

**AMBIENT VOC CONCENTRATIONS IN THE CITY OF BALIKESIR AND ITS
ENVIRONMENT**

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ABSTRACT

AMBIENT VOC CONCENTRATIONS IN THE CITY OF BALIKESIR AND ITS ENVIRONMENT

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The assessment of volatile organic compounds (VOCs) has become an important field of interest in atmospheric pollution. This study quantifies and characterizes the ambient levels and spatial distribution of VOCs in urban and rural areas of Balıkesir. In addition, for the city drinking water dam excess flux from the traffic estimation was done. For these assessments passive sampling of VOCs performed at approximately 50 locations in and around the city of Balıkesir and analyzed with GC-FID system. Tenax TA was used as adsorbent. The sampling periods were in March of 2010 and in August of 2010 which were held for 7 days periods.

25 different compounds were analyzed for summer and winter periods and the most abundant species were compared with the literature. Benzene was measured $2.64 \mu\text{g}/\text{m}^3$ where Toluene was $10.90 \mu\text{g}/\text{m}^3$, Ethylbenzene was $1.30 \mu\text{g}/\text{m}^3$, m&p-Xylene was $1.80 \mu\text{g}/\text{m}^3$ and o-Xylene was $0.73 \mu\text{g}/\text{m}^3$ in average. The literature data was not split into summer and winter concentrations, therefore the average of winter and summer concentrations were taken. Balıkesir concentrations were lower than the industrialized cities Bursa and Kocaeli, where for the other European cities it differs. The median concentrations are also given for winter and summer samplings.

Factor analysis technique is used on the data collected in the study site. Four factors were extracted where first three of them were identified as light-duty vehicles, solvent evaporation and diesel emissions. The last one is suspected to be agricultural vehicles.

Keywords: Volatile organic compounds (VOC), passive sampling, spatial distribution.

ÖZ

BALIKESİR VE ÇEVRESİNDE UÇUCU ORGANİK BİLEŞİKLERİN ORTAM SONUÇLARININ İNCELENMESİ

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Atmosferik kirlilik konusunda uçucu organik bileşiklerin (UOB) değerlendirilmesi önemli bir ilgi alanı olmaya başlamıştır. Bu çalışma Balıkesir'in çevresel seviyeleriyle birlikte, kentsel ve kırsal kesimlerindeki uçucu organik bileşikleri tanımlar ve nicelendirir, ve mekansal dağılımlarını inceler. Bunlara ek olarak şehrin içme suyu barajının trafik emisyonlarından kaynaklı fazladan akımının tahminleri yapılmıştır. Bu hedefe ulaşabilmek için Balıkesir ve çevresinde, yaklaşık 50 noktada UOB'lerin pasif örnekleme çalışması yapılmış ve GC-FID sistemiyle analiz edilmiştir. Tenax TA adsorbent olarak kullanılmıştır. Örnekleme periyotları, kış periyodu olarak Mart 2010 ve yaz periyodu olarak Ağustos 2010 tarihlerinde 7'şer günlük sürelerle yapılmıştır.

25 farklı UOB kış ve yaz periyotları için analiz edilmiş ve en sık karşılaşılan bileşikler literatür çalışmalarıyla kıyaslanmıştır. Bu çalışmada Benzene $2.64 \mu\text{g}/\text{m}^3$, Toluene $10.90 \mu\text{g}/\text{m}^3$, Ethylbenzene $1.30 \mu\text{g}/\text{m}^3$, m&p-Xylene $1.80 \mu\text{g}/\text{m}^3$ ve o-Xylene ise $0.73 \mu\text{g}/\text{m}^3$ ölçülmüştür. Literatürdeki çalışmalarda yaz ve kış olarak ayırım yapılmamıştır bu nedenle kış ve yaz konsantrasyonlarının ortalamaları alınmıştır. Balıkesir deki ölçümler endüstrileşmiş şehirler olan Bursa ve Kocaeli'ne göre daha düşük değerlerdedir. Kış ve yaz ortanca değerlerine de bu çalışmada yer verilmiştir.

Çalışma sahasından toplanan veriler için faktör analizi tekniği kullanılmıştır. Dört faktör belirlenmiş olup, bunlardan ilk üçü sırasıyla küçük araçlar, solvent buharlaşması ve motorin yayılımları olarak belirlenmiştir. Sonuncusunun ise tarımsal araçlar olmasından şüphelenilmektedir.

Anahtar Kelimeler: Uçucu Organik Bileşikler (UOB), pasif örnekleme, mekansal dağılım.

To My Family...

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List of Abbreviations

ARF	Absolute Response Factor
BDL	Below Detection Limit
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
CMB	Chemical Mass Balance
EC	European Commission
EPA	Environmental Protection Agency
FA	Factor Analysis
FID	Flame Ionization Detector
GC	Gas Chromatography
MDL	Method Detection Limit
METU	Middle East Technical University
PCA	Principle Component Analysis
PMF	Positive Matrix Factorization
QA	Quality Assurance
QC	Quality Control
VOC	Volatile Organic Compound

CHAPTER 1

INTRODUCTION

1.1. Background

World atmosphere is in a change due to the gaseous pollutants emitted into the troposphere as a result of human activities. After 1950s world started to realize the damage on the atmosphere and many legislations started to be issued. First legislations including air pollution acts were in middle of 1950s for both Europe and North America. Inorganic pollutants such as nitrogen oxides (NO_x), sulphur oxides (SO_x) and carbon oxides (CO_x) were taken into consideration till the last decades. The main reason behind it is because they contribute to acid deposition on clouds or fog. With the development of the technology, volatile organic compounds (VOCs) started to be monitored and the effects are taken into consideration. The compounds may be emitted from solids and liquids which are commonly used by human and some of these compounds may create short and long term health effects. According to United States Environmental Protection Agency's (U.S. EPA) studies some of the effects can be irritation of eyes, nose, and throat, headaches, loss of coordination, nausea, and damage on liver, kidneys, and central nervous system. (EPA#1) The indirect contribution to the tropospheric ozone formation can be seen as another effect of the VOCs.

Volatile organic compounds are defined as any organic compound having at 293.15 K a vapor pressure of 0.01kPa or more or having a corresponding volatility under the particular conditions by EC Directive 1999/13/EC of 11 March 1999, Article 2 sub 17. VOCs are found in atmosphere in gaseous and particulate phases. These gaseous phase organic compounds get into reactions by photolysis with OH, NO_3 and O_3 (Atkinson and Arey, 2004). These reactions needed to be understood since there are many adverse effects. The rate constants and the mechanisms of the reactions with VOCs were researched in the last three decades and rates are mostly understood or can be estimated.

In the presence of the sunlight O_3 is produced with very complex reactions involving VOCs and NO_2 in the atmosphere. (Simpson, 1995) There are many studies trying to explain the mechanism and the relationship with the meteorological conditions and other pollutants but there is still a little knowledge about the roles of VOCs and NO_x in the formation of ozone. (Sillman et al. 2001)

U.S. EPA found out that biogenic VOC emission is amount to 72% of the total VOC emissions in the USA in 2002. The other 28% is believed to be anthropogenic where wildfires and prescribed burns excluded. The same study shows around 10% of the measurable anthropogenic sources is from non-road vehicles, nearly 42% is from on-road

vehicles, 43% is from industrial processes and the rest 5% is from fuel combustion in other processes which can be called as the emissions from fossil fuel power plants. (EPA#2) Biogenic emissions occur in the natural process of the vegetation.

The major classes of VOCs emitted to the troposphere are alkanes, alkenes, aromatic hydrocarbons, and oxygenated compounds. The vegetative emissions mainly consist of alkenes and oxygenated compounds. In the urban cities of U.S. the non-methane VOC concentrations calculated with the percentage of alkanes around 40-45%; alkenes, 10%; aromatic hydrocarbons, 20%; and oxygenates, 10-15%; plus unidentified VOCs in 1990s. (Atkinson and Arey, 2003)

1.2.Purpose

The main purpose of the study is to investigate the ambient VOC levels in Balıkesir atmosphere both in the rural and urban areas in different seasons. Also estimation of BTEX effects on the drinking water reservoir and in the urban area is another purpose. Aim is to determine the pollution in Balıkesir atmosphere and to understand the factors effecting the spatial distribution of VOCs such as meteorology.

1.3.Novelty and Contribution of the Thesis

Spatial distribution of BTEX compounds and their effects on the city atmosphere is studied in many cities all over the world. The main advancement in this study is the increase in the amount of sampling points and the increase in the compounds analyzed. Most of the studies based on only BTEX compounds and the sampling points were chosen in the urban areas of the cities; however in this study over 25 compounds were analyzed and the points were chosen from the urban areas, the main roads connecting the city to the others, some rural areas and from the Dam where city's drinking water is supplied. In addition, the sampling periods were chosen to examine the difference in winter and summer conditions in approximately 50 locations.

The area covered and the amount of compounds studied makes this study special. Although there are studies made in different meteorological conditions, there is no study which covers over 25 compounds in 50 locations covering most of the urban and rural areas and covering seasonal changes at the same time. Another special part for this study is the estimation of the excess flux on the drinking water reservoir because of the traffic contributed BTEX compounds.

CHAPTER 2

THEORETICAL BACKGROUND

2.1. History of VOC Problem

First photochemical problem occurred in Los Angeles, California in early 1950s. The problem emerged from secondary pollutants such as O₃, nitrogen oxides or reactive hydrocarbons, released from motor vehicles. Haagen-Smit and Fox (1956) were the first ones made connection between the photochemical smog and secondary pollutants (Shallcross, D., 2006). In the industrial cities and urban areas more problems started to occur where first problem in Europe was recorded in 1965 in Netherlands where the ozone concentrations recorded high as in the most of the European cities.

Ozone was found to be the main photochemical oxidant in the early studies where ozone formation involves hydrocarbons, nitrogen oxides and sunlight. In the last half century the contribution of different hydrocarbons on photochemical ozone formation started to be analyzed and different contribution of each hydrocarbon is recognized. (Kuntasal, 2005). In North America, there has been a policy focus on the reactive hydrocarbons creating ozone formation in the urban areas.

In Europe, the policies focused on multiday photochemical episodes and the long range transport rather than the urban photochemical ozone formation. United Nations Economic Commission for Europe decided to fight regional ozone formation problems in those manners. For regulation policy, reactivity is the main factor for hydrocarbons where the non-reactive ones are exempt from regulations (Dewulf *et.al.* 2007). European countries decided to reduce the hydrocarbon emissions by 30% and stop nitrogen oxides emission to reduce the ozone formation potential.

International actions against methane and chlorofluorohydrocarbons (CFCs) emissions, as well as carbondioxide (CO₂) and nitrogen oxides (NO_x) are worked out in Montreal Protocol on Protection of Ozone Layer (1987), London Revisions to do Protocol (1990), and the Protocol of Copenhagen (1992). Also in 1997, reduction of methane carbon dioxide and nitrous oxide is aimed with the Kyoto Protocol. (Dewulf *et.al.* 2007)

2.2. Environmental Effects of VOCs

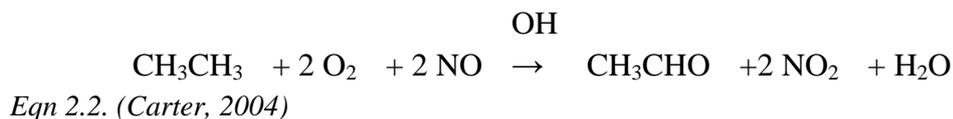
For more than a half century VOCs are of concern because of effects on human health, plants, climate change via stratospheric ozone depletion and tropospheric ozone formation. The details are explained in the following topics.

2.2.1. VOC-NO_x and O₃ Chemistry in Troposphere

VOCs are defined as organic compounds with a pressure higher than 10⁻¹ torr at 25°C and 760mmHg. When these compounds discharged to the environment, they tend to evaporate rapidly to the atmosphere. Atmospheric photochemistry and photo degradation are major removal processes for VOCs. (Mackay *et al.*, 1992)

VOCs include chemicals with different physical and chemical properties. Only carbon and hydrogen containing compounds creates important VOC classes such as alkanes, alkenes, alkynes and aromatics. Also oxygen, chlorine, bromine, phosphorus or other halogens containing hydrocarbons creates other important groups such as aldehydes, alcohols, ketones, chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). (Kuntasal, 2005)

Volatile organic compounds are mainly transformed in the troposphere by the process of photolysis, and also removed by the mechanism of dry and wet deposition. Most of the VOCs are reactive in troposphere with hydroxyl (OH) ions in the presence of sunlight and also in the night time chain reactions occur with NO_x. Furthermore in costal and marine conditions Cl reacts with the VOCs. (Atkinson and Arey, 2003) The overall process of ethane, can be an example in the equation 2.2;



In the past decade the rate constants for the atmospheric reactions of VOCs have been studied and there is a lot of progress in understanding the chemistry between VOCs, NO_x and O₃. For the larger alkanes (≥C₆) there are mostly indoor air studies in room temperature and above but there is much to be studied to totally understand the mechanism. (Atkinson and Arey, 2003)

In the absence of VOCs, NO and NO₂ are the reason for composition and decomposition of O₃ in the troposphere. In the presence of VOCs many mechanisms occur with substituted alkyl peroxy radicals (RO₂•), substituted alkoxy radicals (RO•), OH and HO₂. These mechanisms result in net formation of O₃ in the troposphere as shown in the *Figure 2-1*.

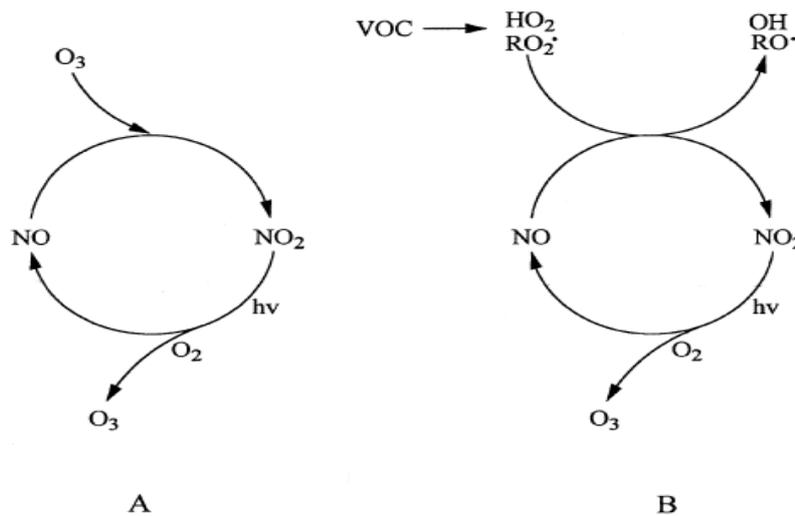


Figure 0.1: Schematics of NO-NO₂-O₃ reactions in the absence of VOCs in (A), and NO-NO₂-O₃ reactions in the presence of VOCs. (Atkinson, 2000)

2.2.2. Effects of VOC on Human Health

Many VOCs are classified as carcinogenic and toxic, so they have many adverse effects on human health. Therefore in many people exposed to VOCs even in low concentrations may suffer from eye, nose and throat irritation, nausea, or damage to kidney, liver or central nervous system. Some of the compounds are suspected to cause cancer in humans and animals (EPA#3). Health effects of VOCs change for each compounds from highly toxic to non-hazardous.

In the Clean Air Act, 185 hazardous air pollutants for human health are listed by US EPA. Most of the compounds are defined as VOCs. In addition The Ministers of Environment of Canada published priority substance lists containing 50 compounds most of which are VOCs. (Kuntasal, 2005)

2.2.3. Effects of VOC on Plants

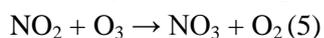
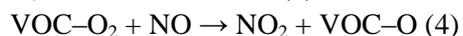
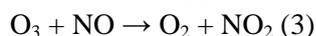
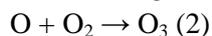
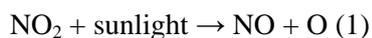
For plants, no direct effects of organic compounds were observed. However in some of the sensitive plants, decreased harvesting pod weight was observed. In the plant tissues, VOCs themselves do not appear where metabolic breakdown products may be found from the leaf to the root which may indicate the potential side effects. One of the side effects is thought to be environmental stress (Cape, 2003). Possible symptoms are given as internode shortening, premature discoloration of leaves, epinasty of leaves, abscission of flowers, chlorosis and necrosis. (Kuntasal, 2005)

2.2.4. Climate Change

Ground level ozone formation is due to nitrogen oxides, VOCs, and hydroxyl radicals. VOCs from fossil fuel combustion are primary ozone formation sources. Also high contribution to non-methane VOC concentrations come from gasoline evaporation. So the VOCs are effective in ozone formation throughout a year although there are some concentration differences in the seasons (Shea *et al.*, 2008). There is no direct effect of VOCs on climate change is observed but the important effect on ozone formation in the troposphere and effect on water vapor affect the climate change in indirect ways.

2.2.5. Stratospheric Ozone Chemistry

Nitrogen oxides (NO_x) is one of the most important ozone depletion species in the stratosphere according to the summarized equation 2.3. Most of the VOCs are not important in the stratospheric ozone chemistry since lifetimes of most of them is not long enough to reach stratosphere. However some of the species like methylchloroform and carbontetrachloride are reactants in the stratospheric chemistry which are introduced as Ozone depleting substances (Sainfeld *et al.*, 1998). Ismail *et al.* (2013) studied stratospheric ozone depletion and found out the following results of VOCs effect on reactions:



Eqn. 2.3. NO_x , VOC, O_3 reactions

The VOCs react with NO and produces NO_2 , which creates both ozone production and depletion where the reactions depend on the VOC and NO_x concentrations in the atmosphere. The reactions are dependent on the levels of VOCs and NO_x where VOC is in higher concentrations NO_x is the limiting reactant if otherwise VOCs are limiting reactants. As a result, it is important to keep the balance of VOC and NO_x levels in low concentrations to keep ozone depletion at low levels. (Ismail *et al.*, 2013)

2.3. VOC Sampling and Analyzing Techniques

In the urban areas, anthropogenic VOC emission to the atmosphere in ppb levels is a known fact. The determination of VOC levels in the air is necessary to learn the transport mechanism of the pollutants and for the health effect studies. But the concentrations of VOCs change in time, so the measurement techniques must be effective against these fluctuations. Also the extreme variety of the complex hydrocarbons in the atmosphere with low concentrations creates a difficulty in determination of the concentration of each VOC. Different techniques for these purposes comes handy looking at the accuracy,

sensitivity and simplicity. Real time instruments like portable gas chromatography or infrared spectrometers are one of the mostly used techniques although there are many limitations. High cost, field calibration problems and power supply problems on the field are main disadvantages of the method. (Harper, 2000). Another technique is based on field study and laboratory study. Air sampling is done in the field with adsorption on selective sorbents or using canisters. Also two different methods are used on adsorption, as active sampling and passive sampling methods. Taking samples of pollutants from the atmosphere with a rate controlled by physical processes such as diffusion through a membrane filter or a static layer is called passive sampling (diffusive). Sample taking with active movement of air through the sampler is called active sampling.

The theory of passive sampling is based on Fick's First Law. The amount (M) of the analyte transported by diffusion with time (t(sec)) when the concentration gradient is linear and the collection efficiency is 100%, can be described by the following relationship (Gorecki et al. 2002):

$$M = U \times t = \frac{DA}{L} C_0 t$$

Eqn 2.4.: Gorecki et al.(2002)

Where;

U: Uptake rate (mol/sec)

t: time (sec)

D: Molecular diffusions coefficients of the analyte (cm²/s)

A: Cross section of the diffusion path (cm²)

L: the total length of the diffusion path (cm)

C₀: analyte concentration of the medium examined (mol/cm³)

The concentration of the analytes can be calculated adsorbed mass determined by gas chromatography, the uptake rate and the sampling time. In ideal conditions the uptake rates are constant for each compound which can be calculated from the geometry of the sample tubes. However it was proven that the experimental uptake rates are different from the theoretical ones (Gelencser et al., 1994). Different environmental conditions in the field and in the laboratory are seem to be an important reason causing the difference. (Tolnai et al., 2001). These disadvantages of passive sampling tried to be eliminated with taking the uptake rates from a parallel study made by Mihriban CİVAN in 2010 which were calculated for all VOCs studied, with the help of online GC-FID. (Civan, 2010)

For passive sampling methodology there are many commercially available passive sampling tubes for both organic and inorganic pollutants. NO, NO₂, SO₂, CO, NH₃, H₂S are some of the examples for inorganic pollutants where most of the organic pollutants can be measured as long as its uptake rate is known. Passive sampling is made by chemical or physical adsorption on an adsorbent medium. The area of use is very broad

because of the ease of use. Indoor and ambient air quality, occupational hygiene are some examples of area passive sampling can be used. Diffusive monitoring is both cost effective and simple since there is no need for sampling pump and attention in the field. There are two types of sampling tube extraction procedure which are solvent extraction and thermal extraction.

For many volatile organic compounds, thermal adsorbent tubes are applicable which can be used in ambient and indoor environments. Also with the applicability, thermal extraction creates an advantage in sensitivity of the results since there is no dilution of the solvents (De Bortoli et al., 1992). The sampling tubes are small in size, easy to transport and store, easy to condition and relatively cheaper than the other processes.

In determination of VOC concentration passive sampling is one of the most effective techniques although there are still many studies going on to determine the uptake rates more accurately. In addition, different adsorbents are used in different studies to increase the effectiveness of the technique (Roche et al., 1999, Ballesta et al., 1992). Skov et al. (2001) compared the sampling techniques on Benzene also with the adsorbents used. The thermal desorption passive sampling methodology seems to be one of the best ways to determine the VOCs, although long sampling time is required and the detection limit is higher than online gas chromatography, BTEX monitors and canisters thermal desorption. At the same study Skov et al. found a linear correlation between BTEX analyzer and Tenax TA filled diffusion samplers with a slope of 1.20 ± 0.13 . Also in another study Wideqvist et al. (2003) found that the diffusive sampling stays in 95% confidence interval for toluene concentrations compared to online GC-FID. But the benzene results were found 25% to 30% higher in passive sampling strategy.

2.4. Natural VOC Sources and Emissions

In every living organism VOCs are present. So, the natural emissions of carbon monoxide (CO), nitric oxide (NO) and non-methane VOCs generally exceed the anthropogenic emissions where they have important role in the composition of the atmosphere. However in the urban atmospheres the anthropogenic emissions are generally more than the natural emissions. (Guenther *et al.*, 2000). Atmospheric chemistry models show that both anthropogenic and biogenic emissions of VOCs have effect on ozone production in the troposphere. (Guenther *et al.*, 1994).

More than 40,000 organic compounds can be found in the plant cells in the different plant species (Guenther *et al.*, 1994). The emission investigations are focused on the reactive hydrocarbons which are dominant in the emissions. Most abundant biogenic organic compounds are listed as methane and isoprene by Guenther *et al.* (2006). Those two dominant emissions are associated with different living species. High percentage of methane emissions is associated with the microbial activities where more than 90% of the isoprene emissions thought to be form terrestrial plants. (Guenther *et al.* 2006).

Each of methane and isoprene emissions accounts to the one third of the annual VOC emissions in the world. The other one third accounts for anthropogenic and biogenic emissions of hundreds of VOCs. However the most important compound is considered as methane since its life time in atmosphere is measured with years where isoprene has a life time between minutes and hours (Guenther *et al.* 2006).

2.5. Anthropogenic VOC Sources and Emissions

Starting from early 1950s the most important air problems have been the high sulphur dioxide and smoke levels because of the combustion of sulphur containing fossil fuels. However, with the increase of the motor vehicles and the filtering of sulphur dioxide in the stacks the major problem became the traffic emissions. Motor vehicles emit high variety of organic and inorganic pollutants such as carbon monoxide (CO), nitrogen oxides (NO_x) and volatile organic compounds (VOC). In EPA study (1993) the motor vehicle emissions for Benzene was calculated around 60% of the total emissions.

Measurements of the inorganic particles such as SO₂, NO_x, and CO, were routine through the world for a long time but for the VOCs only in North America and Europe there were some stations. In North America there are over 4500 monitoring stations for both inorganic and organic pollutants. According to Canadian Ministry of Environment Lands and Parks agency the routine VOC measurements started in 1986 in British Columbia (Canadian Ministry of Environment 1998). Also US EPA initiated the Photochemical Assessment Monitoring Stations program (PAMS) in 1993 including monitoring of 56 hydrocarbons, O₃, and NO_x. (Demerjian, 2000). The monitoring stations for Europe was started in 1992 with a low number but increased rapidly by Swedish Urban Air Quality Network Program (Mowrer *et al.*, 1996).

Many studies were done to determine the emission sources all over the world including the continuous monitoring programs. In Germany 51% of the emissions of VOCs were from solvent use excluding methane in 1995. Also 35% of the emissions was from road traffic, 6% was from industrial processes, 4% was from production and distribution of fuel, and the rest was from other sources which were shown in the figure 2-2. Liebscher (2000). In some countries, emissions from solvent use exceed the emissions from traffic.

VOC - Emissions in Germany 1995 (excl. methane)

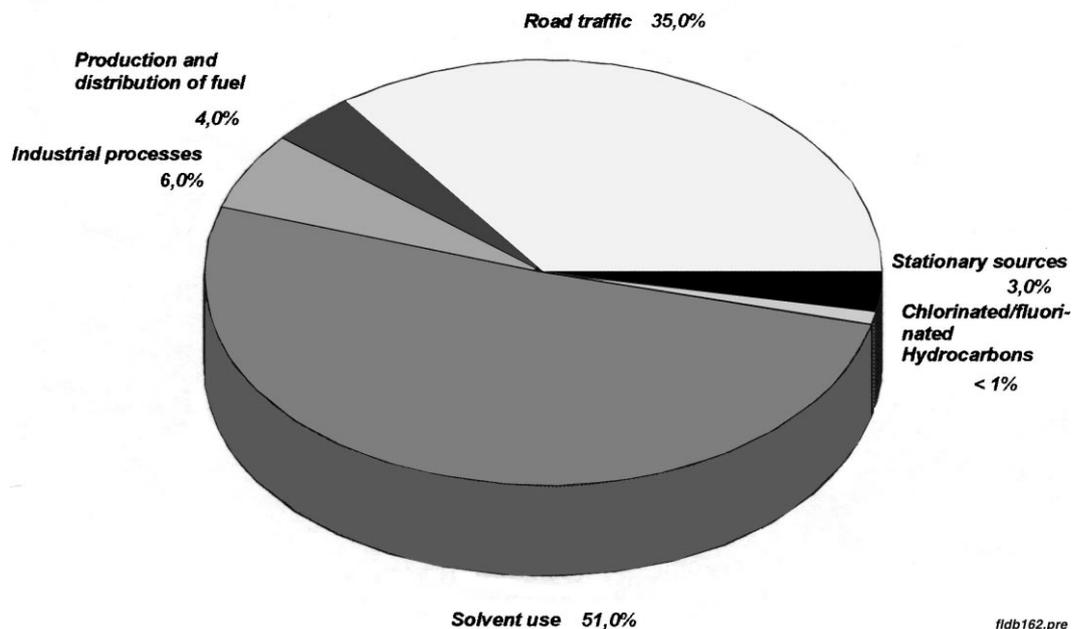


Figure 0.2: VOC emissions in Germany 1995, (Liebscher, 2000)

The main application in solvent used emission is painting processes. 38% of the total 51% emission was from painting processes in Germany 1995. Printing processes, industrial cleaning, chemical industries, pharmaceutical industries were some other important emission sources for solvent used emissions (Liebscher, 2000). Figure 2.3 shows the graphical projection of the major solvent used sectors.

Estimates of VOC-emissions in major solvent use sectors
(Source Umweltbundesamt 1995)

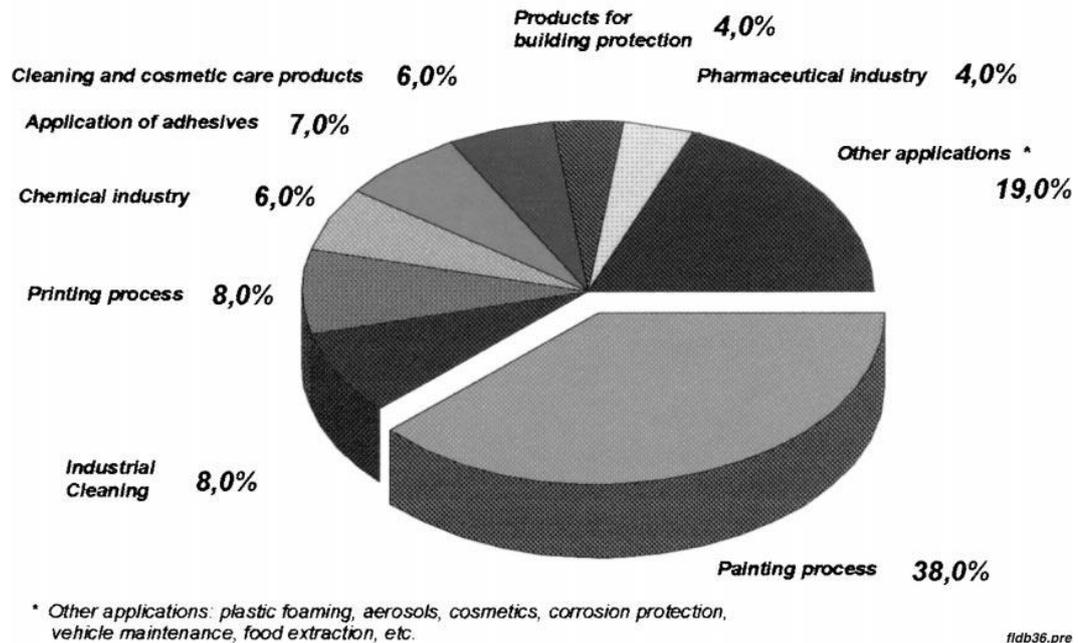


Figure 0.3: Major solvent used sectors. (Liebscher, 2000)

The studies specific for Turkey are also important for filling the data gap between the Asia and Europe. Latest studies show that the legislations and the cultural differences effect the amount of VOC in the ambient air. (Na et al. 2004). Gee and Sollars (1998) revealed that the toluene to benzene ratio is much higher in Asia countries than the European countries and USA. The difference is thought to be originating from the emission sources and strengths of the Asian countries. These evidences show the need for detailed investigation of the sources for different parts of the countries and continents are needed in order to develop effective management plans.

Along with the online monitoring stations many research studies were made on VOCs with different methods. Mowrer et al. (1996) conducted a study in the urban air of Sweden during the winter months with diffusive monitoring methods. The study was to determine the C6-C9 hydrocarbons with diffusive tubes filled with Tenax TA to examine the characteristics of anthropogenic sources in the urban atmosphere. The analyzes were done with the help of Varian Model GC-FID attached with a thermal desorption unit. Detection limits, sample stability during storage and sources of errors were evaluated during the study. In the meantime online gas chromatography was used to confirm the validity of passive sampling method. Another study was done in 1998 by Svanberg et al. which aimed to measure the VOC concentrations in weakly means. The diffusive tubes were also filled with Tenax TA and analyzes were done with Varian GC-FID with an automatic thermal desorption system. Results were analyzed to determine the contribution from regional and local sources and the long range transport of VOCs.

There are various studies for determination of VOC concentrations and sources of VOCs with other methods like active sampling or online gas chromatography. In Hong Kong ambient air Guo et al. (2004) studied concentrations of 51 VOCs, sources and emission rates, and photochemical reactivity of C3-C12 hydrocarbons. The sampling period started in 10th of January and ended in 30th of December, 2001 which covers almost all year. The samplings were done with stainless steel canisters and in the analyze GC-FID is used. Sexton and Westberg (1983) studied with online instruments in seven urban and six rural areas in USA to determine the pollution levels and evaluate the transport mechanism of the pollutants in States.

2.6. VOC Emission Regulations

First emission control guideline was introduced by US EPA in 1971. The aim of the study was both to reduce or stop the emissions of ozone producing substances and also to encourage the use substitute substances. In the first intent was to exempt the VOCs with tolerable adverse effect by Los Angeles Districts Rules. However in 1977 EPA issued a policy which decreased the number of exempted species to 12. These 12 substances have negligible reactivity which does not cause ozone formation in the troposphere. EPA also issued reactivity test methods for compounds which later used to increase the number of compounds with negligible reactivity. In 1992 the list of negligibly reactive compounds increased to approximately 50 compounds with 40 CFR part 51. (EPA#4)

In 1990 California Air Resources Board (CARB) started to work on regulations on VOCs based on reactivity and in 1991 a reactivity scale was incorporated with the regulations. The aim was to control the emissions from vehicles with a clean fuel regulation. The reactivity scale was based on the VOC composition and VOC-NO_x ratios (EPA#4). Currently, CARB is working on regulations for architectural coatings with the use of reactivity scales in other programs.

Canadian Ministry of Environment regulated the “Canada Wide Standards for Particulate Matter and Ozone” in 2000. The aim is to reduce some air pollutants and VOCs with some action plans. In 2004 the “Federal Agenda on the Reduction of Emissions of VOC from Consumer and Commercial Products” was implemented aiming only the VOCs till 2010. Also in 2003, VOCs were met the “toxic” criteria of Canadian Environmental Protection Act (1999).

In Europe the Council Directive 1999/13/EC limiting the VOCs was adopted in 1999 although the studies for the directive started in 1991. The aim of the directive was to reduce the solvent emission in the European Union by limiting the use of solvents in some industrial activities. The main activity that was aimed was painting processes which expected to cut the emissions at least to half of the 1990 levels. (Liebscher, 2000) 20 activities were in the control mechanism of the directive compatible with the USA and Canada. In addition in 2000 the European Commission limited the benzene and carbon monoxide emissions with the Directive 2000/69/EC. And with 2002/3/EC directive the

European Commission focused on the ozone problem in the ambient air. In addition 30 VOCs and NO_x monitoring was recommended by the directive. With the Directive 2008/50/EC the NO_x and benzene limit compliances of the member countries were extended. (EC#1)

The first regulation on air quality in Turkey was issued in 1986 which is the Air Quality Control Regulation. With this regulation the industrial emissions of approximately 10 VOCs were regulated. Also the ozone producing substances were regulated in general. A more detailed regulation about VOCs were issued in 22.07.2006 with the name of “Industrial Sourced Air Pollution Control Regulation”. In this new regulation the carcinogenic VOCs and total hydrocarbons were limited from the industrial emission sources. There were around 120 compounds limited by this regulation. It was renewed in 03.07.2009 with minor changes about VOCs. Also for vehicle emissions “Quality of Gasoline and Diesel Regulation” was issued in 11.06.2004. the regulation limits the percentage of olefins, aromatics and benzene in the emissions of the motor vehicles. Control of Air Pollution Emitted from Heating Purposes Regulation was issued in 13.01.2005 which regulated permissible fuel characteristics limiting hydrocarbons in housing and commercial heating. Some other regulations are in progress, which are parallel to European Union Directives since Turkey is trying to be an EU member.

2.7. Receptor Modeling

Receptor models were started to be used in 1960s when multivariate statistical methods and mass balance both started to be used. These methods are used to calculate the relative contributions of major emission sources in individual monitoring sites (receptors) by utilizing the measurements. The main input parameters for receptor based models are the measurements (EPA#5). Some models like Chemical Mass Balance (CMB) model requires some other parameters like source emission profiles. On the other hand, some advanced models like Positive Matrix Factorization (PMF) do not require source profile inputs, but; the common output of these models is the estimation of contributions of each source for air pollution (EPA#5).

Receptor models have an advantage on source appointment since the data is based on the actual measured results. VOC emission factors and profiles, amount of each specie released from a source can be found in the literature, but the uncertainties in operating conditions, fuel characteristics, etc. increases the necessity of using receptor models (Baldasano *et al.* 1998).

In identification of the sources, receptor models rely on traces. For reliable results the tracers should be measurable for each of the mostly used receptor models. Chemical Mass Balance (CMB), Principle Component Analysis (PCA), Factor Analysis (FA), and Positive Matrix Factorization (PMF) are the four models most commonly used. Factor analysis is used in this study shown in the section 4.5.

Receptor models have been used for the particles for a long time. In addition to particles models have also started to be used for the VOCs for more than two decades. For example in Illinois, USA for 13 toxic VOCs CMB model was used. Also in Chicago 23 non-methane organic compounds were analyzed by Scheff and Wadden. Kupiszewska and Pilling applied factor analysis (FA) in Leeds, UK to 20 VOCs sampled (Baldasano *et al.* 1998). In Turkey, Kuntasal (2005) used PMF modeling for the Ankara VOC samples. In addition, Civan (2010) used FA technique for the samples collected from Bursa and Pekey *et al.* (2011) used the same technique for the data from Kocaeli. Recently in most of the studies the receptor models are being used.

CHAPTER 3

MATERIALS AND METHODS

3.1. Balıkesir Study Site

The sampling site of this study is chosen to cover the urban and rural areas, including the dam the city gets its drinking water. Sampling campaigns were made in two different seasons, in 10-17 March 2010 and 13-20 August 2010. These dates were chosen to cover the winter and summer conditions. In March coal burning in Balıkesir continues and the traffic goes back to the normal conditions after the snowy days, which can be seen as the worst case scenario for the VOC air quality.

Balıkesir is the 17th crowded city in Turkey with a population of 1.150.000 which includes around 700.000 urban citizens. The city is located in the south west of the Marmara Region and has coast both to Marmara and the Aegean Seas. Figure 3.1 shows the place of Balıkesir on Turkey map. Because of the coastal areas city has, the mobility in the city increases in summers. Also the road connecting İstanbul to İzmir, which is one of the most crowded roads, goes through the city. According to TUIK's statistics Balıkesir has the 11th most vehicles used and the 22nd population dense city in Turkey. The main income of the city is from agriculture and the industries based on agriculture, although there are some other sectors including metal casting and some electrical products.

Climate in Balıkesir differs from the coast to the inner parts. In the coastal parts mainly Mediterranean and in the inner parts mainly Anatolian climates seen. Highest precipitation occurs in winters, although there is some contribution in springs. Annual precipitation is below the average of the Marmara Region with the amount of 54,5 cm. Average annual temperature is 14,5 °C. (Tağıl, 2007)

Balıkesir air quality is started to be studied in terms of PM and SO₂ after the year 2000. However for the VOCs there is no data available. To understand the quality of the air better, VOC and inorganic compounds data must be studied. So this study is important since it will be the first VOC data set for Balıkesir.

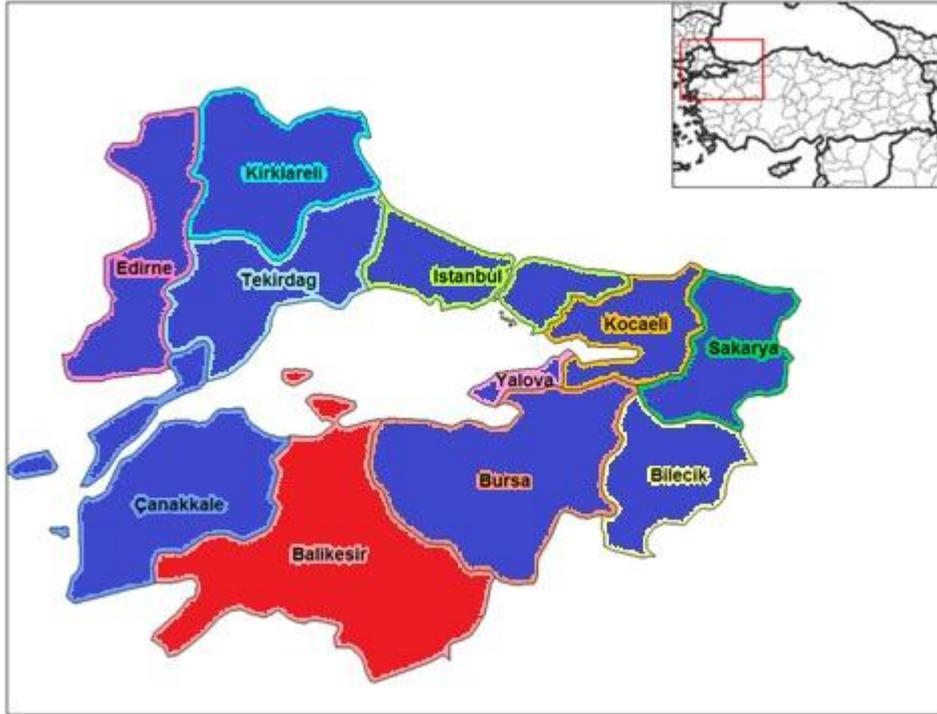


Figure 0.1 Balıkesir on Turkey Map

3.2. Sampling Seasons and Stations

For determination of the VOC levels across the city two different sampling periods were chosen. In March 2010, first samplings were done in 48 points in addition to 6 different blank samples for 7 days period. The aim was to evaluate 50 samples in rural areas, urban areas, city connection roads and background points; however 2 of the sampling stations were lost at the end of 7 days. Other than the lost 2 passive sampling tubes, there were 4 damaged tubes which could not be studied by Gas Chromatography Device (GC). As a result rest 44 samples were used in the evaluation of the VOC levels in Balıkesir between the dates 10-17.03.2010. Table 3.1 represents the sampling dates for the winter and summer periods.

Table 0.1: Sampling Periods

Sampling Name	Sampling Start Date	Sampling Finish Date
Winter Period	10-11.03.2010	17.03.2010
Summer Period	13-14.08.2010	20.08.2010

Second period of study was done between the dates 13-20.08.2010. In this study period 53 passive tubes were deployed to the same locations of the winter with an additional 3 points. The aim of 53 sample points was to evaluate at least 50 data points; however 1 of the sampling stations was lost and 3 of the tubes were damaged to be studied by Gas

Chromatography Device. The evaluated sample amount was 49 for the summer period. Number of sampling tubes collected in the sampling periods is shown in the table 3.2.

Table 0.2: Number of Sampling Tubes

Sampling Tubes					
Sampling Period	Deployed	Stolen or Lost	Collected	Damaged	Total Analyzed
Winter	50	2	48	4	44
Summer	53	1	52	3	49

The extension of the exposure time was planned in the summer sampling campaign since the peak levels of the low concentrated organic compounds would be harder to chase; however the idea was seen to be un-effective as the high concentrated compounds such as benzene and toluene starts to be saturated after 10-14 days exposure. To see the effect of the exposure time on concentrations and to optimize the time that tubes stay on the field, a study was done by Civan (2010). The optimum sampling period was chosen as 7 days in this study.

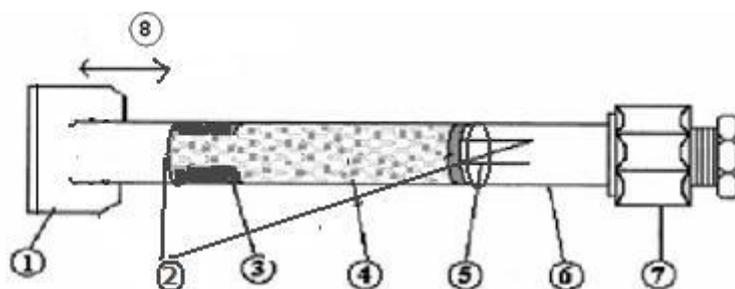
In the seven days winter period, the average temperature was around 8⁰C. There was no precipitation during this time, although the statistics show that precipitation occurs for about 11 days in March. Also for the summer study no precipitation was observed where the average temperature was around 25⁰C for the seven days period in August.

The locations of the sampling points were tried to be carefully selected, to be in one of the three microenvironments as residential, traffic or background. For the residential stations the samplers were tried to placed in the public areas like schools, mosques etc. which were away from the main roads. The aim was to decrease the effect of the traffic while covering the more crowded places. For the traffic affected stations, the samplers were put right next to the main roads of the city, and the İzmir-İstanbul highway. The background stations were selected to be away from the anthropogenic effects except for the 8 statins which were very close to the borders of İkizcetepeler Dam Lake.

There were 13 residential, 13 traffic and 23 background stations where 5 of the traffic stations were very close to the residential areas. The samplers close to the high traffic roads in the residential areas were chosen as traffic samplers. Also for the purpose of estimation of dry deposition, 8 out of 23 background stations were deployed right next to the İkizcetepeler Dam Lake. The sampling points away from the residential and traffic areas were named as background points where they were selected to cover the area between residential area and the drinking water resorvair.

3.3. Sampling Methodology

Passive sampling tubes, imported from Gradko Ltd. were used in the sampling periods. The passive sampling tubes were filled before the winter period with 100 mg Tenax TA (SUPELCO Company) and conditioned in a special made conditioning oven by Kuntasal (2005) for her PhD thesis. Filling process is explained in the next section in details. Tubes has a length of 8.89 cm, an outer diameter of 6.35mm and an inner diameter of 4.10mm. In order to keep the Tenax adsorbent in the sampling tubes, stainless steel screens are planted at the inner bottom and the inner top of the tubes. However the screens at opposite side of the diffusion entrance were not stable so additional screen gouges were put on top of the screen. A figure of a sampling tube is shown in the figure 3.2.



- | | |
|----------------------------|---------------------------|
| 1. Diffusion Cap | 5. Screen Gouge |
| 2. Stainless Steel Screens | 6. Gradko Sampling Tube |
| 3. Additional Screen Gouge | 7. Swage-Lock Storage Cap |
| 4. Adsorbent (Tenax TA) | 8. Diffusion Gap |

Figure 0.2: Scheme of passive sampling tubes. (Civan, 2010)

The details of the conditioning process are explained in the section 3.4. The tubes were conditioned in groups of 5 or 6 and one of each group was analyzed to see if any problems occurred in conditioning. Also the blank samples were chosen from these analyzed tubes. In order to keep the conditioned sampling tubes away from contamination some preservation mechanisms were developed. Screw caps were deployed to the both ends until the sampling period started. In the start of the sampling period the top screw caps were removed and a diffusion caps were installed. In addition to the screw caps, the sampling tubes were put into glass tubes filled with silica gel and activated charcoal at the bottom which is shown in the figure 3.3.2 on the left. Also the glass tubes were kept in activated charcoal filled containers which were kept in the deep-freezer at around -10°C to reduce the contamination in storage period. The conservation mechanism for contamination is in the figure 3.3. For the sampling periods the tubes were transported with a mobile refrigerator at 4°C and the sampling tubes were taken out in each sampling point one by one. In the collection of the tubes the screw caps were deployed after the diffusion caps were removed and the tubes were put into glass tubes again. Same mobile refrigerator was used in the collecting period. Although the tubes kept safely in glass tubes and cold environment, in order to keep contamination minimum the samples were analyzed in 4 days with around 60 hour work time.



Figure 0.3: Sorbent tubes conservation mechanism (Kuntasal, 2005)

3.4.Preparation and Conditioning of Passive Tubes

Empty stainless steel passive tubes were cleaned with 95% pure methanol supplied by Merck & Co. Inc. in the Cole Parmer Model 8892 (Cole-Parmer Instrument Company) ultrasonic shaker for 2 hours. After the cleaning period the tubes were dried in the oven in 100°C. The screens were placed in the tubes to keep the adsorbent chemical, and 100 mg Tenax TA (SUPELCO Company) accurately weighted using high precision scale (Sartorius Model A210V). The filling process of the tubes was made in the clean air room. A glass funnel is used in the filling process. To make homogenous placement of the chemical in the tube mechanical vibration was used. The filling process is shown in the figure 3.4. Powder free gloves and dust mask were used in all these processes in the clean room.



Figure 0.4: Sampling tubes filling process (Civan, 2010)

For an efficient measurement the contaminants have to be removed from the sorbent before the sampling. To make sure that there is no contamination, the tubes were prepared just before the March sampling period and conditioned before moving them to the field. Used sampling tubes were conditioned after the analyzes also to remove the contamination and they were kept in the glass tubes in the deep-freeze for the next sampling. Before the summer period only 10-12 sampling tubes were prepared since there were some stolen or lost tubes in the winter study. In addition the amount of blanks was increased in the summer sampling campaign. In this case Tenax TA adsorbent was kept

under high temperature, high purity N_2 gas flow for a long time. This process was done in the conditioning oven designed by Kuntasal (2005) which is shown in the figure 3.5. The oven has $400^{\circ}C$ heating and a flow rate of max 500 mL/min high purity N_2 gas capacity(Kuntasal, 2005). Although the adsorbent chemical has a max $370^{\circ}C$ temperature limit shown in the catalogue before it starts to lose its specialties, the heating capacity was kept at $320^{\circ}C$ since there were some tubes lost its adsorption capacity when conditioned in $350^{\circ}C$ according to Kuntasal's work in 2005. The high purity gas rate was kept in the range of 70-100 mL/min for all the 5 or 6 tubes in the conditioning oven, since the lower flow rates were not effective where higher flow rates decrease the temperature in the passive tube. In these standards the tubes were kept in the oven for at least 12 hours. For every set of condition at least one of the tubes were analyzed to see, if the conditioning was proper.

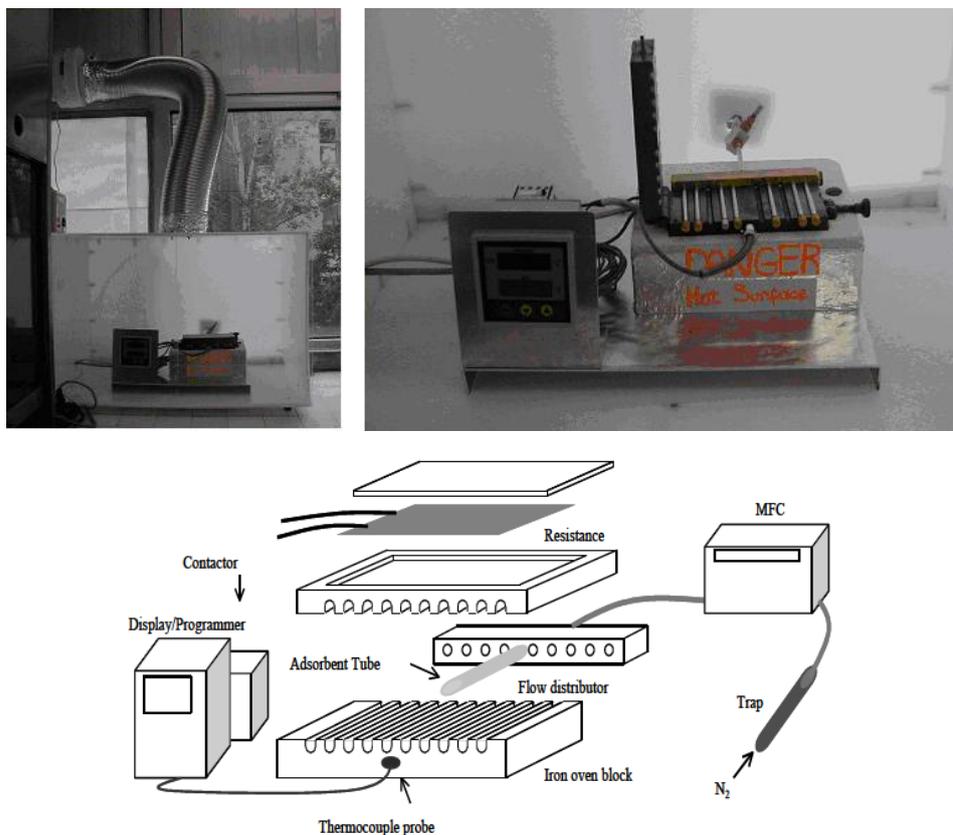


Figure 0.5: Photograph and the schematic representation of conditioning oven designed by Kuntasal (2005)

3.5. Analytical Methodology

In this study the same equipment and the method were used with Mihriban Civan's Bursa study (2010), so the work she had done is summarized in this part. 6990 Gas Chromatography (GC) device (Hewlett- Packrat Company – Agilent Technologies Inc., USA) coupled with Unity Thermal Desorption System (Markes International Limited, UK) was used to analyze the samples. The thermal desorption unit was used to feed the GC-FID system which is compatible with the sampling tubes. The system works by desorbing the analytes on the sampling tubes and collecting them in the cold trap. The desorption unit works at 200⁰C and the cold trap works at -15⁰C both of which were optimized by Civan (2010) for her PhD thesis.

Analyze and quantification of the calibration gas was made by Civan (2010) against the standard reference material SRM 1800 (Non-Methane Hydrocarbon Compounds in Nitrogen) and 1804a (Volatile Organics in Nitrogen) provided by the National Institute of Standards and Technology (NIST) (Gaithersburg, MD, USA). There are 15 and 19 compounds in the SRMs respectively where 3 components (benzene, toluene, and ortho-xylene) are common for both. The calibration standard was used since the compounds were within 30% of their respective nominal values (Civan, 2010).

148 volatile organic compounds were identified to GC-FID system by Civan (2010). However Tenax TA chemical adsorbs the volatile organic compounds between the ranges C5 to C12 which determines the range of this study.

All statistical analyses were performed using SPSS Statistics 17.0 software (SPSS Inc., Chicago, USA) for Windows. The spatial distribution maps of VOC concentrations were generated with MapInfo 10.0.

3.5.1. GC-FID Optimization

GC parameters including desorption temperature, desorption time, cold trap temperature and time, and FID parameters including flow rates of the columns, temperature at the columns etc. were optimized by Civan (2010) for better resolutions of the peaks. FID was very helpful since it reduces the analyzing time especially for the complex mixtures (Civan, 2010). Desorption of the sorbents were made in the thermal desorption unity system which works at 200 ⁰C. The collection mechanism of the GC-FID system is cold trap which is used to get better resolutions for the peaks where the optimized temperature is -15 ⁰C. Compounds lighter than the Hexane go through the Alumina plot capillary column and heavier compounds with a higher molecular weight of Hexane go through the DB1 column with the help of Dean Switch system (Civan, 2010). The special columns supplied by J&W (Palo Alto, CA, USA), which can operate in between 60⁰C and 325⁰C where 300⁰C was chosen as the optimized temperature by Civan (2010).

Nitrogen gas with purity above 99.99% was used as a carrier gas for the GC system. It was supplied by BOS A.Ş. (Ankara, Turkey). Also dry air and hydrogen gases were used for the flame ionization systems ignition. Oxygen and hydrocarbon traps were used to make sure there was no contamination in the gases, although they were supplied with high purity. (Civan, 2010)

3.5.1.1. Sample Tube Desorption Temperature:

Recommended operation values are taken as a base parameter for optimization of the thermal desorption system. Thermal desorption temperature was selected 200⁰C for Tenax filled sample tubes where Civan(2010) calculated the optimum desorption temperature as 200⁰C.

3.5.1.2. Sample Tube Desorption Time:

Tube desorption times effect on analyte recovery. For the complete desorption of the compounds, desorption time should be long enough. The optimum range is identified by Civan (2010) as 5 to 10 minutes and for an effective analyze 5 minutes were chosen.

Flow rate of clod trap desorption rate was used as 50 ml/min and flow rate for the sample tubes was used as 30ml/min while 8/3 split ratio was used.

3.5.1.3. Cold Trap Temperature:

The typical operation temperature is around 300⁰C, but for the recovery of ultra-volatile compounds -10 to -15⁰C temperatures were analyzed by Civan (2010) and operation temperature is selected as -15⁰C.

3.5.1.4. GC Parameters:

Parameters of GC-FID and thermal desorption was optimized before the field study as mentioned in Bursa filed study by Civan (2010). The summary of the results were given in the table 3.3. Since retention time is the main parameter effecting the peak identification on FID detectors the study took a very long time, effort and resources, so for this study another optimization was not made.

Optimized parameters in Civan's study (2010) was used as:

Table 0.3: GC-FID Parameters Used

Thermal Desorption	Dry Purge flow rate	120 ml/min
	Dry Purge Tm-Prepurge Time	1 min- 1 min
	Tube Desorption Temp	200 °C
	Tube Desorption Time	5 min
	Tube Desorption flow rate	50 ml/min
	Cold Trap min temp	-15 °C
	Cold trap max temp	300 °C
	Cold trap desorption time	3 min
	Cold Trap Heat Time	MAX >40 °C/sec
	Cold trap hold	3min
GC-FID	Transfer Line Temp	120 °C
	Column1	DB-1, 60m ÷ 0.25 mm ÷ 1µm
	Column2	HP Al/S,50m÷0.32 mm ÷ 8µm
	Flow Rate for Column1	2.8 ml/min
	Flow Rate for Column2	5.2 ml/min
	Temperature Program	40 °C hold for 5min 5°C/min to 195 °C, hold 10 min
	Valve Position	Off at 13.2 min On at 45.5 min
	FID Parameters for Column1:	
	Temperature	300 °C
	Hydrogen Flow	30 °C
	Air Flow	300 °C
	Make-up (N2) flow	2ml/min
	FID Parameters for Column2:	
	Temperature	300 °C
	Hydrogen Flow	30 °C
Air Flow	300 °C	
Make-up (N2) flow	2ml/min	

3.5.2. Quantification

External standard method is used for quantification. This method is based on plating area or height response against concentrations of the analytes in the standard. Ratio of the concentrations to the area or the height is calculated as the calibration factor where the ratio is constant for a wide range of concentrations. By comparing the unknown with the linear range of the curve, the concentration of the analyte is calculated. (Kuntasal, 2005).

3.5.3. Target Analytes

The method developed in the GC-FID unity thermal desorption system was identified for a wide range of VOCs including aromatics, halogenated compounds, paraffins, olefins that were most widely detected in ambient air. In this study the target analytes were selected as the most common of compounds in ambient air. Table 3.4 gives a list of the targeted analytes with some of their physicochemical properties

Table 0.4: List of the target analytes with some physicochemical properties

Compound Name	Molecular Formula	CAS Number	Molecular Weight	Boiling Point (°C)	Vapor Pressure (Pa at 25°C)
Hexane	C ₆ H ₁₄	110543	86.17	68.95	20200
Methylcyclopentane	C ₆ H ₁₂	96377	84.16	71.80	18300
Benzene	C ₆ H ₆	71432	78.11	80.10	12700
Cyclohexane	C ₆ H ₁₂	110827	84.16	81.00	95
2-Methylhexane	C ₇ H ₁₆	591764	100.21	90.00	8780
3-methylhexane	C ₇ H ₁₆	589344	100.21	92.00	8210
c-3-Heptene	C ₇ H ₁₄	7642106	98.19	95.70	12830
Methylcyclohexane	C ₇ H ₁₄	108872	98.19	100.90	6180
Toluene	C ₇ H ₈	08883	92.13	110.60	3800
Octane	C ₈ H ₁₈	111659	114.23	125.70	1800
Ethylbenzene	C ₈ H ₁₀	100414	106.20	136.20	1270
meta,para-xylene	C ₈ H ₁₀	108383 106423	106.20	138.00	1100
Styrene	C ₈ H ₈	100425	104.15	145.00	667
ortho-xylene	C ₈ H ₁₀	95476	106.20	144.00	1170
Nonane	C ₉ H ₂₀	111842	128.26	150.80	1330
n-propylbenzene	C ₉ H ₁₂	103651	120.20	159.20	450
Camphene	C ₁₀ H ₁₆	79925	136.23	158.90	320
1-decene	C ₁₀ H ₂₀	124180	140.27	172.00	
1,2,4- trimethybenzene	C ₉ H ₁₂	95636	120.20	169.40	270
n-decane	C ₁₀ H ₂₂	124185	142.28	174.00	
Benzylchloride	C ₇ H ₇ Cl	100447	126.59	179.30	
1,2,3-trimethybenzene	C ₉ H ₁₂	526738	120.20	176.10	200
1-undecene	C ₁₁ H ₂₂	28761275	154.20	162.00	
1,2,4- trichlorobenzene	C ₆ H ₃ Cl ₃	120821	181.45	214.40	
Napthalene	C ₁₀ H ₈	91203	128.16	218.00	134

3.5.4. Quality Assurance and Quality Control System (QA/QC)

Control of the instruments performance was done before starting the analyses. Conditioning of the instruments like GC oven, injection point and cold trap were done before the sampling periods in order to eliminate the contamination. Methods performance was evaluated according to method detection limit (MDL), desorption efficiency precision, and recovery. The evaluation of the methods performance was done according to following titles and the results are given in the table 3.5.

3.5.4.1.Method Detection Limit

Making seven replicate measurements of the same compound close to the expected detection limit, computing the standard deviation for the results and multiplying the result with 3.14 (i.e. the Student's t value for 99% confidence) is defined as Method detection limit (MDL) (Kuntasal, 2005). According to this procedure MDL values ranged between 0.04 $\mu\text{g}/\text{m}^3$ and 0.24 $\mu\text{g}/\text{m}^3$ with an average of 0.11 $\mu\text{g}/\text{m}^3$.

3.5.4.2.Desorption Efficiency

Known mass of gas phase analyte was injected to a sample tube in order to determine the desorption efficiency After the injection the tube was analyzed by using GC-FID. The result of the analysis showed the desorption efficiency changed between 84% and 100% with an average of 92%.

3.5.4.3.Precision of Linearity

Six replicate measurements were evaluated for determining the precision level of the system. Also with the correlation coefficient (R^2) the linearity of the calibration curve was determined by drawing the regression line with six points. Relative standard deviation of the system changes between 1.36% and 17.98% with an average of 6.11%.

3.5.4.4.Laboratory and Field Blanks

For QA/QC procedure laboratory and field blanks were kept. The internal standard was injected to the blank samples, and the samples were kept in the refrigerator both in the field and in the laboratory. 13 laboratory and 9 field blanks were kept and analyzed during the sampling periods. The results showed that there is around 1% to 6% contamination in the field, so the contamination levels were deducted from the field study results.

3.5.4.5.Storage Efficiency

In Bursa study made by Civan, the same solvent-free refrigerator was used. In her study she used nine sample tubes to analyze the efficiency of storage with analyzing three of them after two days after the injection and she found the recovery between 98% and 101% with average of 99%. The samples were analyzed after four and nine days and the recovery of those were calculated by Civan (2010), between 90% and 98% with an average of 93% after four days, and calculated between 81% and 92% with an average of 87% after nine days (Civan,2010). The collected samples were analyzed in three days after collection from the field so there is no significant loose of analytes were expected in this study according to Civan's results.

Table 0.5: Methods Performance Parameters

No	Compound Name	MDL ($\mu\text{g}/\text{m}^3$)	Linearity	Precision (%)	Recovery (%)	Contamination (%)
1	Hexane	0,13	0,997	10,77	92,0	2,1
2	Methylcyclopentane	0,11	0,996	4,74	90,0	2,2
3	Benzene	0,09	0,994	4,05	91,0	1,4
4	Cyclohexane	0,13	0,997	7,01	94,0	1,1
5	2-methylhexane	0,13	0,990	12,38	96,0	0,9
6	3-methylhexane	0,09	0,994	5,16	99,0	1,9
7	c-3-heptene	0,13	0,994	3,44	91,0	5,7
8	Methylcyclohexane	0,04	0,994	4,69	97,0	4,4
9	Toluene	0,24	0,993	4,57	91,0	1,4
10	Octane	0,16	0,996	9,74	97,0	3,2
11	Ethylbenzene	0,16	0,993	5,91	99,0	2,2
12	m,p-xylene	0,11	0,992	11,58	91,0	2,1
13	Styrene	0,10	0,998	13,18	95,0	1,7
14	o-xylene	0,17	0,992	8,07	91,0	2,4
15	Nonane	0,04	0,989	11,34	100,0	2,4
16	n-propylbenzene	0,09	0,990	6,16	97,0	1,7
17	Camphene	0,12	0,997	3,85	93,0	3,0
18	1-decene	0,09	0,993	6,77	99,0	1,1
19	1,2,4-trimethylbenzene	0,26	0,992	7,39	100,0	1,9

No	Compound Name	MDL ($\mu\text{g}/\text{m}^3$)	Linearity	Precision (%)	Recovery (%)	Contamination (%)
20	Benzylchloride	0,21	0,993	4,95	91,0	2,2
21	n-decane	0,13	0,990	7,29	91,0	3,6
22	1,2,3-trimethylbenzene	0,13	0,990	7,79	89,0	3,2
23	1-undecane	0,09	0,991	7,99	91,0	2,0
24	1,2,4-trichlorobenzene	0,21	0,998	9,14	93,0	1,0
25	Naphthalene	0,04	0,996	17,98	95,0	1,8

CHAPTER 4

RESULTS AND DISCUSSION

4.1.VOC Data Evaluation

VOC data was collected in two different seasons with two sampling periods in Balıkesir. 103 tubes were deployed in total and 100 of them collected back. However, only 93 of them were analyzed using GC-FID, because of the deformations on the sampling tubes. The instruments were calibrated for fifty five VOCs. However 25 of the compounds were detected in more than 60% of samples. Statistical summary of 25 VOCs at Balıkesir atmosphere are given in Table 4.1. The detailed investigation of seasonal and spatial distribution of the data set will be at the following sections.

Toluene and Benzene is found to be the most abundant volatile organic compounds in the Balıkesir atmosphere. These two compounds were measured in all samples without any exception. In city center road sides Toluene goes up to 85.9 $\mu\text{g}/\text{m}^3$ where it goes down to 1.43 $\mu\text{g}/\text{m}^3$ in the background stations. Benzene can be found in lower concentrations compared to Toluene which changes between 0.29 at some of the rural stations and 14.77 $\mu\text{g}/\text{m}^3$ in the city.

Table 0.1: Statistical Summary of Most Abundant Species

Compound Name	Winter Period			Summer Period		
	Mean ($\mu\text{g}/\text{m}^3$)	Median ($\mu\text{g}/\text{m}^3$)	Range ($\mu\text{g}/\text{m}^3$)	Mean ($\mu\text{g}/\text{m}^3$)	Median ($\mu\text{g}/\text{m}^3$)	Range ($\mu\text{g}/\text{m}^3$)
n-hexane	1.64	0.83	0.21 - 14.44	0.19	0.14	0.05 - 0.95
Methylcyclopentane	1.11	0.69	0.23 - 3.68	0.39	0.28	0.05 - 1.62
Benzene	4.50	2.80	1.72 - 14.77	0.79	0.75	0.29 - 1.67
Cyclohexane	1.57	1.40	0.48 - 3.57	0.41	0.27	0.13 - 1.25
2-Methylhexane	2.12	1.92	1.09 - 4.89	0.47	0.36	0.16 - 1.75
3-Methylhexane	1.12	0.92	0.30 - 2.57	0.30	0.29	0.04 - 0.99
c-3-Heptene	0.22	0.18	0.06 - 0.64	0.10	0.08	0.05 - 0.25
Methylcyclohexane	0.18	0.15	0.07 - 0.45	0.12	0.11	0.06 - 0.25
Toluene	15.77	6.53	2.96 - 85.90	6.00	3.94	1.43 - 40.01
Octane	0.94	0.69	0.21 - 4.70	0.61	0.54	0.09 - 1.77
Ethylbenzene	1.32	0.73	0.26 - 8.18	1.26	0.27	0.05 - 16.74
m,p-xylene	5.05	1.64	0.66 - 37.94	2.55	1.56	0.08 - 13.77
Styrene	2.48	1.82	0.45 - 8.40	1.49	0.88	0.17 - 5.34
o-xylene	0.89	0.39	0.15 - 3.33	0.57	0.35	0.08 - 1.86
Nonane	0.97	0.70	0.27 - 3.12	0.63	0.45	0.05 - 3.74
n-propylbenzene	1.25	0.50	0.16 - 7.38	2.46	1.82	0.40 - 13.11
Camphene	3.66	3.03	0.10 - 13.95	3.18	2.29	0.08 - 17.14
1-decene	2.74	2.62	0.46 - 7.80	2.12	1.91	0.06 - 9.82

Compound Name	Winter Period			Summer Period		
	Mean ($\mu\text{g}/\text{m}^3$)	Median ($\mu\text{g}/\text{m}^3$)	Range ($\mu\text{g}/\text{m}^3$)	Mean ($\mu\text{g}/\text{m}^3$)	Median ($\mu\text{g}/\text{m}^3$)	Range ($\mu\text{g}/\text{m}^3$)
1,2,4- trimethylbenzene	0.57	0.50	0.21 – 1.45	1.81	0.86	0.19 – 14.45
n-decane	0.43	0.29	0.07 – 1.53	0.21	0.15	0.05 – 1.48
benzylchloride	1.33	1.01	0.31 – 11.61	0.32	0.19	0.06 – 1.45
1,2,3-trimethylbenzene	0.56	0.38	0.18 – 2.43	0.20	0.17	0.06 – 0.57
1-undecene	3.65	2.77	1.10 – 10.61	8.18	3.65	0.21 – 74.87
1,2,4- trichlorobenzene	11.33	7.08	1.35 – 74.05	16.20	10.48	0.72 – 88.01
naphthalene	1.66	1.04	0.39 – 6.42	0.45	0.42	0.06 – 1.09

4.2. Comparison of Results with Literature

VOC concentrations in different parts of the world measured in time with different studies. In most of the studies various characteristics of locations were taken into consideration such as urbanization, industry or traffic. Effect of many parameters should be also considered in the comparison since analytical protocol including sampling duration, sampler height, sampling technique and particularly sampling location have effect on ambient concentrations. Since VOC concentrations are sensitive to all these parameters, comparison between VOC levels measured in different studies is not straightforward.

In figure 4.1. toluene concentrations in different parts of Europe is given just to put concentrations measured in this study into a perspective. In most of the Europe, the toluene concentrations change between $3 \mu\text{g}/\text{m}^3$ and $9 \mu\text{g}/\text{m}^3$ in annual observations. In Vlachokostas et al. (2012) study strong correlation between toluene and Benzene and CO was found. The red and green bars in the figure 4.1 shows the estimated toluene levels from benzene and CO measurements respectively which was given with $\text{toluene}=\text{f}(\text{benzene})$ and $\text{toluene}=\text{f}(\text{CO})$ equations.

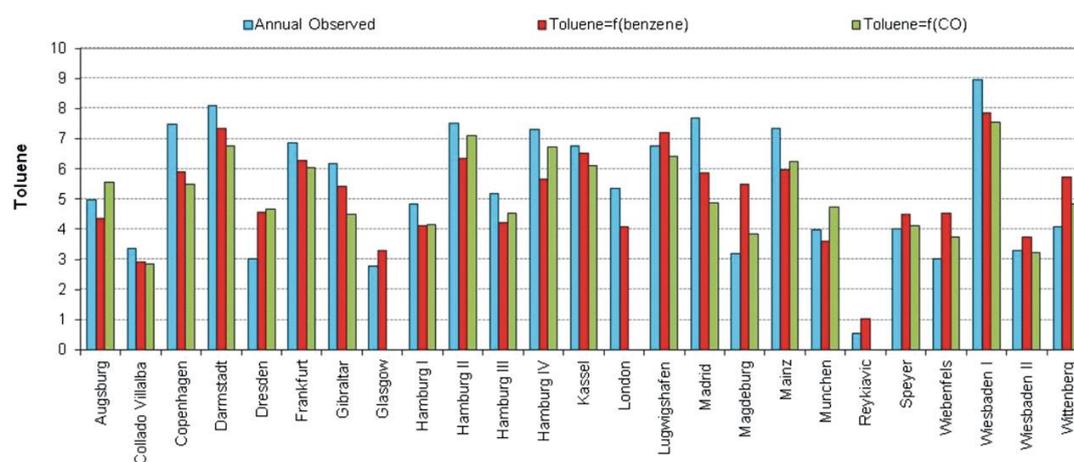


Figure 0.1: Toluene concentrations measured in different cities in Europe. (Vlachokostas et al., 2012)

Ambient VOC concentrations were much higher in early 1990s since there were no restrictions in USA and Europe like USEPA, 1999 or EEA, 2003. Also winter concentrations are higher than the summer concentrations in most of the studies like Ankara, (Kuntasal, 2005), Kocaeli (Pekey, 2008) and Bursa (Civan, 2010). Therefore it is important to know the year and season of the data since they both effect the comparison of the data with the literature.

Concentrations of BTEX compounds measured in this study were compared with corresponding data generated elsewhere in Turkey and Europe in Table 4.2. BTEX compounds, rather than VOCs were included in the comparison, because it is easier to

find BTEX data in literature as all VOCs are not frequently measured. The sites used in the comparison are selected based on their similarities with this study. However, it should be noted that it is almost impossible to find studies which are identical to each other, and some of the differences observed can be attributed to differences in analytical methodology or siting of sampling points. Consequently, in the following paragraphs studies chosen for comparison are discussed explaining the similarities they have with the study.

Civan, (2010) measured VOC levels in Bursa atmosphere in four periods at approximately 65 sampling sites, which includes sites at industrial areas, urban residential areas, urban traffic sites and rural locations. Samples were collected using passive samples, which are identical with the samplers used in this study and analyzed by GC-FID. Active sampling methodology also used in a separate study in Bursa, but those measurements were not used in Table 4.2. Since Bursa passive sampling study is very similar to the Balıkesir study both in sampling and analytical procedures, data generated in these two studies are comparable and represent the differences in emissions demography in the two geographies.

Parra et al. (2009) measured VOC levels in a medium sized city Navarre, Spain. In the study 40 sampling points were used in one year period from June 2006 to June 2007. The analyze technique was same with this study and Civan (2010). Thermal desorption passive sampling by GC-MS technique was used to determine spatial distribution of VOCs. Although the city is bigger than Balıkesir, the sampling area has mostly the same characteristics.

Roukos et al. (2009) measured VOC levels in Dunkerque, France. Two sampling campaigns were conducted, during summer and winter seasons, using 36 sampling points. The main BTEX levels were represented in rural, urban and industrial areas. High VOC concentrations were found in industrial areas. However, concentrations of VOCs at urban and roadside sites were lower and similar to each other.

Pilidisa at al. (2005) measured benzene and toluene concentrations at nine sampling locations in four passive sampling campaigns at Ioannina, Greece. Although the city is small in size and there is no significant industrial activity, fairly high concentrations of benzene and toluene were measured, which is attributed to close proximity of sampling points to traffic activity in the city.

Pekey et al. (2010) studied on İzmit Bay VOC levels. The city is highly industrialized and includes one of the busiest highway in Turkey. Sampling and analytical methods were identical to the methodologies used in this study. The sampling was conducted at 50 points mostly chosen at urban and industrialized areas.

Under the different circumstances of the cities BTEX concentrations are lower compared to European and Turkish cities. However, the differences between the city industries and traffic density should be analyzed to compare the results correctly. Furthermore the

differences in the sampling techniques and the meteorology should also be considered when comparing the results.

Table 0.2: Literature comparison of the average BTEX concentrations ($\mu\text{g}/\text{m}^3$)

	This Study	Literature				
	Balıkesir	Bursa, Turkey ¹	Dunkerque, France ²	Navarre, Spain ³	Ioannina, Greece ⁴	Kocaeli, Turkey ⁵
Benzene	2.64	5.2	2.84	1.90	12.3	2.26
Toluene	10.90	24.3	13.26	6.02	41.2	35.51
Ethylbenzene	1.30	3.5	2.15	1.43		9.72
m&p-Xylene	3.80	9.9	3.38	4.60		36.87
o-Xylene	0.73	1.4	2.63	1.73		12.46

¹Civan (2010), ²Roukos et al. (2009), ³Parra et al. (2009), ⁴Pilidisa et al. (2005),

⁵Pekey et al. (2010)

BTEX concentrations measured in this study are comparable to the corresponding concentrations measured in European cities, except for Pilidisa et al (2005) study in Greece. However BTEX concentrations measured in two Turkish cities, namely Bursa and Kocaeli are higher than BTEX concentrations measured in this work. As pointed out before, average VOC concentrations in urban areas depends on a number of factors, like locations of sampling points. However, it should be noted that VOC data generated in different cities are more comparable when average concentrations are calculated from passive sampling campaigns, because those average values are probably generated from VOC data measured at large number of locations in the city. Since average BTEX concentrations that are given in Table 4.2.2 are all generated from passive sampling campaigns and include data from 9 – 50 different locations in those cities, data in the table are representative for cities and can be compared.

Data in the table demonstrate that BTEX concentrations measured at the Balıkesir are comparable to concentrations reported for cities with comparable sizes in Europe. Higher BTEX levels at Bursa and Kocaeli is probably due to heavier traffic density, larger population and more intensive industrial activity in these two cities compared to Balıkesir.

One point this comparison revealed is that passive sampling in many points around cities is a good way of comparing pollution status in those settlement areas, because passive sampling appears to be the only way of generating data that is representative for an area. Temporal representativeness of data generated by passive sampling is a different issue.

The results are also compared with the Turkish, U.S. EPA and European regulations. All of these regulations limit the VOC concentrations at the release point or in indoor air, so the comparison may not be effective. However the concentrations we measured has a great difference with the regulation limits, which gives an idea about the situation. The

comparison is given in the table 4.3. In the comparison the winter mean values were used since higher concentrations were measured for most of the compounds in winter.

Table 0.3: Results comparison with the regulations.

Compound Name	Mean ($\mu\text{g}/\text{m}^3$)	Limit Values ($\mu\text{g}/\text{m}^3$)		
		Turkish Regulations ¹	U.S. EPA ²	EC Directive ³
n-hexane	1.64		3500	700
Methylcyclopentane	1.11			
Benzene	4.50	75	30	
Cyclohexane	1.57			8000
2-Methylhexane	2.12			8000
3-Methylhexane	1.12			8000
c-3-Heptene	0.22			
Methylcyclohexane	0.18			8000
Toluene	15.77	75	150	1000
Octane	0.94			
Ethylbenzene	1.32	75	1000	1000
m,p-xylene	5.05	75	350	1000
Styrene	2.48		450	70
o-xylene	0.89	75	350	1000
Nonane	0.97			10000
n-propylbenzene	1.25	5		1000
Camphene	3.66			1000
1-decene	2.74			2000
1,2,4- trimethybenzene	0.57	5		1000
n-decane	0.43			2000
benzylchloride	1.33			
1,2,3-trimethybenzene	0.56	5		1000
1-undecene	3.65			10000
1,2,4- trichlorobenzene	11.33		300	
napthalene	1.66		4.5	500

¹Industrious Air Pollution Control Regulation, ²California Air Resources Board Regulations, ³European Council Directive 1999/13/EC

The comparison shows that there is no exceeding value for the Balikesir results. Although the limitations are for indoor air quality or for the release point measurements, the values are at least 4 times higher than the measured concentrations.

4.3. Seasonal Variations of VOCs

Passive sampling methodology is not an ideal way to identify the seasonal variations of pollutants since the sampling tubes are left in the field for 7 to 10 days once in every season where representatives of this time are questionable. Increasing the frequency of the sampling periods in a season can be a better way to take the averages of the season and assess the seasonal variations. On the other hand, passive sampling gives high spatial resolution of the data which helps to determine the city average better. In most studies seasonal variations are assessed by a few fixed stations in a city which is not enough to take the average of the city general compared to 40 to 50 sampling points of passive sampling. Averages of the measurements based on large number of stations are more representative for a city, as also pointed out in the previous section.

In Balıkesir two different sampling periods were performed as discussed before. The seasons were divided into two as summer and winter, since one of the period was in March and the other one was in August. In Turkey 15th of April to 15th of October is considered as non-heating season and 15th of October to 15th of April is considered as heating season. This rule is accepted after the air pollution crisis in Ankara in 90s. Ankara municipality established the rule as heating units should not be used in non-heating seasons. It is accepted as a general rule and heating units continued to be operated between April and October, even after air pollutions ceased to be a serious problem. Seasons in this study was also based on this rule. The period between 15th of April to 15th of October was considered as “summer” (or non-heating period) and the period between 15th of October to 15th of April was considered as “winter” (or heating period) season.

Concentrations measured in summer and winter campaigns were used to determine the seasonal variations of VOCs in Balıkesir. Although median is a better representation for a log-normally distributed data population Arithmetic average concentrations of the data were used in the table, since in most of the studies the results are given in mean concentrations. The median values are also given in the table although they were not discussed thorough.

Winter concentrations are higher than the summer concentrations of VOCs in most of the studies. This study is also consistent with the other work. Concentrations of 25 measured VOCs in Balıkesir atmosphere are given in the table 4.4. The higher winter concentrations can be explained by several reasons. One of the reasons may be higher emissions in winter (Na et al, 2005). Although some of the VOCs can be emitted from stationary sources, such as power plants and industrial activities, which can have higher emissions in winter due to the higher demand for electricity in winter for heating purposes. The main source is heavy and light-duty traffic for VOCs. In metropolitan cities traffic emissions can be lower in summer due to migration of population to coastal areas in summer months. In Ankara, for example, number of vehicles on the roads decrease by 30% in June, July and August, because of that reason (Kuntasal et al., 2013). However for Balıkesir study no traffic counts were performed and since it is a coastal city traffic emissions may increase in the summer months. Therefore it will be a wild guess to

try to explain the seasonal variations in the Balikesir atmosphere with traffic. Another reason can be more extensive photochemical destruction of VOCs in summers (Kuntasal, 2005). However, it should be noted that some of the VOCs, particularly the ones that are intermediates in oxidation mechanism are also produced faster in summer. The most likely source for observed winter high concentrations is the seasonal variation in meteorology, particularly the mixing height. The mixing height depicts a well-defined seasonal variations, with approximately a factor of two-to-three higher values in summer (Civan, 2010). Since mixing height defines the volume in which pollutants are dispersed, higher mixing height results in a larger volume, which in turn results in dilution of VOCs and lower concentrations in summer.

But if it is accepted that the mixing height is the only factor for the summer winter difference, it would not be possible to explain the differences between the summer-winter ratios of most VOC. These differences indicate that there are factors other than variations and mixing height, which affects seasonal variations in VOC concentrations.

Table 0.4: Seasonal differences of 25 measured VOCs in Balikesir atmosphere

Compound Name	Winter Period		Summer Period		Winter/Summer Ratio
	Mean ($\mu\text{g}/\text{m}^3$)	Median ($\mu\text{g}/\text{m}^3$)	Mean ($\mu\text{g}/\text{m}^3$)	Median ($\mu\text{g}/\text{m}^3$)	
n-hexane	1.64±1.56	0.83±1.56	0.19±0.16	0.14±0.16	8,63
Methylcyclopentane	1.11±0.87	0.69±0.87	0.39±0.27	0.28±0.27	2,85
Benzene	4.50±3.25	2.80±3.25	0.79±0.29	0.75±0.29	5,70
Cyclohexane	1.57±0.97	1.40±0.97	0.41±0.25	0.27±0.25	3,83
2-Methylhexane	2.12±1.25	1.92±1.25	0.47±0.36	0.36±0.36	4,51
3-Methylhexane	1.12±0.66	0.92±0.66	0.30±0.15	0.29±0.15	3,73
c-3-Heptene	0.22±0.13	0.18±0.13	0.10±0.06	0.08±0.06	2,20
Methylcyclohexane	0.18±0.11	0.15±0.11	0.12±0.07	0.11±0.07	1,50
Toluene	15.77±14.58	6.53±14.58	6.00±7.18	3.94±7.18	2,63
Octane	0.94±0.70	0.69±0.70	0.61±0.41	0.54±0.41	1,54
ethylbenzene	1.32±1.45	0.73±1.45	1.26±1.69	0.27±1.69	1,05
m,p-xylene	5.05±4.55	1.64±4.55	2.55±2.92	1.56±2.92	1,98
Styrne	2.48±4.06	1.82±4.06	1.49±1.60	0.88±1.60	1,66
o-xylene	0.89±2.62	0.39±2.62	0.57±0.43	0.35±0.43	1,56
Nonane	0.97±0.66	0.70±0.66	0.63±0.67	0.45±0.67	1,54
n-propylbenzene	1.25±1.15	0.50±1.15	2.46±2.92	1.82±2.92	0,51
Camphene	3.66±2.16	3.03±2.16	3.18±2.66	2.29±2.66	1,15
1-decene	2.74±1.94	2.62±1.94	2.12±1.90	1.91±1.90	1,29

Compound Name	Winter Period		Summer Period		Winter/Summer Ratio
	Mean ($\mu\text{g}/\text{m}^3$)	Median ($\mu\text{g}/\text{m}^3$)	Mean ($\mu\text{g}/\text{m}^3$)	Median ($\mu\text{g}/\text{m}^3$)	
1,2,4- trimethylbenzene	0.57±0.38	0.50±0.38	1.81±2.14	0.86±2.14	0,31
n-decane	0.43±0.24	0.29±0.24	0.21±0.16	0.15±0.16	2,05
benzylchloride	1.33±1.70	1.01±1.70	0.32±0.30	0.19±0.30	4,16
1,2,3-trimethylbenzene	0.56±0.44	0.38±0.44	0.20±0.14	0.17±0.14	2,80
1-undecene	3.65±2.67	2.77±2.67	8.18±6.71	3.65±6.71	0,45
1,2,4- trichlorobenzene	11.33±12.56	7.08±12.56	16.20±13.83	10.48±13.83	0,70
naphthalene	1.66±1.36	1.04±1.36	0.45±0.24	0.42±0.24	3,69

According to winter to summer ratio the VOCs separated to two different groups. First group includes VOCs, which have winter to summer ratio < 1.0 . These are the VOCs with higher concentrations in summer. The second group includes VOCs with winter-to-summer ratios > 1.0 , which are the VOCs that have higher concentrations in winter.

Most of the 25 VOCs measured in this study are in the second group. The only VOCs that have higher concentrations in summer are; n-propylbenzene, 1,2,4- trimethylbenzene, 1-undecene, 1,2,4- trichlorobenzene.

The other group, which have winter-to-summer ratios > 1.0 includes n-hexane, Benzene, 2-Methylhexane, benzylchloride, Cyclohexane, 3-Methylhexane, naphthalene, Methylcyclopentane, 1,2,3-trimethylbenzene, Toluene, ethylbenzene, c-3-Heptene, n-decane, m,p-xylene, Styrene, o-xylene, Octane, Nonane, Methylcyclohexane, 1-decane and camphene.

As pointed out before, compounds which have the same emission rate both in summer and winter seasons are expected to have higher winter concentrations, due to shallower mixing height in winter. Compounds with higher concentrations in summer are expected to have stronger source contributions in summer. These higher concentrations may be because of the higher emissions of the compounds which is also present in winters or may be because of operation of additional sources.

It is well documented that in urban atmosphere, traffic is the most important VOC source. Although traffic counts were not performed in this study, other studies performed in different Turkish cities showed that traffic emissions, particularly by light duty vehicles, decrease in summer. However, this pattern may not be true for the city of Balıkesir since it is a coastal city. Also most of the traffic from İstanbul to coastal areas goes around the city where we had eight traffic VOC measuring stations. This could be an explanation for the higher summer concentrations of some of the heavy hydrocarbons. The traffic effects will be discussed later.

In the industrial perspective, industrial operations do not change significantly with seasons, VOCs that are emitted from industrial operations are expected to have higher concentrations in winter, thus should take place in the second group.

In addition to the traffic, one of the mechanisms that have stronger emissions in summer season is the solvent evaporation. Solvents used in paints, inks etc. are known sources of VOCs. Since evaporation is enhanced during hot summer months, the compounds that are extensively used as solvents in paints inks etc. can have higher concentrations in summer, as in the first group of VOCs pointed above.

4.4.Spatial Distribution of VOCs

Spatial distribution of VOC concentrations in the study area is very convenient first step to identify sources contributing to measured VOC levels. Passive sampling approach is an ideal way for determining the spatial distribution, since it is possible to deploy many tubes to the sampling area. For this study, concentration data from fifty sampling locations were used for determining the spatial distributions of measured VOCs. Distribution maps were generated only for the compounds, which were detected in most of the sampling points. There were eleven such including benzene, cyclohexane, 2-Methylhexane, Toluene, Ethylbenzene, m,p-xylene, Styrene, o-xylene, Nonane, 1-decene, 1,2,4-trichlorobenzene. Data were entered to the MapInfo Professional 10.0 GIS software for Winter and Summer campaigns separately and pollutant maps were generated by interpolation.

As a first step in source apportionment median concentrations of VOCs in different microenvironments are compared. In the design of the experimental part of this study, locations of sampling points were tried to be carefully selected, to be in one of the three microenvironments. Consequently each station is a member of the residential, traffic and background microenvironments. However in some points it is very hard to separate the residential and traffic stations since there is always traffic in the residential areas. Median and mean concentrations of measured VOCs in these groups of stations are given in Table 4.5.

Table 0.5: Median and mean concentrations of measured VOCs at residential, traffic impacted and background stations.

Compound Name	Residential ($\mu\text{g}/\text{m}^3$)		Traffic ($\mu\text{g}/\text{m}^3$)		Background ($\mu\text{g}/\text{m}^3$)	
	Mean	Median	Mean	Median	Mean	Median
n-hexane	1.63	0.85	0.87	0.59	0.72	0.42
Methylcyclopentane	1.14	1.09	0.68	0.54	0.61	0.34
Benzene	4.98	4.64	2.11	1.96	1.82	1.52
Cyclohexane	1.11	1.01	0.97	0.89	0.89	0.79
2-Methylhexane	1.95	1.73	1.15	1.09	0.97	0.80
3-methylhexane	1.01	0.94	0.58	0.54	0.60	0.53
c-3-heptene	0.24	0.21	0.14	0.13	0.13	0.10
Methylcyclohexane	0.20	0.18	0.13	0.12	0.12	0.10
Toluene	17.1	17.8	13.9	6.51	6.20	3.37
Octane	1.08	0.99	0.79	0.61	0.65	0.48
Ethylbenzene	1.56	1.28	0.99	0.52	0.67	0.25
m,p-xylene	6.27	5.22	3.92	2.55	2.43	0.84
Styrne	2.35	1.95	1.53	0.93	1.66	1.03
o-xylene	1.22	1.09	0.69	0.34	0.37	0.23
nonane	0.96	0.96	1.03	0.99	0.63	0.50
n-propylbenzene	1.99	1.69	2.27	1.13	1.74	1.08
Camphene	4.04	3.09	2.33	2.20	2.67	2.11
1-decene	2.40	2.13	2.13	1.95	1.98	1.75

Compound Name	Residential ($\mu\text{g}/\text{m}^3$)		Traffic ($\mu\text{g}/\text{m}^3$)		Background ($\mu\text{g}/\text{m}^3$)	
	Mean	Median	Mean	Median	Mean	Median
1,2,4- trimethylbenzene	0.70	0.63	1.22	0.82	1.01	0.75
n-decane	0.45	0.39	0.19	0.18	0.19	0.16
benzylchloride	1.14	1.15	0.61	0.51	0.76	0.37
1,2,3-trimethylbenzene	0.45	0.42	0.21	0.20	0.31	0.23
1-undecene	3.87	2.94	3.15	1.84	2.52	1.81
1,2,4- trichlorobenzene	10.7	6.54	19.1	7.55	6.44	6.41
naphthalene	1.57	1.35	0.71	0.64	0.78	0.66

Sampling stations are densely located in the city of Balıkesir and around İkiçetepeler Dam Lake. Stations that were classified as “residential” are the stations within the city and that are not in the immediate vicinity of major roads. There were 13 residential stations used in the study. “Traffic” stations are the stations that are in the immediate vicinity of the roads in the city. Traffic stations also include stations around the Izmir highway outside the city. There were 13 traffic stations and 5 of them were within the city and 8 were in the close proximity of the Izmir highway. “Background” stations included 23 stations that were located outside the city. Eight of these stations were carefully situated around İkiçetepeler Dam lake, because one of the objectives of this study was to evaluate if deposition of VOCs from traffic on the Izmir – Istanbul highway is important for human health. Because, the lake provides tap-water for the city. Remaining 15 background stations were located between the city and the lake.

VOC concentrations shown in the table demonstrate an interesting pattern. Concentrations of light hydrocarbons, which includes; n-hexane, methylcyclopentane, benzene, cyclohexane, 2-methylhexane, 3-methylhexane, methylcyclohexane, toluene, octane, ethylbenzene, m,p-xylene, styrene and o-xylene have systematically the highest concentrations in residential stations. Traffic impacted stations have the second highest concentrations and lowest concentrations were observed in the Background stations. This pattern is consistently observed in all of these compounds. A different pattern is observed in concentrations of heavier hydrocarbons. Heavy hydrocarbon group included Nonane, n-propylbenzene, Camphene, 1-decene, 1,2,4- trimethylbenzene, n-decane, benzylchloride, 1,2,3-trimethylbenzene, 1-undecene, 1,2,4- trichlorobenzene and naphthalene. These compounds have consistently higher concentrations at traffic impacted stations.

These two different patterns observed for light and heavy hydrocarbons are due to their different sources in the study area. It is well documented that light hydrocarbons are associated with gasoline engine emissions (light duty vehicles), whereas heavy hydrocarbons are associated with diesel emissions from heavy-duty vehicles. Many of the “traffic” stations used in this study are located around Izmir – Istanbul highway, which has a very dense truck activity. Because of that, heavy HC’s have higher concentrations in those stations.

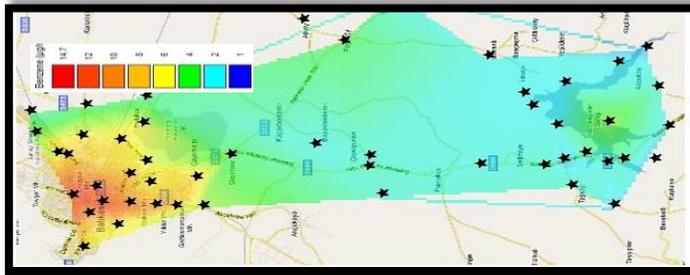
Concentrations of light hydrocarbons are high in residential stations, because most of the residential stations are located within the city, because light duty vehicle emissions dominate VOC concentrations in the city. Although our initial objective was to differentiate between traffic and non-traffic VOC sources, we were not very successful, because, no matter where you put the sampler, it is close to a road in the city. Because of this, all stations in the city are traffic impacted stations. Since the traffic that impacts stations in the city is largely gasoline vehicles, concentrations of concentrations of light HCs are higher in city stations (city-traffic + city residential stations).

Spatial distributions of the concentrations of pollutants, including VOCs can provide valuable information on their sources, because their concentrations are expected to be

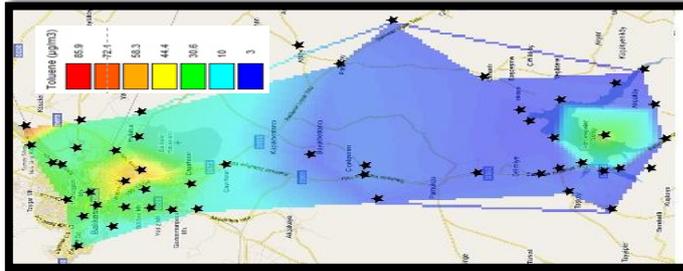
high in the areas close to sources. In this study, pollution maps were prepared for individual VOCs by interpolating spatially distributed passive VOC data. Pollution maps generated using winter and summer BTEX concentrations are given in Figure 4.2. Maps for other VOCs are not included in the figure, because they are fairly similar to BTEX figures.

In the generation of the figures thematic map option of MapInfo Professional 10.0 was used. The interpolation was done with the Grid TIN interpolator where zero values were ignored. The legends were divided into equal values.

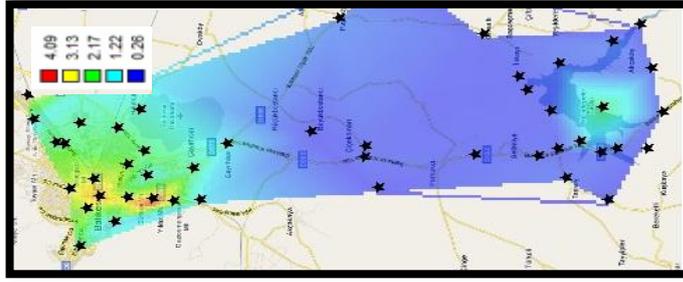
Benzene winter



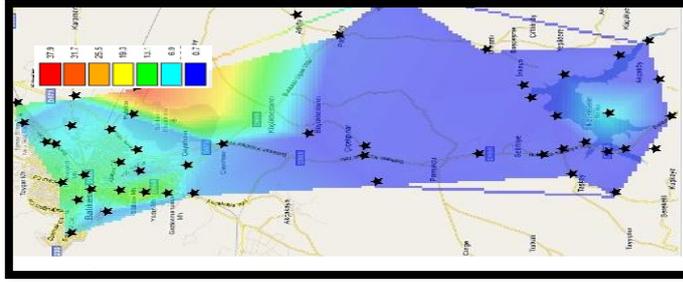
Toluene winter



Ethylbenzene winter



M-p, xylene winter



O-xylene winter

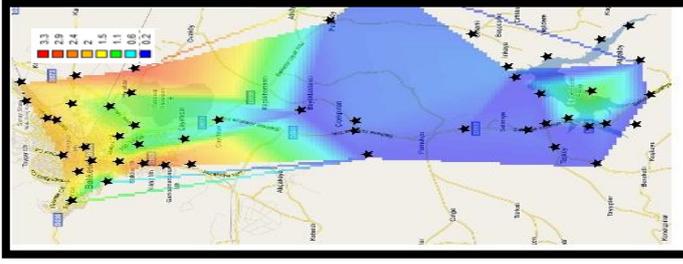


Figure 0.2: Spatial distribution of BTEX compounds in and around the city of Balıkesir

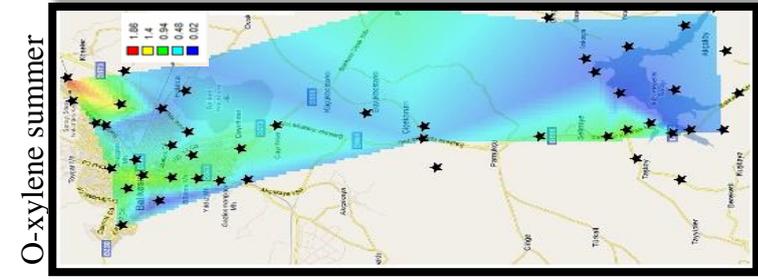
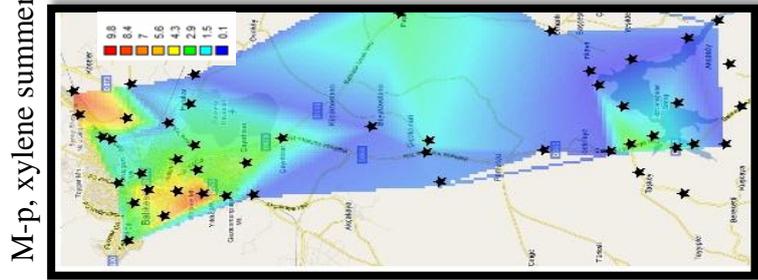
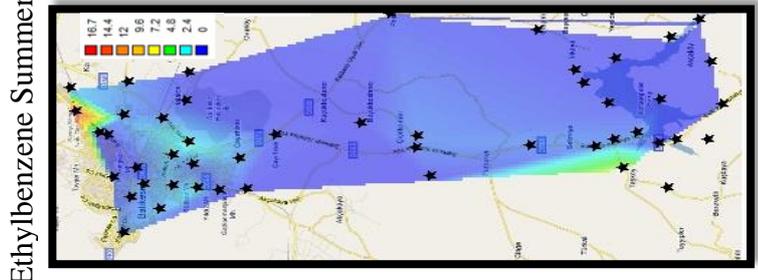
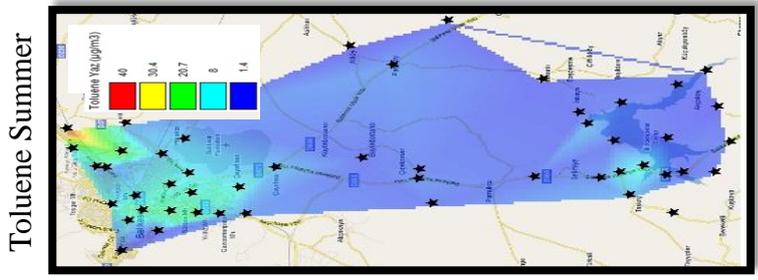
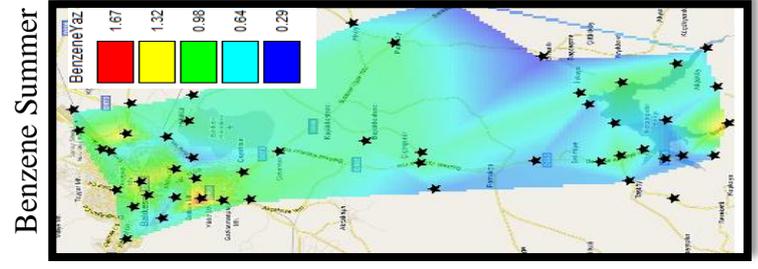


Figure 4.2. Spatial distribution of BTEX compounds in and around the city of Balıkesir

Distributions of BTEX compounds in the study area have some common features worth noting. The most obvious feature that is common in all distribution maps is higher concentrations observed in the city. All VOCs measured in this study have higher concentrations in the passive stations located within the city. This is obviously due to heavy traffic activity within the city. As pointed in previous section, our initial attempt was to differentiate sources affecting stations in the residential areas of the city and sources affecting stations close to the roads. We were not able to differentiate these two source groups, because there is no location in the city that is free from the impact of traffic emissions. Consequently, high concentrations of BTEX and other VOCs in the city are due to dense traffic in the city.

Another interesting point in the figure is relatively higher concentrations of BTEX compounds at the stations around İkizcetepeler Lake. This is important because one of the important motivation for this study was to evaluate if deposition of VOCs emitted from traffic activity on the İzmir – Istanbul highway is significant. High concentrations observed around the lake implies that some extra dry deposition of BTEX compounds along with some heavy hydrocarbons occur due to traffic across the lake.

Crude estimation of BTEX and some other heavy hydrocarbons fluxes and annual loads to the lake are given in Table 4.6. Average concentrations of the compounds in two background station groups were used to calculate fluxes and loads of VOCs to the lake. One group consisted of passive sampling stations that are outside the city and far from roads and lake. The second group included stations located around the İkizcetepeler Lake. Deposition fluxes were calculated using the following relation:

$$F = C \times v_d$$

Where F is the flux (in $\mu\text{g m}^{-2} \text{sec}^{-1}$), C is the VOC concentration in $\mu\text{g m}^{-3}$ and v_d is the dry deposition velocity. In this work 0.3 cm sec^{-1} was used as v_d . (Waite et al. 2002)

Deposition calculations were performed both for the stations around the lake and background stations not too close to the lake. The difference was assumed to be due to traffic activity across the lake. Annual loads to the lake (in kg yr^{-1}) were calculated assuming the surface area of the lake is 9.6 km^2 .

Table 0.6: Dry deposition of BTEX and some heavy hydrocarbons to Ikizcetepeler Lake

	Background		Lake		Excess deposition to lake %
	Flux $\mu\text{g m}^{-2} \text{s}^{-1}$	Load kg/yr	Flux $\mu\text{g m}^{-2} \text{s}^{-1}$	Load kg/yr	
Benzene	4.0×10^{-3}	128	6.0×10^{-3}	189	32.3
Toluene	1.15×10^{-2}	367	1.20×10^{-2}	375	1.9
Ethylbenzene	9.8×10^{-4}	30.6	1.3×10^{-3}	40.2	23.2
m,p-xylene	2.7×10^{-3}	87.0	3.8×10^{-3}	120	27.2
o-xylene	5.3×10^{-4}	16.8	8.7×10^{-4}	27.0	38.3
1-decane	2.0×10^{-3}	64.5	2.7×10^{-3}	88.1	26.7
1-undecene	2.4×10^{-3}	79.2	3.5×10^{-3}	115	30.4
1,2,4-trichlorobenzene	9.0×10^{-3}	288	1.3×10^{-2}	412	30.2

Results of this calculation demonstrate that emissions from traffic on the Izmir – Istanbul highway causes approximately 30% excess deposition of benzene onto the lake. Contribution of highway traffic on deposition of other VOCs varied between 1.9 % for toluene and 38% for o-xylene. Some of the heavy hydrocarbons were also analyzed to see the effects of diesel engine emissions on the lake. 1-decane, 1-undecene, and 1,2,4-trichlorobenzene were chosen because they had the highest differences between the background and around lake concentrations. These figures indicate that, there is an excess dry deposition of VOCs to the lake due to traffic emissions on the road. Implications of this deposition flux for the water supply to the Balıkesir has to be investigated.

With the same equation, the excess BTEX concentrations in the urban area tried to be estimated assuming the area of the city is 30 km². In this case the residential concentrations of the BTEX were taken into considerations which were compared with the background concentrations. Flux and annual load for BTEX compounds were calculated and excess deposition for the city is estimated as can be seen in the table 4.7.

Table 0.7: Dry deposition of BTEX in the urban area

	Background		Residential		Excess deposition to residential area %
	Flux $\mu\text{g m}^{-2} \text{s}^{-1}$	Load kg/yr	Flux $\mu\text{g m}^{-2} \text{s}^{-1}$	Load kg/yr	
Benzene	5.4×10^{-3}	541	1.3×10^{-2}	1422	62.5
Toluene	1.2×10^{-2}	1162	3.4×10^{-2}	3327	65.1
Ethylbenzene	1.1×10^{-3}	120	2.5×10^{-3}	268	56.2
m,p-xylene	3.5×10^{-3}	301	8.9×10^{-3}	779	61.2
o-xylene	7.7×10^{-4}	75.9	2.6×10^{-3}	251	69.7

In the urban area the excess deposition of the BTEX changes between 56% and 70%. This was an expected result since the residential concentrations are much higher than the background concentrations. There are lots of studies about the health effects of VOCs, so the data should be interpreted with those studies to see the effects on population in Balıkesir. Since the flux and the loads depend on the selected deposition velocity and on the estimated ground area which have the same value for each compound, the excess deposition percentages can also be estimated by only using the concentrations. In the table 4.8 the excess traffic and residential loadings percentages are shown.

Table 0.8: Excess residential and traffic loading percentages.

Compound Name	Excess Residential Loading (%)	Excess Traffic Loading (%)
n-hexane	56	17
Methylcyclopentane	46	10
Benzene	63	14
Cyclohexane	20	8
2-Methylhexane	50	16
3-methylhexane	41	
c-3-heptene	46	7
Methylcyclohexane	40	8
Toluene	64	55
Octane	40	18
Ethylbenzene	57	32
m,p-xylene	61	38
Styrne	29	
o-xylene	70	46
nonane	34	39
n-propylbenzene	13	23
Camphene	34	
1-decene	18	7
1,2,4- trimethybenzene		17
n-decane	58	
benzylchloride	33	
1,2,3-trimethybenzene	31	
1-undecene	35	20
1,2,4- trichlorobenzene	40	66
napthalene	50	

O-xylene has the highest excess loading percentage with 70% for the residential area which is consistent with the excess deposition estimated from the calculated flux. The lowest percentage for the residential area is 1,2,4- trimethybenzene where there is no excess load. For the traffic loadings, there are 7 compounds with no excess loading where

the highest loading is estimated for 1,2,4- trichlorobenzene with 66%. BTEX compounds and 1,2,4- trichlorobenzene have the highest excess loadings in overall.

4.5. Factor Analysis

Factor analysis is a multivariate statistical tool, which is widely used in source apportionment studies. The objective in FA is to explain the variance of the system with minimum number of reduced variables, which are called “Factors”. In urban FA studies these reduced variables or factors generally represent sources affecting concentrations of measured parameters, which are VOCs in this study. Thus parameters (VOCs) associated with these factors are thought to be the VOCs emitted from that particular source.

Although its application of FA (or multivariate tools in general) to spatially distributed data is limited, impressive results were observed in some studies like Atgin et al. (2000), where FA was applied to sediment samples collected at approximately 100 points in İzmir Bay, Civan (2010), where FA was used to apportion sources affecting VOC concentrations measured at 50 locations, by passive sampling at Bursa and Pekey et al. (2011), where sources affecting spatially distributed VOC concentrations at Kocaeli. Looking at these studies, in passive sampling of VOCs, Factor Analysis (FA) technique decided to be used although it is rare in this kind of studies.

Factor analysis do not tolerate for missing data points in the data set. Samples with even a single missing data for any of the VOCs should either not be included in the FA or that missing data has to be filled in with one of the available techniques. It should be noted that missing data, which can be due to below detection limit values of the VOCs or due to samples that were not measured with one of the analytical techniques used in the study, is very common in environmental studies. If samples with missing data are not included in the FA, one can end up with very few samples. Because of this, missing data is generally filled in. There are different methods, such as using half of the detection limit value, detection limit value or a random number between zero and detection limit value can be used to fill in missing data points due to BDL values of parameters used in FA. Missing points due to lack of measurement with a certain analytical technique can be filled in with geometric mean value (assuming data is log-normally distributed), or most frequently measured value. In this study missing data points are due to below detection limits of VOCs, because GC-FID was the only analytical tool used and it was applied to all samples. Because of this, missing points were filled with a value equal to half of the method detection limits (MDL) of each VOC. The MDL values are given in the table 3.5.

In this study only 10 of the 25 VOCs were detected in all of the samples (48). All remaining VOCs had one or more BDL values [Cyclohexane had 5 missing points (25% of data), 2-Methylhexane had 3, 3-Methylhexane had 7, Methylcyclohexane had 12, Styrene and o-xylene had 10, n-propylbenzene had 1, Camphene had 16, 1-decene had 4, 1,2,4- trimethylbenzene had 12, n-decane had 8, 1,2,3-trimethylbenzene had 17, 1-undecane had 15, 1,2,4- trichlorobenzene had 10 and naphthalene had 11 missing points]. Although any number of missing data points can be, theoretically, filled in with the techniques mentioned in earlier paragraphs, large number of missing points cannot be filled in, because FA, and other multivariate tools, rely on covariance of parameters. If large number of data points are filled in variance in the data for that particular parameter is reduced. This can degrade the quality of FA exercise. In this study VOCs with missing points higher than 20% of complete data were not included in the FA exercise.

Six VOCs, including Methylcyclohexane, Styrene, Camphene, 1,2,4- trimethybenzene, 1,2,3-trimethybenzene and 1-undecane, were included in FA with this criterion.

Too many missing points were also the reason for why FA was not applied to summer data. Concentrations of VOCs were lower in summer season, as pointed out in previous sections. This resulted in too many missing points for many VOCs. Summer data was not used in FA, because using 20% criterion would lead to a very small data set for FA.

The FA was performed twice and results of the second run are used in this manuscript. In the first attempt FA was run with all available data (excluding five VOCs listed above). After the first run, high factor scores were searched and samples that correspond to very high factor scores are excluded and FA is run for the second time. Generally scores larger than seven are considered "very high". In this study there were no scores >7 in the first FA run. However, there was a score in Factor 2 for the sampling point #18, which was smaller than 7 (the preset criterion to exclude a sample), but which was much higher than rest of the factor 2 scores. The presence of this relatively high value affected distributions of scores. Sample #18 was then excluded from the data set and FA was run for the second time. This exclusion did not affect composition of factors, including Factor 2, but significantly improved appearance of the distribution of factor 2 scores. Results of this second run were used in this manuscript.

Only factors with eigenvalues μ 1.0 were extracted (Kaizer criterion). This resulted in four factors, which explained approximately 80% of the system variance. VOC loadings in these four factors are given in Table 4.9. Distribution of factor scores, which were used to identify sources corresponding to each factor is depicted in Figure 4.3. Distribution of scores are prepared by interpolation (triangulation) using a GIS software. Since distributions of scores (and also concentrations) can be affected by a high score (or concentration) at one single point, bar graphs of scores are also presented in the same figure.

Table 0.9: VOC loadings of the four factors.

	Factor 1	Factor 2	Factor 3	Factor 4	communality
n-hexane		0,53			0,39
Methylcyclopentane	0,53	0,54	0,34		0,70
Benzene	0,84	0,38			0,87
Cyclohexane	0,45				0,77
2-Methylhexane	0,83	0,40			0,88
3-Methylhexane	0,79	0,39	0,29		0,88
c-3-Heptene	0,73		0,31		0,65
Toluene		0,87			0,83
Octane	0,57		0,70		0,85
Ethylbenzene	0,70	0,66			0,95
mpxylene	0,62	0,74			0,95
oxylene	0,36	0,75			0,70
Nonane			0,87		0,83

n-propylbenzene		0,88		0,80	
1-decene	0,39		0,79	0,86	
n-decane	0,35	0,87		0,91	
Factor 1 Factor 2 Factor 3 Factor 4 communality					
benzylchloride	0,36	0,82		0,85	
1,2,4-trichlorobenzene			0,86	0,75	
naphthalene	0,83		0,29	0,79	
eigenvalue	10,6	2,33	1,27	1,05	
Variance explained (%)	55,5	12,3	6,67	5,51	79,99

Factor 1, which explained approximately 50% of the system variance, is loaded with relatively light hydrocarbons. Benzene, methylhexanes, and BTEX compounds, which are heavily loaded in Factor 1 are all good indicators of light duty vehicle emissions (Kuntasal et al., in press). Scores of this factor is high in the city and low in urban areas. Slightly higher scores are also observed around the lake. The bar graph corresponding to Factor 1 (Figure 4.3) demonstrate that this increase in scores around the lake is not due to high scores at a single point around the lake. Slight shading around the lake is due to slightly higher score values at more than one station around the lake. The pattern was also observed in distributions of concentrations of many VOCs.

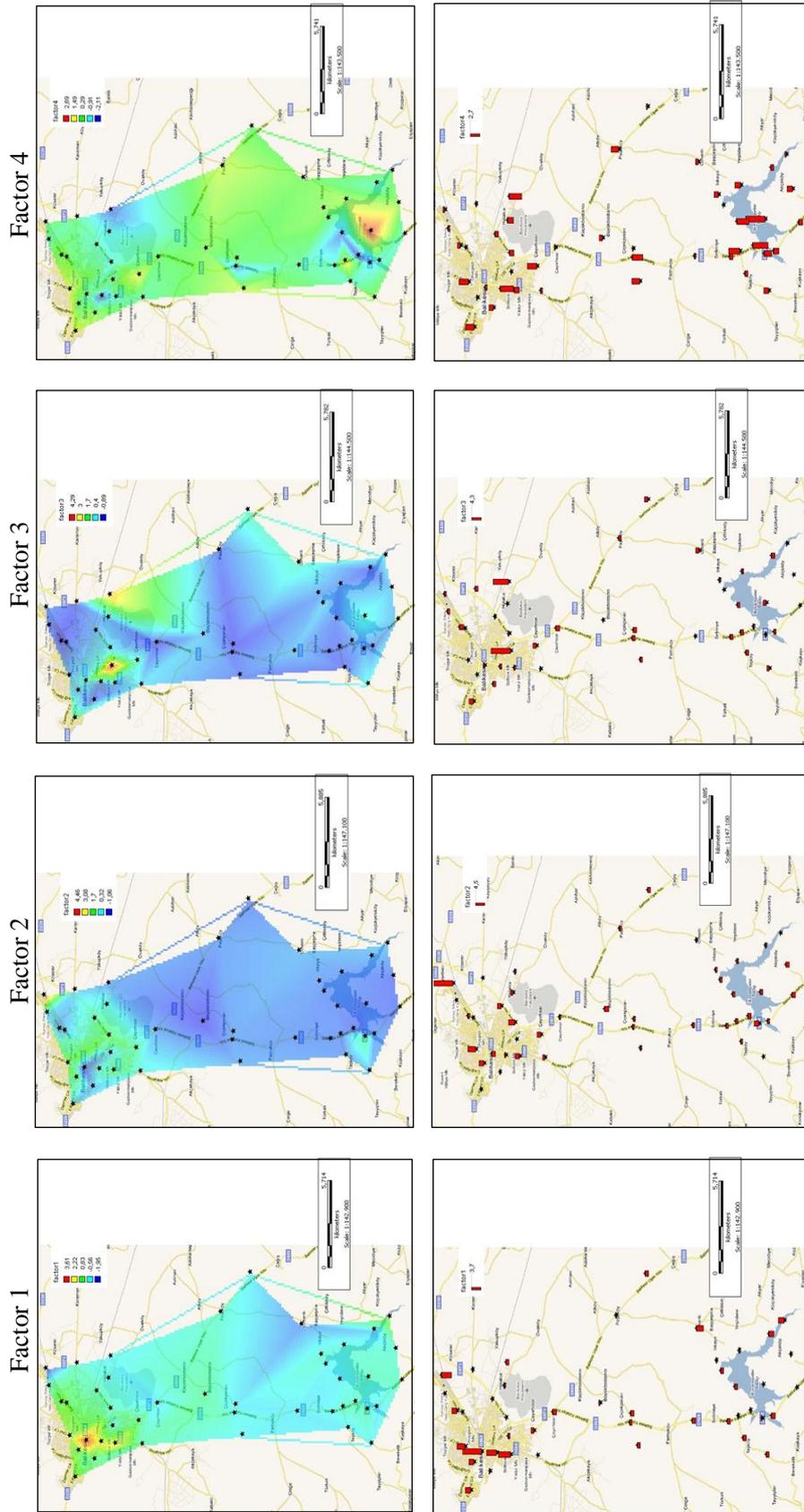
Scores of factor 1 are higher at stations close to the roads then scores at off - road stations. This is true both in the city and in rural areas. Both higher loadings of light hydrocarbons in this factor and higher score values around roads suggest that Factor 1 represent emissions from light duty traffic. In most of the studies on VOC source apportionment, largest fraction of variance is always explained by gasoline engine, which is the dominant source of light VOCs in urban atmosphere. Our assignment of light duty vehicle source to Factor 1 which explains half of the system variance agrees with this general trend.

Factor 2 explains 12% of the system variance. This factor loaded with both light and heavy hydrocarbons. Factor 2 scores are higher in the city, but there are no sharp gradients due to presence of roads. Factor 2 does not look like a traffic factor. Presence of hexane, toluene and o-xylene in factor 2, but lack of benzene confirms the non-traffic source for factor 2, as these compounds, particularly toluene, are good markers for solvent evaporation. Thus Factor 2 is identified as solvent evaporation source.

Factor 3 includes heavy loadings of Octane, Nonane and 1,2,4-trichlorobenzene. These heavy hydrocarbons are known markers of diesel emissions. Factor 3 distribution map demonstrated that Factor 3 scores are higher in the city. Furthermore, average values of factor 3 scores in traffic impacted stations are higher than average values of VOCs at residential and background stations. With these indications, Factor 3 was identified as diesel traffic factor.

Factor 4 had high loadings only for 1-decane. Loadings of all other VOCs included in FA exercise had loadings less than 0.3, indicating that those VOCs are not strongly associated with this factor. Distribution of Factor 4 scores was interesting because bar graphs shown in Figure 4.3 were high around roads and particularly high around the dam.

Although it is not easy to assign a specific source for factor 4 with only 1-decane as an indicator, from distributions, we suspected that Factor 4 is related to emissions from agricultural vehicles, such as tractors and other work machines. However, for the time being this is only a speculation and must be investigated further in future studies.



CHAPTER 5

CONCLUSION

The sampling periods were chosen to cover winter (heating) period and summer (non-heating) period in 2010 in Balıkesir atmosphere. Passive sampling tubes were placed in residential areas, intercity roadsides, around the dam lake which is used for irrigation and drinking purposes and at background places in order to measure VOC levels. In the winter period, the sampling tubes were deployed to 50 points but only 44 of them could be analyzed because of the lost and damaged tubes. For the summer period the sampling tube number was increased and deployed to 53 points where the results were taken only from 49 of them.

The aim of the study was to determine the ambient levels and spatial distributions of 25 VOCs in 50 points and also to estimate the excess dry deposition of the BTEX on the İkiçetepeler Dam Lake. For these purposes over 50 compounds were scanned and the ones which were found in more than 60% of the points were taken into account. The other compounds were not analyzed since most of the concentrations were under the detection limit for most of the points. For only 11 of the compound's spatial distribution map were generated for winter and summer conditions separately. Since all the maps were fairly similar to each other, maps for the other compounds were not generated. The analyzes were made with GC-FID system attached with a unity thermal desorption where ChemStation software was used to finalize the results. Also MapInfo Professional 10.0 software was used for the spatial distribution maps and SPSS Statistics 17.0 software was used for the statistical works.

The results were investigated in terms of seasonal variations. The most abundant specie was found to be Toluene with an average concentration of $15.77 \mu\text{g}/\text{m}^3$ in winter and $6.00 \mu\text{g}/\text{m}^3$ in summer which was measured in 100% of the sampling points. The only other compound found in all the sampling stations was Benzene which has a concentration of $4.50 \mu\text{g}/\text{m}^3$ in winter and $0.79 \mu\text{g}/\text{m}^3$ in summer. The highest average concentration was measured for 1,2,4- trichlorobenzene with $11.33 \mu\text{g}/\text{m}^3$ in winter and $16.20 \mu\text{g}/\text{m}^3$ in summer, however the compound was measured only in 65% of the sampling points over the detection limit. Most of the compounds showed seasonal variations. The BTEX compounds in addition to 1,2,4- trichlorobenzene were accounted for around 57% of the total amount of VOCs in winter but in summer the ratio goes down to 52%.

Excess dry deposition of BTEX on the İkiçetepeler Dam Lake was also taken into account in this study. With a rough estimation of the lake area and deposition velocity the excess deposition percentages were found. The highest deposition percentage is in o-Xylene with 38.3% where the lowest one is in Toluene with 1.9%. Same calculations were also done for the residential area and higher percentages were observed for the same compounds. The highest percentage was calculated for o-xylene, as in the lake estimation with 70%, where the lowest one was ethylbenzene with 56%.

Factor analysis was also done for the collected data and four factors were extracted which had eigenvalues greater than 1.0 (Kaizer criterion). Three of these factors were identified as light-duty vehicles, solvent evaporation, and diesel emission respectively where these three factors explain 74% of the factor scores. The fourth factor, which explains 5.5%, is suspected to be from the agricultural vehicles. However to prove this idea further studies are needed to be done.

CHAPTER 6

RECOMMENDATIONS FOR FUTURE STUDIES

The study was successful in determining the spatial distribution and seasonal differences of the VOCs. But it could not reach the aimed number of VOCs because of the high detection limit of the passive sampling theory. Also for 14 compounds the spatial distribution map could not be analyzed because of the very low levels and the missing points because of the detection limit. For the future studies in Turkey the following recommendations are provided:

- ✓ More sampling periods or continuous monitoring should be performed to see the VOC change more clearly with physical effects like wind or temperature.
- ✓ The sampling points should be chosen close to the chemical factories or fossil fuel burning plants and the number of the points should be increased as the factory number increases. The aim should be to see the effect of the industry on the residential areas.
- ✓ For each city in Turkey a VOC emission inventory should be prepared.
- ✓ Studies on public exposure and health risks of VOCs are needed since Turkey is in an industrialization process.
- ✓ More of these studies should be done in different parts of Turkey to see the contamination in a larger scale.

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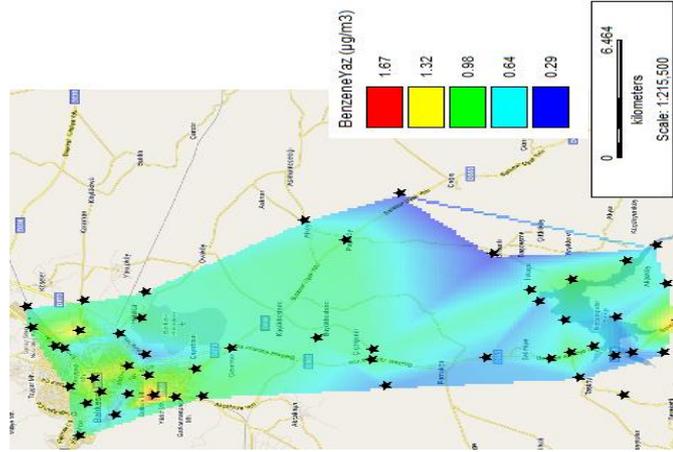
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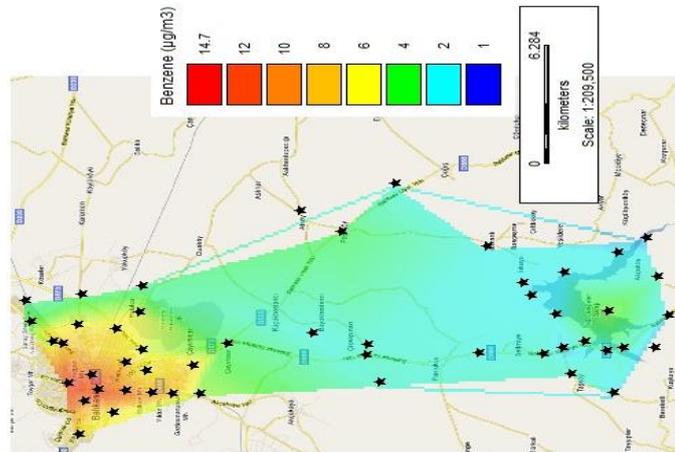
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APPENDIX A

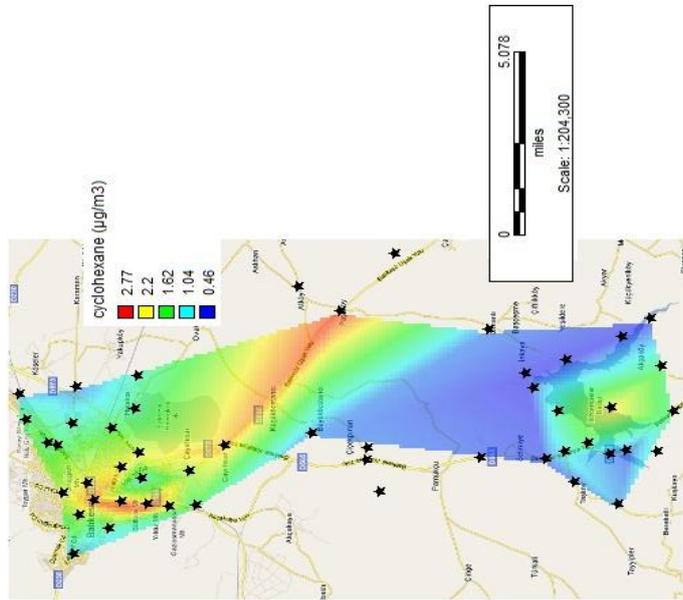
Maps of the VOCs.



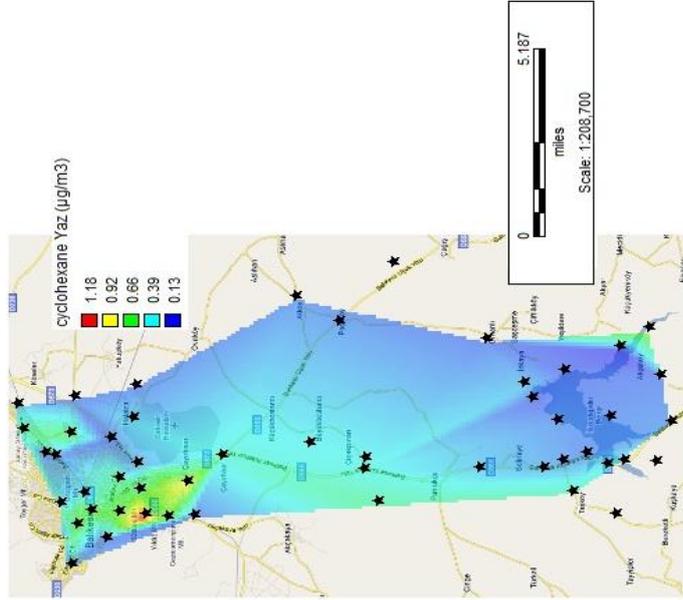
Benzene summer



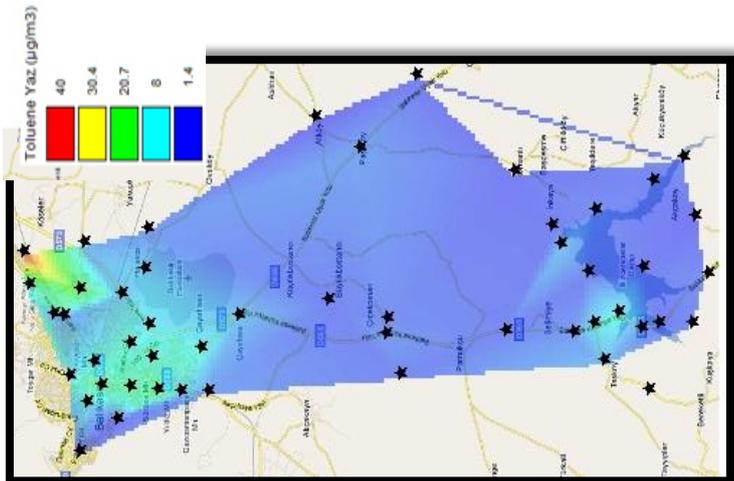
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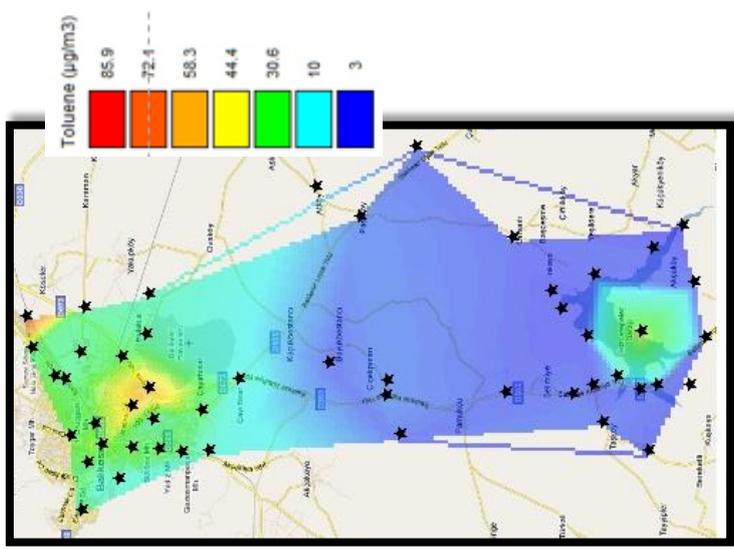
Cyclohexane winter



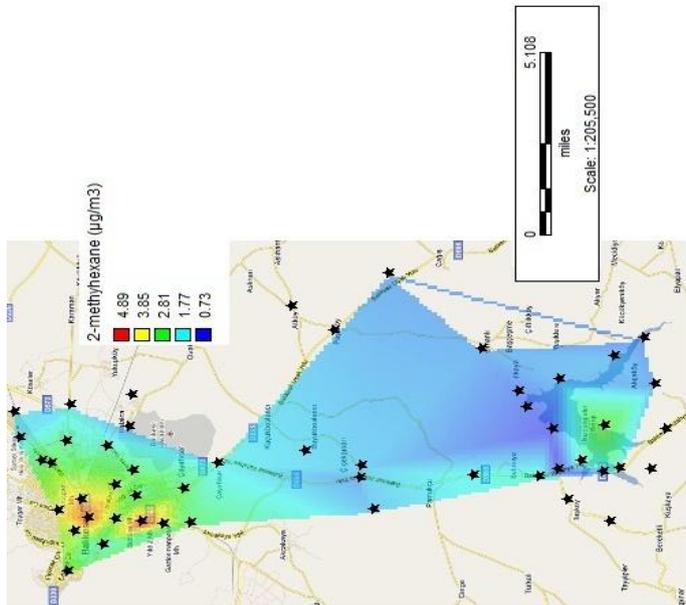
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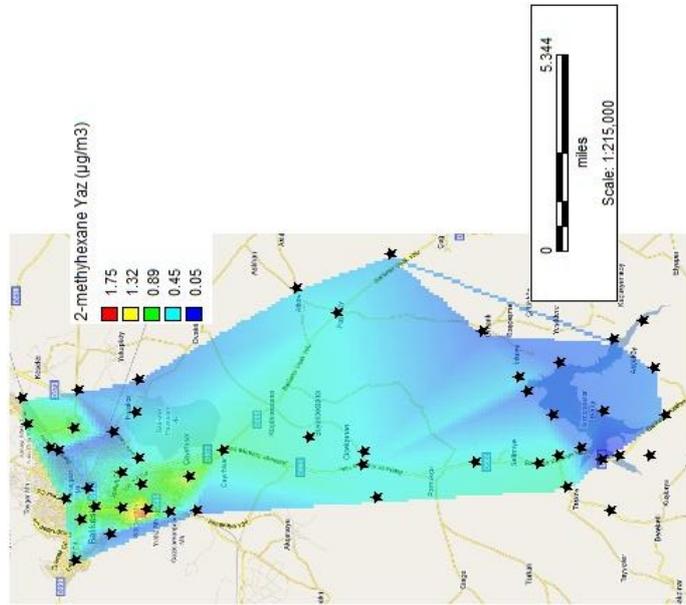
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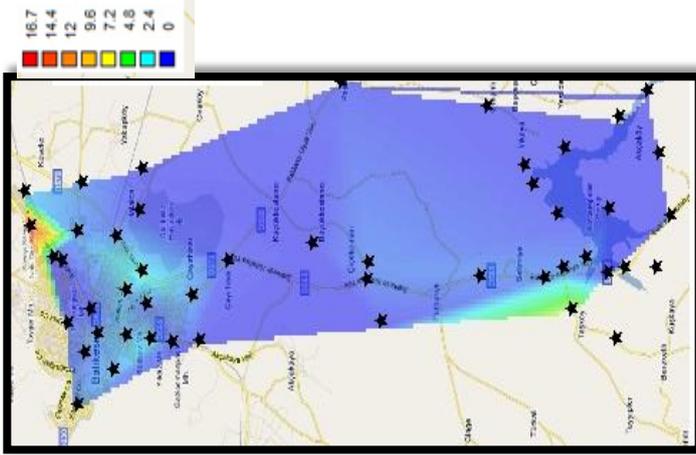
Toluene winter



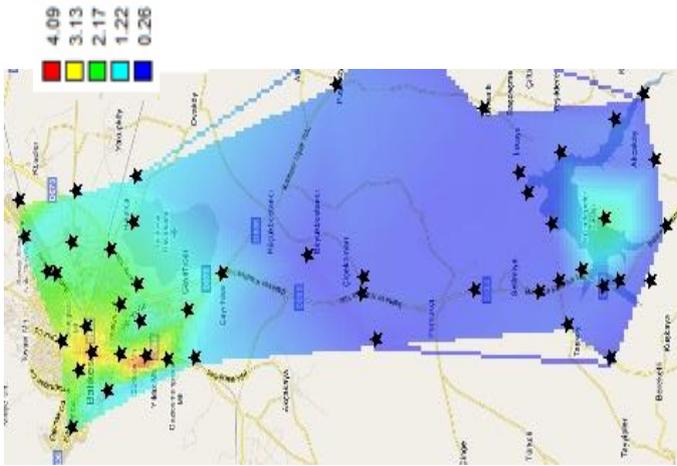
2-methyl hexane winter



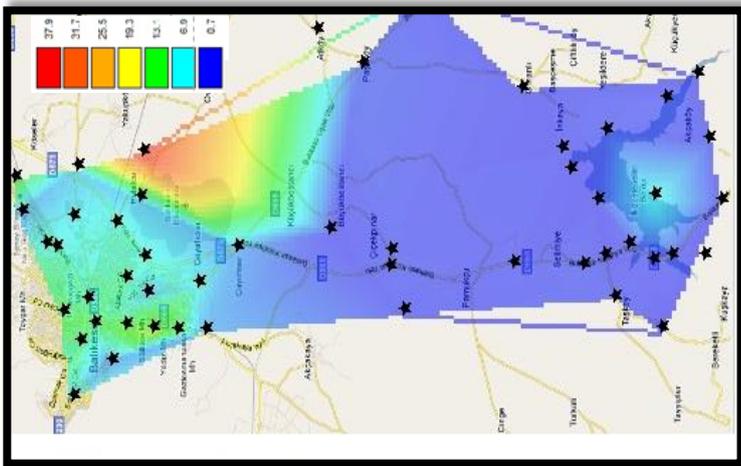
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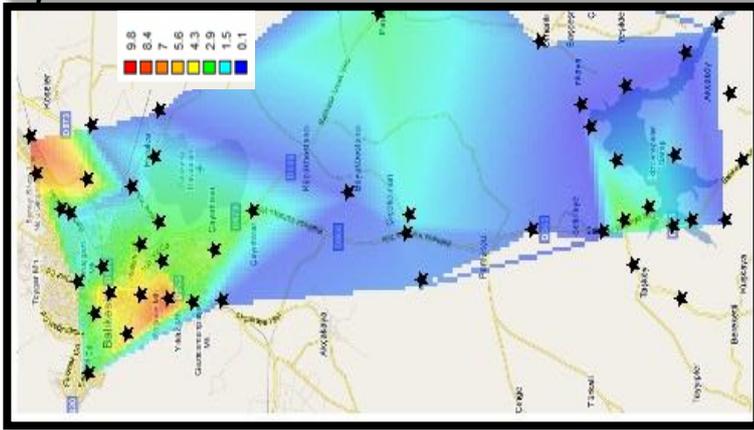
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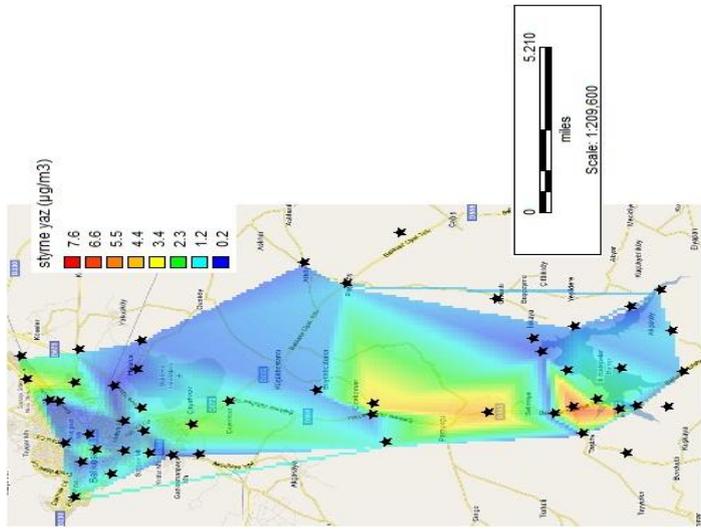
ethylbenzene winter



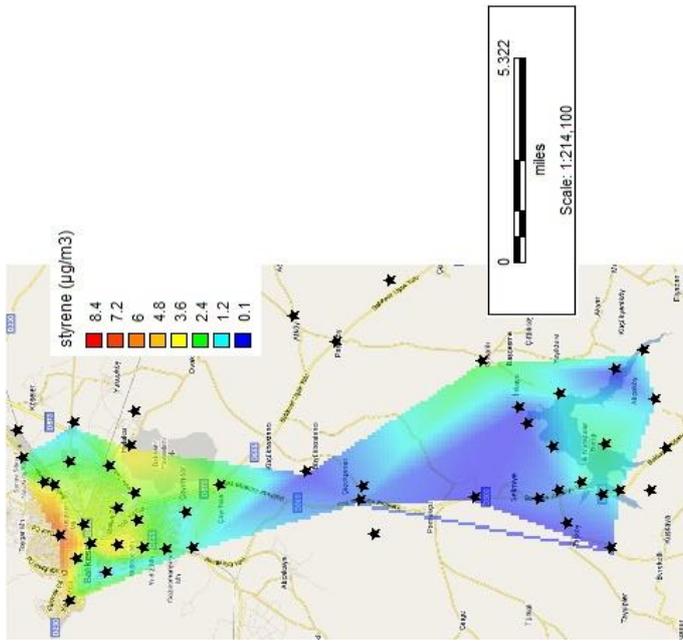
M-p, xylene winter



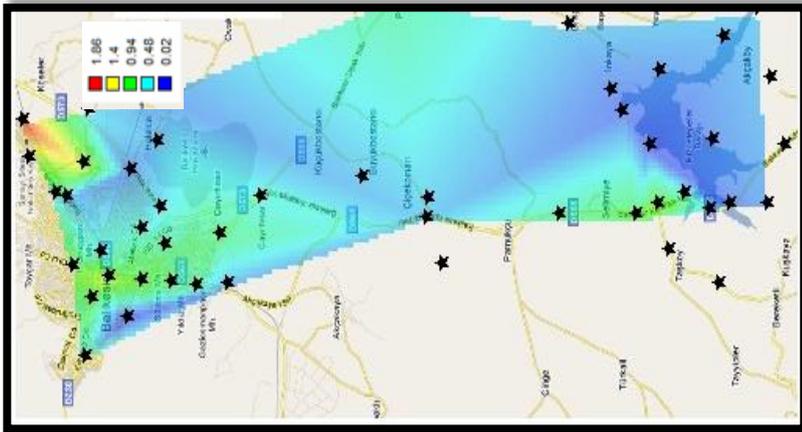
M-p, xylene Summer



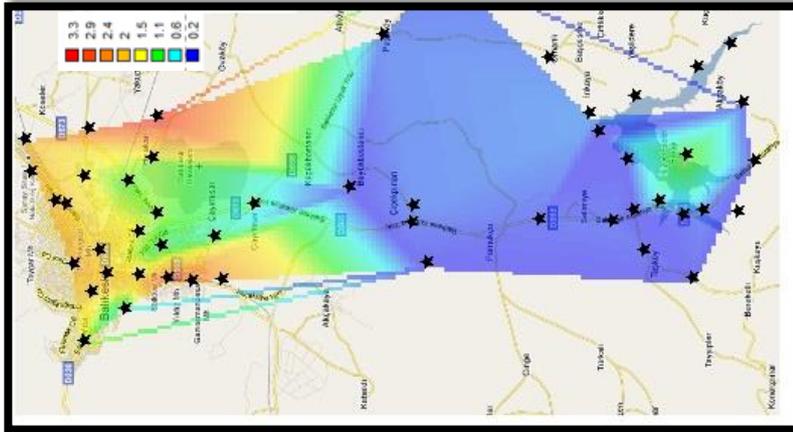
Styrene summer



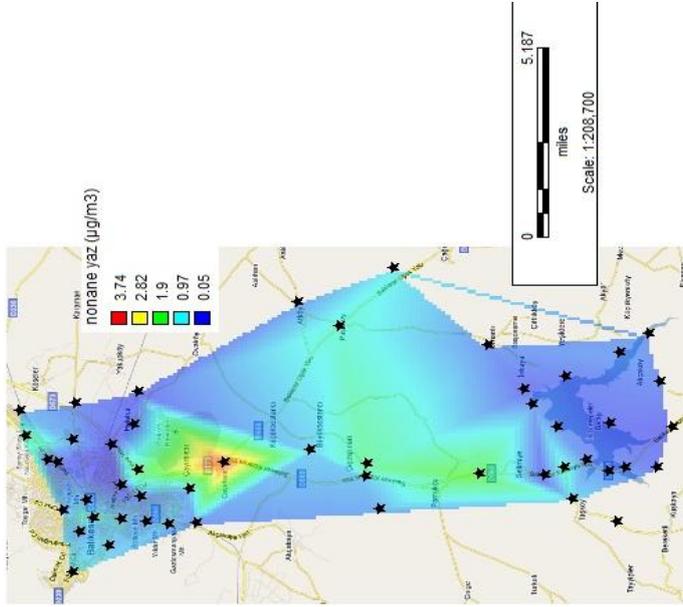
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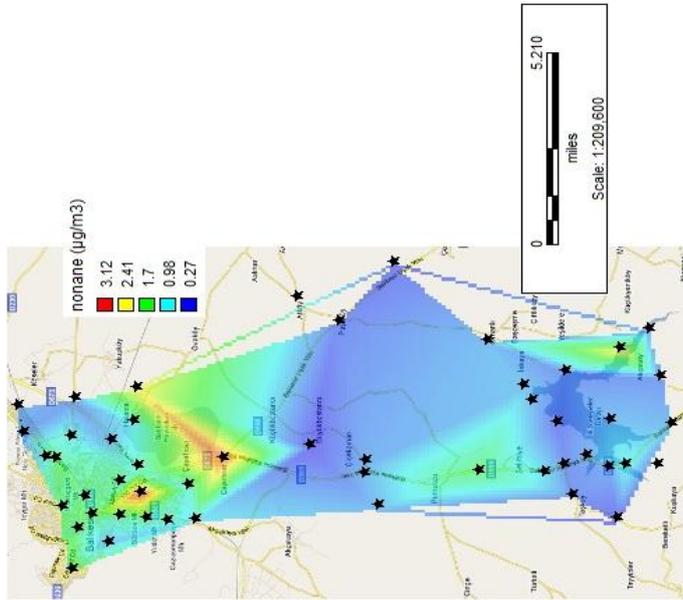
O-xylene summer



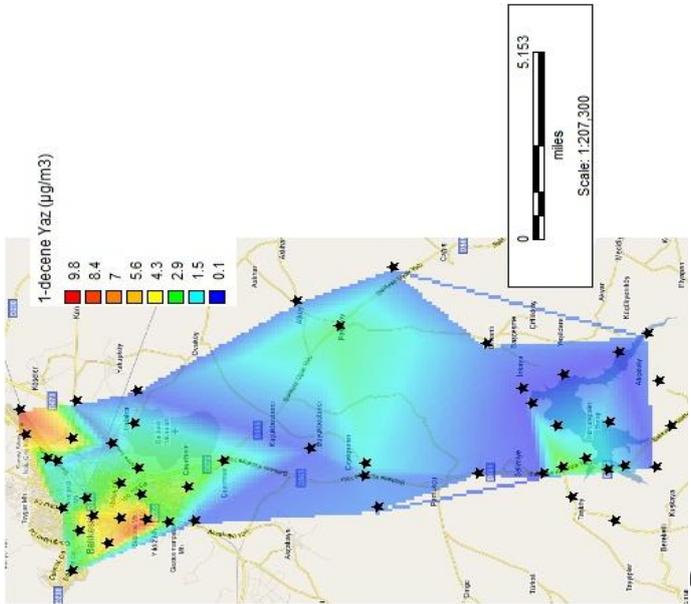
O-xylene winter



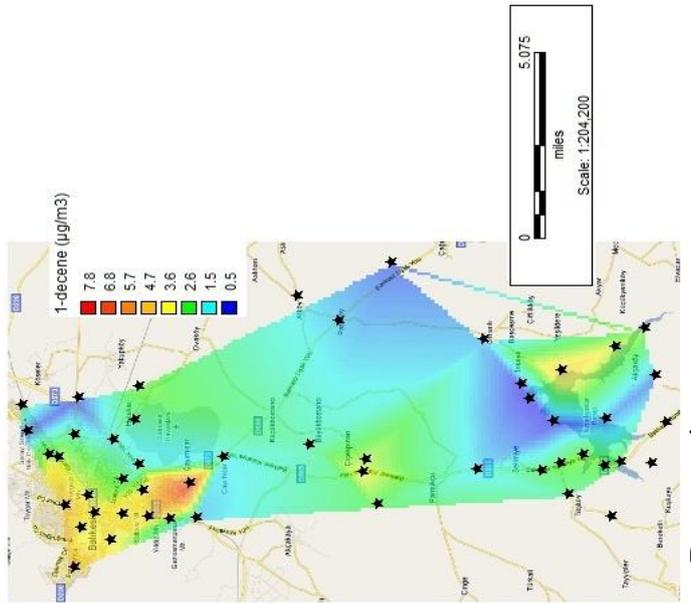
Nonane in summer



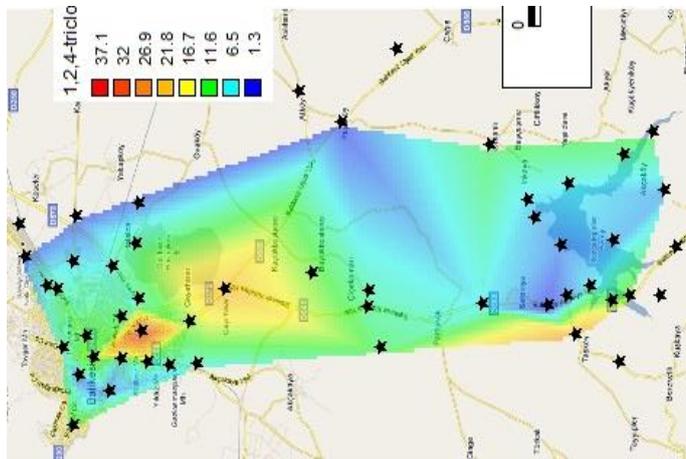
Nonane winter



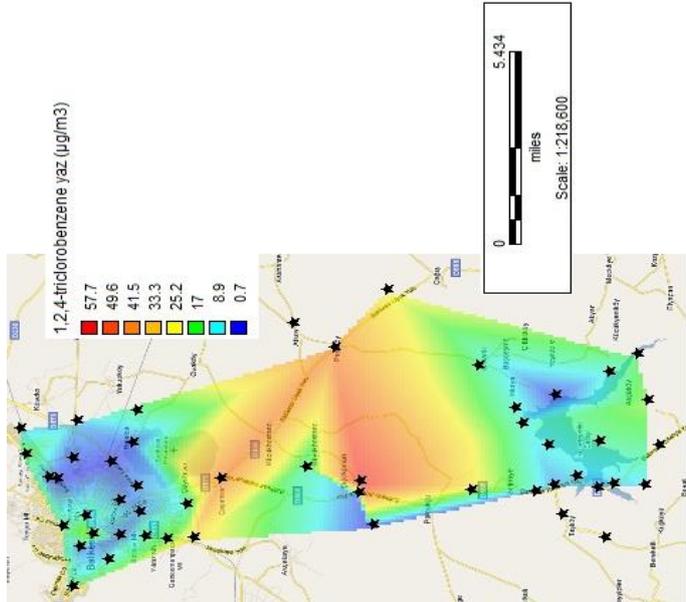
Decane summer



Decane winter



Trichlorobenzene winter



Trichlorobenzene summer