SPATIAL AND TEMPORAL DISTRIBUTION OF INORGANIC AND ORGANIC POLLUTANT CONCENTRATIONS AT NORTHWESTERN ANATOLIA

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ABSTRACT

SPATIAL AND TEMPORAL DISTRIBUTION OF INORGANIC AND ORGANIC POLLUTANT CONCENTRATIONS AT NORTHWESTERN ANATOLIA

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Concentrations of inorganic pollutants including NO_2, SO_2, O_3 and organic pollutants including benzene, toluene, ethylbenzene, o-xylene and m&p-xylene, which are known as BTEX compounds were measured on a seasonal basis in 13 cities located in the Central and Northern parts of Anatolian Plateau. Cities included in measurements were Ankara, Bartın, Bolu, Çankırı, Düzce, Eskişehir, Karabük, Kastamonu, Kırıkkale, Kırşehir, Kütahya, Yozgat, and Zonguldak. Sampling was performed in four seasonal campaigns in each city between July 2014 and June 2015 by using passive VOC and inorganic samplers prepared in METU. Sampling and analysis of collected samples were completed. In this work, data generated in the above mentioned campaigns were statistically evaluated to understand how BTEX and conventional inorganic pollutants concentrations are related to demographic conditions at central Anatolian Plateau. Since each pollutant was measured in more than one location in each city, urban averages were established as the first step. How pollutant concentrations vary between residential, traffic-impacted and industrial parts of the cities were evaluated. Variation in concentrations of organic and inorganic pollutants between cities were evaluated related to demographic differences, such as differences in population, traffic intensity. To measure the air pollution in these cities, new station locations and numbers were determined and suggested according to regulation on Air Quality Assessment and Management to protect human health by the ArcGIS software program by using Inverse Distance Weighted (IDW) interpolation method.

Keywords: Organic pollutants, inorganic pollutants, spatial and temporal distribution

ÖZ

ORGANİK VE İNORGANİK KİRLETİCİ KONSANTRASYONLARININ KUZEYBATI ANADOLU’DA MEKANSAL VE ZAMANSAL DAĞILIMI

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Grubumuzca daha önce yapılan bir çalışma çerçevesinde Orta ve Kuzey Anadolu’da yer alan 13 şehirde (Ankara, Bartın, Bolu, Çankırı, Düzce, Eskişehir, Karabük, Kastamonu, Kırıkkale, Kırşehir, Kütahya, Yozgat and Zonguldak) Haziran 2014 – Temmuz 2015 ayları arasında inorganik kirleticiler olan SO_2, NO_2 ve O_3 ile organik kirleticiler olan benzen, toluen, etilbenzen, o-ksilen ve m&p-ksilen konsantrasyonları mevsimlik bazda ölçülmüştür. Bu çalışmada oluşturulan veri setine kentlerin içerisinde ve kentler arasında ölçülen inorganik ve organik kirletici konsantrasyonları açısından farklılıklar olup olmadığı incelendi ve kirletici düzeyler ile demografik koşullar arasındaki ilişki ortaya çıkartıldı. Hava Kalitesi Değerlendirme ve Yönetimi yönetmeliğinde insan sağlığını korumak için gerekli limit değerlerine göre ArcGIS programı ve Ters Ağırlıklı Ortalama yöntemi kullanılarak belirlenen illerde hava kirliliği parametrelerini ölçmek için illerde kurulacak istasyon yerleri ve sayıları önerilmiştir.

Anahtar Kelimeler: Organik kirleticiler, inorganik kirleticiler, mekansal ve zamansal değişim

To my family

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The data of this study was taken from the Air Quality Preliminary Assessment Project (2015) run by Dokay Engineering and Consultancy Ltd. Co. for Ministry of Environment and Urbanization. This project was affiliated to Ankara Clean Air Center in 2014 Investment Program of Ministry of Environment and Urbanization and it was carried out in 13 cities which are Ankara, Bartın, Bolu, Çankırı, Düzce, Eskişehir, Karabük, Kastamonu, Kırklareli, Kırşehir, Kütahya, Yozgat and Zonguldak.

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CHAPTER 1

INTRODUCTION

Using motor vehicles and increased industrial activities in urban environment cause many problems. Air quality is increasingly concerned because of having relation with human health, environment and climate. Sulphur dioxide, nitrogen dioxide, tropospheric ozone and volatile organic compounds are among the most important atmospheric pollutants (WHO, 2005).

Air pollution defined by World Health Organization (WHO) is a mixture of man-made and natural substances in the air that we breathe. It can be considered as indoor and outdoor air pollution. Indoor air pollution includes exposures to carbon oxides, particulates and other pollutants which is carried by indoor dust or air. Sources of indoor air pollution are gases, building materials like asbestos, formaldehyde, lead, household products and chemicals, tobacco smoke, pollen and mold. Outdoor air pollution includes exposures which take place outside of the built environment. Outdoor air pollution sources are noxious gases like nitrogen oxides, sulfur dioxides, carbon monoxide, fine particles resulting from combustion of fossil fuels, for example petroleum and coal used in energy production, manufacturing factories, oil refineries, agricultural and municipal waste sites and incineration, and ground level ozone (WHO, 2019).

United States Environmental Protection Agency (U.S. EPA) defines volatile organic compounds as any compound of carbon, excluding carbon dioxide, carbon monoxide, metallic carbonates, carbonic acid and ammonium carbonate. World Health Organization (WHO) categorized the volatile organic compounds (VOC) as very volatile, volatile and semi-volatile organic compounds. As organic compound becomes more volatile, it will be more emitted from a product into the air. Measuring the very volatile organic compounds is difficult because they are found almost all as gases in the air. There are many volatile organic compounds but, in this study, only benzene, toluene, ethylene and xylene are measured because these compounds have significant health problems for human.

Sulphur dioxide (SO_2), nitrogen dioxide (NO_2) and ozone (O_3) are inorganic air pollutants. Organic and inorganic air pollutants' sources are both natural and anthropogenic. They can affect both human health and environment. Concentrations of air pollutants in sampling sites that are indicative of public exposures should be calculated and necessary precautions should be taken by authorized institutions (WHO, 2005).

1.1. Aim of the Study

The aims of this study are;

- to compare with seasonal variations of measured sulphur dioxide, nitrogen dioxide, ozone, benzene, toluene, ethylbenzene and xylene concentrations by passive sampling in Bartın, Ankara, Bolu, Çankırı, Düzce, Eskişehir, Kırıkkale, Karabük, Kastamonu, Kırşehir, Kütahya, Zonguldak and Yozgat
- to observe variations in these air pollutants between cities
- to compare the results with regulatory requirements
- to determine and suggest site, number and type of the monitoring stations and compare the existing air pollution measurement stations

1.2. Layout of the Study

In Chapter 2, typical features of sulfur dioxide, nitrogen dioxide, ozone, benzene, toluene, ethylbenzene and xylene are briefly explained. Also, information about different sources of emissions, effects on human health and environment of these air pollutants are given. Moreover, national and international regulations on the emission and management of these pollutants are provided.

In Chapter 3, sampling locations are introduced, and sampling time information is given. Then, sampling and analytical methodologies are provided.

In Chapter 4, meteorological parameters that influence the results are given. Descriptive statistics of data which was taken in this study are given. Furthermore, data is compared with previous studies in various cities in Turkey and the world. Temporal variations in air pollutants concentration are provided. Finally, number and location of the stations that will be established are discussed.

In Chapter 5, whole study is elucidated briefly, and suggestions are offered for future studies.

CHAPTER 2

LITERATURE

2.1. Inorganic and Organic Pollutants

One of the most important environmental problem is air pollution. According to United States Environmental Protection Agency, most especially, industrial activities, increasing population and using motor vehicles in urban environment cause to increase in the amount of atmospheric pollutants. In terms of environment and human health, atmospheric pollutant concentration is important. Sulphur dioxide (SO_2), nitrogen dioxide (NO_2) and ozone (O_3) are the most common and significant inorganic air pollutants. SO_2 and NO_2 among these inorganic pollutants are primary pollutants since the main sources of them in the atmosphere are industrial emissions, domestic heating and road traffic. Gaseous sulphur oxide concentrations in the atmosphere is much lower than the SO_2. Therefore, SO_2 indicates the main group of gaseous sulphur oxides. Using sulfur containing fuels like coal for domestic aim in urban areas increases SO_2 concentration in atmosphere. Vehicles and combustion of fossil fuels like coal, fuel oil and natural gas cause increasing concentration of NO_2 (Bozkurt et al., 2018).

On the other hand, since the ozone forms in the atmosphere and is not emitted directly from a source, ozone is a secondary pollutant. Volatile organic compounds react with nitrogen oxides and they form ozone when power plants, cars, refineries, chemical plants, industrial boilers and other chemical sources emissions react with sunlight. Ozone that is at the ground level is detrimental air pollutant because ozone is the large ingredient in smog. On hot sunny days, ozone reaches the unhealthiest levels. Wind is also important factor for ozone transportation long distances. Stratospheric ozone forms in the upper atmosphere naturally. It protects the Earth from the harmful ultraviolet rays of the sun.

U.S. EPA states that volatile organic compounds are emitted as gases from liquids or solids. Volatile organic compounds (VOCs) involve chemicals that may have long and short-term health effects. When fuels, paints, pesticides, organic solvents, varnishes, aerosol sprays, cosmetic products, hobby and degreasing products, cleaning and disinfecting products and wood preservatives are used, organic compounds are released. In this study, only benzene, toluene, ethylene and xylene which are called as BTEX are measured and examined. Benzene, toluene, ethylene and xylene are the most important VOCs because of possibility their high abundance in ambient air and carcinogenic effects. Benzene, toluene, ethylbenzene and xylenes are specified to evaluate air pollution caused by traffic. The traffic emissions are indicated by toluene and benzene ratio. These are part of liquid fuels that are released by vehicles and these are emitted from industrial areas (Bozkurt et al., 2018).

2.2. Emissions of Organic and Inorganic Pollutants

There are different sources for releasing of organic and inorganic pollutants to the atmosphere. These sources can be categorized as biogenic (natural) and anthropogenic sources.

Table 2.1 shows that air pollutants and their sources in terms of natural and anthropogenic sources.

Table 2.1. *Air Pollutants and Their Sources*

Pollutants	Major Sources
Sulphur dioxide (SO_2)	Fossil fuel combustion, natural emission (volcanos, atmospheric oxidation of sulphur compounds emitted from microbial activity)[1]
Nitrogen dioxide (NO_2)	Fossil fuel combustion processes[1]
Ozone (O_3)	Generated from NOx, VOCs, and CO, as well as natural processes (e.g. stratosphere)[1]
Benzene, Toluene, Ethylbenzene, Xylene (BTEX)	Vehicular exhaust, gas stations, industrial activity and combustion for domestic heating[2]

[1] WHO, 2016, [2] Denghani et al., 2018.

2.2.1. Emissions from Natural Sources

VOCs are emitted range from about 1200 to 1600 TgC/yr from both anthropogenic and biogenic sources. Most of the released amount of VOCs is from biogenic sources (Kumar et al., 2018). Natural sources of organic pollutants are freshwater bodies, decomposition of organic material, oceans, sediments and soil and vegetation that is the most important emitter (Zemankova and Brechler, 2010).

According to International Agency for Research on Cancer (IARC, 2016), natural sources of SO_2 include microbial activities in the ocean, decomposition of organic material and volcanoes. Microbial activity in soils is natural source of NO_2 and stratospheric oxidation is natural sources of NO_2 and ozone.

2.2.2. Emissions from Anthropogenic Sources

Derwent (1995) categorized anthropogenic air pollution sources as industrial processes, motor vehicle exhaust, solvent usages, food manufacture, landfilled wastes, agriculture, oil refining, petrol storage and distribution, petrol vapors from motor cars. Industrial processes and motor vehicle exhaust are the two major sources of air pollutants. Motor vehicle exhaust is the dominant source of air pollution especially in areas that include high traffic densities and industrial activities (Odhiambo et al., 2010). As a result of the incomplete combustion of fuels, air pollution grows up. Air pollutant emission increases when the reaction is more incomplete. Vehicle speed, fuel type, motor load and air temperature are the factors that affect the exhaust gas emission (Friedrich and Obermeier, 1999). While emissions from cars which are using gasoline fuel without catalysts are assessed 18.92 g HC/kg fuel and with catalysts 0.68 g HC /kg fuel, emission amount is 1.32 g HC/kg of fuel for diesel engines (Williams and Koppmann, 2007).

Another major contributor for the anthropogenic air pollution source is industrial processes. Globally, organic air pollutant amount produced by industrial processes such as using consumer goods, adhesives, paints is 27 Tg/year (Williams and Koppmann, 2007).

2.3. Effect of Organic and Inorganic Pollutants

2.3.1. Effects of Organic and Inorganic Pollutants on Human Health

Hazardous pollutants contaminated environment is very important issue around the world because this would affect the human health directly or indirectly. Air pollution that is a major public health concern because human can be easily exposed them by breathing and skin. According to World Health Organization (WHO), there are six major air pollutants include particle pollution, carbon monoxide, nitrogen oxides, sulfur oxides, ground-level ozone and lead. Short or long term exposure to air suspended toxicants has different toxicological impact on human including cardiovascular and respiratory diseases, skin diseases, the eyes irritation and long term chronic diseases. Also, air pollution is considered as the major environmental risk factor for some diseases such as lung cancer, asthma, Alzheimer’s and Parkinson’s diseases, autism, fetal growth, retinopathy, low birth weight and some psychological complications (WHO, 2016).

Gaseous pollutants mainly affect the respiratory system but benzene that is a chemical species of VOCs causes cancer and hematological problems (Kampa and Castanas, 2008). According to IARC, benzene, toluene, ethylbenzene and xylenes are classified as group 1 which is carcinogenic to humans (IARC, 2014).

2.3.2. Effects of Organic and Inorganic Pollutants on Environment

Air pollution not only effects the human health but also effects the environment. Ground level ozone and toxic air pollutants can harm wildlife, crops, trees, lakes. Also, aquatic life is affected by those pollutants (U.S. EPA, 2007). Massachusetts Department of Environmental Protection states that acid rain which includes sulphuric and nitric acids, eutrophication because of emission of nitrogen oxides from vehicles, power plants and other sources, haze because of emitted sulphur dioxide and nitrogen oxides are the other environmental effects of organic and inorganic pollutants (Massachusetts Department of Environmental Protection, n.d.). According to Bourguignon (2018), ground level ozone contributes to global warming directly.

2.4. Regulations on Organic and Inorganic Pollutants Emission

In previous sections, effects and sources of SO_2, NO_2, O_3 and BTEX were summarized. Since these air pollutants are emitted from different sources with increasing amounts and their effect on environment and human health is a known reality, there are several regulations to control the emissions of SO_2, NO_2, O_3 and BTEX. In this section, current regulations managing these air pollutants, which are viewed as important for this study, will be summarized.

2.4.1. Turkish Regulations on Organic and Inorganic Pollutants

SO_2, NO_2, O_3 and VOCs are regulated in accordance with the Air Quality Assessment and Management Regulation (AQAMR) (Official Gazette No: 26898, dated 06.06.2008) which entered into force in 2008. This regulation was prepared in parallel with the directives of the European Union. (MoEU, 2008). In Appendix II of the AQAMR, there is a list for advocated VOCs to be determined under ozone precursor measurements. This list involves the thirty VOCs such as toluene, benzene, xylene, ethylbenzene and hydrocarbons not containing total methane. Only benzene has a concentration limit that is 5 $\mu g/m^3$ for annual average amount among these thirty VOCs.

Regulation on Control of Air Pollution Originating from Industry (Official Gazette No: 27277, dated 03.07.2009) which entered into force in 2009 situates air quality limits around petroleum refineries, fuel and petroleum storage facilities and petrochemical industries as short term and long term values. Sulphur dioxide, nitrogen dioxide, benzene, toluene, ethyl benzene and xylene are used for assessment of air quality (MoEU, 2009).

Regulation on Control of Air Pollution Caused by Heating (Official Gazette No: 25699, dated 13.01.2005) situate maximum concentration of sulphur dioxide. This regulation covers properties of combustion plants to be used in heating, the quality criteria of the solid, liquid and gas fuels to be used in the combustion plants and the emission limits (MoEU, 2005).

2.4.2. European Union Regulations on Organic and Inorganic Pollutants

There are many directives related with SO_2, NO_2, O_3 and BTEX in European Union. Implementation the most effective pollution reduction measurement at national, and local level, protect the human health and environment are main purpose of these directives. As a result, European Union directives obtain importance to reach appropriate aims for ambient air quality. Therefore, Turkish legislation gained further significance in terms of the environment chapter of acquis because of

European Union membership process (Coşkun et al., 2010). The most relevant directives to the content of this study are listed as follows:

- ‘‘Directive 2003/35/EC of European Parliament and Council on the Reduction of National Emissions of Certain Atmospheric Pollutants” (European Commission, 2003).

- ‘‘Directive 2008/50/EC of European Parliament and Council on Ambient Air Quality and Cleaner Air for Europe’’ (European Commission, 2008).

- ‘‘Directive 2004/42/CE of the European Parliament and of the Council on the Limitation of Emissions of Volatile Organic Compounds due to the Use of Organic Solvents in Certain Paints and Varnishes and Vehicle Refinishing Products’’ (European Commission, 2004).

- ‘‘Directive 2003/17/EC of the European Parliament and of the Council Relating to the Quality of Petrol and Diesel Fuels’’ (European Commission, 2003).

- ‘‘Directive 2016/802/EC of the European Parliament and of the Council Relating to a Reduction in the Sulphur Content of Certain Liquid Fuels’’ (European Commission, 2016).

2.4.3. U.S. EPA Regulations on Organic and Inorganic Pollutants

U.S. EPA puts the limits on certain air pollutants under the Clean Air Act. Also, the Clean Air Act authorizes the U.S. EPA to limit the emissions of air pollutants which come from steel mills, chemical utilities and plants. States may have their more rigid air pollution laws, but they are not allowed to apply limits lower than the U.S. EPA.

Clean Air Act necessitates U.S. Environmental Protection Agency to set National Ambient Air Quality Standards (NAAQS) for six air pollutants which are carbon monoxide, sulphur dioxide, nitrogen dioxide, ozone, particulate matter and lead. Benzene, toluene, ethylbenzene and xylene are regulated under the air quality standards for ozone (U.S. EPA).

2.5. Overview of Air Sampling

Particle sample collection often requires attention and is difficult. According to Lodge (1988), particles are sampled for many reasons such as to determine the emissions levels from a source, to determine the effectiveness of control programs in decreasing ambient concentration of pollutant, to determine the sources furnishing to pollution, to recognize pollutant in the atmosphere, to determine concentration of hazardous pollutants.

Sulphur dioxide, nitrogen dioxide and ozone have significance criteria for air pollutants. There are several studies that claim link between long and short term exposure to SO_2, NO_2 and O_3 and increased mortality, morbidity and hospital admissions for pulmonary and cardiovascular diseases. Also, these pollutants cause photochemical smog and acid deposition. Therefore, monitoring of these pollutants is useful for finding out spatial and temporal changes in health impact assessment and air quality (Bari et al., 2015).

Type of pollutants, expected pollutant level, availability of trained personnel, averaging time of specified by air standards, available sources and presence of interfering media in the air are factors effects the choice of method for air monitoring (Schnelle and Brown, 2002).

Analysis and sampling are the key roles of the success of air monitoring. Continuous monitoring which makes both analysis and sampling can perform continuously and resulted in less loss of sample and less contamination is the most reliable air monitoring. However, this monitoring method is very expensive, and it is limited with urban areas (Wongniramaikul, 2012). This method is expensive since it requires more complicated maintenance and calibration. And maintenance personnel and operators must be more technically trained. Continuous monitoring involves taking the sample and analyzing sample at the same time. Also, it requires less laboratory support. Output of the measurements can be sent to central point electronically. Therefore, common way of the air monitoring is sampling the air and then carrying to the laboratory. There are two methods to sample the air which are active or continuous monitoring and passive sampling (Schnelle and Brown, 2002).

2.5.1. Active Sampling

Active sampling is a conventional method. It is done by pumping the air samples. Since flow meter to measure the volume rate of air and flow rate, active pump and sampling media are required, active sampling method is costly. Power supply and the instrument maintenance are required for active pump. Therefore, active sampling cannot be used in remote area (Wongniramaikul, 2012; He and Balasubramanian, 2010).

2.5.2. Passive Sampling

Passive sampling can be defined as monitoring technique that based on diffusion of analyte molecules easily flow from sampled media to collecting media due to their concentration differences (Gorecki and Namiesnik, 2002).

Passive sampling is a favored environmental method because of some effective advantages. One of them is that this method is cheap and portable. Therefore, it allows to use in variety area easily. The second one, the passive sampling method does not need any human power and supervision to work and also does not need any electrical power. That’s why, it is a thrifty method. The third one, it does not make voice pollution. Taking into consideration all advantages of using passive sampling, it can be seen that it is a useful method for environment (Wongniramaikul, 2012). Also, it is operated without risk of clogging, power loss and leaks that may affect the pumped tube or canister and it ensures exact results for a large range of sampling time (Grosse and McKernan, 2015). Although, there are advantages of passive sampling, there are also disadvantages of this monitoring. The main disadvantage is its low diffusive transport rate. Therefore, it cannot provide diurnal fluctuations or short term information, it can only provide on average concentrations based on the long exposure period. Another disadvantage is passive sampling does not provide real time values. (Varshney, Singh, 2003).

In addition to these disadvantages, there are two more problem related with passive sampling using. Interference effect that is one of them. Other chemical components in the atmosphere can interfere with adsorbent in the tube. The second one is sampling rate of the passive sampling can be effected by relative humidity, wind direction, wind speed, temperature, collection media and sampler’s structure (Tang et al.,1999).

Passive sampling method can monitor wide variety of inorganic and organic gases. According to Wongniramaikul (2012), limitation of passive sampling for different sample types can be exampled on sulphur dioxide and nitrogen dioxide. Chemical adsorbent is used for nitrogen oxide may react with sulphur dioxide which cause the reduction of adsorption of nitrogen oxide. Likewise, the used reagent for ozone can be interfered with other atmospheric air pollutants.

CHAPTER 3

MATERIALS AND METHODS

3.1. Sampling Locations

Concentrations of inorganic pollutants including NO_2, SO_2, O_3 and organic pollutants including ethylbenzene, toluene, benzene and xylene, which are known as BTEX compounds in the Central and Northern parts of Anatolian Plateau data will be used in this study. In figure 3.1, cities included in measurements are Bartın, Ankara, Bolu, Çankırı, Eskişehir, Karabük, Düzce, Kastamonu, Kırıkkale, Yozgat, Kırşehir, Kütahya and Zonguldak. In table 3.1, it is shown that locations and surface areas of cities.

Figure 3.1 Sampling Locations

Table 3.1. *Locations and Surface Areas of Cities*

Cities	*Latitude (N)*	*Longitude (E)*	*Surface Area (km2)*
Ankara	39.57	32.53	25632
Bartın	41.37	32.22	2143
Bolu	40.57	31.57	8313
Çankırı	40.60	33.61	7542
Düzce	40.84	31.15	2492
Eskişehir	39.77	30.52	13960
Karabük	41.20	32.62	4142
Kastamonu	41.38	33.78	13064
Kırşehir	39.14	34.17	6584
Kırıkkale	39.84	33.51	4791
Kütahya	39.41	29.98	11634
Yozgat	39.81	34.81	13690
Zonguldak	41.45	31.79	3342

(Ministry of Environment and Urbanization, 2015)

3.2. Sampling Period

Sampling of stations at these thirteen cities started at January 2014 and continued until May, 2015. During this sampling period, data were collected from total 341 stations. These 13 provinces are in the Ankara Clean Air Center which is affiliated to Ministry of Environment and Urbanization.

3.3. Sampling Methodology

Within the scope of the project, SO_2, NO_2, O_3 and BTEX concentrations were measured with TS EN 13528-1.2.3 methods. For SO_2 and NO_2 parameters, samplings were collected every two weeks and two times in a month in autumn and winter. In spring and summer seasons, samplings were collected every four weeks and one time in a month. For O_3 and BTEX, samplings were collected every two weeks and two times in a month in spring and summer and samplings were collected every four weeks and one time in a month in autumn and winter.

Sampling and analysis procedures for all parameters to be measured by passive sampling method were performed in accordance with TS EN 13528-1, TS EN 13528-2 and TS EN 13528-3 standards. In the NO_2, SO_2, O_3 and BTEX analyzes performed by the Middle East Technical University Environmental Engineering Department, air pollution laboratory, clean room and ion chromatography laboratory were used. Air Pollution Laboratory is a place where all operations that do not require to be overly clean with its large areas. Since gas chromatography (GC) devices are also present in this laboratory, the air pollution laboratory is also a site for GC analysis.

The clean zone is an area where there is a risk of contamination. This area, which was previously only clean for trace elements, was also cleaned of organic pollutants by the measures taken and it was started to be used as a sample preparation area for organic analyzes. The clean room consists of two interconnected rooms in the basement connected by a door. Both rooms do not have windows. The outer chamber is treated as a storage zone, where processes are carried out which do not involve a high risk of contamination. The interior clean room is the place where all operations involving the risk of contamination is performed. Here, the walls, and all surfaces that produce dust, are covered with wooden planks, making them dust-free. One of these modules passes the air drawn from outside the room through the HEPA filter into the clean room. Once filtered room air is taken up by other modules in the room and passed through HEPA filter for the second time, it is returned to the room. Therefore, the air under the modules is the air passed through the HEPA filter twice. Sample preparation studies are carried out under these modules.

Since the system described above holds particulate matter with a diameter> 1.0 atmosphere in the atmosphere with an efficiency of 99.9%, the PM and the associated trace element concentrations in the room go down to very low levels. In 2013 measurements, it was observed that the number of particles under the cleanroom modules > 0.3 μm in diameter was 27 particles/m^3. The number of particles at the points inside the clean room which is not below the clean room modules was 3700 particles/m^3. During these measurements, the number of particles outside the clean room (in the region where air is drawn into the clean room) was found to be 27x10^6 particles/m^3. Although the clean zone is very effective in reducing dust and trace element concentrations, since the HEPA filters do not retain organic gases, the concentration of organic pollutants in the gas phase such as BTEX in the clean room is not very different from the concentration outside the clean room. To correct this, one of the modules in the clean room was fitted with a carbon filter in addition to the HEPA filter. In an effort to understand the effectiveness of the application, benzene was measured using online GC outside the clean room and under the carbon filter. Outside the chamber, the benzene concentration was 3.2 μg m^{-3}, while no benzene was observed on the carbon filter.

In this study, in the passive sampling of both organic and inorganic gases, coating and drying of the steel wire coated with the holding medium is carried out under a carbon filter.

Ion chromatography (IC) used in the measurement of SO_2 and O_3 is available in a different laboratory. In this study, samples were prepared in the air laboratory and brought to the IC laboratory where IC analyzes were performed.

3.3.1. Information on Passive Samplers

Passive samplers used in this study were obtained by modification of GRADKO samplers.

In the figure 3.2, passive sampling tube was shown.

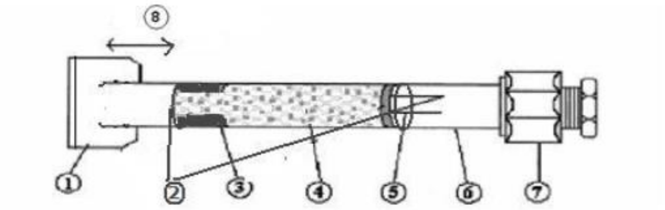

Figure 3.2 Passive sampling tube scheme (Civan, 2010)

1. Diffusion Cap
2. Stainless Steel Screens
3. Additional Screen Gouge
4. Adsorbent
5. Screen Gouge
6. Gradko Sampling Tube
7. Swagelock Storage Cap
8. Diffusion Gab

The SO_2 passive sampler consists of an acrylic tube with an inner diameter of 11 mm and a length of 71 mm. The outer surface of the tube is wrapped with Al tape. At one end of the tube, there are two small porous steel cage wires. The lower wire is absorbed with Triethanolamine (TEA) solution. How the TEA is absorbed will be discussed in the following sections. The retaining of the wires is ensured by a plastic cover placed on them.

The risk of contamination is minimized by closing the end of the passive sampler with a plastic cap until the sampling arrives to the place. When the sampler arrives, this cover is removed and replaced with a different cover with a hole in the middle and a “glass fiber” filter inside. The reason for installing a filter in front of the SO2 sampler is to prevent SO_4^{-2} containing particles from entering the sampler and interfering with the SO_2 measurement.

The NO_2 sampler used in the study is no different from the SO_2 sampler in geometry. The NO_2 sampler consists of an acrylic tube with an inner diameter of 11 mm and a length of 71 mm. At one end of the acrylic tube, there are two steel cage wires, one of which is coated with TEA. A plastic cover attached on the wire layers makes the wire cages in place. NO_2 passive sampler was not wrapped with aluminum tape. The lower end of the sampler, which is open during sampling, is sealed with a plastic cap to minimize the risk of contamination until the tube is moved to the area and sampling begins.

Like the NO_2 and SO_2 samplers, the ozone passive sampler consists of an acrylic tube with an inner diameter of 11 mm and a length of 71 mm. At one end of the tube are two steel cage wires, one of which is coated with adsorbent. The cage wires are fixed at the end of the tube by means of a plastic cap attached to them. The ozone sampler is also wrapped with aluminum tape to slow down the photochemical degradation of ozone. The end of the tube to be left open for sampling is closed with a plastic cap until it is taken to the area, and instead of the cap, a fiber glass filter with a central hole is fixed by means of a plastic cap. As with the SO_2 sampler, the purpose of the filter in ozone sampling is to prevent the interference of particulate matter by measurements.

The passive sampling tubes of BTEX passive sampler made of stainless steel with a surface area of 0.18 cm2, a diffusion depth of 1.5 cm, an inner diameter of 4.8 mm and a length of 100 mm were obtained from Gradko. There is a TENAX adsorbent starting at 150 mm from the sampling end of the pipe. The pouring of the adsorbent was prevented by the steel cage fixed at the top and bottom of the adsorbent.

One end of the steel tube is sealed with a brass blank plug. The other end of the tube is also closed with a similar blank plug to prevent air from entering and causing contamination while the sampler is being taken to the area. When the sampler is placed in the station at the station, the blank plug at the sampling end is removed and replaced by a diffuser to laminate the airflow.

3.3.2. Preparation of Passive Samplers

The preparation of passive samplers includes the steps of cleaning and preparing tubes, impregnating Whatman GF/A Fiber glass filter filters with adsorbent solutions, drying and placing them in tubes, assigning identifier numbers to the tubes and packing them to the field. Although the processes applied are similar for passive samplers other than BTEX samplers, the retention solutions to be coated may be different from each other. The coating methods for each tube are briefly described below.

In passive samplers to be used for NO_2 measurement, triethanolamine is used as the trapping agent. In this study, Whatman GF/A glass fiber filters were impregnated with 20% triethanolamine (TEA) aqueous solution. For the impregnation process, filters cut across the tubes were left in a 20% TEA solution for 5 minutes. The 20% TEA solution was prepared by deionizing 5 mL of TEA (Merc) and diluted to 25 mL with ultra-pure water ($R>17$ MΩ). The filters were then removed from the solution and dried in a clean zone and under an activated carbon filter for 20 minutes. The dried filters were pre-cleaned, placed in acrylic tubes and fixed by closing a gray cap.

Glass-fiber filters used as holding medium in ozone passive samplers were impregnated with 1% $NaNO_2$, 2% Na_2CO_3 and 2% glycerol aqueous solution. For the preparation of a mixture of $NaNO_2$, Na_2CO_3 and glycerol, which allows ozone to be retained on the Glass-fiber filter, 1 g of $NaNO_2$ (Merck), 2 g of Na_2CO_3 (Merck) and 2 g of glycerol were weighed and each of them made up to 100 ml with deionized purified water ($R> 17$ MΩ). The resulting solutions were combined. For impregnation, the cut-off filters were left in a mixture of 1% $NaNO_2$, 2% Na_2CO_3 and 2% glycerol for 5 minutes. The filters were then removed from the solution and dried in a clean zone and under an activated carbon filter for 20 minutes. The dried filters were pre-cleaned, placed in acrylic tubes and fixed with a black cap on them.

The other end of the sampler was also covered with a gray plastic cap to reduce the risk of contamination. The prepared samplers were placed in polyethylene bags in bags of 50 and the bags were stored in boxes containing activated carbon. Unlike NO_2 samplers, glass fiber filters placed in the middle of the hole covers were prepared and packaged together with the samplers. When the field was reached, the caps at the sampling end of the samplers are removed and the caps containing the filter are placed. The purpose of the filter used in ozone samplers is to prevent particulate matter from entering the sampler and interfering with ozone.

In passive samplers to be used in SO_2 measurement, triethanolamine is used as the retention agent as in NO_2 samplers. In this study, Whatman GF/A glass fiber filters were impregnated with 20% triethanolamine (TEA) aqueous solution and used to capture SO_2 in the samplers.

For the impregnation process, filters cut across the tubes were left in a 20% TEA solution for 5 minutes. The 20% TEA solution was prepared by deionizing 5 mL of TEA (Merck) and diluting it to 25 mL with ultra-pure water ($R>17$ MΩ). The filters were then removed from the solution and dried in a clean zone and under an activated carbon filter for 20 minutes. The dried filters were pre-cleaned, placed in acrylic tubes and fixed by closing a white cap.

The other end of the sampler was also covered with a white plastic cap to reduce the risk of contamination. The prepared samplers were placed in polyethylene bags in bags of 50 and the bags were stored in boxes containing activated carbon. Glass fiber filters placed in the middle holes were prepared for SO_2 samplers as well as ozone samplers and packaged together with the samplers. When the field is reached, the caps at the sampling end of the samplers are removed and the caps containing the filter are placed. The purpose of the filter is to prevent the SO_4^{-2} containing particulate matter from entering the sampler.

BTEX samplers are different from the passive sampler used to sample inorganic gases, the inorganic passive samplers discussed in the previous sections. The sampler consists of a steel tube having an inner diameter of 4.8 mm and a length of 100 mm.

The tube was filled with Tenax TA (60/80 mesh) adsorbent from Supelco. 350 ± 2.6 mg Tenax TA is placed in each tube. Both sides of the adsorbent were closed with a steel cage wire and pouring was taken to the sampler area to prevent pouring. The filled tubes were cleaned by passing high purity nitrogen gas at a flow rate of 100 ml/min for 2 hours at 320 ^{0}C according to the manufacturer's recommendation. The risk of contamination is minimized by closing the brass caps at both ends of the tubes, except for sampling times. All tubes were stored in glass tubes with active carbon and silica gel, refrigerated at + 4 ° C, except for sampling time. Passive tubes were prepared for sampling and EN13528-2 standard method was followed during sampling. Each passive tube was sent to the area by sending a diffuser. The diffuser is required to laminar air flow entering the sampler. During sampling, the brass cap on the sampling end is removed and replaced with a diffuser. At the end of the sampling, the diffuser is removed, and the brass cap is closed again.

3.3.3. Placement and Collection of Passive Samplers in Stations

During passive sampling, shelves of 5 cm*12 cm dimensions were made according to EN 13528-3 standard in order to prevent the tubes from being affected by adverse environmental and climatic conditions (rain, etc.). Before and after the installation, the relevant personnel carried out the relevant controls and the control data were recorded in the Diffusion Tube Field Sampling Checklist. Warning labels were affixed to the poles to which the tubes were installed. At the highest level, occupational health and safety measures were taken and Occupational Health and Safety Practices Training on Height was given to the field team before each period.

3.3.4. Preparation and Analysis of Passive Samplers for Laboratory Analysis

Preparation of passive samplers for analysis involves the process of passing the analytic trapped on the glass-fiber filters in the samplers to the solution for contaminants other than BTEX.

Since the BTEX samplers are directly connected to the thermal desorption unit, no preparation is performed for benzene, toluene, ethylene, m, p-xylene and o-xylene.

The procedures for preparing, analyzing and calibrating the collected samples for analysis conform to EN13528-2 and EN13528-3 standards.

Since the collected NO_2 samples are determined spectrometically, the collected samples need to be colored as well as solubilized. Coloring process is provided with Griess-Saltzman solution. To prepare the solution, first, 0.1 g of N- (1-Napthyl) ethylene diamine dihydrochloride is dissolved in 100 ml of ultra-pure water (0.1%). In a separate beaker; 5 g of sulfanilic acid are dissolved in water (heating and stirring) containing 140 ml of glacial acetic acid (Merck). To this solution, 20 ml of 0.1% N- (1-Napthyl) ethylenediamine dihydrochloride solution and 10 ml of acetone are added and the solution is completed to 1 L with ultra-pure water. The glass-fiber filters removed from the samplers are solubilized by stirring in an ultrasonic bath with 5 ml of absorber solution prepared as described above for 40 minutes. Absorbance values of the solubilized samples are measured on UV/VIS Spectrophotometer (Shimadzu 2450) and 550 nm wavelength. The calibration of the spectrophotometer was carried out with NaNO2 solution at 0.1, 0.2, 0.4 and 0.8 ppb concentrations. Calibration R^2 values> 0.99. The absorbance values obtained from the samples are converted to concentration values using the calibration curve.

In ozone passive samplers, ozone in the atmosphere is kept as nitrate on the filters. Thus, after solubilization, it is measured as nitrate in ion chromatography and the measured areas are converted to concentration using calibration curves prepared with nitrate.

In order to solubilize the samples collected on glass-fiber filters, the filters removed from the samplers and the samples on which the sample is placed are placed in 25 mL of high density polyethylene beakers and 5 mL of ultra-pure water (deionized water with resistance > 18 MΩ) is added. The beakers containing the samples were placed in the ultrasonic bath and ultrasonic stirred for 20 minutes. Solubilized samples are analyzed by ion chromatography. Prior to the analysis, the IC is calibrated with 0.1, 0.3, 0.5 and 1 ppm NO^{-3} standard solutions prepared by dilution from 100 ppm NO^{-3} stock solution. The areas obtained from the IC analysis are converted to concentration values using the calibration curve.

In SO_2 passive samplers, SO_2 in the atmosphere is kept as sulphate on the filters. Thus, after solubilization, it is measured as sulfate in ion chromatography and the measured areas are converted to concentration using calibration curves prepared with sulfate.

Solubilized samples are analyzed by ion chromatography. Prior to the analysis, the IC is calibrated with 0.1, 0.3, 0.5 and 1 ppm SO_4^{-2} standard solutions prepared by dilutions from 100 ppm SO_4^{-2}stock solution. The areas obtained from the IC analysis are converted to concentration values using the calibration curve. The samples were analyzed by using Agilent 6890 model Gas Chromatography (GC) and Unity brand thermal desorption device. The organic pollutants held in the Tenax adsorbent were dissolved at 300 ^{o}C for 3 minutes and the volatile organic compounds exiting the thermal desorption device were collected in the cold trap at -15 ^{o}C. Then, the temperature of the cold trap was increased to 350 ^{o}C within one or two seconds and the collected volatile organic compounds were transferred to GC device.

The GC system consists of two detectors (FID) and two columns. In fact, this system works like two GCs. FID-1 measures light hydrocarbons (<C5) and FID-2 measures heavy hydrocarbons (> C5).

The heating program (or oven program) used in the GC is given below.

Step 1. Bring the oven to 40 °C and wait at this temperature for 5 minutes,

Step 2. At the end of five minutes the temperature is increased by 5 ^{o}C to 195 ^{o}C,

Step 3. The oven is kept at 195 °C for 10 minutes.

The GC/FID system used was calibrated with a standard gas mixture from the Department of Environmental Analysis and Air Quality of Canada containing 148 alkanes, alkene, alkyne, aromatic and halogenated aromatic organic compounds.

On each analysis day, one of the mid-point standards is given to the GC before the analysis of samples is performed to check the performance of the instrument. If the obtained area is different from the day of calibration, the analyzes are stopped and the device is recalibrated. BTEX analysis and calibration of the device are carried out in accordance with EN13528-2 standard.

3.3.5. Calculation of Concentrations

The absorbance values (for NO_2) and the area values obtained from the IC formed by the analysis of contaminants collected in the samples were converted to the $\mu g\ mL^{-1}$ values in the solution using the calibration curves described in the above sections. The $\mu g\ mL^{-1}$ was then multiplied by the volume of the solution (mL) to convert the total mass of contaminants in the filters. The transition from the mass of the wrist to the concentration of the same compound in the air was carried out using the following equation of the 2nd Fick's law.

$C_0 = Q \text{ x } (L / (D \text{ x } A \text{ x } t)$

In this equality

Q: the amount of component absorbed (μg),

t: sampling time (s),

A: cross-sectional area of the diffusion path (cm^2),

D: diffusion coefficient of the pollutant component ($cm^2\ s^{-1}$),

L: total length of diffusion path (cm),

C_0: concentration of pollutant component in the sampled medium ($\mu g\ m^{-3}$).

The most critical of the above parameters is the diffusion coefficient (D). D is a temperature dependent parameter.

In this study, the diffusion constants of the measured parameters at 298 K were obtained from the literature, and the values corresponding to the temperatures at the time of sampling were found with the help of the above equation and NO_2, SO_2, O_3, benzene, toluene, ethylbenzene, m&p-xylene and was used in the calculation.

The diffusion constants of the parameters used for 298 K are 0.154 cm^2 sec^{-1} for NO_2, 0.155 cm^2 sec^{-1} for O_3 and 0.176 cm^2 sec^{-1} for SO_2. As mentioned above, these values were changed according to the temperatures at the time of sampling.

In this calculation, the concentration value for ozone was multiplied by 0.77 (48/62). This is because ozone is measured as NO_3 in IC and the molecular weights of NO_3 and O_3 are different. This is a standard procedure used all over the world.

3.3.6. Determination Limit of Dedection

Although the method has different definitions of the limit of detection, the most common is the concentration value corresponding to three times the standard deviation of the absorbance or peak areas to be obtained by reading the blank parameters 10 consecutive times. In this study, the determination limits of the parameters were determined in accordance with the above definition.

The determination limits of the methods were found to be 0.49 µg m^{-3} for NO_2, 1.24 µg m^{-3} for O_3 and 0.76 µg m^{-3} for SO_2. These values are about 2% of the samples based on the average of the concentration values measured in the analyzes performed to date for NO_2. Similarly, the determination limits for SO_2 and ozone are less than 1% of the values seen in the samples.

It is a common phenomenon that the limits of method determination are so low. Because this parameter shows how reproducible the analytical method is, rather than low levels can actually be determined.

3.3.7. Repeatability

To determine the reproducibility of the measured parameters, five SO_2, NO_2, O_3 and BTEX passive samplers were placed side by side for two weeks and then brought to the laboratory and analyzed by normal methods. Using the following equation, coefficient of variance (or relative standard deviation - RSD%) values were calculated.

$\% \text{ RSD} = (\sigma / x_a) \times 100$

In this equation, %RSD is the relative standard deviation (or variance constant), σ is the standard deviation, and x_a is the arithmetic mean.

The coefficients of variance determined using the aforementioned procedure were 10.5% for NO_2, 12.4% for O_3 and 8.6% for SO_2. These values indicate that there will be no significant problem in terms of reproducibility in the analysis.

3.3.8. Blank sample Values

Field and laboratory blank samples were collected separately and evaluated in the evaluation of blank samples. However, in all of the measured parameters, no blank levels above the limit of detection were observed as a result of the measures taken in the laboratory. Although the concentrations observed in the field blank samples were considerably lower than those in the field blank samples, concentrations above the detection limit were still found.

The determined area blank sample levels were 2.1 ± 0.8 for NO_2, 6.3 ± 3.5 for O_3, and 5.7 ± 3.2 µg m-3 for SO_2. These values correspond to a blank sample extraction of between 5% and 10%. This shows that subtraction of field blank sample values will not be a significant problem in the analysis.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Meteorology of Study Areas

Meteorology is important in atmospheric science as it enhance or suppress dilution process or provides information about the directional dependence of pollutant transport to receptor. Among many meteorological parameters mixing height, temperature, wind speed and solar radiation are particularly important and must be considered in data treatment. Hence, this section is allocated to meteorological conditions that were operational during study period at Bartın, Ankara, Bolu, Çankırı, Karabük, Kastamonu, Düzce, Eskisehir, Kırıkkale, Yozgat, Kırşehir, Kütahya and Zonguldak. Data for meteorological parameters were obtained from General Directorate of Meteorology.   Meteorological conditions prevailed in each city during the study is discussed and a comparison is provided at the end of this section.

Typical inland climate, with high summer and low winter temperatures prevails in Ankara. The hottest month is Jul-August and the coldest month is January. Precipitation amounts in the region change in the South and North. Especially in winter, because of the nature of region, the fog event is quite common and it effects life in Ankara (Ankara Provincial Directorate of Culture and Tourism, 2019). Ankara had a population of 5,270,575 in 2015 (Turkish Statistical Institute, 2019). According to long term meteorological parameters of General Directorate of Meteorology (2019), the lowest temperature was -24.9 ^{o}C and the highest temperature was 41^{o}C.

The average temperature in the provincial scale is 12°C in terms of long meteorological data. The dominant wind is seen to change depending on the terrain structure in Ankara. 29.2 m/sec is the highest wind speed detected in Ankara. Annual rainfall amount is 406 mm in long term meteorological parameters.

Bartın is cool in winters and warm in summers because of prevailing of Black Sea climate. The mountain ranges are parallel to the shore and proximity of the sea increase the humidity and decrease the temperature differences on the coastline. The hottest month is July-August and the coldest month is January. (Bartın Provincial Directorate of Culture and Tourism, 2019). Bartın had a population of 190,708 in 2015 (Turkish Statistical Institute, 2019). According to long term meteorological data annual rainfall amount is 1035.1 mm.

Although Bolu (population 291,095 in 2015 - Turkish Statistical Institute, 2019) is located approximately 50 km from the Black Sea coast, administratively and geographically it is included in the Black Sea region of the country. The climate is a typical Black Sea climate, which is relatively mild, with annual average temperature of 10.5°C. The coldest temperature recorded in winter and the highest temperature recorded in summer, in last 90 years (between 1929 – 2018) are -34°C (in January) and 39.8°C (August), respectively. However, Bolu does not receive as much rain as other cities on the Black Sea coast. Annual rainfall is 553.5 mm.

Çankırı, which is located approximately 160 km from the Black Sea coast is included in the Central Anatolia region of the country. The city has a population of 185,945 (Turkish Statistical Institute, 2019) and experiences Central Anatolian (or inland) climate (Çankırı Provincial Environmental Status Report, 2015), where summers are mild, but winters are cold. According to long term meteorological parameters of General Directorate of Meteorology (2019), the coldest month is January and the hottest month is July. The lowest and highest temperatures recorded between 1929 and 2018 were -25°C and 42.4°C, respectively. The average temperature in the same period was 11.3°C. Çankırı, like all cities located at the Central Anatolia, do not receive as much rain as cities in coastal regions of the country. Annual rainfall in last 90 years is 405 mm.

Typical Black Sea climate prevails in Düzce, which is approximately 25 km from the Black Sea coast and has a population of 360,388 in 2015 (Turkish Statistical Institute, 2019). The lowest and highest temperatures recorded in last 60 years (Since 1959) are -20.5°C and 42.4°C, respectively (General Directorate of Meteorology, 2019). Sixty year average annual rainfall is 815,3 mm, indicating that Düzce receiver fair amount of rainfall when compared with other Turkish cities, particularly with cities located on the Anatolian Plateau.

Eskişehir is a typical Central Anatolian city, with a population of 826,716 in 2015 (Turkish Statistical Institute, 2019). Climate prevailing at Eskişehir is very similar to that in Ankara, with extreme cold temperatures in winter and moderate temperatures in summer. January is the coldest month (The minimum temperature recorded since 1928 is -27.8°C) and the hottest month is July and August (record high temperature measured in last 90 years is 40.6°C). Average temperature in the same period is 10.9 ^{o}C and average annual rainfall is 468 mm in terms of long meteorological data.

Karabük, with its mere 60 km distance from the Black Sea coastline, is a Black Sea city where climate reflects characteristics of the climate along the Black Sea coast, with relatively mild temperatures (average temperature in last 65 years is 13.3°C). Since Karabük is behind the mountain range, which extends along the coast, it does not receive is much rain as coastal Black Sea cities do. 65-year average annual rainfall at Karabük is 468 mm. The coldest temperature recorded in winter since 1965 is -15.1°C and the hottest temperature recorded in the same period is 44.1°C.

Topographic and geographic characteristics of Kastamonu is very similar to those of Karabük. Both cities are approximately 60 km from the coast, both behind the mountain range, which modifies coastal climate. Population of Kastamonu is 372,373 in 2015. Historical high and historical low temperatures are 42.2 and -26.9, respectively (historically refers to lowest and highest temperatures recorded between 1930 and 2018). Annual rainfall is 488.4 mm.

In Kırıkkale, the coldest month is January and the hottest month is July. The lowest temperature was -22.4 ^{o}C and the highest temperature was 41,8 ^{o}C. The average temperature in the provincial scale (average between 1963 and 2018) is 12.5 ^{o}C in terms of long meteorological data. Fifty-five year average annual rainfall is 379,2 mm.

In Kırşehir, the coldest month is January and July is the hottest month. The lowest temperature was -28 ^{o}C and the highest temperature was 40.2^{o}C. The average temperature in the provincial scale is 28.4 ^{o}C in terms of long meteorological data. According to long term meteorological data annual rainfall amount is 381.6 mm.

In Kütahya, January is the coldest month and the hottest month is July and August. The lowest temperature was -28.1 ^{o}C and the highest temperature was 39.5^{o}C. The average temperature in the provincial scale is 14.1 ^{o}C in terms of long meteorological data. According to long term meteorological data annual rainfall amount is 560.4 mm.

In Yozgat, the coldest month is January and July and August are the hottest months. The lowest temperature was -24.4 ^{o}C and the highest temperature was 38,8 ^{o}C. The average temperature in the provincial scale is 9 ^{o}C in terms of long meteorological data. According to long term meteorological data annual rainfall amount is 585.6 mm.

In Zonguldak, the coldest month is January and the hottest month is July and August. The lowest temperature was -8 ^{o}C and the highest temperature was 40.5 ^{o}C. The average temperature in the provincial scale is 13.6 ^{o}C in terms of long meteorological data. According to long term meteorological data annual rainfall amount is 1198.8 mm.

Annual, summer and winter averages of temperature, wind speed (WS) and rainfall are given in Table 4.1. Averages in the table are average values measured during the study period. Long term annual averages of these parameters are also given in the same table. Long term averages are the average values generated by General

Directorate of Meteorology (MGM) using meteorological data generated since the commissioning of the meteorological station in each city. The length of this period is different for each city. It is approximately 90 years (1929 and 2018) for Ankara, Bolu, Çankırı, Eskişehir, Kastamonu, Kırşehir and Kütahya, 80 years (between 1939 – 2018) for Yozgat and Zonguldak and between 54 and 60 years for Düzce, Bartın, Karabük and Kırıkkale. Since averages calculated using very long time periods, these average values are quite sturdy and do not change too much over the long-run.

Table 4.1 Annual, Summer and Winter average temperature, average wind speed and total rainfall measured during study period

	Rainfall (mm)				Temp (°C)				WS (m s^{-1})			
	Annual Long-term	Annual	Summer	Winter	Annual Long-term	Annual	Summer	Winter	Annual Long-term	Annual	Summer	Winter
Ankara	406	515	114	111	12.0	12.9	23.6	3.4	2.0	2.5	2.8	2.6
Bartın	1035	1154	304	337	12.7	13.5	22.3	6.1	1.3	1.1	1.3	1.0
Bolu	554	624	124	230	10.6	11.6	20.6	3.3	1.5	1.4	1.5	1.2
Çankırı	406	532	77	130	11.2	12.0	23.0	2.4	1.1	1.6	1.8	1.4
Düzce	815	1063	268	347	13.3	13.8	22.6	5.8	1.0	1.1	1.3	1.0
Eskişehir	366	452	114	184	11.3	12.4	22.5	3.1	2.1	1.8	1.9	1.8
Karabük	490	469	92	132	13.4	13.1	22.9	4.1	1.2	1.4	1.8	1.0
Kastamonu	482	718	214	127	9.8	10.3	20.1	1.2	1.3	1.5	1.7	1.3
Kırıkkale	380	469	111	104	12.6	12.9	24.2	2.7	2.1	1.9	2.3	1.9
Kırşehir	382	197	33	48	11.4	12.8	23.8	3.5	1.9	2.6	3.2	2.4
Kütahya	562	392	40	145	10.8	11.6	21.5	2.8	1.3	1.6	1.7	1.6
Yozgat	586	294	54	72	9.0	10.1	20.2	1.3	1.9	1.6	1.7	1.7
Zonguldak	1219	662	142	254	13.6	14.0	22.0	7.7	2.3	2.0	1.9	2.3

Temperature measured during our study period do not depict large variations from one city to another. Annual average temperatures vary between 10.1°C at Yozgat and 14°C at Zonguldak. Cities that are located on the coast, such as Zonguldak and Bartın, have slightly higher annual average temperatures than cities located on the Anatolian Plateau, such as Kütahya and Yozgat. Intercity variation in temperature during summer and winter seasons closely follow the annual variability. In summer season temperatures in this part of the country varies between 20.1°C at Kastamonu and 24.2°C at Kırıkkale; and between 1.2°C at Kastamonu and 7.7°C at Zonguldak. This variation in summer and winter seasons indicate fairly uniform distribution of seasonal temperatures when this study was performed.

Is the meteorology in these cities, recorded during our study period is typical for the region, or was the study performed under very unusual meteorological conditions in 2014? This is an important question that should be answered, because if the study was performed under very unusual meteorological conditions, then concentrations of pollutants measured during the study may not be representative for that city over a long time period.

Annual average wind speed, temperature and rainfall measured during the study period are compared with long-term averages of these parameters.

Average temperature measured during the study period in each city is compared with long-term averages reported for the cities in Figure 4.1. The difference between study-period and long term average temperatures are not very different in all cities that are included in this study. Difference varies between 0.3°C at Kırklareli and 1.4°C at Kırşehir. The figure demonstrates that temperatures in all cities that are measured during study period can be considered as “typical” for the region and for each city. It should be noted that although ΔT between study period and long-term averages is not much, current temperatures were consistently higher than long-term averages in all cities. This is due to increasing population in cities and known as “urban heat island” effect. Urban heat island effect increased in time with increasing urbanization.

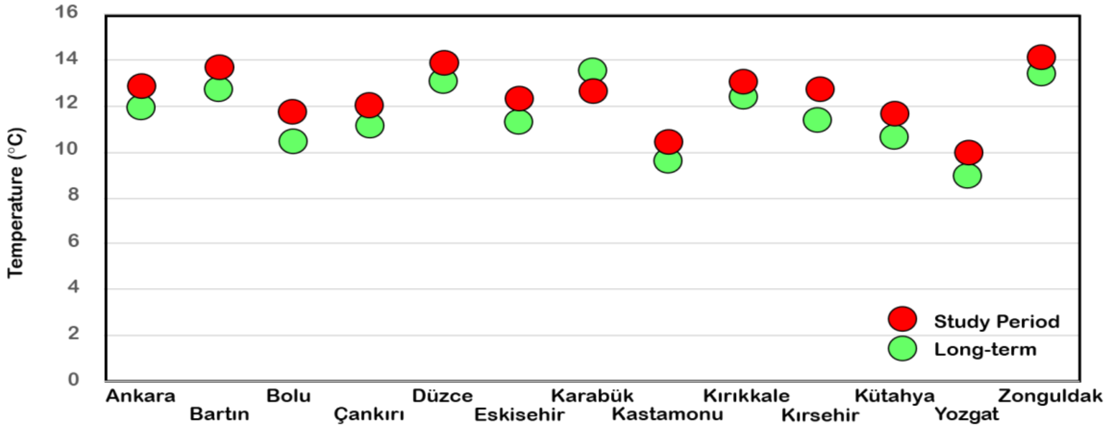

Figure 4.1. Comparison of average temperature in cities during the study period with corresponding long-term average temperature

Investigation of variability of wind speed between cities revealed that average wind speed are extremely low in all cities. This statement is true for both summer and winter winds. In summer WS varies between 1.3 m s^{-1} at Düzce and 3.2 m s^{-1} at Kırşehir. In winter it varies between 2,6 m s^{-1} at Ankara and 1.0 m s^{-1} at Bartın Düzce and Karabük. These are very low wind speeds, meteorologically WS < 1.0 m s^{-1} is considered as calm. In most of the cities average wind speed is very close to this criteria. As can be anticipated, such low wind speeds is not a favorable condition for accumulation of pollutants over the city.

Average wind speed measured during this study are compared with long term average wind speed in each city in Figure 4. 2. With few exceptions, long-term average wind speed in cities are not significantly different from average wind speed measured during this study. In Ankara, Çankırı and Kastamonu current WS is 20% - 30% higher than long-term averages in these cities. For the remaining cities the difference is <10%.

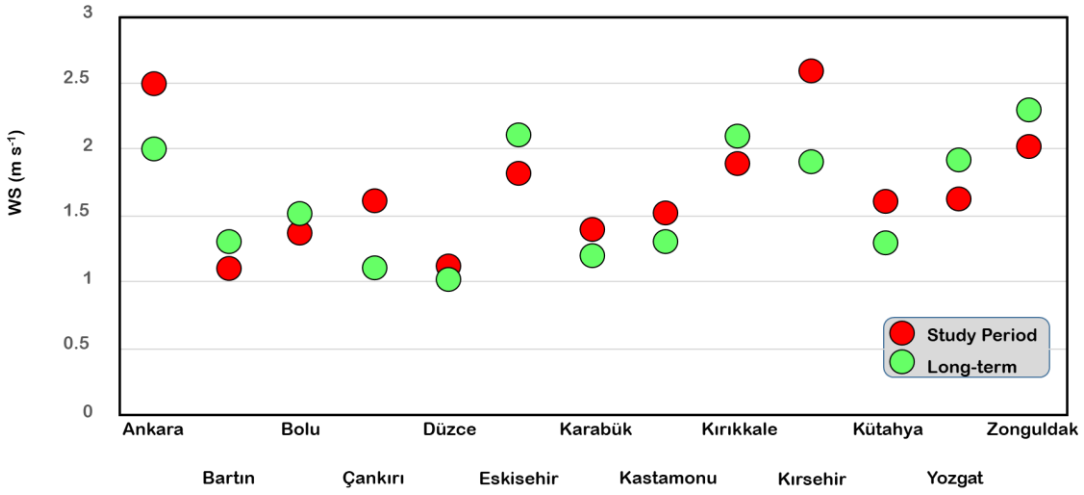

Figure 4.2 Comparison of average WS measured during the study period with corresponding long-term average WS in cities.

Rainfall is the most variable parameter among the three. Annual rainfall varies between 1154 mm at Bartın and 197 mm at Kırşehir. There is a consistent pattern in variability of rainfall among cities. Bartın, Düzce, Kastamonu and Zonguldak are the cities that received highest rainfall during the study. All of these are the cities that are close to the Black Sea coast. They are at most 50 km from the shoreline. Kırşehir, Yozgat, Kütahya and Eskisehir are the cities, which received lowest rainfall. These are the cities that are not in the immediate vicinity of the Black Sea. Kırşehir is 325 km, Yozgat is 246 km, Kütahya is 200 km and Eskişehir is 160 km from the Black Sea coastline. Apparently, the mountain range that extends along the Black Sea coast have profound influence on the annual rainfall cities receive. Cities that lies on the coastal side of the mountains receive rainfall close to or higher than 1000 mm. However, rainfall received by cities, which are located behind the mountain is less than half of the annual rainfall experienced at coastal cities.

Annual rainfall measured during the study are compared wıth long-term average annual raınfall in Figure 4.3. For 9 out of 13 cities included in this work precipitation recorded during the study is higher than long term average rainfall in these cities. Four cities where long term average rainfall exceeds current rainfall are Kırşehir, Kütahya, Yozgat and Zonguldak. For Bartın and Bolu this difference is small (approximately 10%), in Ankara, Düzce and Çankırı. Precipitation recorded during study is 23 – 31% higher than long-term average precipitation in these cities. In Eskişehir, Kastamonu, Yozgat, Kırşehir and Kütahya the difference between current and long-term average rainfall varies between 46% and 54%. The difference is 70% in Zonguldak.

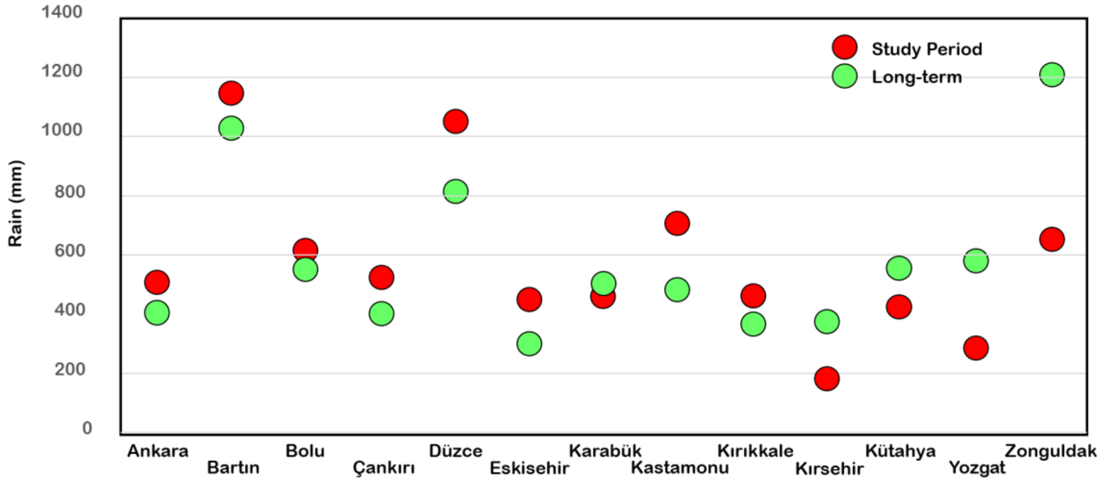

Figure 4.3 Comparison of annual rainfall received in cities during the study period with corresponding long-term average annual rainfall

Discussions in this section demonstrate that study period is reasonably typical for most cities in terms of temperature and wind speed, however long term average precipitation in cities differ from precipitation data recorded during the study, at least for some of the cities.

4.2. General Feature of DATA

Annual average SO_2, NO_2, O_3 and BTEX (benzene, toluene, ethylbenzene, m&p-xylene and o-xylene) concentrations are given in Table 4.2. Number of stations which were used for passive sampling of these parameters are also included in the table. Two numbers that are shown in parenthesis, for each city, are number of sampling stations where inorganic and organic pollutants are measured. In all cities passive sampling of organic pollutants (BTEX) was conducted in fewer stations, due to difficulties involved both in their sampling and analysis, relative to inorganic pollutants.

Table 4.2 Summary statistics (concentrations are in µg m-3)

	mean ± σ	Median	Max	Min
Ankara (66*, 21)**				
SO_2	41 ± 28	33	220	0.05
NO_2	63 ± 42	53	290	1.9
O_3	38 ± 27	32	158	2.17
Benzene	2.7 ± 3.0	1.4	14.8	0.03
Toluene	32 ± 62	12	481	0.15
Ethylbenzene	2.2 ± 3.0	1.1	21	0.002
m&p-xylene	3.7 ± 5.3	1.7	38	0.008
o-xylene	2.2 ± 3.1	1.0	21	0.007
Bartın (15*, 7)**				
SO_2	36 ± 42	30	304	4.32
NO_2	42 ± 29	36	139	6.23
O_3	40 ± 18	39	80	6.50
benzene	3.6 ± 4.2	1.8	18	0.49
toluene	54 ± 119	18	652	0.79
ethylbenzene	1.9 ± 3.2	1.3	18	0.08
m&p-xylene	3.0 ± 4.9	1.9	27	0.14
o-xylenelene	1.7 ± 2.5	1.2	14	0.04
Bolu (20*, 8)**				
SO_2	34 ± 28	29	125	1.59
NO_2	46 ± 33	37	159	6.22

Table 4.2 (cont'd)

O_3	46 ± 25	44	131	4.28
benzene	7 ± 21	2	126	0.20
toluene	10 ± 18	4	86	1.24
ethylbenzene	0.95 ± 1.88	0.48	11	0.10
m&p-xylene	1.52 ± 3.05	0.71	18	0.14
o-xylene	0.83 ± 1.45	0.38	8.0	0.06
Çankırı (20*, 6)**				
SO_2	34 ± 21	29	118	4
NO_2	27 ± 22	21	110	0.001
O_3	46 ± 25	39	128	2.85
benzene	3.47 ± 2.80	2.54	10.86	0.38
toluene	8.92 ± 6.06	7.73	23.97	0.81
ethylbenzene	1.06 ± 0.70	1.04	2.40	0.11
m&p-xylene	1.68 ± 1.11	1.64	3.97	0.14
o-xylene	1.26 ± 0.92	1.10	3.26	0.06
Düzce (25*, 8)**				
SO_2	29 ± 25	32	131	0.10
NO_2	57 ± 38	53	234	5.83
O_3	36 ± 17	33	88	6.47
benzene	7 ± 9	2	44	0.65
toluene	51 ± 56	31	250	1.83
ethylbenzene	2.58 ± 2.38	2.02	14	0.24
m&p-xylene	3.91 ± 3.31	3.15	17	0.28
o-xylene	2.26 ± 1.88	1.79	6.84	0.15

Table 4.2 (cont'd)

Eskisehir (30*, 8)**				
SO_2	33 ± 30	26	195	3.1
NO_2	43 ± 33	33	189	0.8
O_3	48 ± 27	46	195	9.2
benzene	2.3 ± 2.1	1.4	8.2	0.3
toluene	26 ± 19	23	78	2.6
ethylbenzene	1.6 ± 1.1	1.3	6.8	0.1
m&p-xylene	2.5 ± 1.8	2.0	10	0.1
o-xylene	1.6 ± 1.3	1.1	6.7	0.0
Karabük (25*, 7)**				
SO_2	38 ± 35	30	200	1.35
NO_2	40 ± 28	37	137	1.35
O_3	41 ± 19	34	145	7.0
benzene	11 ± 12	6.1	54	0.8
toluene	15 ± 15	7.9	59	1.7
ethylbenzene	1.1 ± 1.0	0.7	4.3	0.2
m&p-xylene	2.0 ± 1.8	1.4	8.6	0.3
o-xylene	1.0 ± 1.1	0.7	5.3	0.2
Kastamonu (30*, 6)**				
SO_2	33 ± 19	28	94	2.6
NO_2	32 ± 21	28	94	0.3
O_3	56 ± 29	56	173	1.7
benzene	3.2 ± 2.7	2.6	11.4	0.5
toluene	24 ± 54	9	305	1.4
ethylbenzene	1.2 ± 1.4	0.9	8.2	0.1

Table 4.2. (cont'd)

m&p-xylene	1.9 ± 2.1	1.5	12.5	0.2
o-xylene	1.1 ± 1.1	0.9	6.2	0.1
Kırıkkale (15*, 9)**				
SO_2	36 ± 28	25	161	5.49
NO_2	32 ± 26	24	127	2.34
O_3	46 ± 43	35	243	2.81
benzene	2.7 ± 2.5	1.7	10	0.10
toluene	12 ± 16	5	80	0.4
ethylbenzene	0.9 ± 0.7	0.9	2.9	0.04
m&p-xylene	1.5 ± 1.2	1.1	4.9	0.1
o-xylene	1.1 ± 0.8	0.9	3.2	0.0
Kırsehir (20*, 7)**				
SO_2	32 ± 25	20	107	2.37
NO_2	22 ± 15	20	69	0.68
O_3	67 ± 49	49	326	25
benzene	2.7 ± 2.5	1.9	13	0.13
toluene	4.8 ± 6.4	3.2	38	0.51
ethylbenzene	0.50 ± 0.50	0.34	2.88	0.04
m&p-xylene	0.83 ± 1.03	0.57	6.45	0.15
o-xylene	0.59 ± 0.72	0.32	4.00	0.13
Kütahya (24*, 6)**				
SO_2	35 ± 29	30	217	0.59
NO_2	30 ± 29	23	147	0.27
O_3	37 ± 19	33	113	0.50
benzene	1.6 ± 2.2	0.7	9.8	0.37

Table 4.2 (cont'd)

toluene	4.0 ± 5.8	1.7	27	0.19
Et-benzene	0.68 ± 0.96	0.32	3.83	0.00
m&p xylene	0.91 ± 1.42	0.41	6.9	0.05
o xylene	0.73 ± 1.03	0.36	4.9	0.01
Yozgat (21*, 6)**				
SO_2	37 ± 35	23	269	7.69
NO_2	27 ± 28	21	207	0.27
O_3	60 ± 45	45	297	2
benzene	2.8 ± 1.9	2.6	7.5	0.4
toluene	10 ± 12	6	57	0.79
ethylbenzene	1.2 ± 1.4	0.8	7.9	0.14
m&p-xylene	1.8 ± 2.0	1.3	10	0.27
o-xylene	1.1 ± 1.2	0.8	5.4	0.10
Zonguldak (30*, 6)**				
SO_2	38 ± 23	33	115	7.2
NO_2	49 ± 25	48	124	6.23
O_3	31 ± 21	27	100	0.38
benzene	3.8 ± 2.9	2.8	11	0.44
toluene	7.6 ± 4.4	7.3	16	0.56
Et-benzene	1.0 ± 0.8	0.8	3.4	0.08
m&p xylene	1.4 ± 0.9	1.4	3.6	0.11
o xylene	0.9 ± 0.6	0.8	2.1	0.12

***Number of passive sampling stations for SO_2, NO_2 and O_3**

****Number of passive sampling stations for BTEX**

Number of stations where inorganic pollutants are measured varied between 15 at Kırıkkale and 66 at Ankara. Similarly, number of stations where BTEX compounds were measured varied between 21 at Ankara and 6 at Kastamonu, Kütahya, Yozgat and Zonguldak. Population of cities played an important role in selecting number of passive sampling stations in that city.

Concentrations of SO_2, NO_2 and O_3 measured at Ankara are 41 ± 28, 63 ± 42 and 38 ± 27 μg $m^{-3,}$ respectively. These are annual averages, which were obtained by averaging all measurements at each station. In the second step annual averages in all of the 66 stations were also averaged. Median concentrations of SO_2, NO_2 and O_3 are 33, 53 and 32 μg $m^{-3,}$ respectively. In this study we were not able to do frequency analysis, because there was not enough data to generate frequency histograms. However, smaller median concentrations of measured parameters than average concentrations in most of the cities suggested right skewed distributions for most of the parameters, in most of the cities.

Concentrations of benzene, toluene, ethylbenzene, m&p-xylene and o-xylene concentrations at Ankara are 2.7 ± 3.0, 32 ± 62, 2.2 ± 3.0, 3.7 ± 5.3 and 2.2 ± 3.1, respectively. Since the main source of BTEX compounds is traffic concentrations of benzene, toluene, ethylbenzene, m&p-xylene and o-xylene in urban atmosphere is determined by number of cars in traffic. In that sense Ankara is expected to have higher concentrations of BTEX compounds.

Annual average SO_2 concentrations in remaining cities varied between 38 μg m^{-3} at Karabük and Zonguldak and 29 μg m^{-3} at Düzce. Median concentrations on the other hand vary between 20 μg m^{-3} at Kırşehir and 33 μg m^{-3} at Zonguldak. As pointed earlier lower median concentrations (than averages) is due to right skewed distribution of SO_2 concentrations in cities. One point to note about SO_2 concentrations is that it is not highly variable between cities. Normally strength of residential heating source is expected to be significantly different between cities due to different populations. However, the expected difference was not observed. This may indicate that, since most of the cities are heated by natural gas, space heating is no longer the main source of SO_2 in urban atmosphere. Sources other than space heating, particularly traffic should be seriously considered as main SO_2 source. Genç et al (2010) reported a typical diurnal traffic pattern in SO_2 concentrations measured in monitoring stations at Ankara. Although there is no similar reports in other cities, change in mode of heating in cities may affect main SO_2 sources in Turkish urban atmosphere.

Annual average NO_2 concentration in cities varied between 22 µg m^{-3} at Kırşehir and 57 µg m^{-3} at Düzce. Median concentrations, on the other hand varied between 20 µg m^{-3} at Kırşehir and 53 µg m^{-3} at Düzce. Smaller median NO_2 concentrations than averages is again due to right-skewed distribution of NO_2 concentration. Unlike in case of SO_2, NO_2 concentrations are variable between cities. This is probably due to different influence of traffic emissions in cities. For example, NO_2 concentration at Düzce, which is a city with 377,000 population is similar with annual average NO_2 concentration measured at Ankara, which is a city with 5.4 million population. Please note that Düzce is located in close proximity of the highways that connect Istanbul and Ankara (TEM and toll-road). Probably, NO_2 concentrations measured at Düzce is affected from vehicle emissions coming from those roads. The role of neighboring emissions on NO_2 concentrations measured in other cities should also be taken into account.

Ozone concentrations varied between 31 µg m^{-3} at Zonguldak and 67 µg m^{-3} at Kırşehir. These values are lower than we anticipated, because in a country with plenty of sunshine higher ozone concentrations is expected. Limit ozone concentration in our country is 120 µg m^{-3} according to Air Quality Regulation. Average O_3 concentrations measured in this study is not even close to this standard. Relatively low O_3 concentrations measured in all cities can be due to number of factors. (1) In urban atmosphere high ozone concentrations are observed at suburbs, not at the city center due to a process called “ozone distillation”. Ozone distillation refers to ozone destruction at areas where NO concentration is high, with the following reaction (1):

(1) $NO + O_3 \rightarrow NO_2 + O_2$

This process does not allow ozone built up at the city center. Therefore, ozone concentration is higher at far away from city center (Üzmez, 2018). (2) There is approximately 4 – 5 hour gap between emission of ozone precursors from traffic (NO_2 and hydrocarbons) and formation of ozone maximum. Ozone precursors are emitted during morning rush hour (between 8 and 10 am), but ozone maximum is observed at 13:00 - 14:00 hours. During this time winds move O_3 containing air over the city to suburbs. Since our stations are mostly within the city we probably missed high ozone concentrations outside the city. (3) Most O_3 standards are designed for day-time ozone concentrations, to avoid low night-time ozone concentrations. This means that ozone concentrations that will be compared with standards has to be measured only during day-time. However, it is not possible to differentiate between night and day time O_3 concentrations when samples are collected with passive sampler. Since passive samplers are left at the field for about a week, concentrations measured is average of entire week, without discriminating between day and night time concentrations. All of these three factors results in low ozone concentrations within the city where all of our BTEX passive samplers are located.

Benzene concentrations in 13 cities included in this study vary between 1.6 $\mu g\ m^{-3}$ at Kütahya and 11 $\mu g\ m^{-3}$ Karabük. Most of the VOC studies performed by our group in different locations in Turkey demonstrated that BTEX levels are low in Turkish cities compared to BTEX concentrations measured in equally sized European and US cities. This was attributed to smaller number of cars in our cities (Kuntasal et al., 2013). Although benzene concentrations in most of the cities were low, there are cities such as Bolu, Düzce and Karabük where benzene concentrations were > 7 $\mu g\ m^{-3}$. Since traffic is the dominating source for most VOCs including BTEX compounds concentrations of these compounds measured at a station depends strongly on the distance between the sampling points to the nearest major road, which can be the reason for relatively high benzene concentrations reported for some of the cities.

General patterns observed in concentrations of other BTEX compounds, namely toluene, ethylbenzene, m&p-xylene and o-xylene were not significantly different from pattern observed in benzene concentration.

4.3 Comparison of Data with Literature

Comparison of data with literature part includes a three-stage comparison method. SO_2, NO_2, O_3, BTEX and their sources that they reflect can be seen from table 4.2. At the first stage, SO_2, NO_2, O_3, BTEX concentrations which were measured in thirteen cities in this study were compared with the concentrations measured with other cities in Turkey. This comparison is very significant to observe the differences of air pollutant concentration of other cities.

At the second stage, measurement results of SO_2, NO_2, O_3, BTEX concentrations in thirteen cities in this study were compared with the concentrations measured with similar studies at different regions around the world.

At the final stage, results of measurements of this study were compared with regulatory standards both national and international.

4.3.1 Comparison of data obtained in this study with other cities in Turkey

In this section, the measured concentrations of inorganic pollutants including nitrogen dioxide, ozone and sulfur dioxide and organic pollutants including toluene, benzene, ethylbenzene, m-xylene, o-xylene and p-xylene in 13 cities in Central and Northern Anatolia are compared with other cities of Turkey in order to assess the pollution level.

Ercan et al. (2019) studied spatial and seasonal variations of atmospheric SO_2, NO_2, O_3 and BTEX concentrations in Istanbul. In this study, there was no variation observed for SO_2 concentration. Meteorological conditions have important effect on the distribution of air pollutants. The highest NO_2 concentration was observed in winter season and lowest concentration in summer because of photochemical reactions and residential heating. The highest O_3 concentration was observed in summer in İstanbul. In this study, maximum geometric mean concentrations of

BTEX, O_3, NO_2 and SO_2 were 5476.4, 110.12, 35.86, 9.44 μg/m^3 and minimum geometric mean concentrations of BTEX, O_3, NO_2 and SO_2 were 2.42, 32.85, 5.96, 0.04 μg/m^3 respectively. The geometric mean concentration of O_3, NO_2 and SO_2 were 72.04, 15.80 and 1.66 μg/m^3.

Pekey and Özaslan (2013) measured SO_2, NO_2 and O_3 concentrations by using passive sampling method in an industrial city of Turkey. Ambient concentrations of SO_2, NO_2 and O_3 were measured at 51 sampling point in Kocaeli. SO_2 concentrations were higher in winter because of residential heating in winters, NO_2 concentrations were also higher in winter because of combustion of fossil fuels and other sources which are vehicles, residential heating, chemical processes and incinerations. O_3 concentrations were higher in summer season because of higher temperatures photochemical reactions which are promoted with light intensity. Ozone levels were measured high in rural areas because of reaction between ozone and nitrogen oxide. In summer, average concentration of SO_2 was 8 μg/m^3 and maximum concentration was 82 μg/m^3, average concentration of NO_2 was 14 μg/m^3, maximum concentration was 40 μg/m^3 and average concentration of O_3 was 86 μg/m^3 and maximum concentration was 61 μg/m^3. In winter, average concentration of SO_2 was 25 μg/m^3 and maximum concentration was 61 μg/m^3, average concentration of NO_2 was 50 μg/m^3 and maximum concentration was 100 μg/m^3.

Bozkurt et al. (2018) measured SO_2, NO_2, O_3 and BTEX concentrations by using passive sampling method in Düzce. Concentrations of SO_2 were measured higher in winter than in summer because of using coal for domestic heating. Concentrations of NO_2 and BTEX were measured also higher in winter than in summer because of high traffic density in winter. Because of photochemical reactions of O_3, higher O_3 concentrations were measured in summer season. Annual average concentrations of SO_2, NO_2, O_3 and BTEX were 23.91, 22.63, 33.62 and 7.71 μg/m^3 respectively. When compared with our study, it can be said that annual average NO_2 concentration in Kırşehir was close to annual average concentration NO_2 of Düzce. Kastamonu and Zonguldak had the close concentration of SO_2 and O_3 with Düzce.

Üzmez (2018) studied atmospheric concentrations of SO_2, NO_2 and O_3 by using passive sampling in Eskişehir. The highest NO_2 concentrations were measured at city center which have heavy traffic, urban and residential characteristics. SO_2 concentrations were similar NO_2 in terms of spatial variations. However, highest O_3 concentration were measured at far from the city center.

Pekey and Yılmaz (2011) measured BTEX concentration with passive sampling method in Kocaeli. BTEX concentration showed high concentration in major roads, city centers and near industrial areas. Concentrations of BTEX ranged from 3.7 to 335.5 $\mu g/m^3$ at 49 sampling points. Mean values of BTEX was 95.69 $\mu g/m^3$.

Tecer et al. (2017) measured BTEX and NO_2 concentration by using passive sampling method at 40 stations in Yalova. These pollutant concentrations were found to be higher in highway passing through the center of city. Apart from benzene, other BTEX compounds concentrations were observed in high concentration in industrial areas. At main road stations, mean BTEX concentration was 2.55 $\mu g/m^3$, at industrial and rural area, mean BTEX concentration was 10.64 $\mu g/m^3$ and 1.21 $\mu g/m^3$.

4.3.2 Comparison of Data Obtained in This Study with Other Cities Around the World

The measured concentrations of inorganic pollutants including nitrogen dioxide, ozone and sulfur dioxide and organic pollutants including benzene, toluene, ethylbenzene and xylene which is called as BTEX are also compared with the results of the studies that were performed in other parts of the world. There are slight alterations in the locations of sampling points can result with significant differences in sulfur dioxide, nitrogen dioxide, ozone and BTEX. Thus, the other measurement results of cities around the world can ensure only crude information comparison of data obtained in this study.

In Caballero et al. (2012) study, NO_2 concentration was measured at 79 sites in city of Elche at the southeastern Spain. Concentrations were measured once a month for

2 years and average NO_2 concentration was 32 ± 12 µg/m^3. Minimum NO_2 concentration was measured in summer season and lowest level was 18 µg/m^3.

Xiao et al. (2018) measured SO_2, NO_2 and O_3 concentrations by using passive sampling method in the Inland Basin City of Chengdu, Southwest China. The highest SO_2 and NO_2 concentrations were measured in winter and the lowest concentration in summer because of effect of industrial sources and weather conditions on air pollution dispersion. Mean SO_2 concentrations were measured 28 µg/m^3, 21 µg/m^3 and 16 µg/m^3 in 2014, 2015 and 2016. Mean NO_2 concentrations were measured 41 µg/m^3, 40 µg/m^3 and 43 µg/m^3. The highest O_3 concentrations was measured in summer season which was related with the solar radiation. Mean O_3 concentrations were measured 83 µg/m^3, 96 µg/m^3 and 98 µg/m^3. All 3 years mean O_3 concentrations were higher than 13 cities in our study. Average concentration of three years of SO_2, NO_2 and O_3 were 21,67, 31,33 and 92,33 µg/m^3, respectively.

Bari et al. (2015) studied SO_2, NO_2 and O_3 concentrations by using passive sampling method in Alberta, Canada. The highest concentration of SO_2 and NO_2 were measured in winter because of greater frequency of mixing height and high atmospheric stability conditions during winter. In rural Alberta, industrial emissions and fossil fuel combustion and wood combustion for residential heating affect the SO_2 and NO_2 concentrations more in winter than summer. Dominant O_3 concentration was observed in spring and early summer period.

Iovino et al. (2009) measured BTEX concentration with passive sampling in Naples metropolitan area. This study indicated that there is high linear correlation between BTEX concentration and vehicular traffic. Also, there is a correlation with hottest months of the year due to transport by local seasonal winds. Average atmospheric benzene concentration was higher than the European Union limit value for 2010. Annual BTEX concentration was measured as 9,16 µg/m^3 in Naples in 2010. Kırşehir and Kütahya showed that close value with 9,67 and 9,88 µg/m^3.

Zabiegala et al. (2010) measured BTEX concentrations by passive sampling in Tricity area and Tczew in Poland in 2007. For selected passive samplers, annual average concentration of benzene exceed the limit values of benzene recommended

European Union directive. Not only road traffic but also industrial activities could have effect on BTEX concentration. Benzene concentration was lower than European Directive, which specifies a limit of 5 µg/m^3.

Kerchich and Kerbachi (2012) studied on BTEX concentration by passive sampling in semirural sites, urban sites and indoor air in Algiers City. High benzene concentrations were observed in tunnel, roadside and inside the car. In this study, there is a good correlation between road traffic flow and BTEX concentration. There were more than 27 sampling points and concentrations were measured in 2009 spring. Average BTEX concentration was measured that 238,9 µg/m^3. This value is much higher than average BTEX concentration of 13 cities in our study.

Brocco et al. (1997) measured BTEX concentration in Rome during 1992-1993. Average BTEX concentration was 232 µg/m^3 and this value is also higher than average BTEX concentration of 13 cities in our study.

Astel et al. (2013) measured BTEX concentration by passive sampling method at 21 different sampling sites placed in Tristine that is the city of Italy. Higher BTEX concentrations were observed in winter than the summer and sources of BTEX compounds were associated with traffic impacts. 7 years' average BTEX concentration was measured as 122.10 µg/m^3.

Duan and Li (2017) studied that BTEX sources and its distribution in China. Atmospheric BTEX concentration were higher in winter than in summer. Main factors that affects the seasonal differences of BTEX are temperature, precipitation, wind speed and wind direction. Also, vehicle emission was related with high BTEX concentration. Annual average BTEX concentration was measured as 46.7 µg/m^3 and 20.0 µg/m^3 for the cities in south and north China. Annual average BTEX concentration of Ankara and Bartın is close to average BTEX concentration of south of China. Annual average BTEX concentration of Çankırı and Kırıkkale is close to north of China.

4.4. Spatial Variation of Pollutant Concentrations

In this section inter-city variability of annual average concentrations of pollutants measured in the study is evaluated. Distribution of SO_2 in 13 cities is depicted in Figure 4.4. As pointed in previous sections SO_2 concentrations do not change significantly from one city to another. Annual average SO_2 concentrations measured at Ankara, Düzce, Kütahya and Zonguldak are slightly higher than SO_2 concentrations measured in other cities, but student t-test demonstrated that difference between SO_2 means in these cities are not statistically significant. Please note that student t-test is designed to establish statistically significant differences between data sets with Gaussian distribution. Although we were not able to establish frequency distribution in our data set (there was not enough stations to construct a valid frequency distribution), it is very likely that it is not gaussian. If the data frequency distribution is not Gaussian, then reliability of t-test becomes questionable. However, it is clear in Figure 4.4 there is not much difference between SO_2 concentrations measured in cities. This also is reflected in very low coefficient of variation (8.9%) calculated using average SO_2 concentrations in cities.

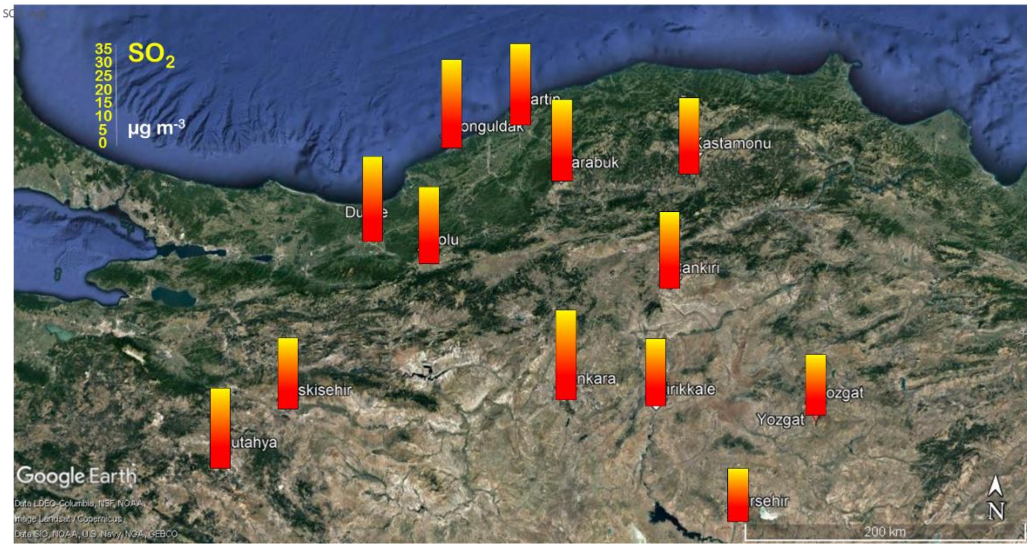

Figure 4.4. Distribution of annual median SO_2 concentrations in cities included in this study

Distribution of NO_2 concentrations between cities is depicted in Figure 4.5. NO_2 is not distributed as uniformly as SO_2 in Northwestern Anatolia. Coefficient, which is 31.4%, reflects this variability. Highest NO_2 concentrations are measured in Ankara, Düzce and Zonguldak and lowest concentrations are reported for Çankırı and Kırşehir. Main source of NO_2 in urban atmosphere is traffic emissions. High NO_2 concentration in Ankara is expected due to higher number of cars on the roads. Although traffic density in Düzce is significantly smaller than traffic density in Ankara, NO_2 concentrations in both cities are comparable. Although traffic density in Düzce is not high, due to its modest population (378,000), the city is only 2 km from the Anadolu highway, which is a toll road that connects Ankara and Istanbul. TEM highway, which is another highway connecting Ankara and Istanbul, passes from the city. High NO_2 concentration measured at Düzce demonstrate that the city is affected from traffic emissions on these crowded highways. Similarly, the results were found in Çoban’s (2009) study. Marmara region has the most of the population in Turkey and industry is developed in comparison to other regions.

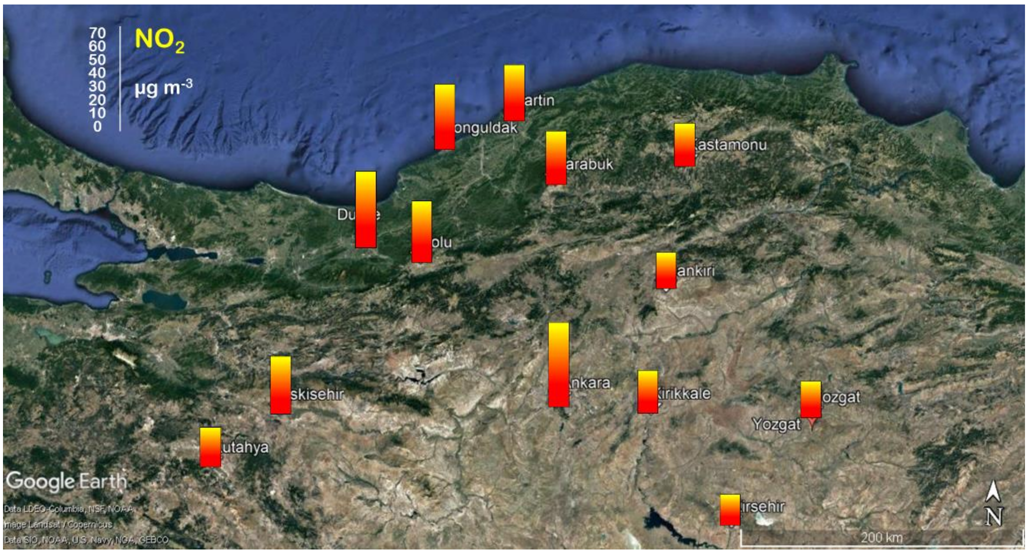

Figure 4.5. Distribution of annual median NO_2 concentrations in cities included in this study

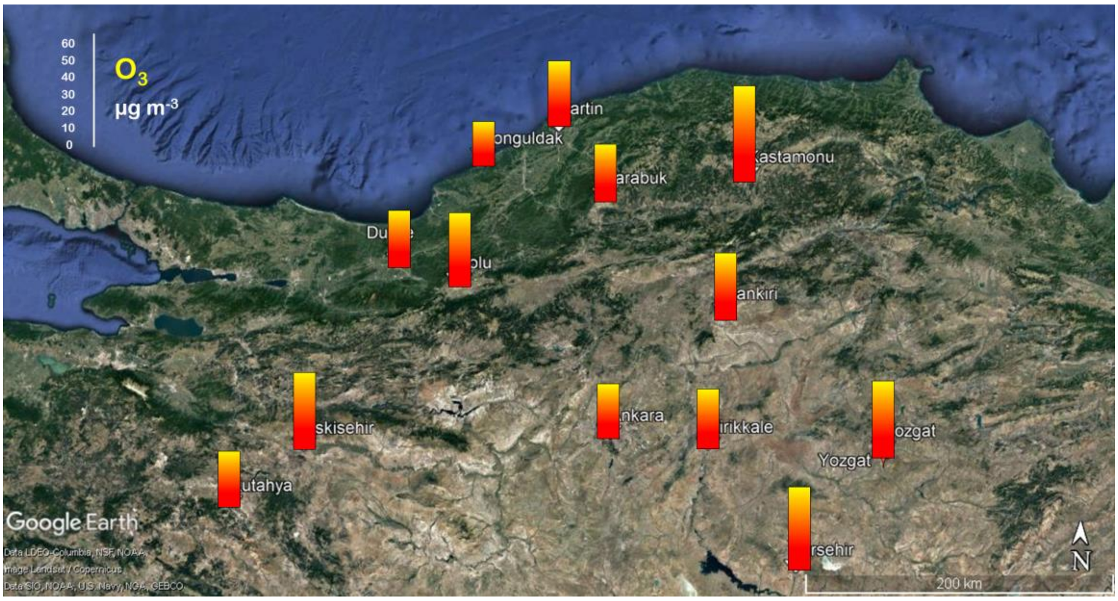

Figure 4.6. Spatial distribution of O_3 concentrations in Northwest Anatolia

Distribution of O_3 concentrations in 13 cities is depicted on Figure 4.6. Please note that O_3 concentration in the city is not the highest O_3 levels in an urban airshed. Maximum in O_3 concentration is always observed at outskirts of the city, at suburbs due to ozone distillation, which was discussed in previous section. Since most of our stations are located within the city, city average O_3 concentrations given in Table 4.2 and Figure 4.6. do not show the highest O_3 levels in these cities. Coefficient of variation is 30.1%, indicating that O_3 concentrations do not change significantly from one city to another. One interesting feature noted in Figure 4.6. is the inverse relation between O_3 and NO_2 concentrations. High concentrations of NO_2 were measured in Ankara, Düzce and Zonguldak. It can be seen in Figure 4.6 that these cities have low average O_3 concentrations, which is the manifestation of ozone distillation at high NO concentrations.

Spatial distribution of measured VOCs in our study area are given in Figures 4.7, 4.8, 4.9, 4.10 and 4.11 for benzene, toluene, ethylbenzene, m&p-xylene and o-xylene respectively. Spatial variability of BTEX compounds is very similar to each other, except for benzene.

Benzene concentration is the highest at Karabük (average is 11 ± 12 µg m^{-3} and median is 6,1 µg m^{-3}). This average value is at least a factor of two hıgher than average benzene concentration measured in other cities. Source of unusual benzene concentration at Karabük is not known.

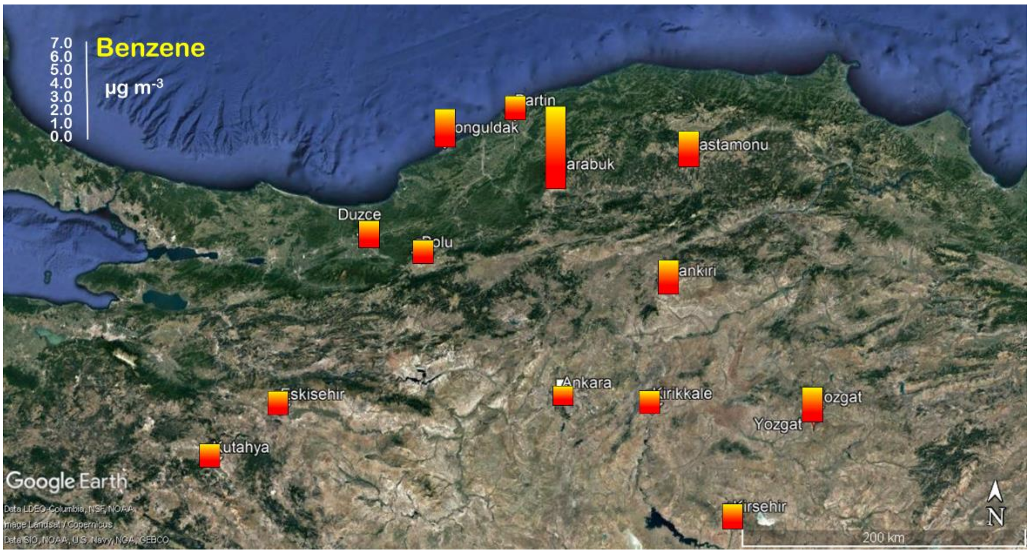

Figure 4.7. Spatial distribution of benzene concentrations in Northwest Anatolia

Highest concentrations of remaining BTEX compounds were measured at Düzce, Ankara, Bartın and Eskişehir, but the difference between these cities and others are not as dramatıc as the difference observed in benzene concentrations. We expected to similar spatial dıstribution for all BTEX compounds, because the dominating source of these compounds is traffic, particularly light duty traffic emissions. Higher concentrations were observed. High BTEX concentrations were measured in highly populated cities like Ankara and in cities that are affected from nearby highways, like Düzce. Distribution of BTEX compounds resemble the variation in NO_2 concentrations, which is not surprising due to traffic source for both BTEX compounds and NO_2.

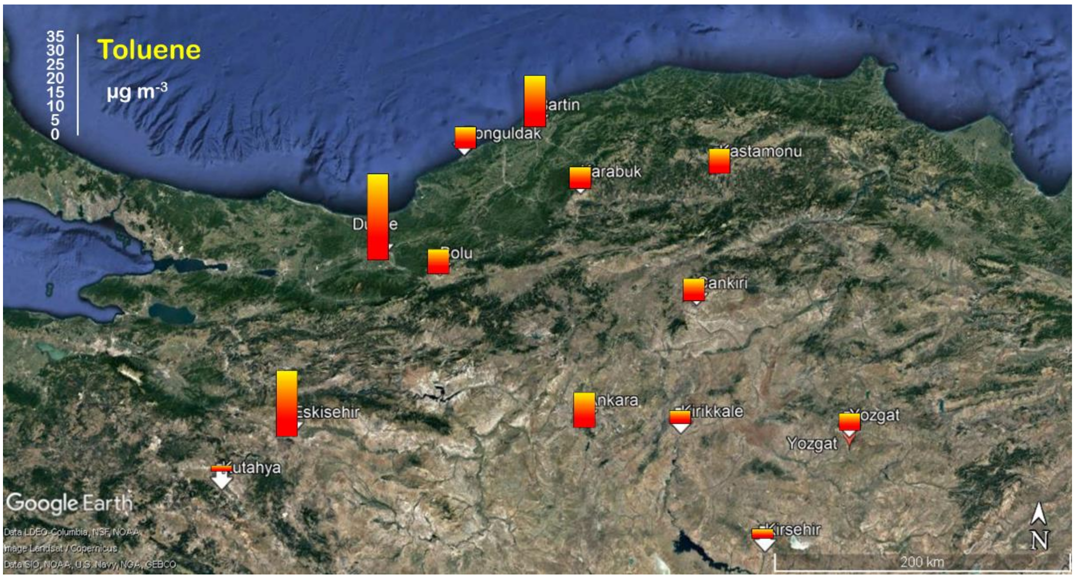

Figure 4.8 Distribution of toluene concentration between 13 cities included in this study

Coefficient of variation for benzene, toluene, ethylbenzene, m&p-xylene and o-xylene were 61%, 84%, 47%, 47%, 42%, respectively, indication fair amount of intercity variability in their concentrations.

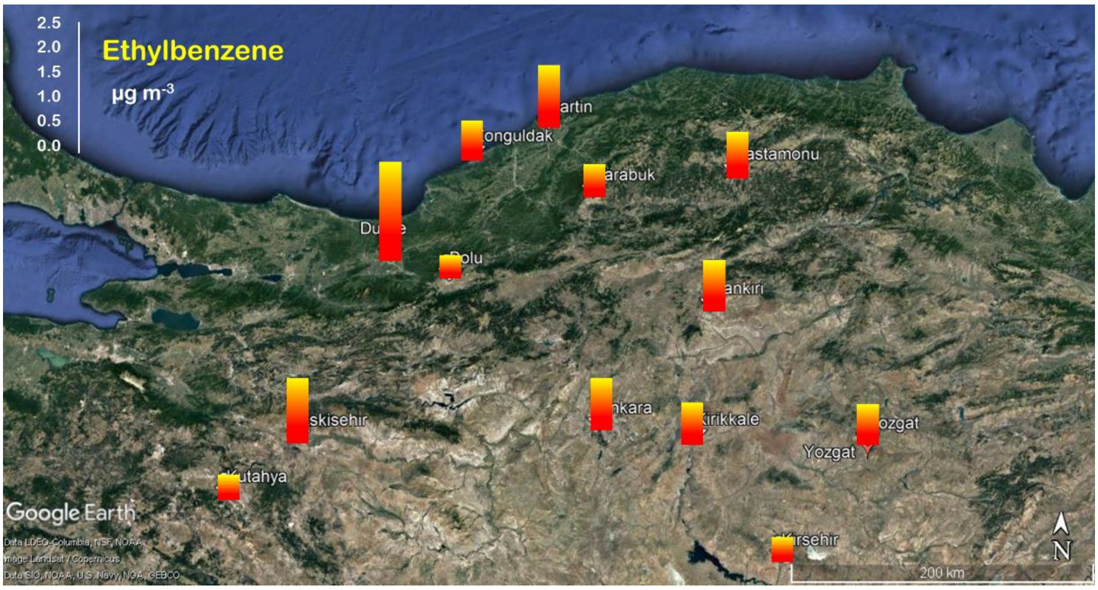

Figure 4.9 Spatial distribution of ethylbenzene in the study area

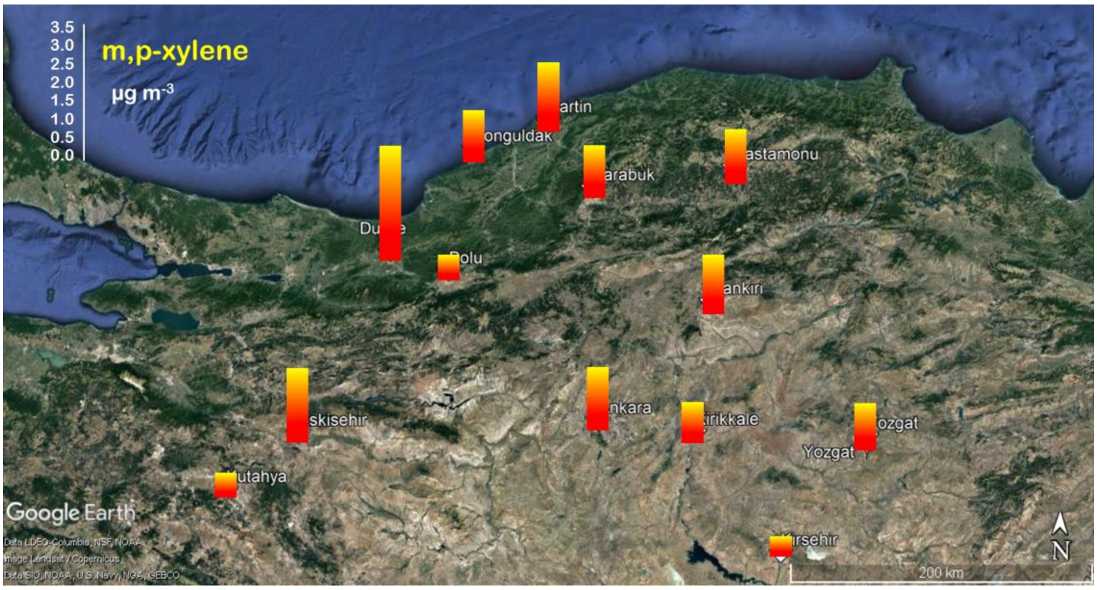

Figure 4.10 Distribution of m&p-xylene concentration in 13 cities included in this study

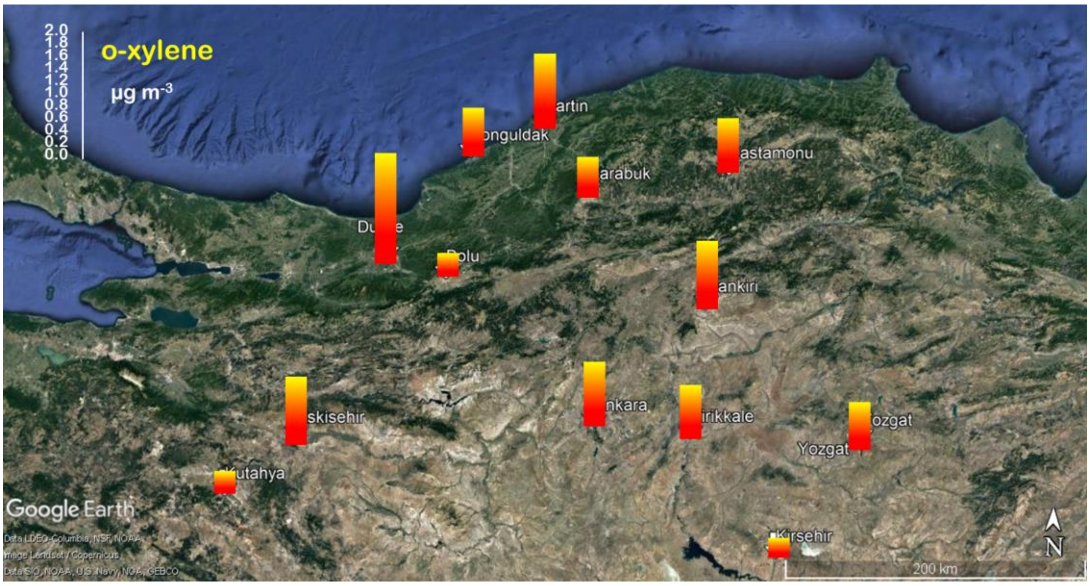

Figure 4.11 Distribution of o-xylene concentration in 13 cities included in this study

4.5. Comparison of Measured Concentrations of Pollutants with Regulatory Standards

The easiest way to assess level of pollution in an urban atmosphere is to compare measured concentrations with regulatory standards. Since most of the standards are designed to protect human health, any incompliance with standard is a clear indication of the polluted atmosphere. However, there are some exceptions to this statement. Sometimes natural sources can be the source of incompliance. For example, most of the incompliance cases for PM_{10} at the Mediterranean region is due to dust transport from Sahara Desert or deserts in Middle East and Arabic Peninsula. These are natural sources and humans cannot do anything to avoid them. Since no EU country on the Mediterranean Coast can comply with existing EU standards a provision was added to EU air quality directive stating that “if an exceedance is shown to be due to dust transport, that event can be excluded from exceedances”. Please note that Turkey adopted 2008/50/EC directive, this provision also apples to exceedances in our country as well.

Gases included in this study have also natural sources, like forest fires, but since it is almost impossible to demonstrate that a forest fire is naturally started (because humans also start fires), it is not possible to include forest fires to provision discussed above.

Relevant table in Turkish Air Quality Regulation (AQR) is given in 4.3. The AQR was modified several times since the first one, which became effective in 1986. Finally, our regulation was matched more or less exactly with EU 2008/50/EC directive in 2018 and currently adopted regulation is effective in our country. Only parameters measured in this study was included in the table.

Table 4.3 Regulatory standards that are in effect in Turkey and elsewhere (concentrations are in (µg/m3)

Regulation	Pollutants	Limit Values		
		Hourly	Daily	Annual
AQR	SO_2	380	150	20 (for ecosystem health)
	NO_2	260		44
	O_3		120*	
	Benzene			5

Table 4.3 (cont'd)

WHO	SO_2**	500	20	50
	NO_2**	200		40
	O_3**	100		
	Benzene***			
EU Directive	SO_2	350	125	$20^{\S}$
	NO_2	260		44
	O_3	120*		
	Benzene			5
USEPA	SO_2			80
	NO_2			100
	O_3	70****		
	BTEX			

AQR: Air Quality Assessment and Management (2015)

* Maximum 8-hour daily average per year.

** WHO guidelines of air quality for sulphur dioxide, ozone, particulate matter, nitrogen dioxide and, WHO Global Update, 2005.

*** World Health Organization Air Quality Guidelines for Europe Second Edition, 2000.

**** Annual fourth highest daily maximum 8 hour average concentration, average over 3 years.

§ The hourly limit value (350 µg m^3) cannot be exceeded more than 24 times a year and the daily limit value (125 µg m^3) cannot be exceeded more than 3 times a year.

Hourly average, which should not be exceeded by data with one-hour integration time is 380 µg m^{-3}. Limit value for daily and annually averaged data are 150 µg m^{-3} and 20 µg m^{-3}, respectively. There is one point worth noting about these SO_2 standard. Annual limit, which is 20 µg m^{-3} is defined as "… for ecosystem health". It is unrealistically low value to meet in urban atmosphere in Turkey. Annual limit (20 µg m^{-3}) is lower than EPA annual limit and WHO annual guideline value. Since our regulation is adopted from 2008/50/EC directive, annual SO_2 limit in EU is also 20 µg m^{-3} and also defined as "for ecosystem health", but it is probably is used for ecosystem health and not for human exposure. In EU directive there other criteria that is used for human exposure. The directive states that hourly limit (350 µg m^{-3})

should not be exceeded more than 24 times in a year and daily limit value can not be exceeded more than 3 times in a year. These are the human health related standards. Unfortunately, these exceedance based limits do not exist in our regulation.

Hourly and annual limit for NO_2 is 260 and 44 µg m^{-3}, respectively. There is no daily limit for NO_2. Problems encountered in SO_2 standard do not exist in NO_2, because annual limit, which is 44 µg m^{-3} is defined as “for human health”

Ozone standard is 120 µg m^{-3}. This value should not be exceeded when 8-hr average is taken between 8:00 and 16:00 hours. Among VOCs there is a limit value for benzene, which is 5 µg m^{-3} annually.

Comparison of our data is problematic for all parameters. Since our sampling with passive samplers is 15-days long and repeated 4 times in a year, we can only compare them with annual averages.

Annual average concentrations of SO_2, NO_2, O_3 and benzene and their status relative to annual limit value are depicted in Figure 4.12. City-average SO_2 concentration is higher than annual limit in our AQR. This is due to unrealistically small SO_2 annual limit value (20 µg m^{-3}). This limit value is exceeded in almost all stations in every city included in this study. The annual average concentrations in cities comply with EPA annual limit value and WHO annual guideline value.

For NO_2, city average concentrations exceed annual limit value only in Ankara, Düzce and Zonguldak. Annual averages in Bolu, Bartın, Eskişehir and Karabük are very close to annual limit value, but do not exceed it.

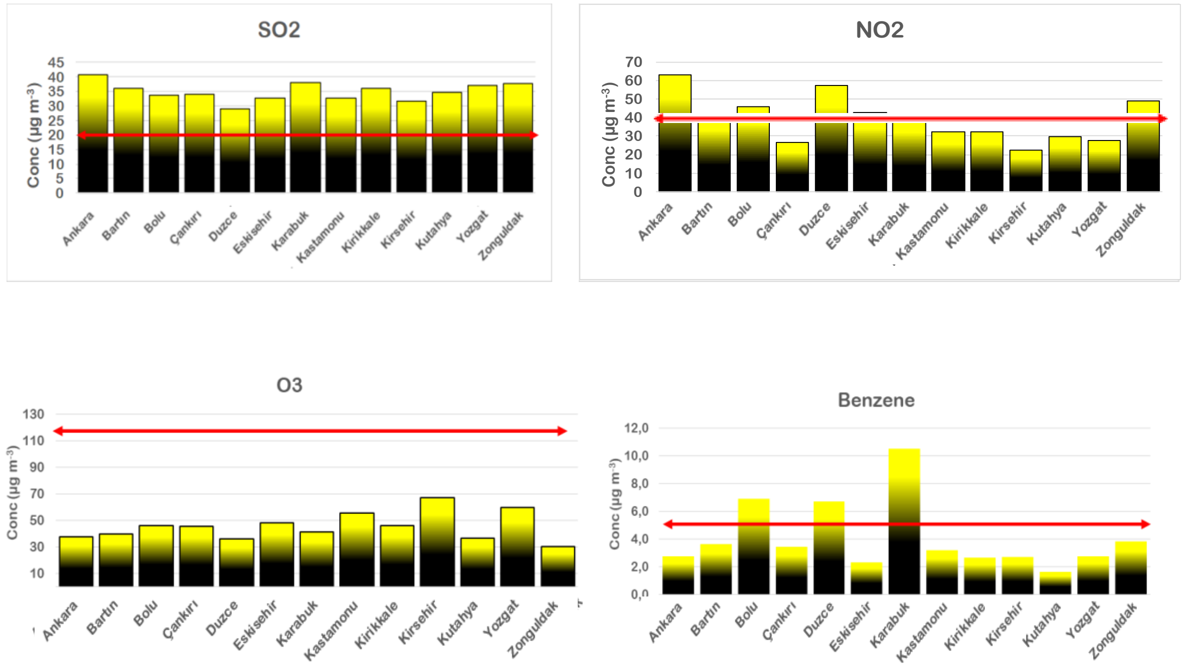

Figure 4.12 Annual average concentrations of pollutant measured in this study relative to annual limits for those

Annual average ozone concentrations measured in our cities are substantially lower than ozone limit value (120 µg m^{-3}). Please note that sampling and analysis method used in this study is not exactly compatible with methods recommended in AQR. In order to generate average ozone concentrations that can be compared with ozone limit value in standard, ozone must be measured 8-hours between 8:00 and 16:00 hours every day and these concentrations must be averaged, we continuously measured for 15 days using passive samplers. Our sampling scheme averages both day-time and night-time concentrations. Since ozone is secondary specie, which is produced by photochemical reactions, its night-time concentrations are significantly smaller than its day-time concentrations. When these low night-time concentrations are included in averages, one ends up with low annual values.

Annual average benzene concentrations exceeds long term limit only at Karabük. Very large iron and steel plant and traffic activity around that plant probably contributes to that high value. As pointed out before, our regulation is adopted from EU directive. EU standard is designed by taking into account traffic density in EU countries, but number of cars in traffic is approximately factor of four smaller than number of cars in western European countries and Countries in North America. Please note that benzene standard in our regulation is 5 μg m^{-3}. Benzene standard is the only limit value that increased when we adopted EU directive. Since it was 5 μg m^{-3}, it was exceeded in Karabük, Bolu and Düzce as well. Most of the studies performed in our group demonstrated that benzene levels in Turkish cities will rarely exceed benzene limit value.

Number of stations at which annual average concentrations of measured parameters exceeds annual limit values are given in Table 4.4. As discussed previously, annual average SO_2 concentrations exceeded annual limit value (20 μg m^{-3}) in almost all stations in all cities.

Table 4.4 Number of Measurement Results Exceeding the Limit Value

	SO_2	NO_2	Benzene
Ankara	65 (98%)	55 (83%)	1 (2%)
Bartın	15 (100%)	9 (60%)	2 (13%)
Bolu	20 (100%)	12 (60%)	3 (15%)
Çankırı	20 (100%)	5 (25%)	2 (10%)
Düzce	25 (100%)	19 (75%)	6 (24%)
Eskişehir	29 (97%)	15 (50%)	0
Karabük	24 (96%)	12 (48%)	5 (20%)
Kastamonu	30 (100%)	8 (27%)	1 (3%)
Kırıkkale	15 (100%)	3 (20%)	1 (7%)
Kırşehir	19 (95%)	2 (10%)	1 (5%)
Kütahya	23 (92%)	4 (16%)	0
Yozgat	20 (91%)	5 (73%)	0
Zonguldak	29 (97%)	24 (80%)	2 (7%)

The NO_2 limit value is exceeded in > 50% of stations at Ankara, Bartın, Bolu, Düzce, and Zonguldak. Exceedances are particularly high at Ankara, Düzce and Zonguldak. These cities are under strong influence of traffic emissions. It is interesting to note that Düzce is relatively small city but it shows the sign of strong influence of traffic emissions, indicated by high concentrations of not only NO_2, but also VOCs measured in this study. The only explanation to this is proximity of Ankara – Istanbul pay-road and TEM highway to the city. Parts of these highways between İstanbul and Kocaeli have very high traffic density, which obviously affect NO_2 and BTEX concentrations at Düzce.

Annual limit value of benzene (5 µg m^{-3}) is regularly exceeded in most cities. Number of stations where these exceedances are observed depends on the distance between the station and the nearest road. Benzene limit value are exceeded in few stations in each city, indicating that VOCs are not a significant problem in most of the cities.

Ozone limit value is not exceeded in any of the station in any of the cities. The reason, as pointed out before, is the way ozone averages are calculated in our measurement system and in regulatory process.

4.6. Seasonal Variation in Concentrations of Measured Parameters

Seasonal median concentrations of inorganic pollutants measured in this study are given in Table 4.5 and summer-to-winter concentration ratios are depicted in Figure 4.13. Concentrations of SO_2 are higher in winter season in all cities without any exception. Indicating influence of space heating on SO_2 concentrations. Although most of the cities included in this study are heated by natural gas, coal combustion is not entirely phased out, particularly at outskirts of cities where there is no infrastructure to use natural gas for heating. These low-income districts of cities are still heated by coal. Lower mixing height in winter also contribute to high concentrations in winter season.

Table 4.5 Seasonal concentrations of inorganic parameters measured in the study

	SO_2				NO_2				O_3			
	Sum	Fall	Wint	Sprng	Sum	Fall	Wint	Sprng	Sum	Fall	Wint	Sprng
Ankara	51	37	47	24	32	78	47	94	40	45	41	39
Bartın	17	23	74	15	49	23	38	59	55	28	41	40
Bolu	25	30	61	12	50	30	46	60	46	61	50	47
Çankırı	19	37	50	38	10	37	28	32	40	37	42	46
Düzce	16	35	51	5	45	35	59	85	45	32	41	36
Eskişehir	29	30	55	14	26	30	43	71	46	42	70	48
Karabük	27	29	79	17	37	29	41	54	49	35	47	41
Kastamonu	20	43	57	25	17	43	29	39	69	46	50	55
Kırıkkale	15	45	58	48	14	45	26	46	36	27	84	44
Kırşehir	16	28	60	34	13	28	20	28	45	44	118	67
Kütahya	32	46	46	20	2	46	21	52	36	46	34	37
Yozgat	17	32	62	52	11	32	26	40	51	31	53	59
Zonguldak	34	55	61	26	21	55	50	70	33	47	25	31

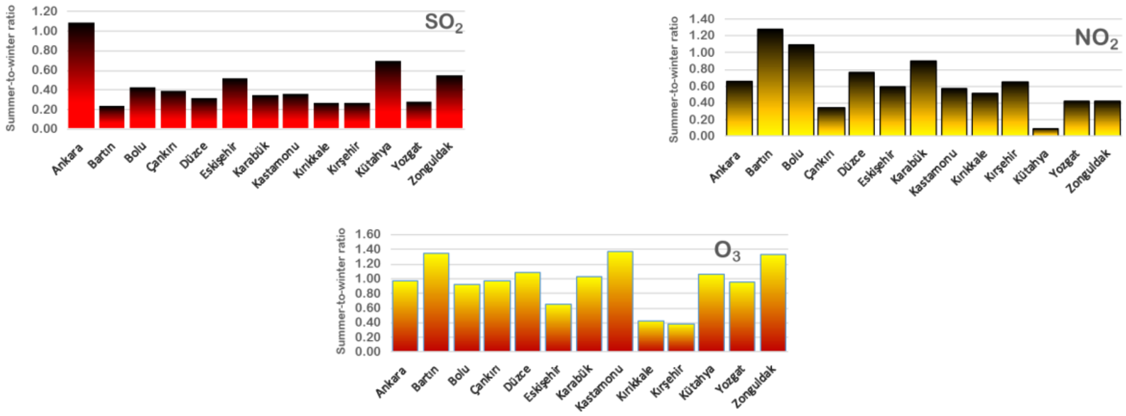

Figure 4.13 Summer-to-winter concentrations ratios of inorganic pollutants measured in this work

There is no consistent seasonal trend in NO_2 concentrations. Main source of NO_2 in urban atmosphere is combustion, particularly combustion at vehicle engine. At very high temperatures in engine NO is formed from atmospheric N_2 gas, which is then quickly oxidize to NO_2 in the atmosphere. Traffic emissions do not show a significant seasonal variation. That is the reason why a consistent trend is not observed in NO_2 concentrations. However, slightly higher concentrations in winter is probably due to lower mixing height in winter.

Since ozone in the atmosphere is produced by photochemical reactions, one would expect to see higher concentrations of O_3 in summer and spring and low concentrations in winter. Measured seasonal ozone concentrations given in the table does not support this hypothesis. There are no very obvious high concentrations in summer season. However, please note that our O_3 data do not show complete picture about ozone levels in these 13 cities. As discussed earlier in the manuscript, highest ozone levels are not observed at the city center, but observed at the peripheral of the city due to ozone distillation process at the city center where NO concentration is high.

Seasonal variation in concentrations of benzene, toluene, ethylbenzene, m&p-xylene and o-xylene are given in Table 4.6 and their summer-to-winter ratios are given in Figure 4.14. Summer-to-winter benzene ratios are < 1 in all cities indicating significantly higher winter-time concentrations of benzene. There are two important sources of VOCs that effect observed VOC concentrations in urban atmosphere; namely traffic emissions and solvent evaporation. Solvent evaporation is not an important source for benzene: it mostly come from light-duty motor vehicles. Motor vehicle emissions do not change significantly between summer and winter; however, lower mixing height in winter can result in higher concentrations in winter. High winter season concentrations (low S-to-W ratio) in all cities is probably due to this meteorological effect.

Table 4.6 Seasonal variation in median concentrations of BTEX compounds (concentrations are in µg m-3)

	Benzene				Toluene				Ethylbenzene				m&p-xylene				o-xylene			
	Sum	Fall	Wint	Spr	Sum	Fall	Wint	Spr	Sum	Fall	Wint	Spr	Sum	Fall	Wint	Spr	Sum	Fall	Wint	Spr
Ankara	1.05	6.24	5.2	0.70	25	74	29	7.5	1.7	5.1	1.8	0.96	2.9	8.9	2.9	1.2	1.5	5.9	1.8	0.6
Bartın	1.09	1.63	9.3	5.85	113	4.3	13	13	3.3	0.37	1.3	1.1	5.1	0.61	2.1	1.6	2.8	0.34	1.3	0.9
Bolu	1.09	1.71	31.2	7.04	6.0	4.3	20	18	0.52	0.39	1.17	2.24	0.78	0.61	2.2	3.5	0.48	0.34	1.3	1.8
Cakiri	0.99	3.51	7.8	2.75	6.8	9.1	11	9.1	1.2	1.1	0.95	0.84	1.8	1.8	1.6	1.3	1.5	1.3	1.0	1.0
Duzce	1.39	1.97	14.7	13.83	67	7.0	39	66	2.5	0.68	3.2	3.5	4.4	1.0	4.5	4.5	2.7	0.7	2.7	2.2
Eskisehir	1.01	1.31	4.6	4.00	36	15	22	20	1.6	1.5	1.9	1.1	2.7	2.3	2.9	1.7	1.7	1.2	2.1	1.1
Karabük	4.50	4.66	20.0	15.98	11	7.4	32	10	0.54	0.73	2.3	0.93	1.1	1.5	4.2	1.7	0.59	0.64	2.1	1.1
Kastamonu	1.36	3.29	7.6	2.55	51	14	12	9.4	1.4	1.4	1.4	0.81	2.2	2.5	2.2	1.3	1.2	1.4	1.1	0.87
Kırıkkale	0.71	3.28	5.5	3.28	13	11	9	12	1.0	0.92	0.85	0.82	1.6	1.6	1.4	1.3	1.4	1.1	0.90	0.82
Kırsehır	0.92	2.50	5.9	3.12	5.9	4.0	5.1	3.8	0.57	0.45	0.58	0.41	1.1	0.80	0.65	0.70	0.66	0.49	0.57	0.59
Kütahya	0.42	4.27	3.5	0.52	0.6	9.2	6.8	3.1	0.09	1.3	1.6	0.43	0.08	2.1	2.0	0.61	0.11	1.4	1.6	0.41
Yozgat	0.86	2.57	5.3	3.43	11	8.6	10	11	1.5	1.1	0.84	1.2	2.0	1.8	1.3	2.0	1.1	1.1	0.9	1.3
Zonguldak	1.96	5.50	6.6	1.35	11	7.3	9.1	3.1	1.9	0.83	0.88	0.31	2.3	1.5	1.5	0.50	1.5	0.83	0.83	0.35

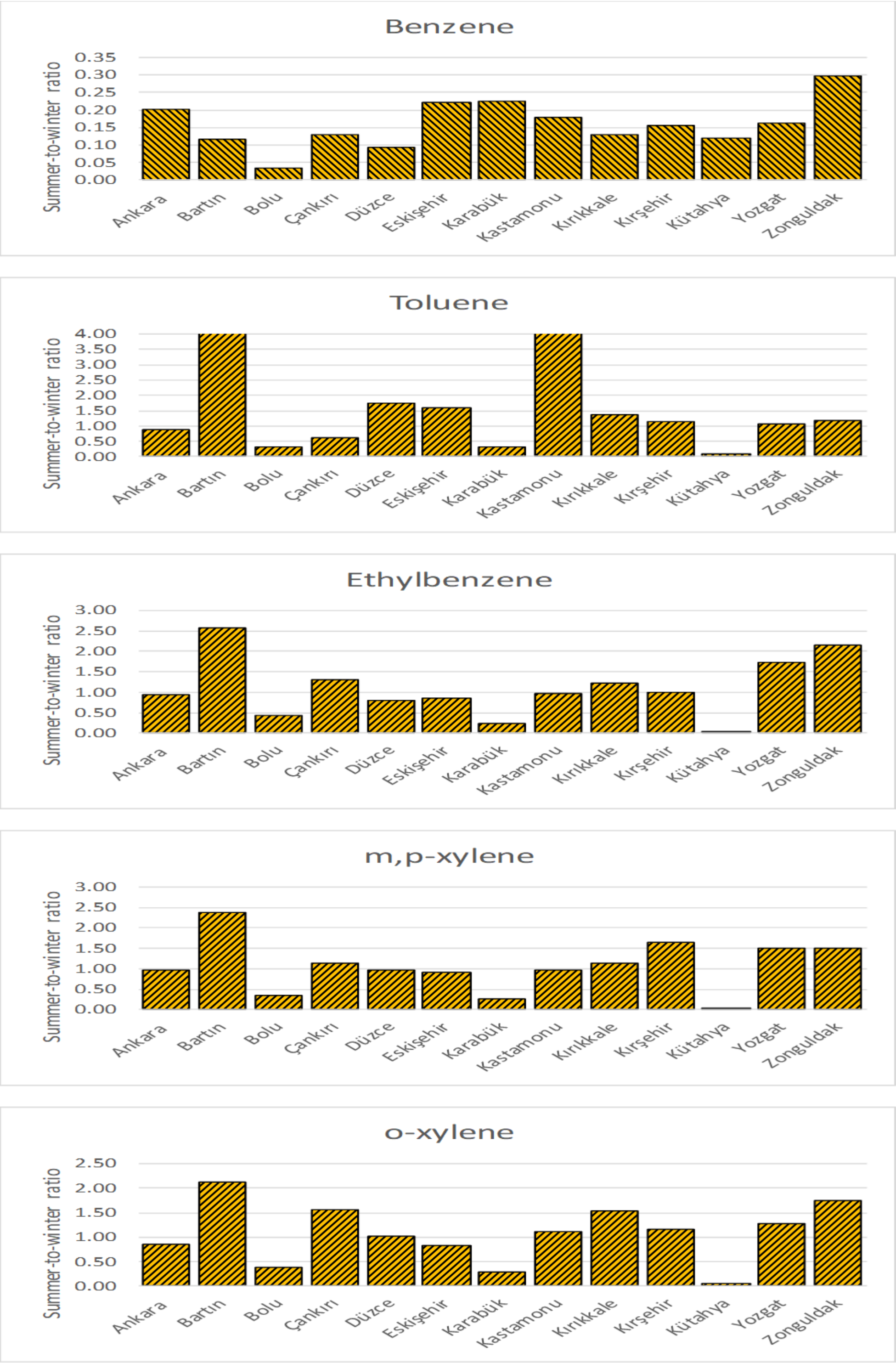

Figure 4.14 Summer to winter ratio of VOC concentrations

For remaining BTEX compounds S-to-W ratios are < 1.0 at Bolu, Çankırı, Karabük and Kütahya. The reason for lower summer season concentrations is similar to that of benzene, which was discussed in previous paragraph. However, summer-to-winter concentration ratios at Bartın, Düzce, Eskişehir and Kastamonu are > 1.0. This observation indicates that evaporative emissions from solvents used in buildings have important contribution to BTEX concentrations measured in these cities.

4.7. Relation between Meteorological Parameters and Concentrations of Measured Parameters

Certain meteorological parameters can increase and decrease concentrations of pollutants in an urban atmosphere. Wind speed, temperature, rainfall are related with decreasing concentrations of organic and inorganic pollutants, whereas mixing height showed inverse relation with pollutant concentrations. In this study, we attempted to relate concentrations of pollutants measured in this study with rainfall, temperature and wind speed.

Variation of SO_2, NO_2 and O_3 concentrations with rainfall is depicted in Figure 4.15. Concentrations of pollutants is expected to decrease with rainfall, as rain washes atmosphere. There are numerous demonstration of wet scavenging process in literature, but most of them demonstrate scavenging of particle bound parameters with rain. Parameters measured in this work are gases. For removal of gases from atmosphere depends on their solubility. Only ozone showed a statistically significant decrease with rain. This should be expected, because O_3 is water soluble gas and thus can be captured by cloud droplets or by falling rain droplets. Nitrogen dioxide and VOCs measured in this study are not water soluble and thus do not show a positive or negative correlation with rainfall.

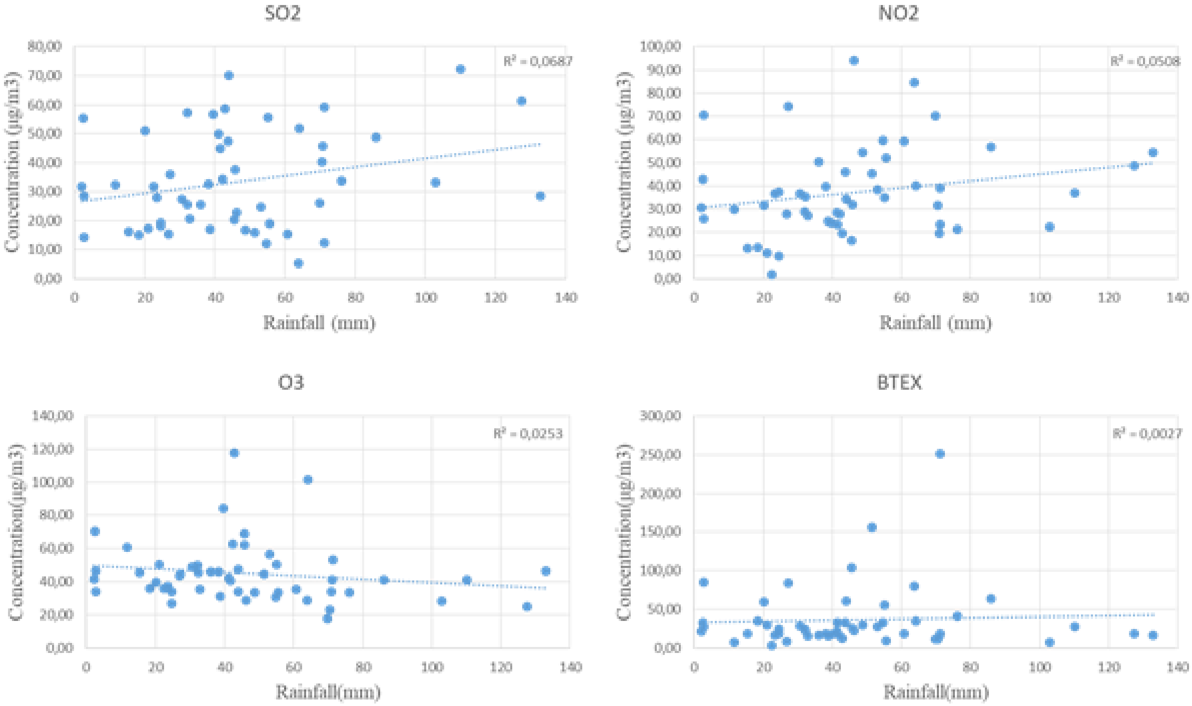

Figure 4.15 Relation between rainfall and measured parameters

Relation between concentrations of SO_2, NO_2 and O_3 and wind speed is shown in Figure 4.16. Interestingly wind speed did not show statistically significant correlation with any of the parameters and p value is bigger than 0,05. It is interesting, because generally WS correlates strongly with decreasing concentrations of pollutants in the atmosphere, because it disperses and dilutes pollutants. The reason for lack of any relation between WS and pollutant concentrations in this study is probably very slow average winds in cities. As pointed out in earlier sections, average wind speed in most of our cities was less than 2 m s^{-1}, which is very close to meteorological definition of “calm”. When WS is very low, pollutants are distributed fairly homogenously over the city and relation between pollutant concentration and WS cannot be established.

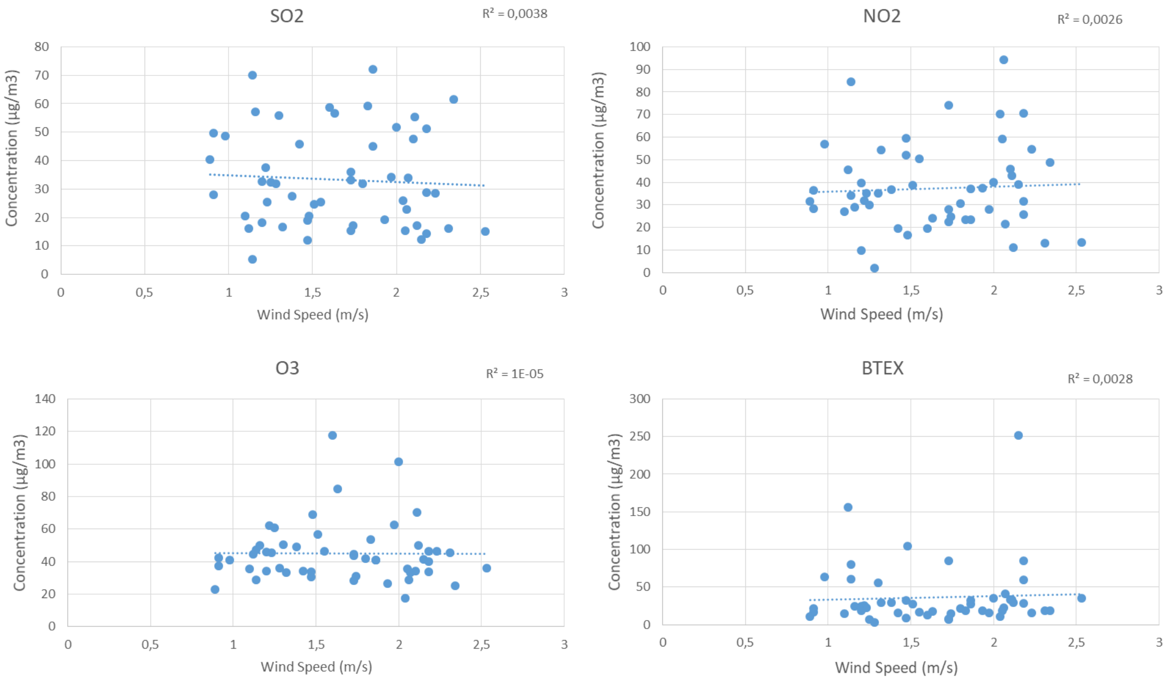

Figure 4.16 Relation between wind speed and measured parameters

The relation between temperature and pollutant concentrations are shown in Figure 4.17. Unlike WS and rainfall, temperature is strongly correlated with concentrations of SO_2, NO_2 and O_3 and p values are smaller than 0,05 which means showing statistically significant correlation. Concentrations of SO_2, NO_2 and O_3 decrease and concentrations of BTEX (sum of the benzene, toluene, ethylbenzene, m&p-xylene and o-xylene concentrations) decrease with temperature.

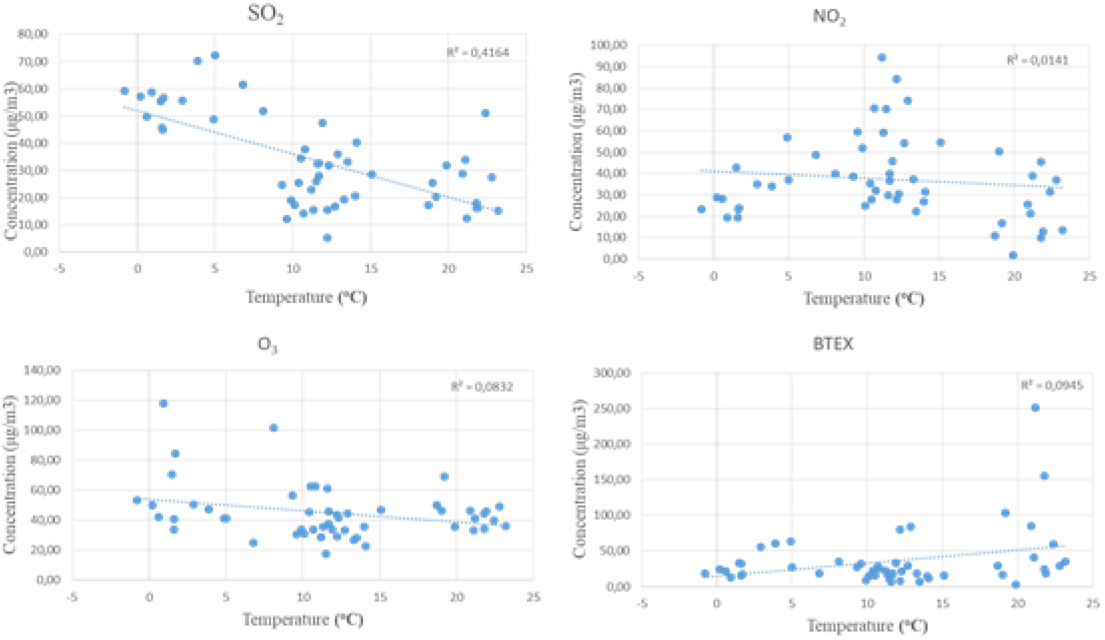

Figure 4.17 Relation between temperature and measured parameters

The decrease in SO_2 concentration with temperature is probably due to burning of fossil fuels in winter for space heating. Although most of the cities are now heated with natural gas, none of them are heated entirely with gas. For example only 60% of the households in Ankara are heated with gas due to lack of necessary infrastructure for natural gas transport at outskirts of the city. Consequently, SO_2 concentrations decrease with temperature (in summer) and p value is smaller than 0,05 which means showing statistically significant correlation. The relation between temperature and NO_2 concentration is very weak, but slight decrease in NO_2 concentration with increasing temperature can be seen. The reason for such a weak decrease is probably the same with SO_2. Main source of NO_2 is traffic. However, some NO also comes from coal combustions or gas combustion. Lack of such combustion process in summer (when temperature is high) is probably the reason for observed decreasing trend.

Unlike inorganic pollutants, BTEX concentrations increase with increasing temperature which means concentrations are higher in summer and p value is bigger than 0,05 which means no statistically significant correlation. Higher summer concentrations of VOCs, particularly Toluene, was discussed previously in relation to their seasonal variations, and attributed to increased evaporation during summer. Toluene is dominating VOC (in terms of concentration) in BTEX group seasonal variation of toluene affects BTEX concentration.

4.8. BTEX Ratios

Chemical species in the atmosphere show different reactivity. As a result of photochemical reactions, concentrations of the reactive compounds will decrease faster than concentrations of less reactive ones (Elbir et al., 2007). Ratios of VOCs with different reactivity and sources can provide information on aging of VOCs and different sources affecting their concentration.

The ratio, which is most widely used to understand aging of air parcels is xylene-to-ethylbenzene ratio (X/E ratio) (Ho et al., 2004; Hsieh et al., 2011). The X/E ratio decrease after the compounds (xylene and ethylbenzene) is emitted to atmosphere, because xylenes react faster with HO radicals (Ho et al., 2004). Hence, low X/E ratios are measured at a receptor which is far from the source (Ho et al., 2004).

Similarly ratios of VOCs with different sources can provide information on relative contributions of these sources. Toluene-to-benzene ratio (T/B ratio) is the most widely used ratio for this purpose. Benzene is emitted exclusively from motor vehicles, particularly from light duty vehicles. Although emissions from motor vehicles are also source of toluene in the atmosphere, it also has non-traffic sources, such as evaporation from painted surfaces. Consequently, high T/B ratios indicate strong contribution of non-traffic sources on the VOC composition of the atmosphere (Guo et al., 2004; Guo et al, 2007; Hoque et al., 2008). Toluene-to-benzene ratios reported for fresh exhaust emissions are approximately 2, but the ratio increases with increasing non-traffic toluene contributions (Sweet and Vermette, 1992; Scheff and Wadden, 1993).

Annual average XE ratios in cities included in this work is depicted in Figure 4.18. Xylene-to-ethylbenzene ratio is very similar in all cities. Its value is constant around 2.5, which indicates a mixture of fresh emissions from nearby roads and aged emissions transported to measurement site. This is not surprising, because in every city both xylene and ethylbenzene are measured in a number of stations distributed in the city. These stations are affected from fresh and aged emissions to different degrees, but on the average a uniform mix of fresh and aged emissions appears in all cities.

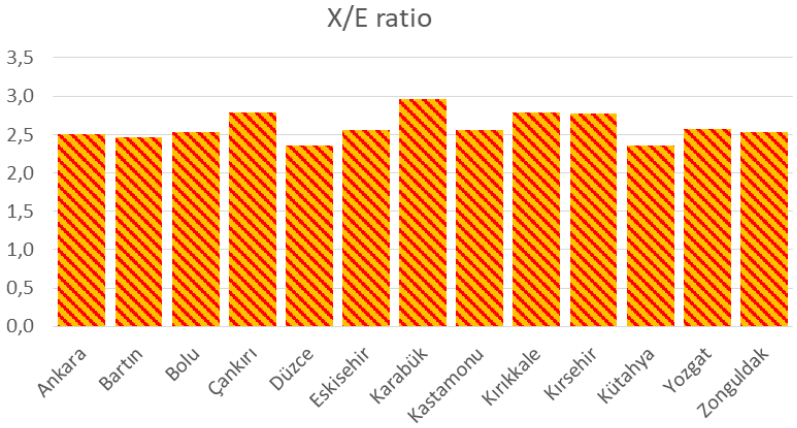

Figure 4.18 Xylene-to-ethylbenzene ratio in 13 cities included in this work

Annual average toluene-to-benzene ratio is depicted in Figure 4.19 for the cities included in this work. As can be seen from the figure, TB ratio is not as uniform as XE ratio among cities. It varies between 1.5 at Karabük and 28 at Bartin. TB ratios well above exhaust ratio (2.0) is observed at Ankara, Bartın, Düzce, Eskisehir and Kastamonu indicating that evaporative emissions from painted surfaces and printing and photocopying activities are influential on measured VOC concentrations in these cities. On the other hand, relatively low TB ratios were measured at Bolu, Çankırı, Karabük, Kırşehir, Kütahya, Yozgat and Zonguldak. Main VOC source in these cities are motor vehicles.

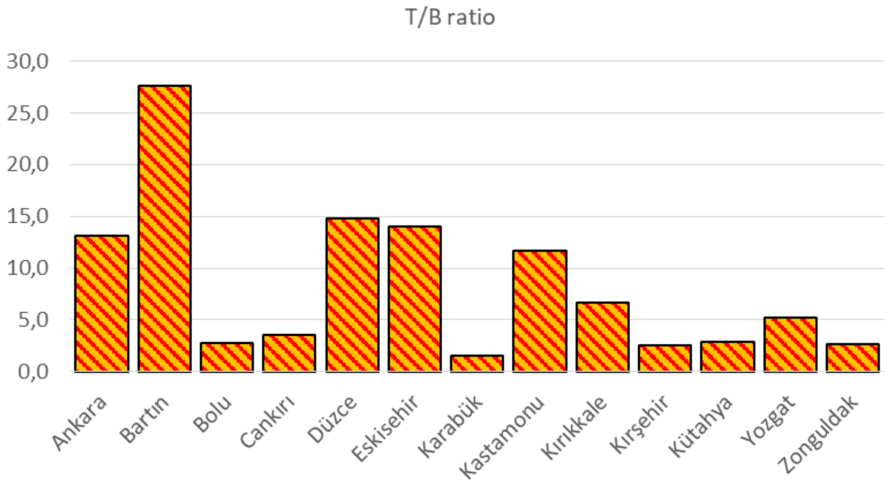

Figure 4.19 Toluene-to-benzene ratio in 13 cities included in this work

Seasonal average toluene-to-benzene (TB) and xylene-to-ethylbenzene (XE) ratios in cities are given in Table 4.7. Xylene-to-ethylbenzene ratios do not change significantly from one season to another demonstrating that air masses with similar aging profile prevails in all seasons. Toluene-to-benzene ratios also do not show too much variability, except for summer season. In summer higher TB ratios are found in most of the cities, due to enhanced evaporation from surfaces at higher temperatures. This also suggest that in most of the cities evaporative sources have non-negligible contribution to VOC composition, but contribution of evaporative sources is small in other seasons.

Table 4.7 Seasonal variation in VOC ratios at 13 cities

	Toluene/Benzene				Xylene/Ethylbenzene			
	Summer	Fall	Winter	Spring	Summer	Fall	Winter	Sprıng
Ankara	24.3	11.9	5.7	10.8	2.6	2.9	2.6	1.8
Bartın	104.3	2.6	1.4	2.3	2.4	2.5	2.7	2.2
Bolu	5.6	2.5	0.6	2.6	2.4	2.4	2.9	2.4
Çankırı	6.8	2.6	1.4	3.3	2.7	2.9	2.7	2.8
Düzce	48.2	3.5	2.6	4.8	2.8	2.5	2.3	1.9
Eskisehir	35.1	11.3	4.8	5.1	2.7	2.4	2.6	2.5
Karabük	2.4	1.6	1.6	0.6	3.2	2.9	2.7	3.0
Kastamonu	37.2	4.4	1.6	3.7	2.4	2.8	2.4	2.6
Kırıkkale	17.9	3.5	1.7	3.6	2.8	3.0	2.7	2.7
Kırşehir	6.4	1.6	0.9	1.2	3.0	2.8	2.1	3.2
Kütahya	1.5	2.2	1.9	6.0	2.3	2.6	2.2	2.4
Yozgat	12.4	3.3	1.9	3.3	2.1	2.7	2.6	2.8
Zonguldak	5.5	1.3	1.4	2.3	2.0	2.8	2.7	2.7

4.9. Spatial Distribution of Measured Parameters in Cities

There are many studies that use Geographical Information System software for modelling and analysing of air pollution (Vienneau et al., 2009; Unwin, D., 1996; Gulliver and Briggs, 2011; Ketzel et al., 2011; Jensen et al., 2001; Cinderby and Forrester, 2005; Kumar et al., 2016; Sohrabinia and Khorshiddoust, 2007; Zhang et al., 2008) The objective in this section is to interpolate pollutant concentrations and use generated pollution maps to determine potential sites for air quality monitoring stations. This software is an efficient instrument to store, manipulate, capture, analyse and manage various kind of geographical data and describe graphical view for understanding easily (Kumar et al., 2016).

Pollution maps were prepared by interpolating concentrations measured at each station using Inverse Distance Weighting (IDW) interpolation method in ArcGis software. IDW is considered good method to study spatial patterns of air quality and it provides good interpolation of air quality (Kumar et al., 2016). Since objective is to find potential sites for monitoring stations winter concentrations were used in interpolation, because it was considered as worst-case distribution of both combustions related (SO_2) and traffic related (NO_2) pollutants.

Input data included coordinate of sampling stations and winter SO_2, winter NO_2 and spring O_3 concentrations. BTEX compounds were not interpolated, because they were measured in only few stations and data were not enough for interpolation. Seven out of 13 provinces with more than 20 stations was used in this exercise. Data of winter SO_2, winter NO_2 of four out of seven provinces was given in Appendix A. Also, spring O_3 concentration distribution of seven province was given in Appendix A. Please note that selection of 25 stations as the minimum number for interpolation is a tentative decision. Higher the number of stations (or data points), lower the uncertainty. In our earlier studies, we typically interpolated data generated at > 100 stations to generate pollution maps. Although 25 stations are not much to generate pollution distributions with reasonably low uncertainty, they are good enough to demonstrate the approach we adopted to select station sites.

The first step in the process is to determine adequate number of stations for each city. The criteria that bases on population is given in (Air Quality Regulation) AQR and also shown in Table 4.8. For each city, there should be at least one “traffic station”. Location of residential station was based on distribution of SO_2 concentration and location of traffic station was based on distribution of NO_2 concentration.

Table 4.8 Criteria for determining the minimum number of sampling points according to AQR

Population in the “sub-region” or “region” (x1000)	Number of sampling points if concentrations exceed the top evaluation threshold for SO_2 and NO_2
0-249	1
250-499	2
500-749	2
750-999	3
1 000-1 499	4
1 500-1 999	5
2 000-2 749	6
2 750-3 749	7
3 750-4 749	8
4 750-5 999	9
> 6 000	10

In this study we adopted a method developed by Bayraktar and Turalioglu (2005). The idea is to define average conditions in the city with a minimum number of stations. So, in our search we tried to determine locations where generated pollutant data can represent average conditions in the city. To accomplish this SO_2 distribution maps were prepared by interpolation and the iso-concentration contour that corresponds to average SO_2 concentration measured in stations was highlighted. This contour shows the parts of the city where SO_2 concentration is expected to be equal to measured average SO_2 concentration in that city. The sites on this counter where the population density is the highest should be ideal locations for residential station. All residential stations in that city can be located at different locations on that "average" contour.

Figures of existing stations, residential and traffic stations and average ozone concentration of 7 provinces are given in the Appendices part of the study.

In the figure 4.20, determination of measurement point for SO_2 is shown for Ankara. Grey lines show the concentration contour that increasing concentrations every 10 $\mu g/m^3$. Each point show stations and green point shows the city center. Black line shows the average winter concentration in the Ankara. Colors specify the concentration of pollution. As the colors change from yellow to red, concentration of pollutant increase. Points on the map shows the passive sampling stations used in this study and black triangles indicate locations of suggested monitoring stations.

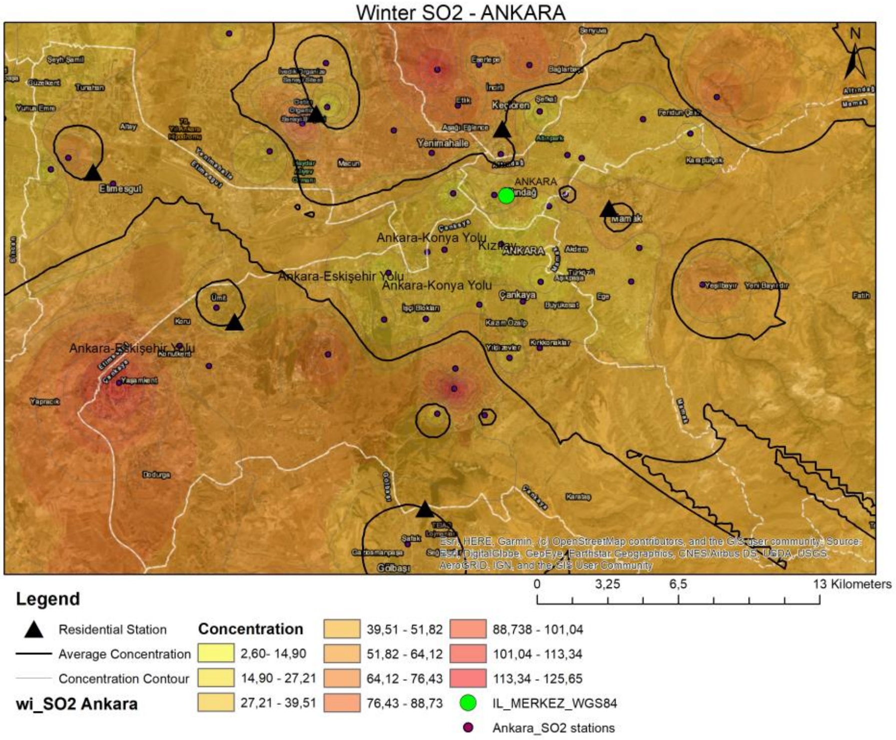

Figure 4.20 Spatial Distribution of SO_2 in Ankara

Population of Ankara was 5,270,575 in 2015. Based on the AQR criteria, a total 9 stations should be installed and 6 of them should be residential stations and three of them should be traffic stations. Average winter SO_2 concentration in Ankara is 46.8 $\mu g/m^3$. The black line on the map is 46.8 $\mu g\ m^{-3}$ contour, calculated by the GIS software. Stations which was labeled by triangle should be installed in the residential area where the pollution caused by heating is high. 6 stations' location was determined in residential areas with the triangles on the average winter SO_2 concentration contour.

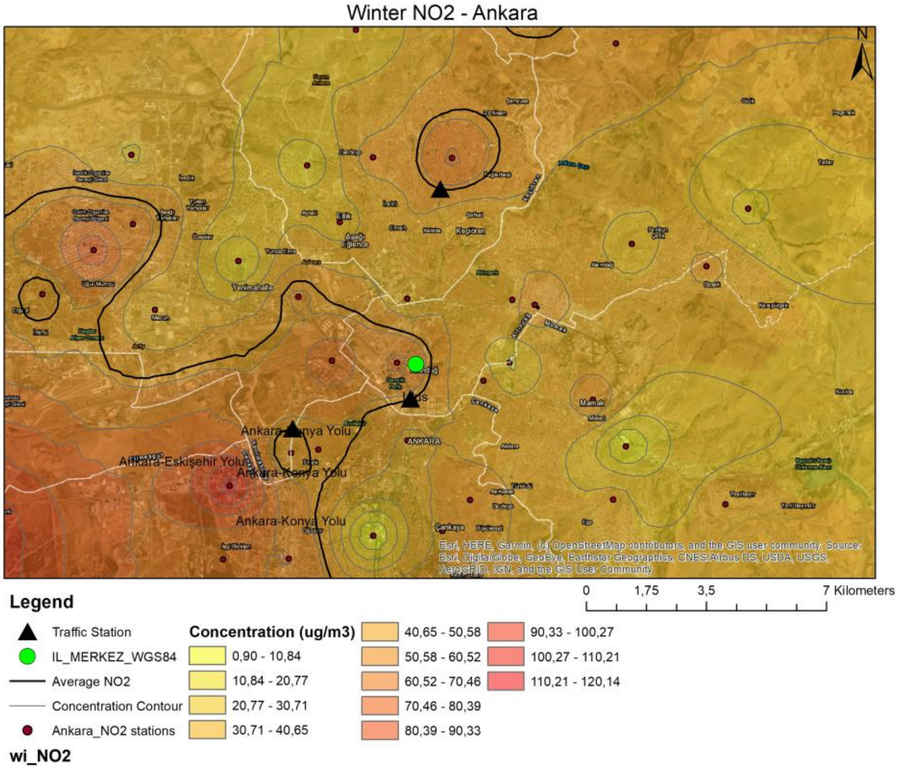

Figure 4.21 Spatial Distribution of NO_2 in Ankara

Figure 4.21 shows the spatial distribution of winter concentration of NO_2 in Ankara. Average winter NO_2 concentration which is shown in black contour in the figure was measured as 47.46 μg/m^3. 3 stations location which was labeled by triangle was determined in Ankara where traffic is heavy on the average concentration contour. Please note that, for a station to be identified as "traffic station" it should fulfill certain criteria such as being close to major roads, should represent high density of pedestrian availability etc. Putting traffic station onto the average SO_2 contour does not mean these criteria can be overlooked.

Population of Zonguldak was 595,907 in 2015. Based on the AQR criteria, a total 2 stations should be installed and one of them should be residential stations and one of them should be traffic stations. Spatial distribution of SO_2 in Zonguldak can be seen from the figure 4.22. Average winter SO_2 concentration in Zonguldak is 61.47 μg/m^3. The black line on the map is 61.5 μg m^{-3} contour, calculated by the GIS software. Station which was labeled by triangle should be installed in the residential area where the pollution caused by heating is high. One location was determined in residential areas with the triangles on the average winter SO_2 concentration contour.

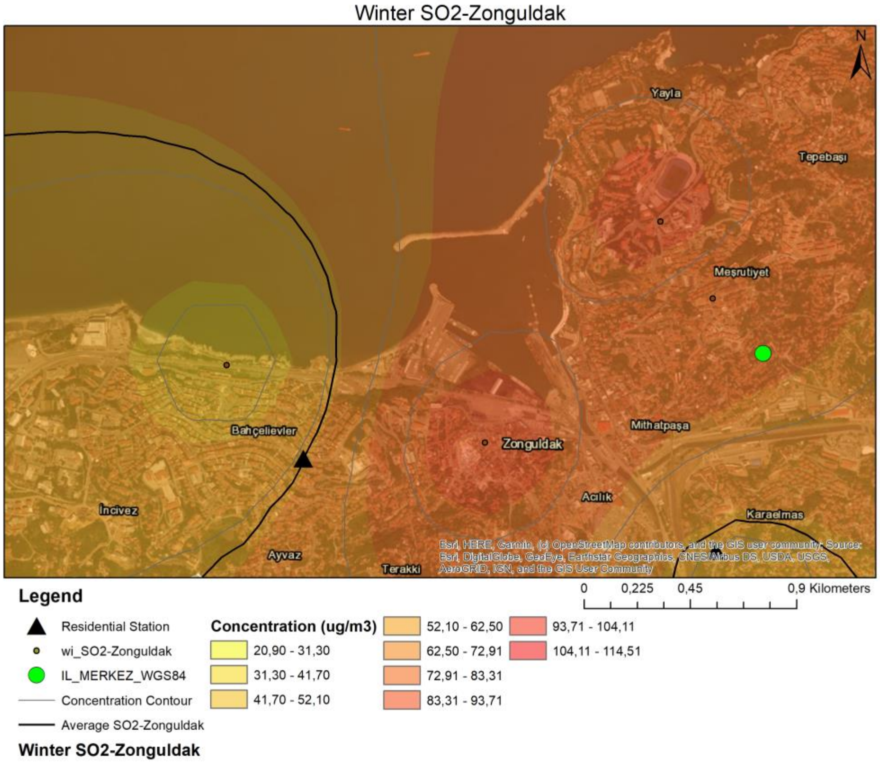

Figure 4.22 Spatial distribution of SO_2 in Zonguldak

Figure 4.23 shows the spatial distribution of winter concentration of NO_2 in Zonguldak. Average winter NO_2 concentration which is shown in black contour in the figure was measured as 49.74 µg/m^3. One station location which was labeled by triangle was determined in Zonguldak where traffic is heavy on the average concentration contour.

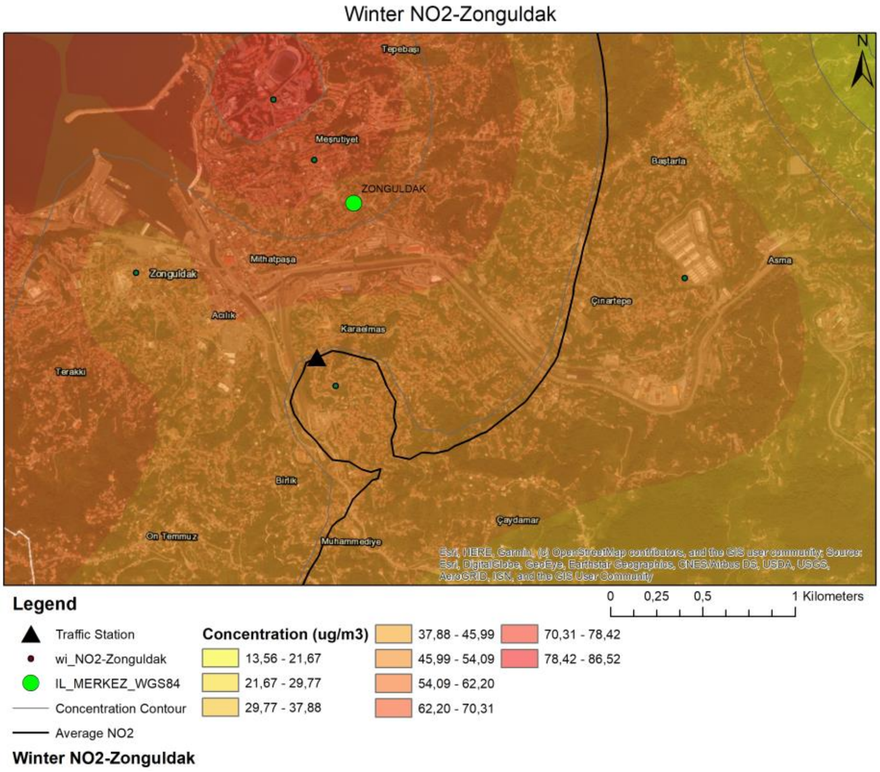

Figure 4.23 Spatial distribution of NO_2 in Zonguldak

Spatial distribution of SO_2 in Eskişehir can be seen from the figure 4.24. Population of Eskişehir was 826,716 in 2015. Based on the AQR criteria, a total 3 stations should be installed and two of them should be residential stations and one of them should be traffic stations. Average winter SO_2 concentration in Eskişehir is 55.40 $\mu g/m^3$. The black line on the map is also 55.4 $\mu g\ m^{-3}$ contour, calculated by the GIS software. Stations which was labeled by triangle should be installed in the residential area where the pollution caused by heating is high. Two locations were determined in residential areas with the triangles on the average winter SO_2 concentration contour.

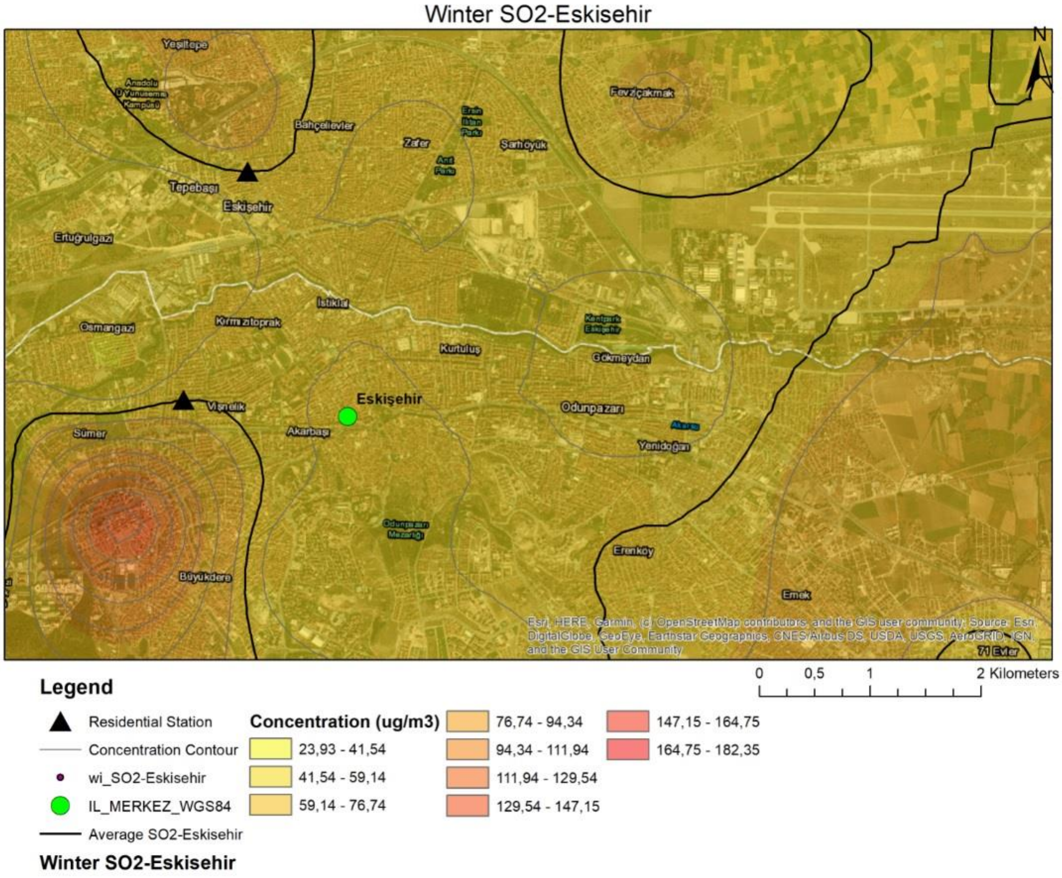

Figure 4.24 Spatial distribution of SO_2 in Eskişehir

Figure 4.25 shows the spatial distribution of winter concentration of NO_2 in Eskişehir. Average winter NO_2 concentration which is shown in black contour in the figure was measured as 42.88 µg/m^3. One station location which was labeled by triangle was determined in Eskişehir where traffic is heavy on the average concentration contour. Please note that, for a station to be identified as “traffic station” it should fulfill certain criteria such as being close to major roads, should represent high density of pedestrian availability etc.

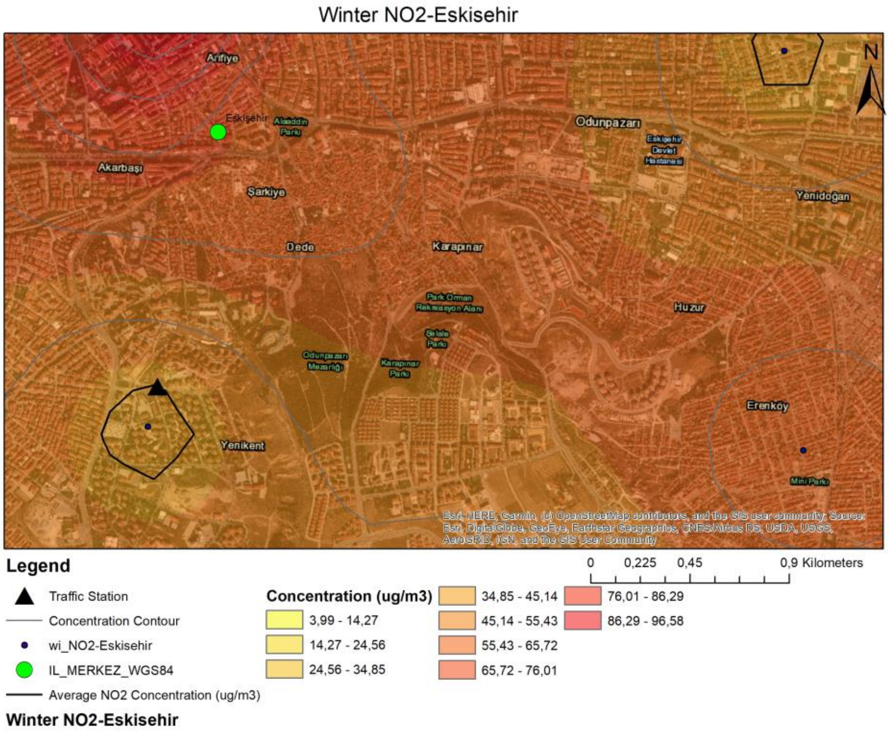

Figure 4.25 Spatial distribution of NO_2 in Eskişehir

CHAPTER 5

CONCLUSION

5.1. Conclusions

351 sampling stations were examined in Bartın, Ankara, Bolu, Eskişehir, Karabük, Çankırı, Düzce Kastamonu, Kütahya, Yozgat, Kırıkkale, Kırşehir and Zonguldak in order to measure SO_2, NO_2, O_3 and BTEX compounds between January of 2014 and May of 2015 ın the scope of this thesis study. In autumn and winter, for SO_2 and NO_2 parameters, samplings were collected every two weeks and two times in a month. Samplings were collected every four weeks and one times in a month in spring and summer seasons. On the other hand, O_3 and BTEX samplings were collected every two weeks and two times in a month in spring and summer and samplings were collected every four weeks and one times in a month in autumn and winter.

Measured SO_2 and NO_2, O_3 and BTEX concentrations were compared with other cities in Turkey and other cities around the world. Also, studied data was compared with regulatory standards.

Temporal variation which was only seasonal variation was observed because results of compounds concentrations were taken by passive sampling method which was once a two week.

Meteorological factors which are temperature, wind speed and rainfall were discussed with SO_2 and NO_2, O_3 and BTEX concentrations with all thirteen cities.

The aim of the study was to determine site, number and type of the monitoring stations that will be established in these cities with measured sulphur dioxide, nitrogen dioxide, ozone, benzene, toluene, ethylbenzene and xylene concentrations by passive sampling in Ankara, Çankırı, Bartın, Bolu, Zonguldak, Düzce, Kırşehir, Karabük, Eskişehir, Kırıkkale, Kastamonu, Kütahya and Yozgat. For this purposes, concentration of 3 inorganic compounds (SO_2, NO_2, O_3,) and 4 organic (benzene, toluene, ethylbenzene and m&p xylene) compounds were measured.

In addition the seasonal variation in concentration of measured parameters, spatial distribution of parameters was examined by interpolating pollution concentrations with ArcGis software. 7 provinces which had minimum 20 stations were selected to determine numbers and station locations to measure SO_2 and NO_2 concentrations. Winter concentrations of these pollutants were used because it was considered as worst scenario distribution of both traffic related (NO_2) and combustions related (SO_2) pollutants. For SO_2 measurement stations, residential areas were chosen and for NO_2 measurement, main road sides were selected to site the stations.

5.2. Recommendation for Future Studies

The sources from which the data were produced influence the results obtained from this study. In this context, the location of the stations from which data sets are provided and population information they represent are important. In order to make more accurate evaluations of the population rates exposed the SO_2, NO_2 and O_3 and BTEX levels in this study, it would be appropriate to have information on what area and population the stations represent. In this sense, establishment of other stations can represent certain parts of the provinces will better reflect the air quality.

Determining the seasonal differences and spatial distribution of SO_2, NO_2 and O_3 but it could not reach number of BTEX station to analyze. More installed passive sampling station would be better for reflecting BTEX measurements of cities. Also, sampling period should be longer than the study to get more accurate results.

In this study, 7 provinces that had minimum 25 stations were selected for interpolation. For 6 provinces, the spatial distribution map could not be analyzed because of the small number of stations. More sampling stations should be installed for spatial distribution of pollutants. Also, if there was enough station in the provinces and sampling periods longer, establishing meaningful relationship with meteorological data would be easier.

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APPENDICES

A: Traffic and Residential Stations and O_3 contour

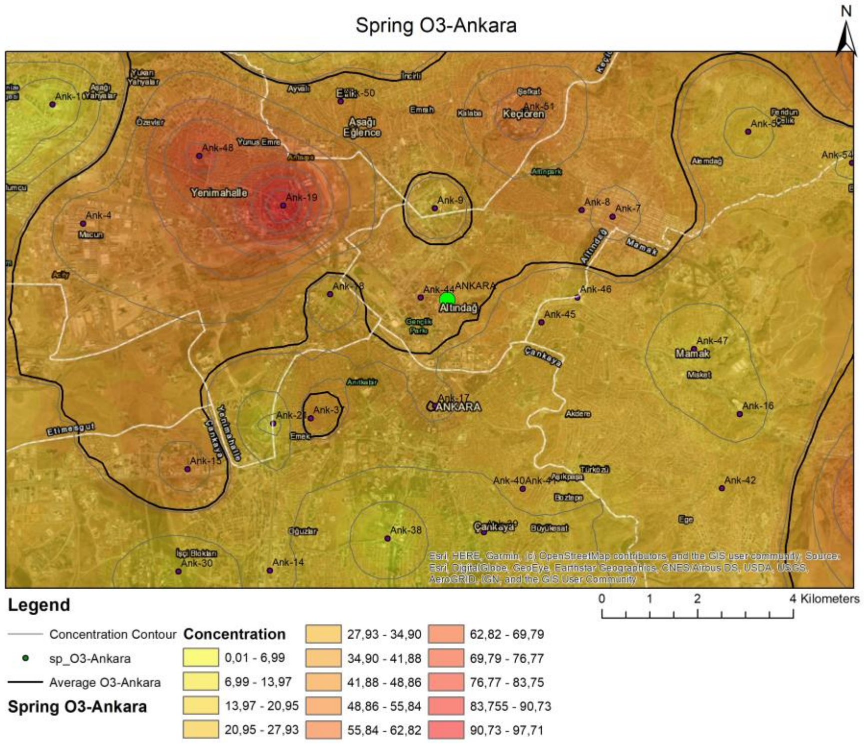

Figure A1 Spatial distribution of O3 in Ankara

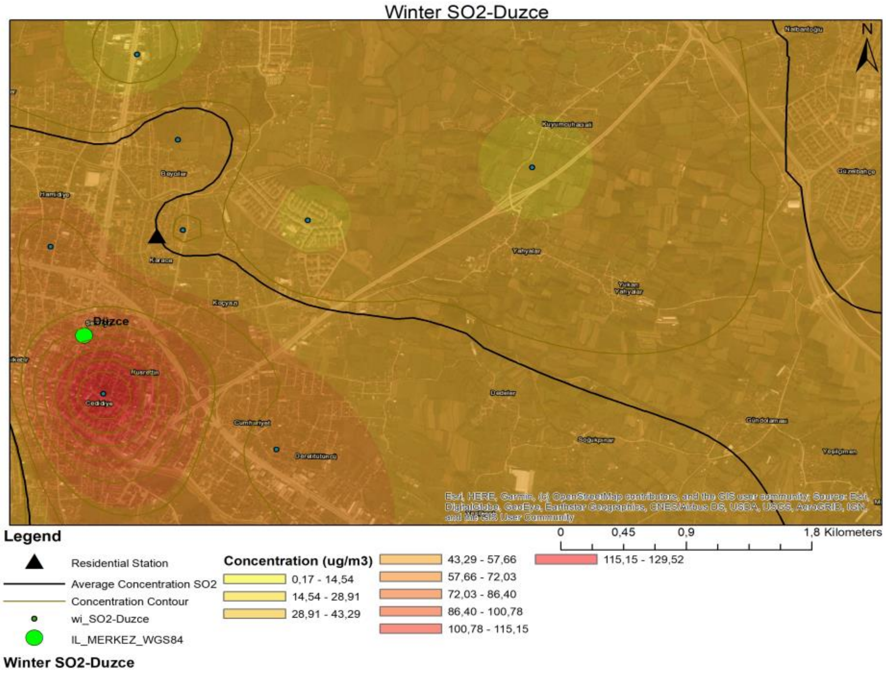

Figure A2 Spatial distribution of SO2 in Düzce

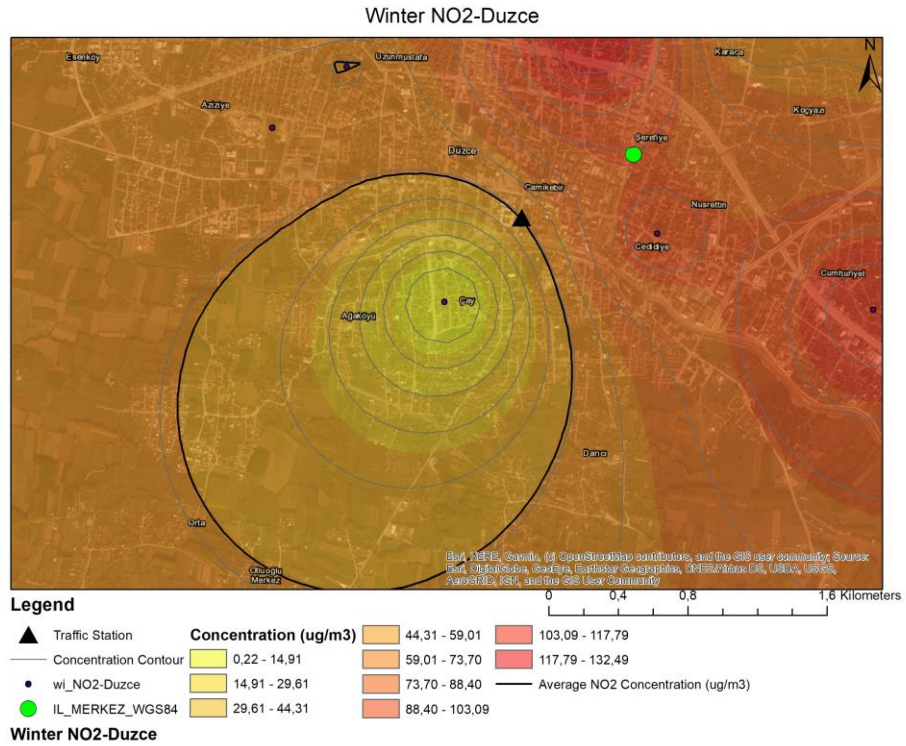

Figure A3 Spatial distribution of NO2 in Düzce

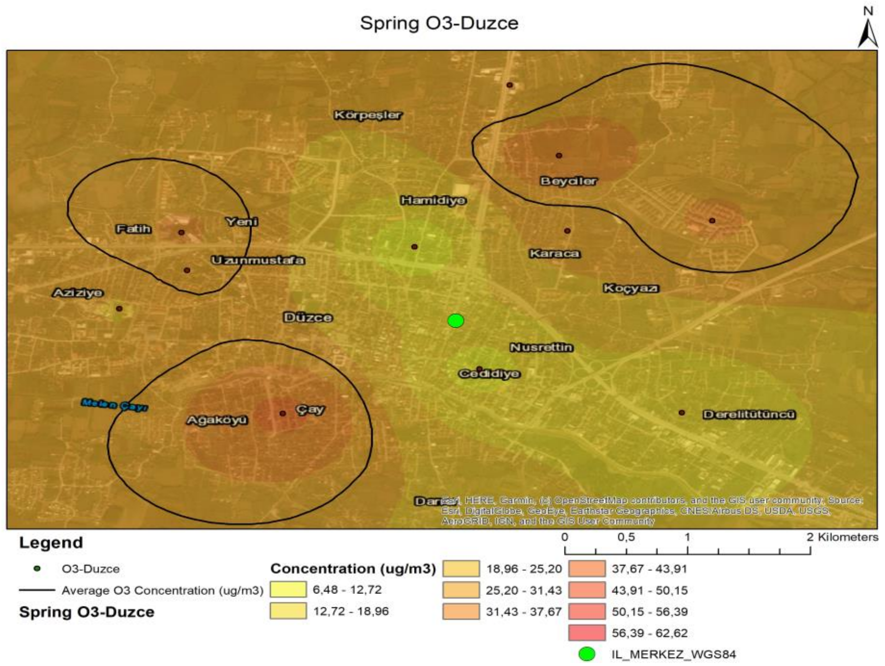

Figure A4 Spatial distribution of O3 in Düzce

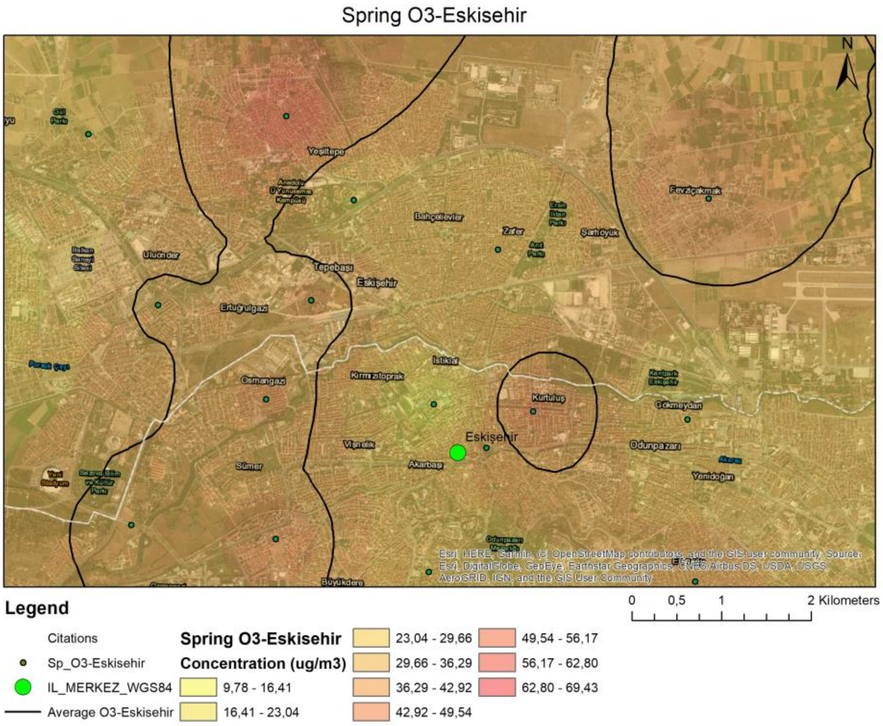

Figure A5 Spatial distribution of O3 in Eskişehir

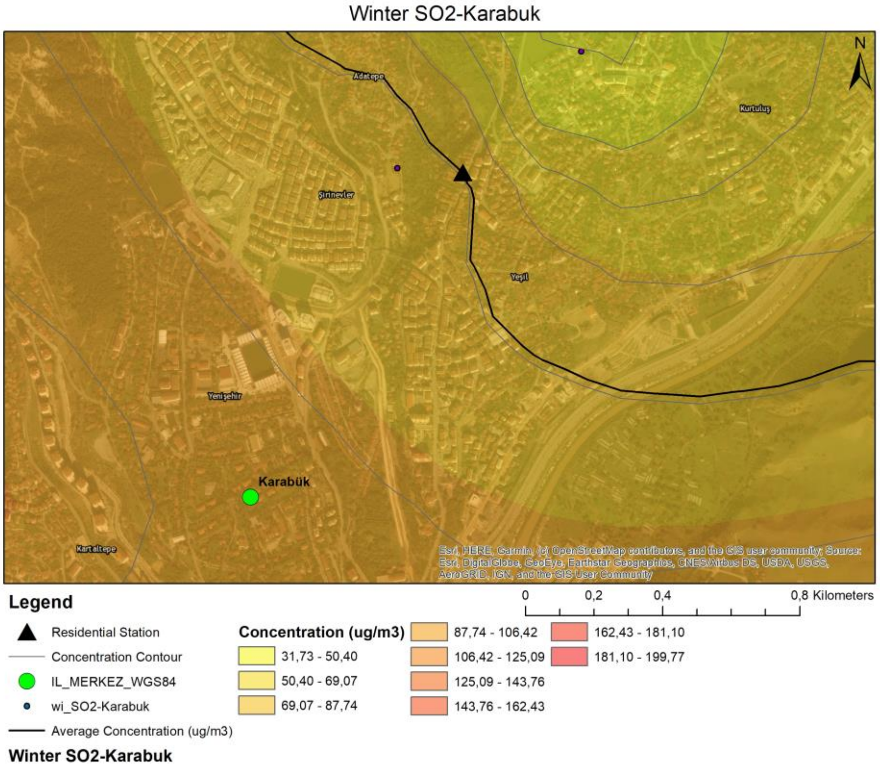

Figure A6 Spatial distribution of SO2 in Karabük

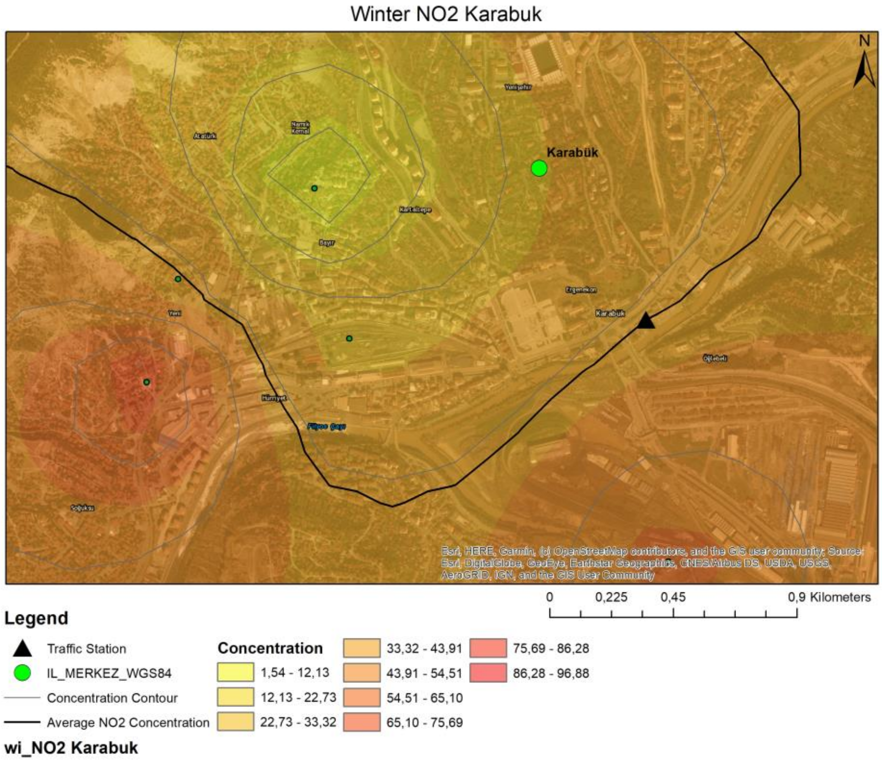

Figure A7 Spatial distribution of NO2 in Karabük

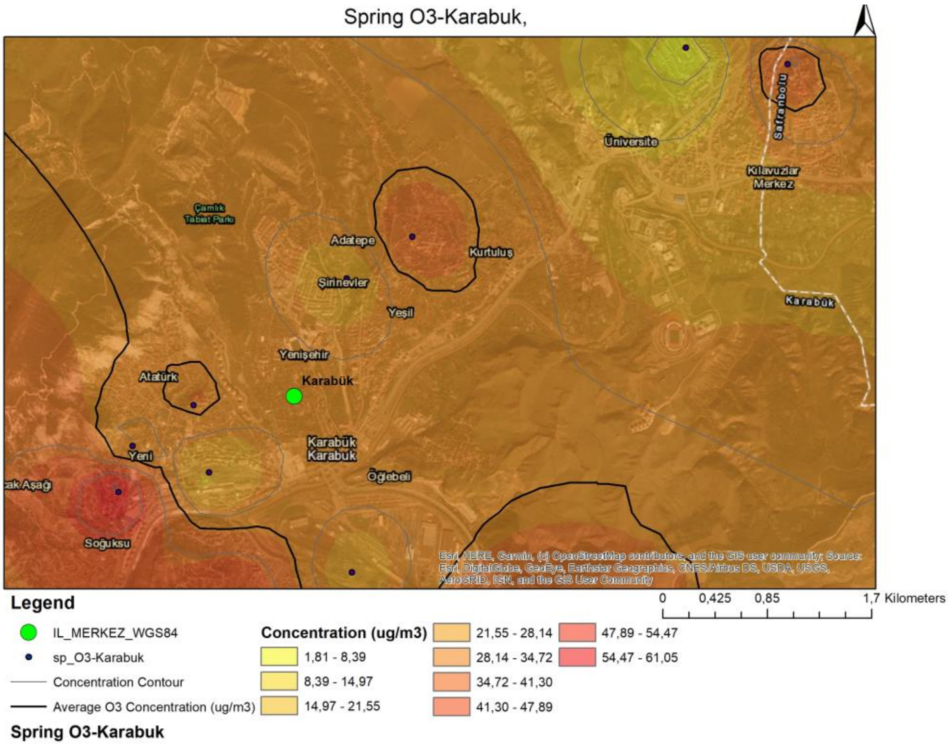

Figure A8 Spatial distribution of O3 in Karabük

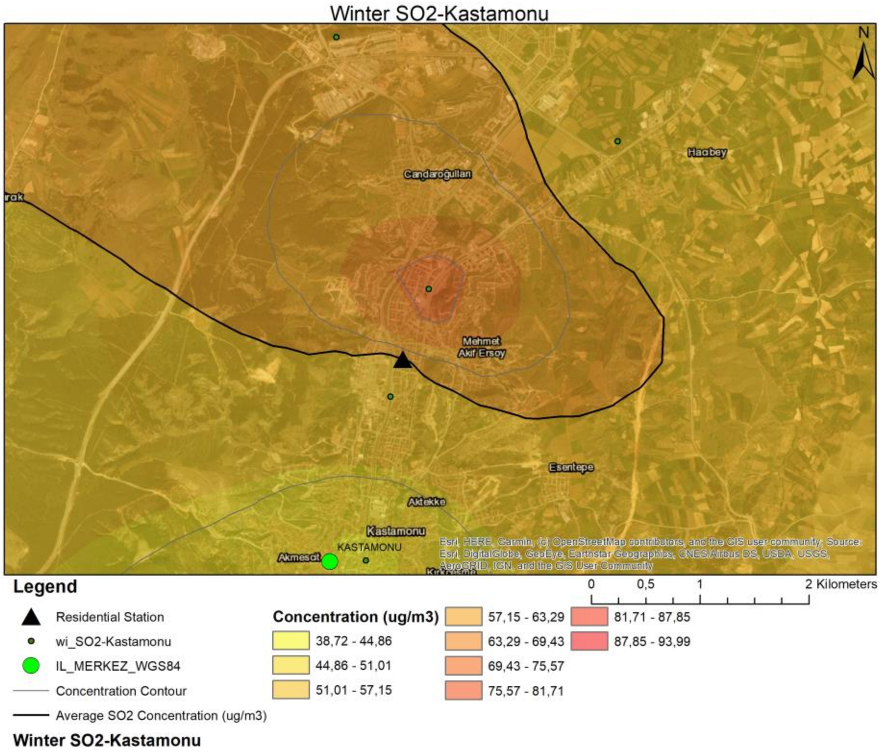

Figure A9 Spatial distribution of SO_2 in Kastamonu

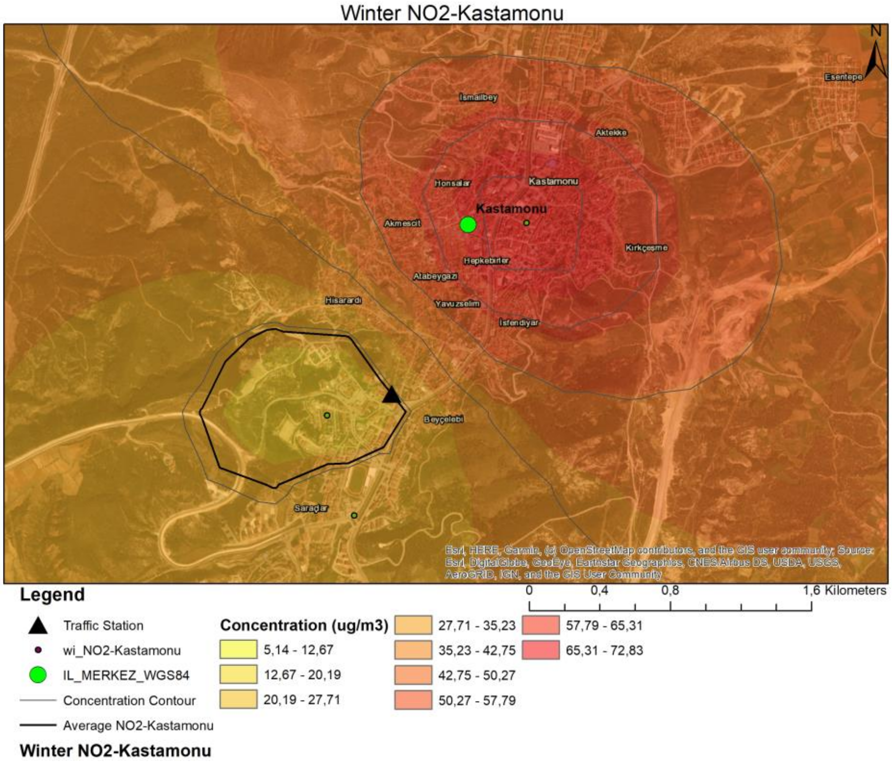

Figure A10 Spatial distribution of NO_2 in Kastamonu

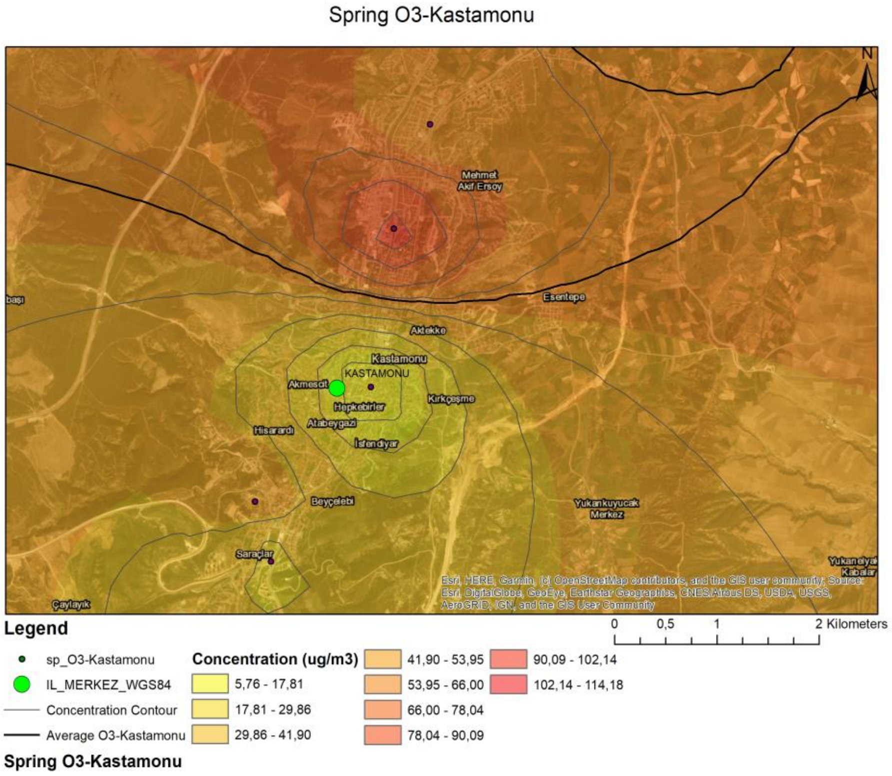

Figure A11 Spatial distribution of O_3 in Kastamonu

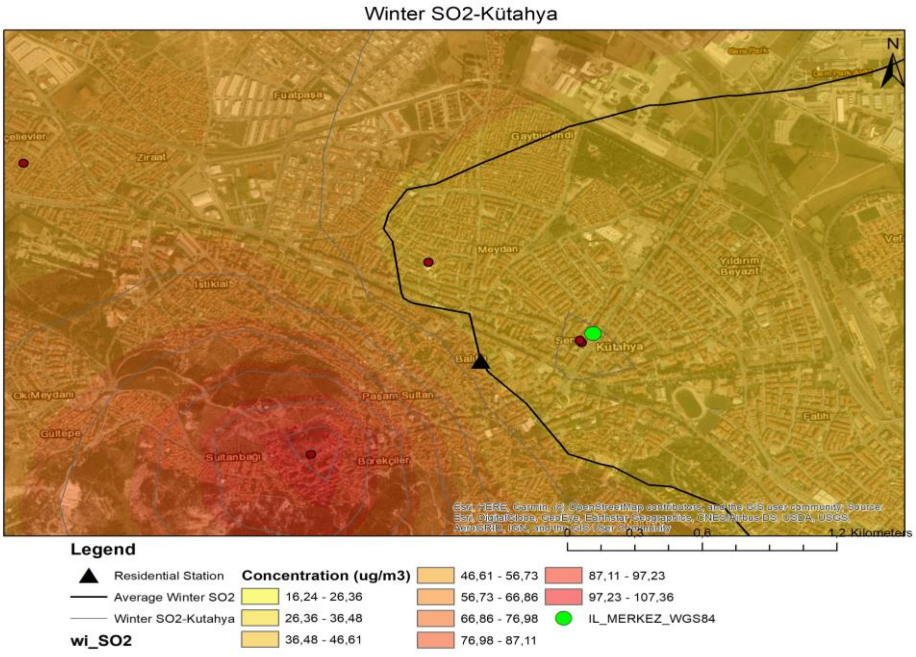

Figure A12 Spatial distribution of SO_2 in Kütahya

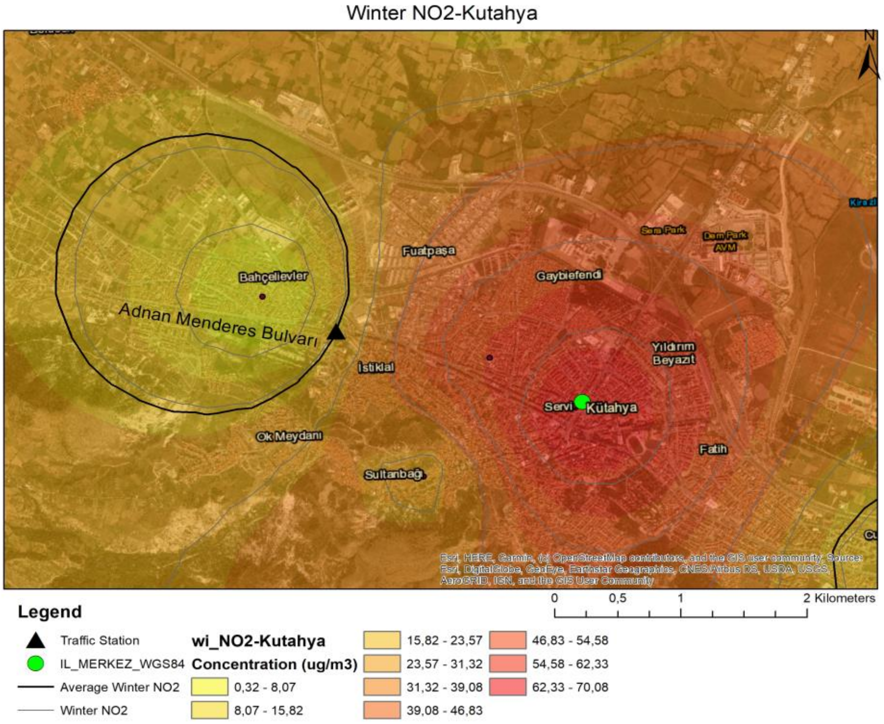

Figure A13 Spatial distribution of NO_2 in Kütahya

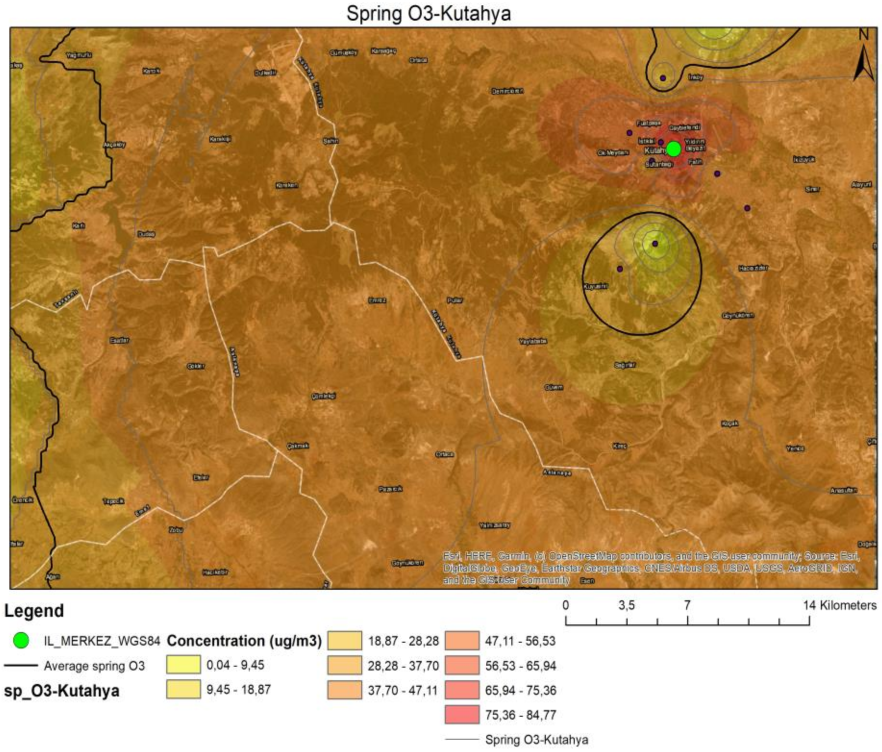

Figure A14 Spatial distribution of O_3 in Kütahya

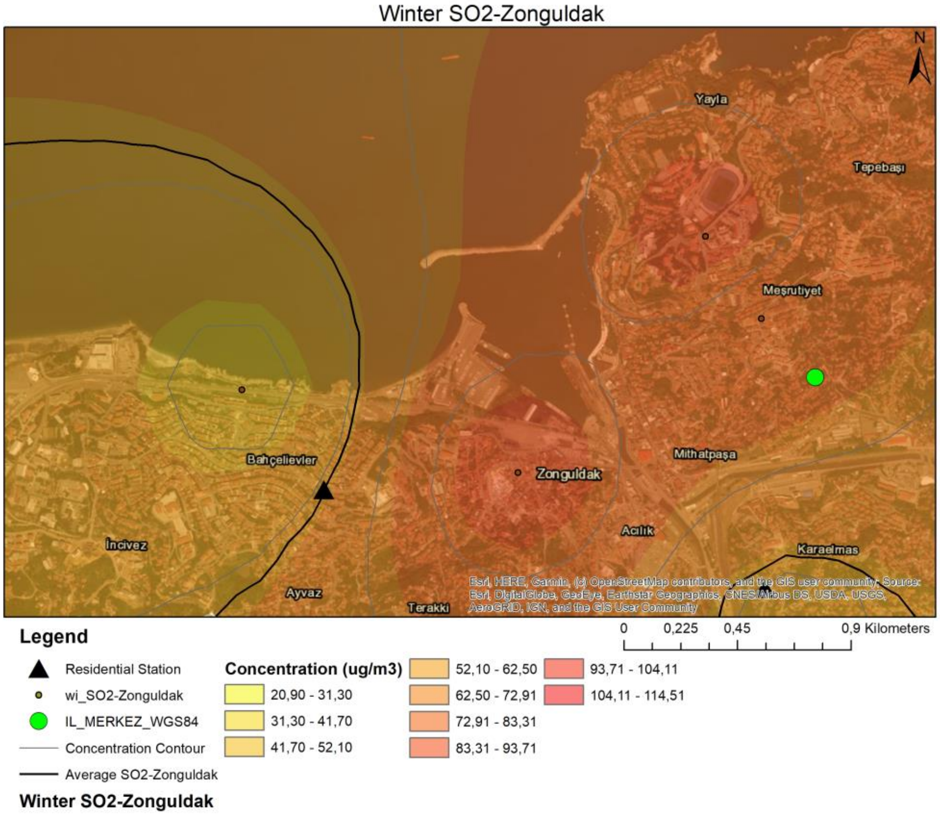

Figure A15 Spatial distribution of SO2 in Zonguldak

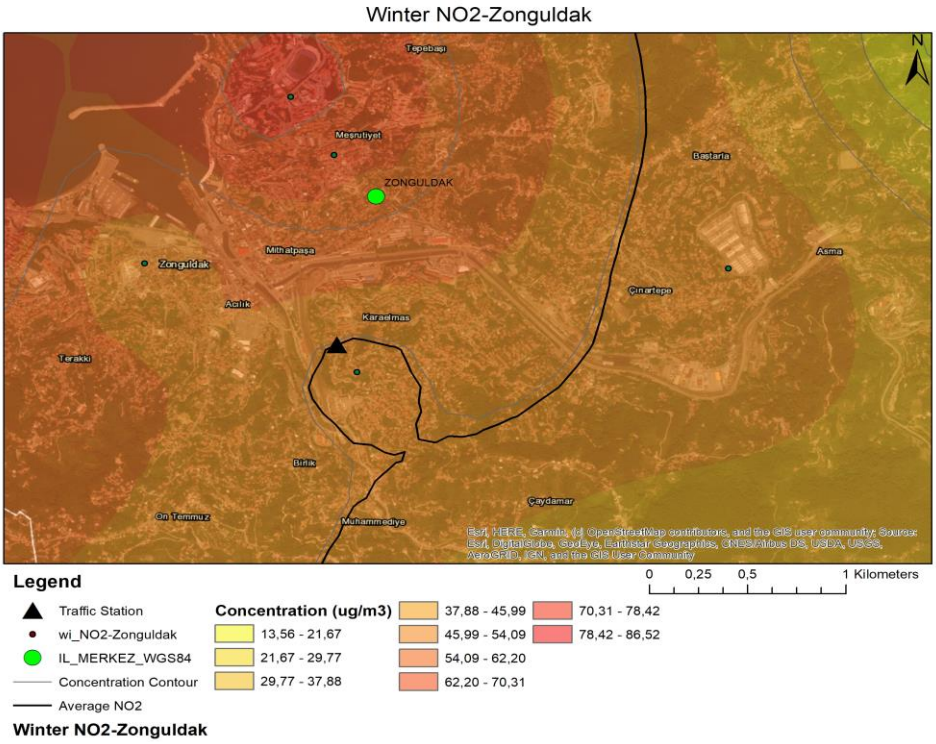

Figure A16 Spatial distribution of NO2 in Zonguldak

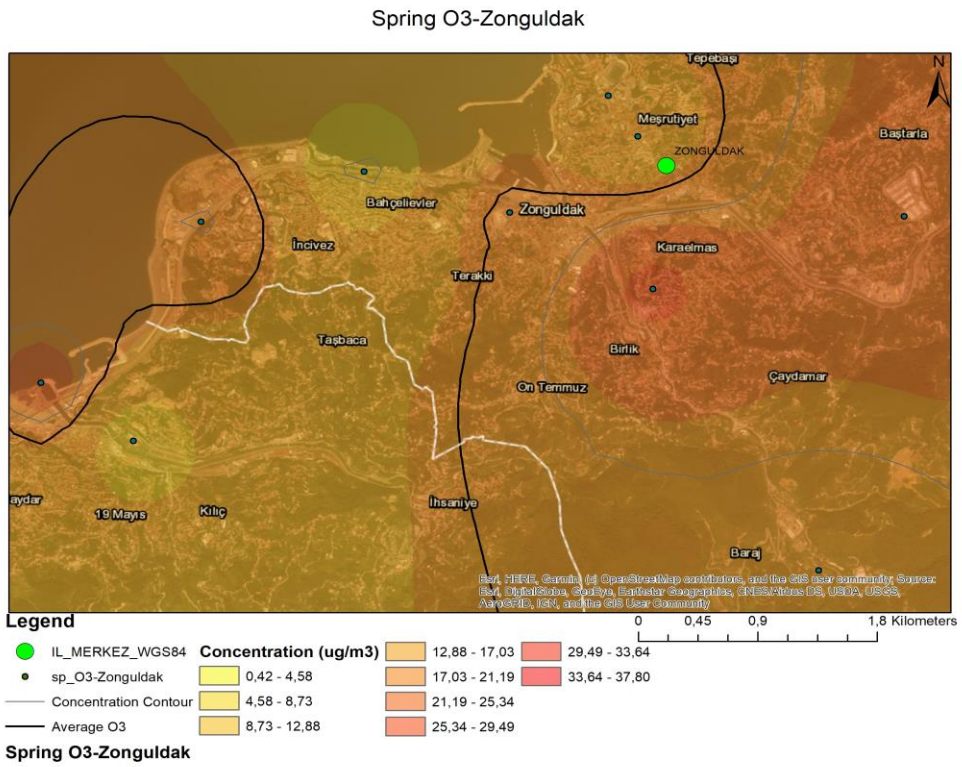

Figure A17 Spatial distribution of O3 in Zonguldak

B: Evaluation of Traffic and Residential Stations with Existing Stations

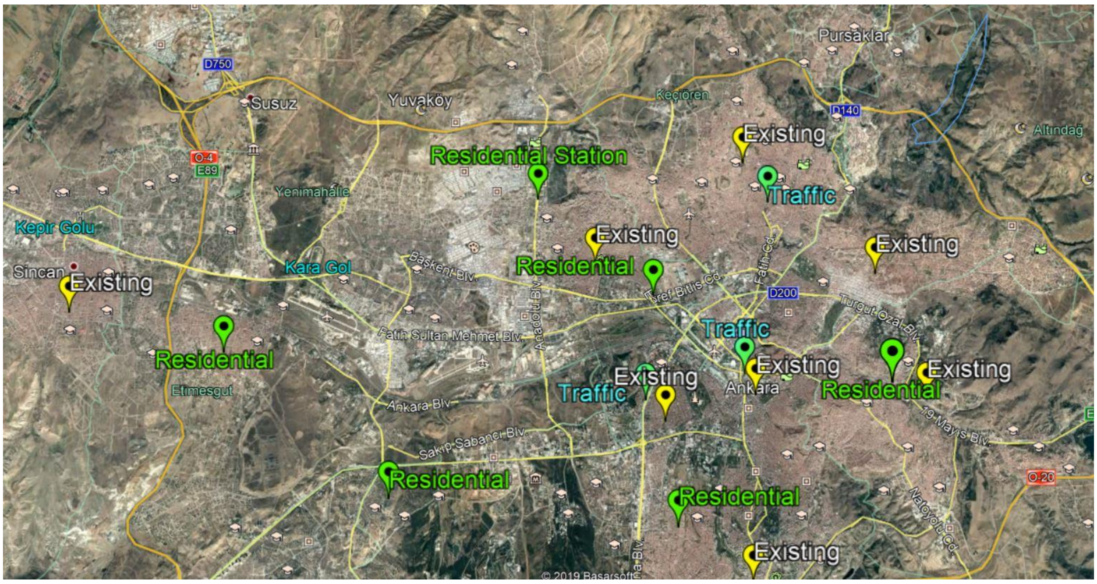

Figure B1 Evaluation of stations in Ankara

Figure B2 Evaluation of stations in Eskişehir

Figure B3 Evaluation of stations in Zonguldak

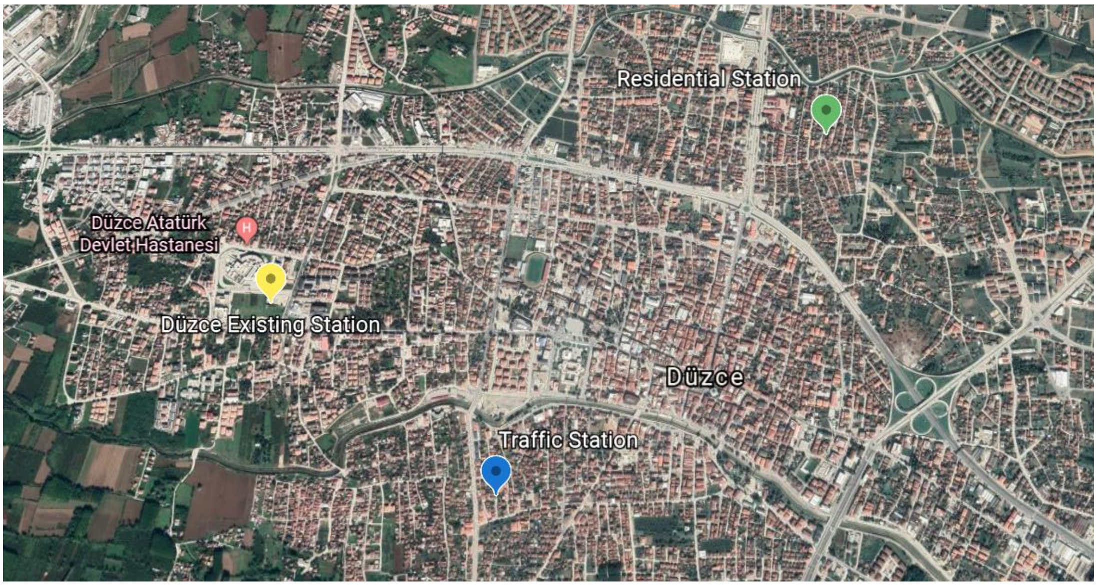

Figure B4 Evaluation of stations in Düzce

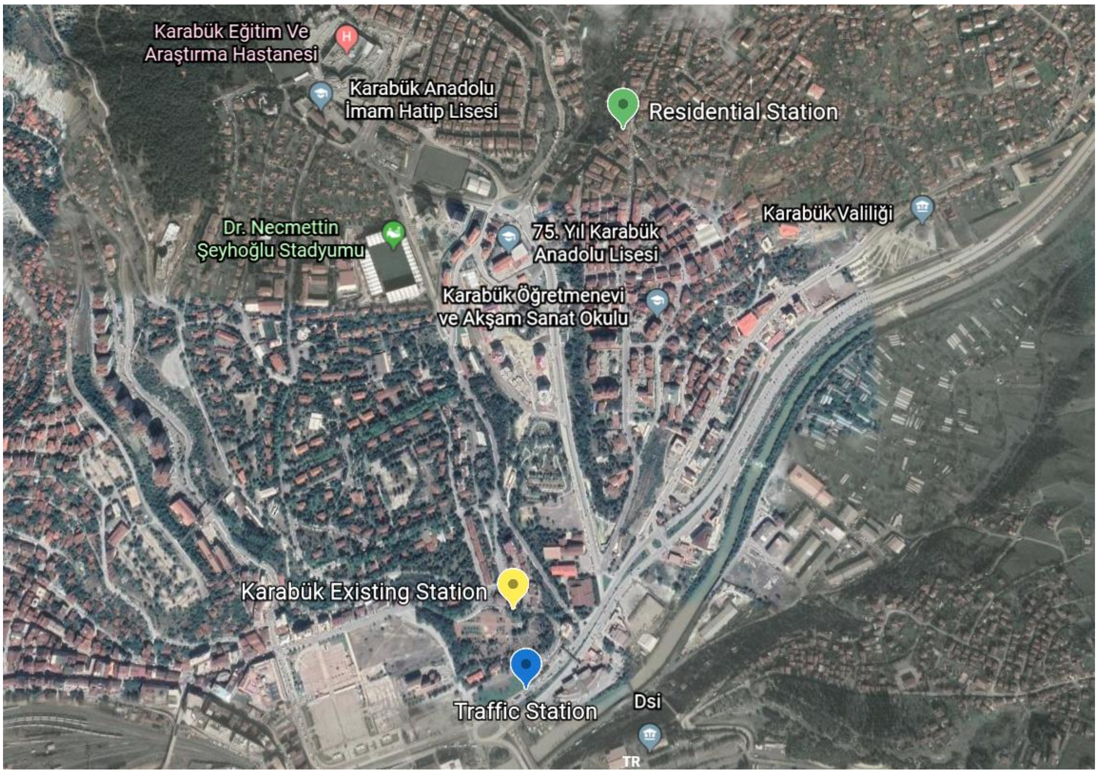

Figure B5 Evaluation of stations in Karabük

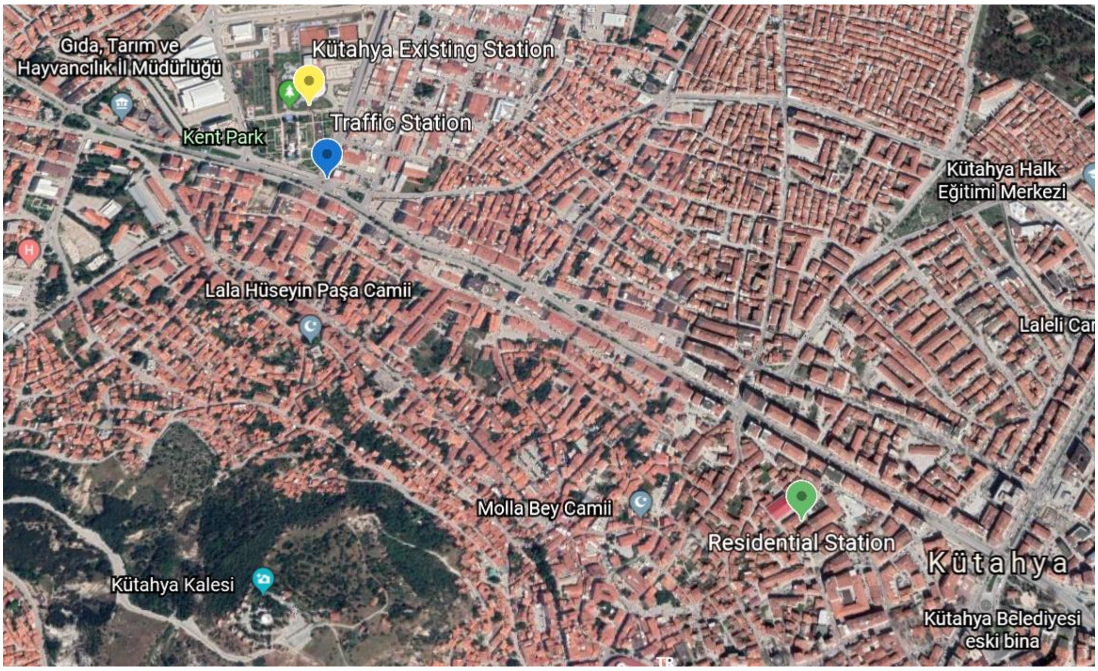

Figure B6 Evaluation of stations in Kütahya

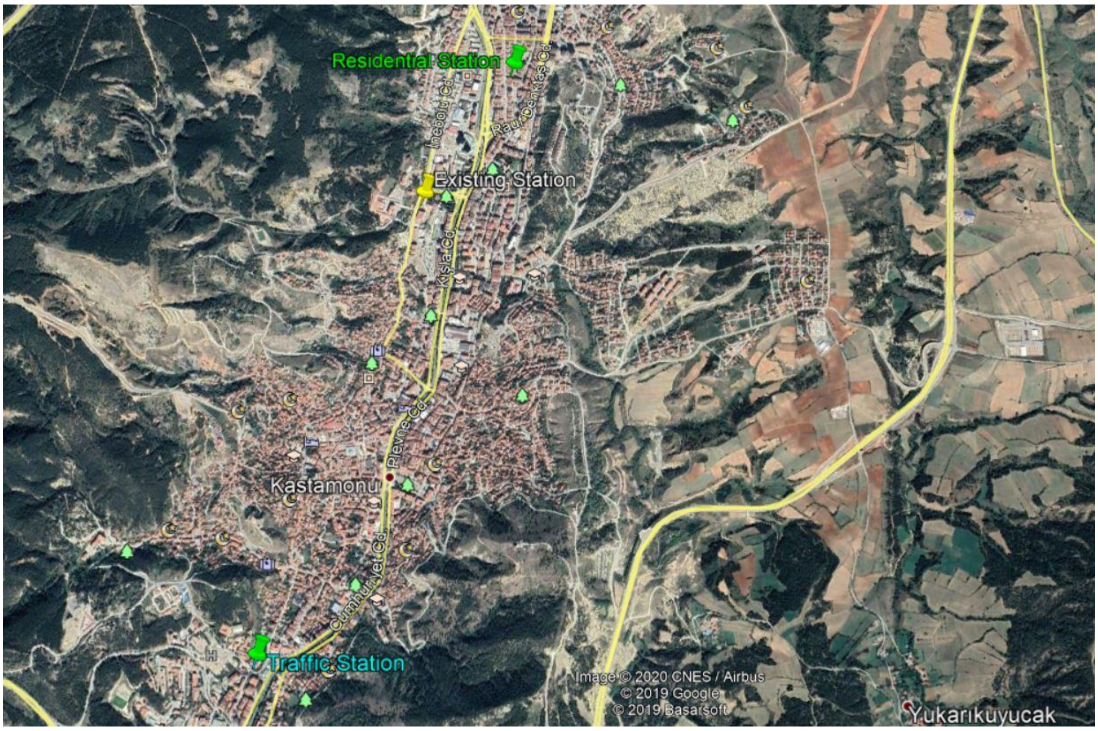

Figure B7 Evaluation of stations in Kastamonu