra MAĞAT TÜRK

Place and Date of Birth **:** Ankara-Altındağ 19th June 1990

Universities

Bachelor's Degree **:** Bolu Abant İzzet Baysal University

e-mail **:** magat.esra06@gmail.com

Address **:** Saglık Quarter, No:4 /15 Bolu/ Turkey

List of Publications **:** Esra Mağat Türk, Özlem Özden Üzmez, Eftade O. Gaga, Tuncay Döğeroğlu, Serpil Yenisoy Karakaş. "Bolu atmosferindeki NO_2, SO_2 ve O_3 gazlarının alansal dağılımı" ICOCEE CAPPADOCIA 8-10 Mayıs 2017 Nevşehir, Conference E – Book), p3301

Hobbies (Optional) **:** Reading a book, riding a bike, swimming and trekking