

**DOKUZ EYLÜL UNIVERSITY**  
**GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**

**DETERMINATION OF VOLATILE ORGANIC  
COMPOUNDS AROUND ALIAGA BY PASSIVE  
SAMPLING METHODS**

**by**  
**Özgün ANDIÇ**

**September, 2008**

**İZMİR**

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COMPOUNDS AROUND ALIAGA BY PASSIVE  
SAMPLING METHODS**

**A Thesis Submitted to the  
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**by  
Özgün ANDIÇ**

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## M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled “**DETERMINATION OF VOLATILE ORGANIC COMPOUNDS AROUND ALIAGA BY PASSIVE SAMPLING METHODS**” completed by **ÖZGÜN ANDİÇ** under supervision of **PROF. DR. AYSEN MÜEZZİNOĞLU** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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# DETERMINATION OF VOLATILE ORGANIC COMPOUNDS AROUND ALIAGA BY PASSIVE SAMPLING METHODS

## ABSTRACT

Volatile organic compounds (VOCs) are most important air pollutants because of their role in the tropospheric chemistry and their adverse effects on human health. In order to determine their ambient VOC concentrations in Aliaga urban and industrial region a grid system with 48 sampling points for weekly passive sampling were established. The five sampling campaign periods that were conducted on December, 19-26, 2005; March 21-28, 2006; June, 19-26, 2006; August 29 – September 5, 2006 and February 9-16, 2007. Twenty-three VOCs were detected and quantified in these five periods, although 55 such compounds were measureable and quantifiable with the method used. In this thesis work, four of the VOCs, namely the benzene, toluene, ethylbenzene and xylene which are altogether called **BTEX compounds** held by the sample tubes were studied in depth. BTEX are the most important group of VOCs for their abundance, common sources and serious health effects.

Styrene was the most abundant volatile organic compound, followed by 2-methylhexane and toluene with an average of  $2.10 \mu\text{g m}^{-3}$ ,  $1.65 \mu\text{g m}^{-3}$  and  $1.44 \mu\text{g m}^{-3}$  at Aliaga region. The highest VOC concentrations were measured at petrochemical and refinery areas.

The levels of BTEX were relatively higher in winter as compared to summer periods. The reason of having lower levels of BTEX might be the effects of higher chemical removal reaction rates by higher temperatures and sunlight.

The average BTEX ratios were 2.5:5.3:1.0:1.5 for period 1, 2.7:4.9:1.0:2.2 for period 2, 2.0:6.7:1.0:2.5 for period 3, 2.5:8.3:1.0:3.6 for period 4 and 13.0:25.9:1.0:3.3 for period 5. Toluene to benzene (T/B) ratio was also studied to identify the possible sources of VOCs. T/B ratios were 2.1 for period 1, 1.8 for period 2, 3.4 for period 3, 3.3 for period 4 and 2.0 for period 5. In winter vehicular

exhaust was the main source of VOCs, however in summer industrial activities also affect the air pollution as source of VOCs. According to T/B ratios, these compounds were more likely originating from the vehicles in traffic in winter, however, they might be more affected by industrial emissions in summer. Although a source detection study was not made in this study, correlations between different BTEX concentrations showed that their major source were the traffic emissions.

Also benzene levels were evaluated for the cancer risk in Aliaga region. Benzene is a known carcinogen and continuous exposure to  $1 \mu\text{g m}^{-3}$  produces a lifetime risk ranging of  $2.2 \times 10^{-6} - 7.8 \times 10^{-6}$  for leukaemia. Usually,  $5 \mu\text{g m}^{-3}$  is considered a practical limit (ENDS, 1996). Average benzene concentrations were 0.66 for period 1; 1.22 for period 2; 0.27 for period 3; 0.13 for period 4 and 0.78 for period 5. Generally speaking, these average values indicate no significant cancer risk due to benzene in the area. However benzene levels were higher than  $5 \mu\text{g m}^{-3}$  at the petrochemical and refinery yards and there was the risk for people which must definitely be studied further.

**Keywords:** Volatile organic compounds, BTEX, Passive sampling method, Aliaga.

# ALIAĞA ÇEVRESİNDEKİ UÇUCU ORGANİK BİLEŞİKLERİN PASİF ÖRNEKLEME METODU İLE BELİRLENMESİ

## ÖZ

Uçucu organik bileşikler (UOB) troposferik kimyadaki rolleri ve insan sağlığı üzerindeki olumsuz etkileri nedeniyle en önemli hava kirleticileridir. Havadaki UOB konsantrasyonlarını belirlemek için, Aliğa kentsel ve endüstriyel alanlarında haftalık pasif örnekleme için, 48 örnekleme noktalı bir dikey hat sistemi kurulmuştur. Beş örnekleme dönemi 19-26 Aralık 2005, 21-28 Mart 2006, 19-26 Haziran 2006, 29 Ağustos – 5 Eylül 2006 ve 9-16 Şubat 2007 tarihlerinde gerçekleştirilmiştir. Kullanılan metod ile 55 bileşik ölçülebilir ve belirlenebilir olmasına rağmen, bu beş dönemde yirmi üç UOB bulunmuş ve ölçülmüştür. Bu tez çalışmasında, örnek tüplerinde tutulan BTEK olarak adlandırılan benzen, toluen, etilbenzen ve ksilen isimli dört UOB üzerinde derinlemesine çalışılmıştır. BTEKler, bolca bulunması, ortak kaynakları ve ciddi sağlık etkileri nedeniyle UOBlerin en önemli grubudur.

Aliğa bölgesinde, ortalama  $2.10 \mu\text{g m}^{-3}$  ile styren en fazla bulunan organik bileşiktir ve bunu ortalama  $1.65 \mu\text{g m}^{-3}$  ile 2-metilheksan ve ortalama  $1.44 \mu\text{g m}^{-3}$  ile toluen takip eder. En yüksek UOB konsantrasyonları petrokimya ve rafineri bölgelerinde ölçülmüştür.

BTEK seviyeleri kış aylarında yazı göre nispeten daha yüksek bulunmuştur. BTEK seviyelerinin düşük olmasının nedeni, yüksek sıcaklık ve güneş ışığı nedeniyle yüksek reaksiyon hızlarının kimyasal giderimi etkisi olabilir.

Ortalama BTEK oranları 1. dönem için 2.5:5.3:1.0:1.5, 2. dönem için 2.7:4.9:1.0:2.2, 3. dönem için 2.0:6.7:1.0:2.5, 4. dönem için 2.5:8.3:1.0:3.6 ve 5. dönem için 13.0:25.9:1.0:3.3 tür. UOB'lerin olası kaynaklarını belirlemek için, toluen / benzen oranı da incelenmiştir. T/B oranları 1. dönem için 2.1, 2. dönem için 1.8, 3. dönem için 3.4, 4. dönem için 3.3 ve 5. dönem için 2.0 bulunmuştur. Kışın trafik kökenli kirlilik ana UOB kaynağı olmakla beraber yazın UOB kaynağı olarak

endüstriyel faaliyetlerin de etkisi görülmektedir. T/B oranlarına göre, bu bileşikler kışın araç trafiğinden kaynaklanabilir olması ile beraber, yazın endüstriyel emisyonların daha fazla etkilediği söylenebilir. Bu çalışmada kaynak belirlenmesi yapılmamasına rağmen, farklı BTEK konsantrasyonları arasındaki korelasyonlar ana kaynağın trafik emisyonları olduğunu göstermiştir.

Aliğa bölgesindeki kanser riskini incelemek için benzen seviyeleri de araştırılmıştır. Benzen kanserojen olarak bilinir ve  $1 \mu\text{g m}^{-3}$  benzene sürekli maruz kalma, kan kanseri için  $2.2 \times 10^{-6} - 7.8 \times 10^{-6}$  arasında değişen risk yaratır. Genellikle  $5 \mu\text{g m}^{-3}$  değeri pratik sınır değer olarak düşünülebilir (ENDS, 1996). Ortalama benzen konsantrasyonları 1. dönem için 0.66, 2. dönem için 1.22, 3. dönem için 0.27, 4. dönem için 0.13 ve 5. dönem için 0.78'dir. Genel olarak, kentsel alanda benzenden kaynaklı önemli kanser riski bulunmamaktadır. Bununla beraber, petrokimya ve rafineri alanlarında benzen seviyeleri  $5 \mu\text{g m}^{-3}$  den yüksektir ve ileride kesinlikle üzerinde çalışması gereken bir risk bulunmaktadır.

**Anahtar Sözcükler:** Uçucu organik bileşikler, BTEK, Pasif örnekleme metodu, Aliğa



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# CHAPTER ONE

## INTRODUCTION

### 1.1 Introduction

Air pollution is a major environmental concern as it affects health and quality of life in urban populations at an increasing trend created by growing industrialization, urbanization and resulting transportation needs. Volatile organic compounds (VOCs) in the air are found in significant quantities contributing to urban atmospheric pollution. These compounds have an important role because of their adverse effects on human health and participation in photochemical reactions resulting in the formation of secondary pollutants of higher significance such as ozone and peroxyacetyl nitrate (PAN).

VOCs are emitted into the atmosphere from anthropogenic and biogenic sources. Major anthropogenic sources are combustion sources (vehicle and fossil-fueled power plant emissions), fuel storage and transport, solvent usage, emissions from industrial operations, landfills and hazardous waste facilities (Atkinson, 2000). Hence, it can be seen that the characteristics of VOC concentrations in ambient air depend on the strength of each emission source (Na & Kim, 2001).

Nowadays, European air quality standards regulate the maximum level of benzene, which is  $10.0 \mu\text{g m}^{-3}$ , from January 2005. Moreover, this limit will be progressively reduced to  $5.0 \mu\text{g m}^{-3}$  by January 2010. However, the health risk of air depends on the type and concentration of each VOC, and they now need to be determined individually (Ras-Mallorquí et al., 2007).

To develop effective strategies on the reduction of ambient levels of VOCs and to determine the effects of VOCs on human health, VOC concentrations should be known. Thus, VOC concentrations were determined in Aliğa town of İzmir, located 50 km north of Izmir ( $38^{\circ} 56' \text{ N}$  ;  $37^{\circ} \text{ S}$  and  $26^{\circ} 53' \text{ W}$ ;  $27^{\circ} 10' \text{ E}$ ), which is one of the most important industrial regions of Turkey. Among the industrial facilities a

large capacity petrochemical refinery, iron-steel industries and gasoline handling workplaces are included. The climate in the area is characterised as Mediterranean, having a mean summer temperature of 25°C, and a mean winter temperature of 7°C. The mean annual rainfall is 700 mm. Aliaga has been experiencing a rapid industrial growth. As a consequence, various air pollution problems arose in Aliaga.

The sampling program for VOCs was conducted between December 2005 and February 2007. Passive sampling tubes were located at 48 different points that were selected and were used to collect one-week air samples at five different campaigns. Collected tubes were thermally desorbed and analyzed by gas chromatography for 55 VOCs in the laboratory. VOC concentrations obtained from the experimental studies were evaluated by comparing them with the values reported in the literature and the limit values set by regulations. In addition, the relationship between meteorological parameters and VOC concentrations was investigated.

## **1.2 Objectives and Scope**

This thesis is designed to investigate atmospheric VOC pollution in Aliaga town with passive sampling method.

The major objectives of this thesis can be summarized as follows;

- To determine VOC concentrations in the air of urban and industrial zones in and around Aliaga town.
- To determine BTEX concentrations of urban atmosphere of Aliaga town and their potential sources.
- To discuss seasonal variations of BTEX concentrations.
- To investigate BTEX ratios and T/B ratios.

- To determine correlations between concentrations of BTEX compounds in order to discuss their sources.
- To discuss health risks of Aliaga town due to benzene emissions.

In the scope of this study, 48 weekly integrated air samples were collected by passive sampling method at five different campaigns during both summer and winter season. Air samples were collected using stainless steel sorbent tubes packed with Chromosorb 106 adsorbent. Ambient concentrations obtained from the experimental studies were evaluated by comparing them to the values reported in the literature.

**CHAPTER TWO**  
**LITERATURE REVIEW**

**2.1 Volatile Organic Compounds**

Volatile organic compounds in the air are consisted of hydrocarbons of C and H only as well as partially oxidized hydrocarbons (organic acids, aldehydes, ketones), and organics containing chlorine, sulfur, nitrogen or other atoms in the molecule. Within this class there are hundreds of individual compounds (Cooper & Alley, 1994). Chemical formulae and some important properties of selected VOCs are given in Table 2.1.

Table 2.1 Chemical formula and some important properties of selected VOCs

<b>Volatile Organic Compounds</b>	<b>Chemical Formula</b>	<b>Molecular Weight (g/mol)</b>	<b>T<sub>m</sub></b>	<b>T<sub>b</sub></b>	<b>Vapor Pressure at 25°C (mm Hg)</b>
Benzene	C <sub>6</sub> H <sub>6</sub>	78.11	5	80	95.2
Toluene	C <sub>7</sub> H <sub>8</sub>	82.14	-95	111	28.4
o-xylene	C <sub>8</sub> H <sub>10</sub>	106.17	-25	144	6.7
m-xylene	C <sub>8</sub> H <sub>10</sub>	106.17	-48	139	8.4
p-xylene	C <sub>8</sub> H <sub>10</sub>	106.17	13	138	8.8
Ethylbenzene	C <sub>8</sub> H <sub>10</sub>	106.17	-95	136	9.5
Isopropyl benzene	C <sub>9</sub> H <sub>12</sub>	120.20	-97	153	4.5
1,2,3-trimethylbenzene	C <sub>9</sub> H <sub>12</sub>	120.20		149	1.5
Ethyl acetate	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	88.10	-83	77	73
n-butyl acetate	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	116.16	-77	126	10
Acetone	C <sub>3</sub> H <sub>6</sub> O	58.08	-95	56	266
Isobutyl methyl ketone	C <sub>6</sub> H <sub>12</sub> O	100.16	-84	116	15
n-hexane	C <sub>6</sub> H <sub>14</sub>	86.18	-94	68	151.3

Of all the classifications of air pollutants, VOCs are the most confusing in terms of understanding the terminology, because of the difficulty in separating out distinct groupings. Although some include methane into the group, according to many VOCs are the sum of non-methane hydrocarbons (NMHC), heavy hydrocarbons and carbonyl compounds. Non-methane hydrocarbons (NMHC), the most predominant group of VOCs in the ambient air, are the C<sub>2</sub> to C<sub>12</sub> (light) hydrocarbons. They include the alkanes (ethane, propane, butane, pentane, hexane, heptane, octane, nonane and decane), the cycloalkanes (cyclopropane, cyclobutane, cyclopentane etc.), the alkenes (ethylene, propene, butene etc.), the alkynes (acetylene, propyne, butyne etc.), the aromatics (benzene, toluene, xylene, styrene etc.) and the numerous derivatives of all of those. Heavy hydrocarbons (C<sub>10</sub> to C<sub>20</sub>) are sometimes termed “semi-volatile” compounds because the >C<sub>15</sub> compounds are often found as both gases and particles (Watson et al., 2001). The gaseous oxygenated hydrocarbons – aldehydes and ketones are defined as carbonyls. The simplest and the most common of the aldehydes found in the atmosphere is formaldehyde, which is a gas at ambient temperatures, whereas other (usually liquid) carbonyls –acetaldehyde, benzaldehyde and acetone- are vaporized at combustion temperatures.

Large quantities of VOCs are emitted into the troposphere from anthropogenic and biogenic sources. Methane is emitted into the atmosphere from both biogenic (natural wetlands) and anthropogenic (domestic ruminants, rice paddies, landfills, biomass burning, and fossil-fuel related emissions) sources. Large quantities of non-methane organic compounds (NMOC), including isoprene (2-methyl-1,3-butadiene), a series of C<sub>10</sub>H<sub>16</sub> monoterpenes, C<sub>15</sub>H<sub>24</sub> sesquiterpenes, and oxygenated VOCs (including methanol, 2-methyl-3-buten-2-ol, 6-methyl-5-hepten-2-one, *cis*-3-hexen-1-ol, *cis*-3-hexenylacetate, and linalool) are emitted from vegetation. NMOC are also emitted into the atmosphere from a variety of antropogenic sources, including combustion sources (vehicle and fossil-fuel power plant emissions), fuel storage and transport, solvent usage, emissions from industrial operations, landfills, and hazardous waste facilities. (Atkinson, 2000)

VOCs have various effects on human beings. Exposure to VOCs might cause eye, nose and throat irritation in addition to damage to the liver, kidney and central nervous system (Wang et al., 2005). Many of them are often considered to be toxic and some, such as benzene, have been identified as important cancer risk factors in urban environment (Fernandez-Villarrenaga et al., 2004) and certain hydrocarbons are known to participate in photochemical reactions resulting in the formation of oxidant such as ozone and peroxyacetyl nitrate (PAN) (Tolnai et al., 2000). In the presence of sunlight, VOCs can react with nitrogen oxides to create ground level ozone and photochemical smog, which can in turn contribute to pollution of the atmosphere.

## **2.2 Sampling and Analyzing Techniques of VOCs**

### **2.2.1 Sampling**

There are two basic methods for collecting gaseous samples: continuous and periodic sampling.

Continuously sampling organic compounds directly into an analyzer enables a detailed picture of how the emission varies with time (Richardson & Gibson, 1998). However, analyzers with such capabilities, like infra-red spectrometers or portable gas chromatographs or their detectors, have limitations of cost, stability, field calibration and power supply which may detract their use (Harper, 2000).

Periodic or intermittent sampling, which is used to collect samples and analyze them in the laboratory, is the practical method for sampling organic compounds. Whole air sampling and sorbent trapping are two main methods of periodic sampling. Canisters or polymer bags are used to collect air samples in whole air sampling. The main advantage of using a canister or a polymer bag is the recovery of air samples and the main disadvantage is the loss of some compounds by adsorption to canister or bag walls. In the sorbent trapping, active (pumped) and passive (diffusive) sampling methods are used to adsorb air samples on active surfaces of sorbents.



Compared to sorbent trapping, the TO-15 method is using canisters and is useful for a wide range of volatiles. However, the cost of canister sampling methods is higher due to the need for the specialized equipment (Wang et al., 2005).

Most studies of ambient VOCs have been performed with active samplers that require an air pump and power supply. Although active samplers have the advantage of being able to collect a precise volume of air in a short time, it makes it difficult to survey the multi points and simultaneously because of they require electricity. Passive air samplers can be used where electricity is not available, and because they are small and silent, they are especially useful for measuring personal exposure and analyzing indoor air. In addition, passive air samplers can be produced inexpensively and used to investigate many sampling points simultaneously and to locate emission sources in a particular area (Kume et al., 2008).

A diffusive (passive) sampler is a device capable of taking samples of pollutants in gas or vapour form from the atmosphere at a rate controlled by a physical process, such as diffusion through a static air layer or permeation through a membrane. However, it does not involve an active or forced movement of the air through the sampler (Brown, 1993).

The principle of passive sampling is based on free flow of analyte molecules from the sampled medium to a collecting medium, as a result of a difference in chemical potentials of the analyte between the two media. Net flow of analyte molecules from one medium to the other continues until equilibrium is established in the system, or until the sampling session is terminated by the user. An ideal collecting medium has 100% collection efficiency, that is analyte concentration near the surface of the medium is zero. In practice, the collection efficiency rarely approaches this ideal efficiency (Gorecki & Namiesnik, 2002).

Diffusion and permeation processes can both be described in derivations of Fick's first law of diffusion (Eq. 2.1), which result in expressions relating the mass uptake by the sampler to the concentration gradient, the time of exposure, and the sampler

area exposed to the pollutant atmosphere (Brown, 1993). The amount,  $M$ , of the analyte transported by diffusion in time,  $t$  (s), when the change in concentration gradient is linear and the collection efficiency is 100%, can be described by the following relationship:

$$M = U * t = \frac{D * A}{L} * C_o * t \quad (\text{Eq. 2.1})$$

where  $U$  is the diffusive transport rate (mol/s),  $D$  is the molecular diffusion coefficient of the analyte ( $\text{cm}^2/\text{s}$ ),  $A$  is the cross section of the diffusion path ( $\text{cm}^2$ ),  $L$  is the total length of the diffusion path (cm) and  $C_o$  is the analyte concentration in the medium examined ( $\text{mol}/\text{cm}^3$ ).

The term  $D*A/L$  is called uptake rate ( $\text{cm}^3/\text{min}$ ). For a device with a defined geometry and at a constant temperature, uptake rate should be constant for a given analyte. Thus, as long as the exact geometry of the sampler ( $A$  and  $L$ ) is known, it should be possible to calculate  $C_o$  based on the literature value of  $D$  (Gorecki & Namiesnik, 2002). Schematic diagram of tube-type diffusion sampler is illustrated in Figure 2.1.

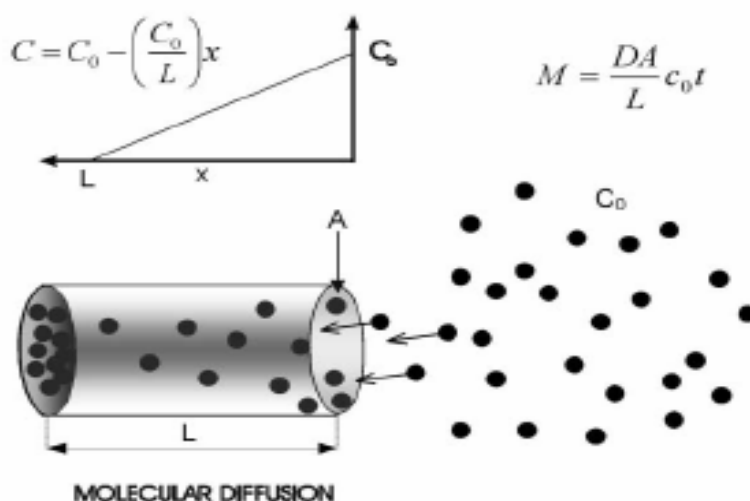


Figure 2.1 Schematic diagram of tube-type diffusion sampler (Gorecki & Namiesnik, 2002).

However, several factors make this approach impractical. The values of the molecular diffusion coefficient for a given compound differ between literature sources, and the data on the temperature dependence of  $D$  are often incomplete. Other factors include analyte losses through sorption to various parts of the sampler, as well as collection efficiency lower than 100%. Thus, in practice, it is often necessary to calibrate each sampler.

### ***2.2.2 Desorption***

Adsorbed compounds could be desorbed by solvent extraction and thermal desorption methods. In solvent extraction, compounds trapped by sorbent are desorbed by utilization of solvent suitable for that compounds. Activated charcoal, silica gel, Anasorb 747, carboxens, porous polymers and carbon molecular sieves are the sorbents preferred for this method (Harper, 2000). Because of the high toxicity and flammability of some solvents such as carbon disulfide and the labour intensive nature of the solvent desorption procedure, a useful alternative is to desorb the collected analyte thermally. Thus, desorption can be fully automatated and analysis is usually carried out by gas chromatography. The main disadvantage of thermal desorption directly into an analyser is that it is essentially a “one-shot” technique. This is why many such methods are linked to mass spectrometry. However, with capillary chromatography it is usually possible to split the desorbed sample before analysis, and if desired the vented split can be collected and re-analysed (HSE, 1993).

Sorbent selection depends on the sorbent characteristics, breakthrough volume and compound of interest. Sorbents used in thermal desorption and their characteristics are presented in Table 2.2.

Table 2.2 Sorbent used in thermal desorption

Sorbent	Analyte range Volatility range	Max. temp. ( <sup>0</sup> C)	Specific surface area (m <sup>2</sup> /g)	Hydrophobic (?)
CarbotrapC CarbopackC AnasorbGCB2	n-C8 to n-C20	>400	12	Yes
Tenax TA	n-C7 to n-C26	350	35	Yes
Tenax GR	n-C7 to n-C30	350	35	Yes
Carbotrap CarbopackB AnasorbGCB1	(n-C4) n-C5 to n- C14	>400	100	Yes
Chromosorb102	bp 50 <sup>0</sup> C-200 <sup>0</sup> C	250	350	Yes
Chromosorb106	bp 50 <sup>0</sup> C-200 <sup>0</sup> C	250	750	Yes
PropakQ	n-C5 to n-C12	250	550	Yes
PropakN	n-C5 to n-C8	180	300	Yes
Spherocarb*	C3 to n-C8	>400	1200	No
CarbosieveSIII* Carboxen1000* AnasorbCMS*	-60 <sup>0</sup> C to 80 <sup>0</sup> C	400	800	No
Zeolite Molecular sieve13X**	-60 <sup>0</sup> C to 80 <sup>0</sup> C	350		No
Coconut charcoal*	-80 <sup>0</sup> C to 50 <sup>0</sup> C	>400	>1000	No

\* These sorbents exhibit some water retention

\*\* Significantly hydrophobic

Source: EPA, 1997

### 2.2.3 Sample Analysis

Gas chromatography (GC) is commonly used to separate the organic compounds. This has a tremendous advantage over other techniques, because a mixture

containing hundreds of compounds can be investigated and the components identified by this technique.

The GC technique is quite simple. The instrument consists of an injection port at one end of a metal column packed or coated with an adsorbent and a detector at the other end of the column. An inert gas propels the sample down to the column. A gas that does not react with the sample or column is essential for reliable results. For this reason, carrier gases of argon, helium, nitrogen or hydrogen are used. To ensure proper separation, the sample must enter the column in a discreet, compact packet. Thus, the sample is injected into the injection port. The injection port is maintained at a temperature at which the sample vaporizes immediately. As the sample moves through the column, the different molecular characteristics determine how each substance in the sample interacts with the column surface and packing. Some of the molecules prefer to be in the gas phase, and others prefer to be absorbed in column. This results in the partitioning of the compounds which is a separation. The compounds that prefer the gas phase reach the end of the column first, the compounds that prefer to be absorbed reach the end of the column later at a time depending on increased temperature. As the compounds emerge from the end of the column, they are detected (Rafson,1998). The detector can be a thermal conductivity detector (TCD), flame ionization detector (FID), an electron capture detector (ECD), a photoionization detector (PID), an electrolytic detector or a mass spectrometer. The signal from the detector is fed to a recorder that plots response with respect to time. The result is the familiar gas chromatogram that consists of a baseline tracing in which each compound is represented by a peak. The area of each peak can be used to determine the concentration of the compound in the original sample.

The amount of time that a compound is retained in the GC column is known as the retention time. The retention time becomes the marker that identifies that compound uniquely and allows the GC technique to qualitatively identify unknown compounds in mixtures.

### **2.2.4 Health Risks**

Benzene is found in the air from emissions from burning coal and oil, gasoline service stations, and motor vehicle exhaust. Acute (short-term) inhalation exposure of humans to benzene may cause drowsiness, dizziness, headaches, as well as eye, skin, and respiratory tract irritation, and, at high levels, unconsciousness. Chronic (long-term) inhalation exposure has caused various disorders in the blood, including reduced numbers of red blood cells and aplastic anemia, in occupational settings. Reproductive effects have been reported for women exposed by inhalation to high levels, and adverse effects on the developing fetus have been observed in animal tests. Increased incidence of leukemia (cancer of the tissues that form white blood cells) have been observed in humans occupationally exposed to benzene. EPA has classified benzene as a Group A human carcinogen. EPA calculated a range of probability of cancer incidence  $2.2 \times 10^{-6}$  to  $7.8 \times 10^{-6}$  as the increase in the lifetime risk of an individual who is continuously exposed to  $1 \mu\text{g}/\text{m}^3$  of benzene in the air over their lifetime (EPA, 2002). This index should be understood as 2.2 – 7.8 persons out of a million population exposed to the unit concentration has the additional risk of having cancer due to inhalation.

### **2.3 Previous Studies**

In a study by Müezzinoğlu et al. (2001), the ambient VOC levels in Izmir, Turkey were measured during daytime and overnight periods between mid-August and mid-September 1998. Stations were located at selected sites with dense traffic roads and junctions far from industrial sources that may contribute to airborne VOCs. Samples were collected by passing air at a constant mass flow rate through activated carbon adsorption tubes. Collected adsorption tubes were cold-stored, brought to the laboratory, extracted into carbon disulfide phase and analyzed in the laboratory by gas chromatography for benzene, toluene, *m,p*-xylene and *o*-xylene (BTX), alkylbenzenes (ethylbenzene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene), n-hexane and n-heptane. Results of this study indicated that Izmir has rather high ambient BTX concentrations compared to many polluted cities in the world. Toluene

was the most abundant VOC in Izmir air and was followed by xylenes, benzene and alkylbenzenes. The concentrations of other VOCs correlated well with benzene concentration at most sampling sites, excluding Gümüldür station located at the beach of a recreation town, indicating that ambient VOC levels were mainly affected by motor vehicle emissions. The toluene to benzene ratios for urban and non-urban sites were in good agreement with previously reported values, indicating a good relationship in between.

In another study by Bayram et al. (2005), the concentrations of volatile organic compounds have been studied in Aliğa region in Izmir, Turkey. Aliğa is surrounded by several major industries, mainly petrochemical industry, refinery and scrap iron smelters. These industries significantly contribute to the air pollution of this region. The active sampling was conducted for 10 sequential days in late March, and 7 sequential days in July, 2005 at two sampling stations concurrently. One of the stations is located at the city center of Aliğa, and the other at Horozgediği industrial area. Total VOCs refer to sum of the concentrations of 36 compounds analyzed with a gas chromatograph equipped with a mass selective detector. Total VOC concentrations in Aliğa were higher than those measured in Horozgediği in summer period. However, this trend was vice versa in winter period. 1,2-Dichloroethane, also called ethylene dichloride was the most abundant VOC, followed by toluene and benzene in Aliğa and Horozgediği.

In a recent study, urban atmospheric samples were collected in A Coruña (NW Spain) and analyzed for VOCs (Fernandez-Villarrenaga et al., 2004). In winter 2000 121 hourly samples were collected. A total of 46 VOC were studied but only 26 of them were detected and quantified. One-hour samples were taken once a week, each at a different hour to cover 24 h cycle. The aim was to study the evaluation of VOC levels along the day. The ambient air was rich in benzene, toluene, ethylbenzene and xylenes (BTX) and especially toluene (mean:  $23.6 \mu\text{g m}^{-3}$ , median:  $14.66 \mu\text{g m}^{-3}$ ), but the presence of chlorinated compounds was also notable. Multivariate analysis of VOC, trace gas ( $\text{NO}_x$ ,  $\text{NO}_2$ ,  $\text{NO}$ ,  $\text{SO}_2$  and  $\text{O}_3$ ) and meteorological variables was applied and correlations between VOC were also studied. Principal component

analysis and correlation analysis confirm traffic as the main source of VOCs in the area, although the importance of evaporative sources is also reflected.

Recently, ambient VOCs samples were collected at three locations during the periods of November 2000 - February 2001 and June 2001 - August 2001 to determine seasonal and diurnal variations of VOCs in the atmosphere of Hong Kong by Ho et al. (2004). Sites were selected for VOC monitoring according to their different landuse categories, populations and traffic densities. Three sampling locations (PolyU campus (PU), Kwun Tong (KT) and Hok Tsui (HT)) were chosen to represent the areas of urban traffic, industrial and commercial mixed and rural background. Sampling was carried out every 6 days and lasted for 24 h at the PU station, while 10 and 6 samples were collected for 24 h during each period at KT and HT stations, respectively. Also the concentrations of VOCs in Cross Harbor tunnel in Hong Kong were obtained in order to determine the vehicular sources of VOCs. Pre-cleaned and pre-evacuated 6-1 SUMMA stainless steel canisters were used to collect samples. VOCs sampled in the canister were concentrated in a NUTECH 3550A cryogenic concentrator and were injected into a HP5890A gas chromatograph coupled to a HP5973 mass-selective detector (GC/MSD). Toluene was the most abundant VOC detected in Hong Kong. At the PU station, which is close to main road, the concentrations of most VOCs were higher in summer than in winter. However, at the background location (HT), the concentrations of all VOCs except tetrachloroethene were higher in winter than in summer. Regional physical dispersion/transportation and mixing depth may be the reasons for higher VOC concentration in winter at HT. The BTEX (benzene:toluene:ethylbenzene:xylene) ratios of PU and KT during winter period were (1.9:10.1:1.0:1.8) and (1.9:10.4:1.0:1.5) and (0.9:29.6:1.0:2.2) and (0.8:29.6:1.0:1.8) for summer season, respectively. The xylene/ethylbenzene (X/E) ratio was used to assess the relative age of the air parcels in this study. The concentrations of VOCs in the atmosphere in Hong Kong were mainly affected by direct emissions from vehicles, evaporation of fuels, photochemical reactions and few industrial emissions. The BTEX ratio in the tunnel was (2:10.4:1:3.2). The BTEX ratios at PU and KT during the winter period were similar to that of the results in the tunnel (except for xylenes). The X/E ratio in



the tunnel was higher than that of in the ambient air. This indicated that the freshly emitted xylenes in the tunnel decayed at different rates from OH-oxidation in the atmosphere. Good BTEX correlations ( $r > 0.8$ ) were found at PU and KT in winter. Vehicular exhaust was the dominant source at PU and KT stations, and less evaporation of fuel or additive occurred at low temperature in winter. Diurnal variations of mean BTEX concentrations at the roadside monitoring station (PU) showed two peaks associated with traffic density and vehicle type.

In another study by Na & Kim (2001), the measurements of C<sub>2</sub>-C<sub>9</sub> volatile organic compounds were carried out at a site in Seoul, the capital of Korea from August 1998 to July 1999. Air samples were collected for 24h in 6 l SUMMA canisters every 6<sup>th</sup> day of weeks. The sampling equipment and procedure conformed with the US EPA TO-14 method. For the analysis of C<sub>2</sub> and C<sub>3</sub> VOCs, a combined gas chromatography/flame ionization detector (GC/FID) system and for the analysis of C<sub>4</sub> to C<sub>9</sub> VOCs, a combined gas chromatography/mass spectrometry (GC/MS) system were used. The species with the highest mean concentration among the 70 identified was propane (7.8 ppb), followed by toluene (6.4 ppb) and ethylene (5.9 ppb). The high concentration of propane was mainly attributed to the emissions by liquefied petroleum gas (LPG) usage for cooking and heating, and butane fuel for transportation. The general trend of the seasonal variation had higher concentrations in winter and lower ones in summer. This behavior was mainly caused by the variations of temperature, and resultant VOC source strengths, coupled with the variations of the mixing depth. According to the analysis of concentration ratios, the seasonal contributions of the major emission sources to the VOC concentrations were influenced by ambient temperature. Further, it was identified that the contributions by the use of solvents, natural gas, LPG, and butane fuel were closely related to the variations of consumption pattern according to season. By correlation analysis of the concentrations between less reactive compounds and highly reactive ones for summer and winter months, it was found that photochemical reactivity affects relative concentration of the reactive compounds.

In a recent study by Kume et al. (2008), passive air samplers were used to investigate VOC levels at multiple sampling sites in an industrial city, Fuji, Japan. The researchers determined the spatial distributions of 27 species of VOCs in three campaigns, March (cold season), May (warm season) and November (mild season) of 2004. In all campaigns, toluene (geometric mean concentration,  $14.0 \mu\text{g m}^{-3}$ ) was the most abundant VOC, followed by acetaldehyde ( $4.76 \mu\text{g m}^{-3}$ ), and formaldehyde ( $2.58 \mu\text{g m}^{-3}$ ). The spatial distributions for certain VOCs showed characteristic patterns: high concentrations of benzene and formaldehyde were typically found along major roads, whereas high concentrations of toluene and tetrachloroethylene (PCE) were usually found near factories. The spatial distribution of PCE observed was extremely consistent with the diffusion pattern calculated from Pollutant Release and Transfer Register data and meteorological data, indicated that passive air samplers are useful for determining the sources and distributions of ambient VOCs.

In another study by Ohura et al. (2005), the regional distributions of VOCs were determined in an industrial harbor city (Shizuoka, Japan) in the summer and winter of 2000. Aromatic hydrocarbons and volatile organic halogenated compounds were collected for 24h by means of passive samplers packed with activated charcoal. The concentrations of VOCs tended to be higher in winter than in summer. Significant correlations were observed between the concentrations of most of aromatic hydrocarbons in both summer and winter, and between the correlations of certain aromatic hydrocarbons and carbonyl compounds in summer, which suggest common emission sources and similar atmospheric behavior for these compounds. The results of principal component analysis indicated that vehicle exhaust and industrial activity were the predominant emission sources of the VOCs.

Concentrations of volatile organic compounds in the air reported by different researchers are summarized in Table 2.3.

Table 2.3 Measured volatile organic compounds in ambient air ( $\mu\text{g m}^{-3}$ )

Reference	Location	Benzene	Toluene	m,p-xylene	o-xylene	Hexane	Heptane	Ethyl benzene	1,3,5-trimethyl benzene	1,2,4-trimethyl benzene
Müezzi noglu et al. (2001)	Bornova	37.0	100.6	91.6	97.1	28.5	59.0	21.3	46.2	38.8
	Basmane	55.9	104.7	82.9	84.7	51.1	35.6	37.2	42.3	34.9
Bayram et al. (2005)	Horozg.W	1.4	1.8	0.4	0.3	-	-	0.1	-	-
	Horozg.S	0.5	1.0	0.2	0.1	-	-	0.1	-	-
	Aliaga W	1.4	1.9	0.4	0.4	-	-	0.2	-	-
	Aliaga S	9.9	6.1	1.4	0.9	-	-	0.3	-	-
Villarre naga et al. (2004)	A Coruña, Spain	3.4	23.6	5.1	2.7	-	1.4	3.3	0.9	4.2
Ho et al. (2004)	PU wint.	5.1	26.4	2.8	2.0	-	-	2.6	0.8	2.2
	PU sum.	3.0	26.2	4.0	3.1	-	-	3.2	1.4	2.6
	KT wint.	4.9	26.4	2.2	1.7	-	-	2.5	0.4	1.6
	KT sum.	1.7	64.3	2.3	1.6	-	-	2.2	0.4	1.5
	HT wint.	2.1	3.2	ND	ND	-	-	0.2	ND	ND
	HT sum.	0.3	1.1	ND	ND	-	-	ND	ND	ND
Na & Kim (2001)	Seoul, Korea	3.2	24.1	10.0	3.5	3.5	2.1	3.0	1.5	3.9
Kume et al. (2008)	Japan	2.1	14.0	1.8	0.6	-	-	1.5	-	-
Ohura et al. (2005)	Shizuoka, Japan									
	Summer	0.5	4.3	1.0	0.4	-	-	0.9	0.1	0.4
	Winter	0.9	6.4	1.5	0.6	-	-	1.6	0.2	0.7

## CHAPTER THREE

### MATERIALS and METHODS

#### 3.1 Sampling Site

The sampling site, Aliğa town, located 50 km north of Izmir ( $38^{\circ} 56' N - 37^{\circ} S$  and  $26^{\circ} 53' W - 27^{\circ} 10' E$ ), is one of the industrial regions with dense chemical and metallurgical industry. A petrochemical complex with as many as 17 plants, a large capacity petroleum refinery, several iron-steel industries, scrap storage and reclamation plants, a large area for ship breaking and petroleum product handling facilities exists in Aliğa. All of these plants are located in and around the Aliğa town which itself has had a quick population growth. This area is characterised by a Mediterranean climate, the mean summer temperature is  $25^{\circ}C$ , the mean winter temperature is  $7^{\circ}C$  and the mean annual rainfall is 700 mm. During the sampling periods, meteorological parameters were taken from Horozgediği monitoring station of the ENKA power plant. Average temperatures were  $2^{\circ}C$  in period 1;  $10.8^{\circ}C$  in period 2;  $26.1^{\circ}C$  in period 3;  $22.5^{\circ}C$  in period 4 and  $4.1^{\circ}C$  in period 5. The predominant wind directions in most part of the year were coming from north-north east and north. Additionally, a southerly direction in summer was noted. Windrose diagrams showing annual, summer and winter wind directions are given in Figure 3.1.

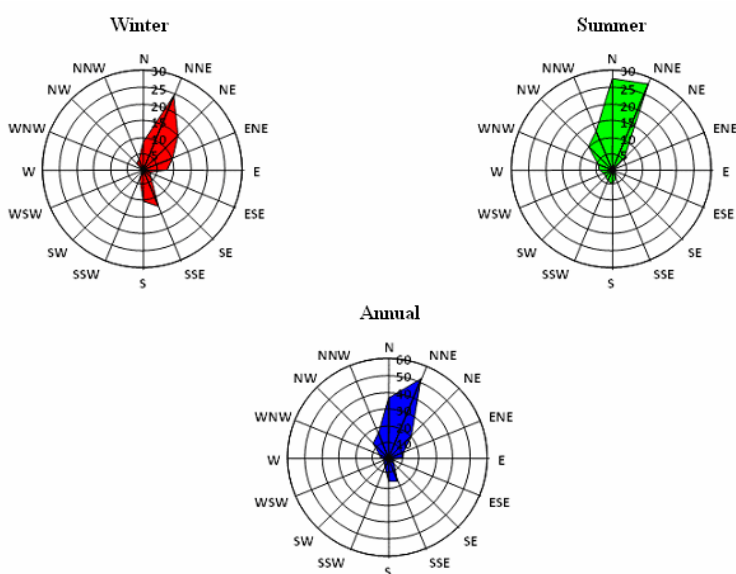


Figure 3.1 Windrose diagrams of Aliaga showing wind directions

A grid of 48 sampling points were selected for VOC sampling to cover different source categories such as stationary and mobile sources and characteristics such as topography and population density. The sampling points were selected at the corners of a 15x20 km<sup>2</sup> rectangular matrix subdivided into 2000 m grids. However, the junction points at which the samplers should have been located in the grid could not always be accessed due to lack of roads or other practical reasons. Therefore, some of the sampling points were somewhat displaced from the junction points of the grid. Location of sampling points is illustrated in Figure 3.2 and names of sampling points are given in Table 3.1.

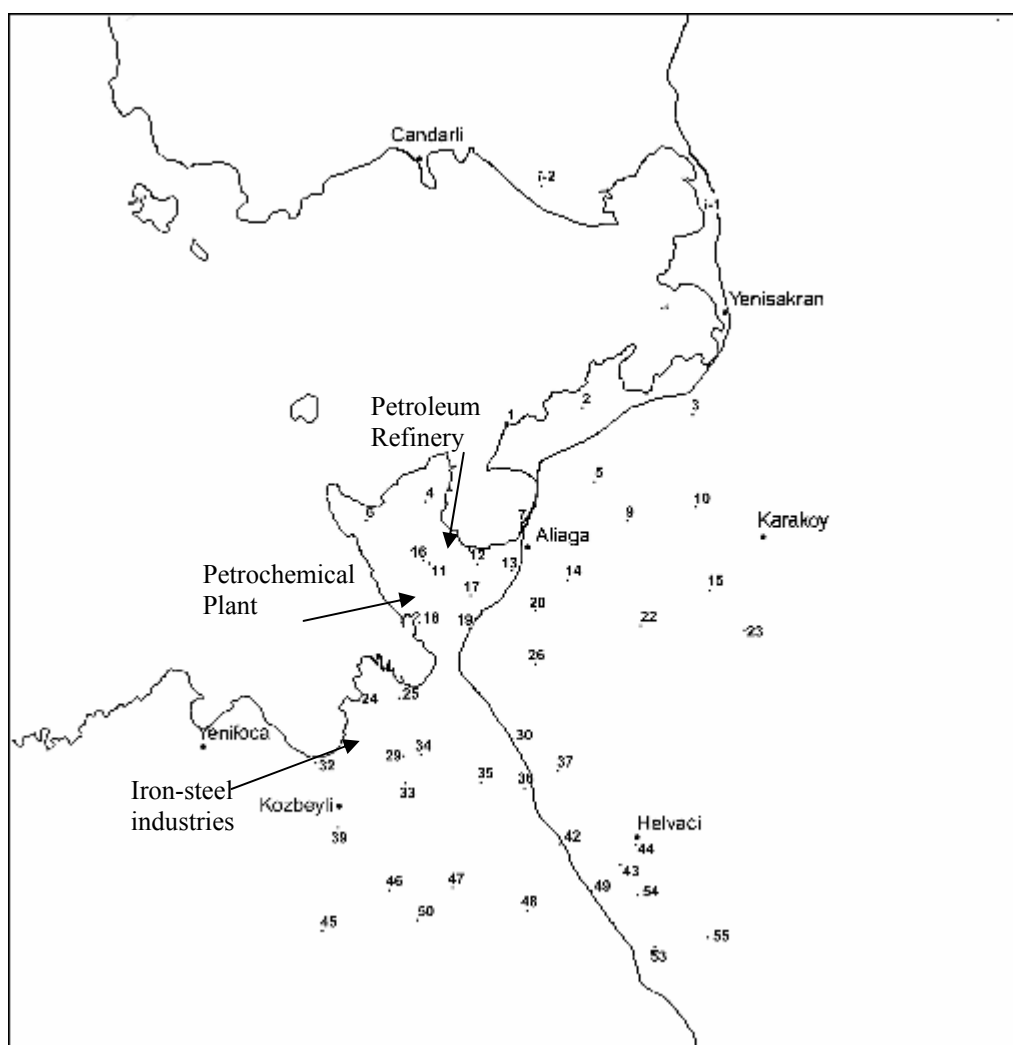


Figure 3.2 Map of Aliaga showing the location of sampling points

Table 3.1 Names of the sampling points

Point	Name	Point	Name
1	Güzelhisar çayı	29	Enka
2	Ormaniçi	30	Yeni Foça yol ayrımı
3	Asfalt Tesisi karşısı	32	Yeni Foça yolu son nokta
4	Tüpraş 2-Güvenlik kapısı	33	Koyun ahılları
5	OSB yolu üzeri	34	Betonsan karşısı
6	Yasak bölge	35	Bozköy
7	Aliağa sahili	36	Opet yanından zeytinlik içi
9	OSB yolu üzeri 2. nokta	37	Şehitkemal köyü
10	OSB merkez	39	Kozbeyli köyü
11	Tüpraş1-Petkim karşısı	42	Egepen levhası
12	Tüpraş 3-Giriş kapisi	43	Hatundere merkez
13	Otogar	44	Helvacı meydan
14	Aliağa hastanesi yol üzeri	45	Mutlu Akü levhası
15	Karaköy yol ayrımı	46	Ulupınar İlköğretim Okulu
16	Petkim çitleri	47	Devekuşu çiftliği
17	Petkim girişi	48	Foçayolu-Terkedilmiş ev
18	Petrol Ofisi liman girişi	49	Hatundere yol ayrımı
19	Petrol Ofisi girişi	50	Foça sunta
20	Hastane sonrası yol ayrımı	53	Buruncuk
22	Çıtak yol ayrımı	54	Türkelli
23	Köy yolu üzeri	55	Buruncuk-Toprak yol
24	Çakmaklı beldesi	A-1	Aliağa-1
25	Liman yolu	I-1	İncirlik
26	Köy içi çeşme	I-2	Asnur Sitesi-Çandarlı

### 3.2 Sampling

Air samples were collected during campaigns each one week period in summer and winter seasons. The five sampling periods were conducted on December 19-26,

2005, March 21-28, 2006, June 19-26, 2006, August 29-September 5, 2006 and February 9-16, 2007.

Ambient VOC air samples were collected using stainless steel sorbent tubes (Gradko Co., England) packed with Chromosorb 106 adsorbent. These tubes are 8.9 cm long and have 4.8 mm diameter and a cross sectional area of 0.18 cm<sup>2</sup>. Characteristics of Chromosorb 106 adsorbent is given in Table 3.2.

Before sampling, all tubes were conditioned by purging with 50 ml/min of pure nitrogen while heating at 225 °C for 15 min on the GC-FID to remove any organic contaminants. Randomly selected 10 tubes were analysed on the GC-FID to control the tubes. Sealed tubes with screw caps were stored and transported inside sealed glass tubes filled with silica gel and charcoal at the bottom.

Table 3.2 Characteristics of Chromosorb 106™

<b>Chromosorb 106™</b>	
Sorbent strength:	Medium
Specific surface area (m <sup>2</sup> /g):	~750
Approximate analyte volatile range:	n-C <sub>5</sub> to n-C <sub>12</sub> Boiling point 50°C to 200°C
Example analytes:	Hydrocarbons, benzene, volatile oxygenated compounds
Sorbent maximum temperature:	225°C to 250°C
Recommended conditioning temperature:	225°C to 250°C
Recommended desorption temperature:	No higher than 200°C
Notes:	High artifacts (=10ng) For trace level analysis condition at 225°C and desorb sample tubes no higher than 200°C to reduce background. Hydrophobic Inert-suitable for labile compounds

Passive sampling tubes were placed 1.5 - 2 m above the ground level with a protective shelter. They were held at the site for one-week sampling period. After sampling period, passive tubes were removed from the shelter box and open side of the tubes were closed with screw caps and put into closed glass tubes to prevent any contamination and desorption. Each sampling period, field blanks were left in place with both sealing end caps through the exposure period. At the end of the exposure period, sample tubes were resealed and stored inside the glass tubes. Passive tubes and field blank tubes were sent to the laboratory in refrigerator with a car. In the laboratory, all tubes were stored in refrigerator at  $-15^{\circ}\text{C}$ . Analyses of samples were completed within four days. European Standard (EN) 13528 was followed during sampling period.

### **3.3 Analysis**

Passive tubes were thermally desorbed by Markes Unity-Air Server Thermal Desorber. The Unity system was coupled to Agilent 6890 two-dimensional gas chromatography with FID detector. The tubes were desorbed at  $200^{\circ}\text{C}$  for 3 min by passing through a stream of pure nitrogen of 50 ml/min. The analytes were sent into cold trap and cooled at  $-15^{\circ}\text{C}$  then trap was heated at  $300^{\circ}\text{C}$  for 3 min. Gas phase analytes were carried to GC-FID for quantification. 2D-GC/FID system provides better resolution with two different types of column. Lighter compounds go through the Alumina Plot capillary column and heavier compounds go through DB1 capillary column. The first column was DB1 (60 m x 0.25 mm) with 0.1  $\mu\text{m}$  film thickness and the second column was HP Al/S (50 m x 0.32 mm) with 8  $\mu\text{m}$  film thickness. The oven temperature was programmed to start from  $40^{\circ}\text{C}$  (hold for 5 min) and increase by  $5^{\circ}\text{C}/\text{min}$  to  $195^{\circ}\text{C}$  (hold for 10 min). The flow rate of carrier nitrogen gas was 2 ml/min for each column. Quantification was performed according to External Standard Method.



### 3.3.1 Uptake Rates

The experimental uptake rates were calculated using hourly online GC-FID results. To do this passive tubes were placed under the same conditions and online GC-FID was started to make the analysis synchronously at site. Air samples were taken using a pump and an air collection system and analysed with online GC-FID to generate hourly data. After sampling programme, passive tubes were analyzed and each data set from analyzed passive tubes and online GC-FID results were compared. Although gas chromatograph was calibrated for 148 VOC species, 55 VOC species for passive tubes and 87 VOC species for online air sampling could be found. Therefore, uptake rates could be calculated for 55 VOC species. Calculated uptake rates of BTEX were  $6.5 \times 10^{-5}$  L.min<sup>-1</sup> (benzene),  $9.2 \times 10^{-5}$  L.min<sup>-1</sup> (toluene),  $9.1 \times 10^{-5}$  L.min<sup>-1</sup> (ethylbenzene),  $9.3 \times 10^{-5}$  L.min<sup>-1</sup> (*m,p*-xylene) and  $9.1 \times 10^{-5}$  L.min<sup>-1</sup> (*o*-xylene). These analyses and calculations were done in Bursa by a team member of the project using the same analytical equipment under the conditions at site.

### 3.4 Quality Assurance and Control

The quality assurance and quality control measures included laboratory and field blanks and surrogate standards. Three field blank samples and a laboratory blank sample were used in sampling period to determine if contamination has occurred during collection, transportation and storage of samples. As surrogate standard 4-Bromofluorobenzene was used to see if there was any problem in passive tubes. Prior to sampling, 1 µl surrogate standard was injected into passive tubes by passing pure nitrogen gas through the tubes at a flow rate of 50 ml/min for 5 min. 10% of samples were analyzed and checked by calculating peak areas before and end of the sampling period. The difference for surrogate standard readings at the pre- and post-sampling was less than 20%.

### ***3.4.1 Calibration***

For method calibration and quantification, a standard calibration gas including 148 VOC species were used. A calibration gas containing 2-20  $\mu\text{g m}^{-3}$  of each compound was prepared in a pressurized 15-L SUMMA polished canister. Although 148 VOC ranging from C2-C12 were identified in GC-FID, Chromosorb 106 provides determination of only 109 compounds ranging from C5-C12 due to its sorbent characteristic.

### ***3.4.2 Sampling tube cleanup***

Prior to sampling, adsorbent tubes were conditioned by passing through a stream of pure nitrogen gas at a flow rate of 50 ml/min for 15 min at 225°C to remove possible contaminants that present in tubes. 20% of conditioned tubes were randomly selected and analyzed to control the tubes. All conditioned tubes were sealed with screw caps and stored in closed glass tubes filled with silica gel and charcoal at the bottom.

### ***3.4.3 Blank samples***

Three field blank samples were used in sampling period to determine that any contamination was occurred or not during collection, transportation and storage of samples. At the end of the sampling period, blank samples stored in closed glass tubes and back to the laboratory with other sampling tubes.

### ***3.4.4 Surrogate standard***

4-Bromofluorobenzene was used as surrogate standard to determine if there was any problem in passive tubes. Prior to sampling, 1  $\mu\text{l}$  surrogate standard was injected into passive tubes by passing pure nitrogen gas through the tubes at a flow rate 50 ml/min for 5 min. 10% of samples were analyzed and check by calculating peak

areas before and end of the sampling period. The difference of surrogate standard between before and end of the sampling was less than 20%.

## CHAPTER 4

### RESULTS and DISCUSSIONS

#### 4.1 VOC Concentrations

Twenty-three VOCs were detected and quantified in Aliaga region during the five sampling periods. The VOCs concentrations are presented in Table 4.2. Styrene was the most abundant volatile organic compound, followed by 2-methylhexane and toluene with an average of  $2.10 \mu\text{g m}^{-3}$ ,  $1.65 \mu\text{g m}^{-3}$  and  $1.44 \mu\text{g m}^{-3}$ . Presence and abundance of VOCs depended on the impacts of emission sources and their proximity to the sampling sites. For example, near the petroleum refinery (sampling point 4, 11, 16, 18) the most abundant VOCs were 2-methylhexane, 3-methylhexane, benzene, toluene and xylenes with an average of  $9.79 \mu\text{g m}^{-3}$ ,  $9.55 \mu\text{g m}^{-3}$ ,  $7.19 \mu\text{g m}^{-3}$ ,  $5.19 \mu\text{g m}^{-3}$  and  $3.58$  and at the urban site at downtown Aliaga (point A1) the most abundant VOCs were styrene, toluene, benzene and n-nonane with an average of  $7.52 \mu\text{g m}^{-3}$ ,  $1.76 \mu\text{g m}^{-3}$ ,  $1.27 \mu\text{g m}^{-3}$  and  $1.23 \mu\text{g m}^{-3}$ . In general, styrene levels were unexpectedly high, in fact the highest among all VOCs measured. Especially, in period 3, levels of styrene were extremely high and they increased the average styrene concentrations for all periods. According to previous studies in this region, levels of styrene were not found as high. In further studies, styrene levels should be investigated and discussed for a final decision about this compound.

#### 4.2 BTEX Concentrations

Average concentrations of BTEX at different periods are given in Table 4.1 and Figure 4.1. Average concentrations of BTEX in winter periods were higher than those measured in summer periods. Highest of the BTEX average concentrations of was in period 2, and the lowest was in period 4. Toluene was found to be the most abundant species varying from 45–60% of the total BTEX at different periods. Benzene (16–30%) has seconded it. Average concentrations of BTEX were  $4.02 \pm 2.29 \mu\text{g m}^{-3}$  in winter and  $1.85 \pm 0.89 \mu\text{g m}^{-3}$  in summer and percentage of toluene

was found 45% in winter and 53% in summer. Similar concentration trends were observed in a study by Bayram et al. (2005) in Horozgediği Village around the iron smelters.

Table 4.1 BTEX Concentrations for the five weekly sampling periods

Periods		Benzene	Toluene	Ethyl benzene	m,p-xylene	o-xylene	BTEX
Period 1 December, 2005	Mean	0.66	1.40	0.27	0.36	0.10	2.79
	SD	0.59	0.94	0.16	0.37	0.09	2.15
	Max	2.58	3.53	0.75	1.80	0.41	9.06
	Min	0.13	0.07	0.02	0.04	0.01	0.26
Period 2 March, 2006	Mean	1.22	2.19	0.45	0.81	0.19	4.86
	SD	2.33	1.72	0.63	1.83	0.37	6.88
	Max	15.34	10.94	4.16	11.51	2.38	44.33
	Min	0.40	0.01	0.14	0.05	0.01	0.62
Period 3 June, 2006	Mean	0.27	0.91	0.14	0.18	0.15	1.65
	SD	0.33	1.02	0.14	0.27	0.29	2.05
	Max	2.20	6.06	0.83	1.40	1.65	12.13
	Min	0.00	0.17	0.01	0.02	0.00	0.21
Period 4 August – September, 2006	Mean	0.13	0.43	0.05	0.12	0.08	0.82
	SD	0.27	0.59	0.12	0.34	0.19	1.51
	Max	1.73	3.73	0.73	2.21	1.10	9.50
	Min	0.00	0.02	0.00	0.00	0.00	0.03
Period 5 February, 2007	Mean	0.78	1.56	0.06	0.13	0.08	2.60
	SD	1.17	2.52	0.12	0.28	0.18	4.29
	Max	7.52	15.80	0.56	1.36	0.90	26.14
	Min	0.05	0.14	0.00	0.00	0.00	0.20

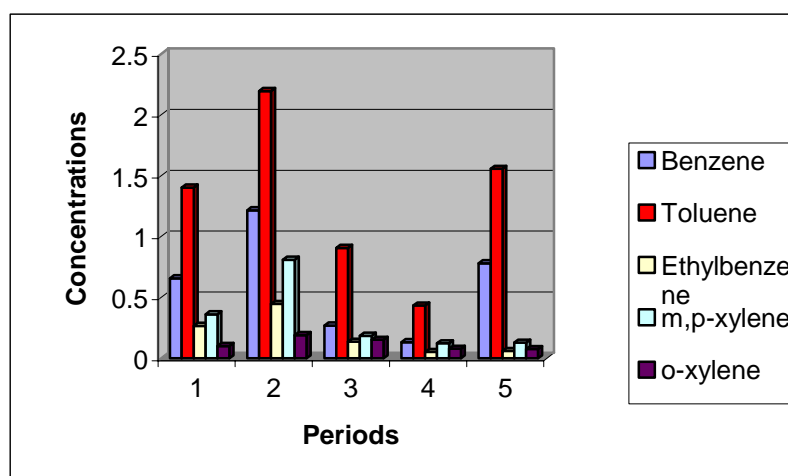


Figure 4.1. Bar diagram of BTEX concentrations measured at Aliğa for five period

Table 4.2 VOC concentrations at sampling points for the five sampling periods

Point	Benzene ( $\mu\text{g m}^{-3}$ )					Toluene ( $\mu\text{g m}^{-3}$ )					Ethylbenzene ( $\mu\text{g m}^{-3}$ )					<i>m,p</i> -xylene ( $\mu\text{g m}^{-3}$ )				
	P1	P2	P3	P4	P5	P1	P2	P3	P4	P5	P1	P2	P3	P4	P5	P1	P2	P3	P4	P5
1	0.4		0.2	0	0.2	0.9	0	0.8	0.1	0.4	0.1	0.1	0.1			0.2	0.1	0	0	
2	1.2	0.4	0	0	0.3	0.4	1.3	0.2	0.1	0.5	0.4	0.2	0		0	0.1	0.2	0	0	0
3	0.5	0.4	0.2	0	0.2	1.3	1.2	0.5	0	0.5		0.2	0.1			0.2	0.2	0.1		
4	2.6	1	0.2	0.4	3.8	3.1	2.9	0.8	1	7.8	0.7	0.5	0.1	0.1	0.6	1.8	0.7	0.1	0.3	1.3
5		0.8	0	0	0.4		1.7	0.2	0.1	0.7		0.4	0		0		0.4	0		0
6	0.2	0.6	0.1	0.1	1.5	0.6	2.7	0.5	0.3	3		0.4	0.1	0	0.1	0	0.7	0.1	0.1	0.2
7	0.3	0.6	0.2	0.1	0.6	3.5	2.2	0.6	0.2	1.1	0.2	0.4	0.2	0	0.1	0.2	0.6	0.3	0.1	0.1
9		0.6	0	0	0.3		1.6	0.3	0.2	0.6		0.3	0		0		0.3	0	0	0
10	0.5	0.5	0.1	0	0.2	1.2	4.1	0.5	0.5	4.5	0.3	0.6	0.2		0	0.3	0.5	0.1		0
11	0.2	15.3	0.6	1.7	7.5	0.9	10.9	4.1	3.7	15.8		4.2	0.8	0.7	0.5	0	11.5	1.4	2.2	1.4
12		0.9	0.3	0.1	0.8		4.9	1.7	1.2	2.6		0.5	0.3	0.1	0.1		0.9	0.4	0.3	0.2
13	0.2	1.3	0.4	0	1.3	1	3.6	1.3	0.4	1.9		0.6	0.3	0.1	0.1	0.1	1.1	0.4	0.1	0.2
14	0.5	0.6	0.1	0	0.4		1.5	0.4	0.1	0.7		0.2	0.1	0	0	0.4	0.3	0.1	0	0
15	0.3		0.2	0	0.2	2.1		0.5	0.1	0.4	0.1		0.1	0		1.5		0.1	0	
16	37	30	0.5	4.1	33.7	3.6	16.3	3.3	4	10.1	2.1	3.7	0.8	0.7	0.7	9	19	1.9	2.3	3.6
17	0.5	3	0.3	0.2	0.5	1.1	4.4	1.6	1.1	1.8	0.2	0.8	0.4	0.1	0	0.2	3.4	0.3	0.1	0.1
18			2.2	0.2	0.8			6.1	1.5	1.8			0.4	0.1	0.1			1.3	0.3	0.1
19		1	0.2	0.7	0.5		2.4	1	0.5	1		0.4	0.2	0	0		0.6	0.2	0.1	0.1
20	1	1.2	0.3	0.1	0.6	1.1	1.8	0.8	0.2	0.7	0.2	0.2	0.2	0	0	0.4	0.4	0.2	0	0
22		0.6	0.2	0	0.4		1.4	0.5	0.2	0.4		0.2	0.1	0			0.3	0.1	0	0
23	0.5	0.4	0.1	0	0.3	0.3	1.1	0.2	0.1	0.4	0	0.2	0	0	0	0.2	0.2	0	0	0
24	0.6	0.9	0.9	0.3	0.4	1.6	0.1	1.7	0.7	0.8	0.2		0.2	0.1	0	0.2		0.3	0.2	0.1
25	0.5	0.9	0.2	0.1	0.4	1.7	2.6	0.7	0.6	1	0.3	0.4	0.1	0	0	0.2	0.7	0.2	0.1	0.1
26	0.5	0.7	0.2	0	0.5	0.3	1.5	0.5	0.3	0.7	0.2	0.2	0.1	0	0	0.4	0.3	0.1	0	0
29	0.1		0.1	0.1	0.4	1.1		0.8	0.6	0.9			0.1	0.1	0	0.2		0.1	0.1	0.1
30	0.6	0.6	0.3	0	0	3.1	1.9	0.7	0.3	0.1		0.2	0.1	0		0.3	0.5	0.1	0.1	
32			0.4	0.2	0.8			1.1	0.2	2.5			0.1	0	0			0.1	0.1	0.1
33	0.5			0.1	0.5	1.7			0.3	1	0.2			0	0	0.4			0	0.1
34	0.5	0.8	0.2	0.1	0.6	2.4	2.3	1.1	0.5	1	0.3	0.4	0.1	0	0	0.6	0.5	0.1	0	0.1
35		1.4	0.3	0.2	1		2.4	0.6	0.4	1.1		0.5	0.1	0	0		0.6	0.1	0	0.1
36	0.3	0.7	0.1	0.1	0.4	0.3	1.8	0.4	0.3	0.6	0.2	0.2	0	0	0	0.2	0.3	0	0	0
37	0.4	0.5	0.2	0	0.3	0.9	1.5	0.7	0.2	0.3	0.2	0.2	0.1			0.1	0.3	0.1	0	
39	0.3	0.8	0.2	0.2	0.6	0.1	1.8	0.8	0.3	1.3	0.1	0.4	0.1	0	0	0.2	0.6	0.2	0.1	0.1
42		0.7	0.2	0.1	0.4		1.7	0.5	0.3	0.7		0.3	0.1	0	0		0.4	0.1	0	0
43	0.8	0.8	0.3	0.1	0.8	1.2	1.8	0.5	0.2	0.8	0.5	0.4	0.1	0	0	0.3	0.4	0.1	0	0
44	2	1.2	0.2	0.1	1.5	2.8	2.9	0.6	0.4	1.6	0.5	0.5	0.1	0.1	0.1	1	0.8	0.1	0.1	0.2
45	0.9	0.9	0.4	0.1	0.9	3	2	1	0.2	1.6	0.3	0.3	0.2	0		0.4	0.5	0.2	0.1	0.1
46		0.9	0.3		0.6		1.8	0.7		1.1		0.3	0.1		0		0.4	0.1		0.1
47	0.2	0.8	0.2	0.1	0.4	1.1	1.9	0.4	0.1	0.7	0.2	0.3	0	0	0	0.2	0.3	0	0	0
48		0.9	0.1	0	0.6		1.8	0.4	0.1	0.9		0.4	0		0		0.4	0.1	0	0.1
49	0.6	0.9	0.1	0	0.3	1.7	2	0.5	0.2	0.8	0.2	0.4	0.1	0	0	0.4	0.5	0.1	0.1	0.1
50		0.8	0.2	0.1	0.5		1.7	0.4	0.2	0.9		0.3	0.1	0			0.3	0.2	0	0
53	0.8	0.7	0.2	0.1	0.6	2.4	0	1.3	0.6	1.5			0.2	0		0.6		0.2	0.1	0
54	1	1.1	0.3	0.1	0.6	1.4	1.7	0.5	0.2	0.6	0.5	0.4	0.1	0		0.4	0.5	0.1	0	0
55	0.4	0.5	0.2	0.1	0.4	0.7	1.4	0.3	0.2	0.7	0.1	0.2	0.1	0	0	0.2	0.3	0	0	0
A1	2.4	0.9	0.5			1.8	1.5	2.1			0.2	0.4	0.3			0.3	0.3	0.4		
I-1	0.6		0.1	0		0.4		0.4	0.2		0.3		0	0		0.2		0.1	0	
I-2	0.2	0.7	0.1	0	0.8	0.5	2.3	0.3	0.1	0.6	0.1	0.3	0			0.4	0.5	0	0	0

Point	o-xylene ( $\mu\text{g m}^{-3}$ )					Styrene ( $\mu\text{g m}^{-3}$ )					2-Methylhexane ( $\mu\text{g m}^{-3}$ )					3-Methylhexane ( $\mu\text{g m}^{-3}$ )				
	P1	P2	P3	P4	P5	P1	P2	P3	P4	P5	P1	P2	P3	P4	P5	P1	P2	P3	P4	P5
1	0	0	0	0			1.2	10.9			0.2		0.1	1.3	0.1	0.3			0.1	0.1
2		0.1	0		0	0.4	0.8		0.2		0.2	0.3		1.1	0.1	0.6	0.6		0.1	0.1
3		0.1	0			1	0.3	14.6			0.1	0.9				3.4	0.7	0.2	0	
4	0.4	0.2	0	0.2	0.9	0.5	0.9	10.2	0.8	1	2.2	1.5		14.2	3.8	3.6	4.1		0.8	6.8
5		0.1	0		0		1.1		0.9	0.3		1.3				0.8		0.1		
6		0.2	0.1	0	0.1	0.6	0.8	6.2	0.4			1.2	0	2.5	1	0.1	1.6	0.1	0.2	1.8
7	0.1	0.1	0.1	0	0.1		0.9	10.8	0.6		0.3	0.4	0.1	1.4	0.1	0.4	1.1	0.2	0.1	0.2
9		0.1	0		0		0.3					1.2		1.5			0.7		0.1	
10		0.1	0			4.6	6.8	30.6			0.3	0.9	0	0.9		0.6	0.7	0.2	0.1	
11		2.4	1.1	1.1	0.7	0.8	2.3	7.8	0.2	2.6		5.9	0.4	26.1	4.8	0.1	10.9	2.4	1.3	9.1
12		0.2	0.3	0.2	0.1		1.4	9.3	0.7			1.3	0.2	14.1	0.3		2	0.4	0.9	0.5
13		0.3	0.4	0.1	0.2	0.6	2	12.5				1.8	0.1	2.1	0.1	0.1	2.1	0.3	0.2	0.2
14		0.1	0		0		0	1.1	0.4			0.5	0.4	1.4	0		1.2		0.1	
15			0.1			1.1		11.4	0.9		0.1		0.1	1.3		0.6		0	0.1	
16	1.4	4.1	1.6	1.4	1.8	1.1	1.4		0.1	1	2.5	9.3	0.7	71.7	2.5	16.7	15.4	3.1	4.4	4.8
17	0.1	0.6	0.3	0.1	0		1.4	2.8	1.5		0.1	14.3	0.1	2.7	0.1	0.5	50.1	0.2	0.4	0.2
18			1.6	0.2	0.1			11.2	1.5				0.5	20.5	0.3			60.4	1.3	0.5
19		0.2	0.2	0.1	0		1.7	6.8				1	0.1	3.2	0.1		1	0.2	0.1	0.1
20	0.1	0.1	0.1	0	0		1.6	11.2	0		0.3	0.6		1.9	0	0.7	1.1	0.4	0.1	0.1
22		0.1	0.1	0			0.2	12.9				0.7		1.2			0.7	0.1	0.1	
23	0.1	0.1	0	0	0	1.4	0.2	1	2.8		0.1	0.7	0.3	2		0.7	0.5		0.2	
24	0.1		0.3	0.1	0			9.7	0.9		0.3	0.2	0.1	12	0.1	1.2	0.2	2.9	0.9	0.1
25		0.2	0.2	0.1	0	0.7	1.6	0.3	0.5		0.4	1.4	0.3	5.8	0	0.8	3.8	0.6	0.4	0.2
26	0.2	0.1	0.1	0	0		0.7	1.7			0.4	0.5	0.1	3	0	0.6	0.6	0.2	0.2	0
29			0.1	0.1	0	0.7		0.7	1.1				0.2	2.5	0	0.1		0.1	0.2	0.1
30		0.1	0.1	0		1.3	0.3	13			0.5	0.5		1.5		0.6	0.6	0	0.1	
32			0.1	0	0			8.3						4.8	0.5			0.7	0.4	0.7
33	0.1			0	0	0			0.5		0.4			2.2	0	0.5			0.2	0.1
34		0.1	0.1	0	0	0.9	1.6	5.5	0		0.6	0.7		2.4	0	0.9	1	0.1	0.1	0
35		0.2	0.1	0	0		2	1.5	0.3	0		0.4	0.2	1.7	0		0.6	0.2	0.1	0
36		0.1	0		0	1.2	0.7	1		0.1	0.3	0.5	0.2	0.6	0	0.6	0.8		0.1	
37	0.1	0.1	0				0.2	6.3	1.5		0.2	0.5		1.3		0.4	0.6		0.1	
39		0.2	0.1	0.1	0	0.4	1.3	1	0.1		0.2	0.5	0.2	4.7	0.2	0.5	1.3	0.8	0.4	0.3
42		0.1	0.1	0	0		0.9	0.7	0.3			0.3	0	1.5	0		0.6	0.2	0.1	
43		0.1	0.1	0	0	0.8	1.7	8.4			0.3	0.9		1.6	0	0.8	0.7	0.1	0.1	0
44		0.2	0.1	0.1	0.1	1.3	2.2	2	0.1	0	0.7	0.8		1.9	0.2	1.5	1.1	0.1	0.1	0.2
45	0.2	0.1	0.1	0	0	0	1	9.9	1.1	0	0.4	0.6	0	20.9	0.2	1.1	1.3	0.6	0.2	0.4
46		0.1	0.1		0		0.6	8.8				0.6			0.1		0.8	0.1		0.1
47	0	0.1	0		0		0.8	2.3	1.3		0.4	0.5	0.2	1.3	0	0.5	0.7		0.1	1.6
48		0.1	0	0	0		1.4	2.3		0.6		0.9	0	1			1	0.6	0.1	0.1
49	0.1	0.1	0.1	0	0		2.7	2.1	0.2		0.2	0.6		1.4	0	0.3	0.9	0	0.1	0
50		0.1	0.1	0	0		1.6	1.4	1.4			0.5	0.2	1.5	0		0.9	0.2	0.1	0.1
53			0.2	0		1.4		1.2			0.1	0.1		1.4	0	10.4		0.1	0.1	0
54	0.1	0.1	0	0	0		5.6	2.9			0.4	0.5	0.4	1.5	0	1.1	0.8		0.1	
55		0.1	0	0	0	0.2	0.4	14.1	1		0.2	0.4	0	1.1		0.3	0.5		0.1	
A1	0.1	0.1	0.4				1.9	13.2			0.5	0.8	0.3			0.5	1.1	0.4		
I-1			0	0		1.6		0.6			0.2			1.8		0.7		0.1	0.1	
I-2	0	0.1	0		0		1.2	1.4			0.2	0.8			0.1	0.2	0.8		0.1	0.1

Point	2,2,4-Trimethylpentane ( $\mu\text{g m}^{-3}$ )					Methylcyclohexane ( $\mu\text{g m}^{-3}$ )					2-Methylheptane ( $\mu\text{g m}^{-3}$ )					N-Octane ( $\mu\text{g m}^{-3}$ )				
	P1	P2	P3	P4	P5	P1	P2	P3	P4	P5	P1	P2	P3	P4	P5	P1	P2	P3	P4	P5
1	0			0		0.1			0	0	0.3	0	0		0	0.4			0	0
2	0.1			0		0.1	0		0			0.3		0.1	0.1	0.6	0.3		0	0
3	0.1	0				0.2	0.1				0.4	0.3	0.1		0	0.5	0.2	0.1		
4	0.2	0		0.1	0.5	1.2	0.2		0.1	1.3		0.5	0	0.4	2.5	5.5	0.4	0	0.6	4.1
5		0		0			0.1		0			0.3			0		0.2			0
6	0	0.1			0.1		0.2		0	0.4	0.1	0.6	0		0.4	0	0.7	0	0.1	0.6
7	0	0		0		0.2	0		0	0		0.4	0.1		0.1	0.1	0.3	0.1		0
9		0		0			0.1		0			0.3					0.2			
10	0	0				0	0.1					0.4	0.1	0.1	0	0.2	0.2	0		
11	0	0.6	0.2	0.1	0.8		2.6	0.8	0.5	2	0.1	3.1	1.3	1.5	1.8	0	3.7	5.2	2.8	3.8
12		0		0.1	0		0.2	0.1	0.3	0.1		0.8	0.2	0.6	0.1		0.7	0.9	1.5	0.2
13	0	0.1	0		0		0.2		0	0	0.1	0.8	0.1		0.1	0	0.6	0.5	0.1	0
14		0		0		0	0.1		0			0.4		0	0	0	0.3	0.1	0	
15	0		0.1	0					0		3		0.1	0		1.2		0		
16	0.3	1	0.3	0.4	0.5	1.9	3.7	1.1	1.2	1.1		6.8	1.7	2.5	1.1	0.6	9.4	9.1	7.3	2.1
17		0.8				0	2	0	0	0	0.3	0.8			0	0	1.4	0.2	0.2	0.1
18			0.7	0	0			1.9	0.1	0.1			0.2		0.1			5.1	0.5	0.1
19		0		0			0.1	0	0	0		0.4	0.1		0		0.2	0.2		0
20	0	0		0		0	0	0	0			0.3	0.1		0	0.2	0.2	0.3	0	
22							0.1		0			0.3	0	0			0.2	0.1	0	
23	0			0		0.1	0.1		0			0.3		0		0.6	0.3		0	
24	0		0	0		0		0.2	0.1	0			0.2	0.3	0	0.4		0.8	0.3	0
25	0	0		0		0	0.1	0	0		0.4	0.4			0	0.3	0.3	0.1	0.1	
26	0	0	0	0		0.1	0		0			0.3		0.1	0	0.1	0.2	0	0.1	
29	0			0					0		0.1				0	0		0	0	
30	0.1	0		0		0.2	0		0		0.6	0.3	0			0.7	0.2	0		
32			0.1	0	0	0.9		0	0	0.1			0.1	0.1	0.1			0.2	0.1	0.2
33				0		0			0	0				0.1	0	0.3			0	0
34	0	0		0		0.1	0.1		0			0.4	0.1		0	0.5	0.3	0.1		
35				0			0		0	0		0.4			0		0.2	0		0
36	0	0				0	0.1					0.3		0.1	0	0.3	0.2			
37		0		0		0	0		0		0.3	0.3	0			0.1	0.2	0		
39		0		0	0	0.1	0.1	0	0	0.1		0.4		0.1	0.1	0.2	0.3	0.2	0.1	0.1
42				0			0		0			0.3			0		0.2	0		
43	0	0		0		0	0.1				0.5	0.4	0	0	0	0.4	0.3	0.1		0
44	0.1	0		0		0	0		0	0	0.9	0.5	0.1		0.1	0.3	0.2	0		0
45	0	0		0	0	0.2	0.1	0	0	0.1	1	0.4	0.1	0.1	0.1	0.8	0.4	0.2	0.1	0.1
46		0					0			0		0.4	0.1		0.1		0.2	0.1		0.1
47		0				0.1	0					0.5		0	0	0.4	0.2			
48		0		0			0.1					0.4			0		0.3			
49	0	0				0	0				0.4	0.4	0		0	0.2	0.3	0		0
50		0		0			0		0	0		0.3	0		0		0.3			0
53	0			0		0			0		0.6	0.1				0.4		0		
54	0			0		0	0		0		0.5	0.3			0	0.3	0.2			
55	0			0		0	0	0.2			0.3	0.3	0	0.1	0	0.1	0.1			
A1	0	0	0			0.1		0				0.4	0.1			0.2	0.2	0.4		
I-1				0		0.1			0							0.6		0		
I-2	0	0		0		0	0			0		0.5		0	0	0	0.2			0



Point	Isopropylbenzene ( $\mu\text{g m}^{-3}$ )					N-Propylbenzene ( $\mu\text{g m}^{-3}$ )					3-Ethyltoluene ( $\mu\text{g m}^{-3}$ )					4-Ethyltoluene ( $\mu\text{g m}^{-3}$ )				
	P1	P2	P3	P4	P5	P1	P2	P3	P4	P5	P1	P2	P3	P4	P5	P1	P2	P3	P4	P5
1	0.5	0.8	0.8	0.1		0.7	0.1		0			0.1	0.1			0	0	0.2		
2	1	0.4		0		0.4	0.1		0	0	0.1	0.1			0	0	0.1			0
3	1.2	0.8	1.4			0.3	0.1	0			0.4	0.1	0.1			0.1	0	0		
4	1.1	1.3	0.7	0.1	0.1	0.1	0.2	0	0.1	0.1	0.2	0.2	0.1	0.1	0.4	0.7	0.1	0.1	0.1	0.2
5		0.9					0.1					0.1					0.1			
6		0.7	0.1	0			0.1	0	0.1	0		0.2	0.1	0	0		0.1	0.1		0
7	0.5	0.9	1.5	0		0.7	0.1	0.1	0		0	0.3	0.2	0	0	0.1	0.2	0.2		
9		0.4	0.1	0			0.1		0			0.1					0.1			
10	1.1	0.5	0	0.1		0.2	0.1	0			0.4	0.1	0.5			0.1	0.1	0.2		
11		2.1	0.9	0.2	0.1		0.4	0.4	0.1	0.1		1	1.1	0.3	0.3		0.7	0.9	0.1	0.2
12		0.8	1.2	0.2			0.1	0.1	0.1			0.3	0.3	0.1			0.3	0.2	0.1	
13		1.2	0.8	0.1			0.2	0.1	0.1	0		0.5	0.4	0.1	0.1	0	0.3	0.2		0
14	0.1	0.4		0.3			0.1	0	0			0.1	0				0.1	0		
15	0.5		1	0.2				0	0		0.2		0.1			1		0.1		
16	0.3	1.7	0.6	0.7	0.1		0.3	0.4	0.2	0.1	0.2	2	1.1	0.5	0.2	0.3	1.3	0.9	0.3	0.1
17	0.1	0.7		0.2		0	0.1	0	0.1		0.1	0.5	0.2	0		0.1	0.3	0.1		
18			1.3	0.1				0.1	0.1				0.3	0.1	0			0.2	0.1	
19		0.8	0.1	0			0.1	0	0			0.2	0.1	0	0		0.2	0.1		
20	0.5	0.2	0.4	0.1		0	0	0.1	0		0.2	0.1	0.2			0.1	0.1	0.1		
22		0.5	0.9	0.6			0.1	0	0			0.1	0.2	0			0.1	0.1		
23	0.9	0.5		0.1		0.3	0.1	0	0		0.1	0	0			0	0	0		
24	0.6		1.2	0.1		0.1		0.1	0		0.2		0.2	0.1		0.1		0.1		
25	0.8	1				0.1	0.2	0	0		0.4	0.3	0.1	0		0.2	0.2	0		
26	0.2	0.4	0.2	0.2		0.2	0.1	0	0	0	0.2	0.1	0			0.1	0.1	0		
29	0			0.7				0	0.2				0	0	0			0	0	
30	0.9	0.5	1	0		0.5	0.1	0	0		0.1	0.1	0.1			0.1	0.1	0.1		
32			1.1					0	0				0.1			0.1		0.1		
33	0.3			0.1					0		0.1					0.1				
34	0.7	1.3	1.4			0.1	0.1	0.1	0		0.2	0.2	0.1			0.1	0.1	0		
35		1.4	0.1				0.2	0	0			0.2	0				0.2	0		
36	0.9	0.6	0.8	0.4		0.1	0.1		0		0.4	0.1			0	0.1	0.1			
37	0.9	0.5	0.7	0.1		0.2	0.1	0	0		0.4	0.1	0			0.1	0.1	0		
39	0.4	1.4		0.1		0.1	0.2	0	0		0.1	0.2	0.1	0		0.1	0.1			
42		0.8	0.3	0			0.1		0			0.1	0				0.1	0		
43	0.7	0.9	1.6			0.3	0.1	0	0		0.3	0.3	0.1			0.2	0.3	0.1		
44	0.7	0.5		0.1		0.3	0.1	0	0.1	0	0.4	0.4	0.1	0.1	0.1	0.4	0.3	0.1	0	0
45	1	0.6	0.5	0.1		0.7	0.1	0	0.1	0	0	0.1	0.1	0		0.2	0.1	0.1		
46		0.6	0.6				0.1			0.2		0.1	0.1				0.1	0.1		
47	0.5	0.7	0.1	0.1		0.5	0.1		0			0.1		0		0	0.1	0		
48		0.9	0.1	0			0.1					0.2	0		0		0.1	0		
49	0.5	0.6	0.2	0.1		0.3	0.1		0.1		0.3	0.2	0	0		0.2	0.2	0		
50		0.7		0.1			0.1		0			0.2		0					0	0
53	0.6			0		0		0	0		0.3		0.2	0		0.4		0.1		
54	0.4	0.6	0.2	0.1		0.3	0.2	0	0		0.2	0.4	0			0.2	0.3	0		
55	0.2	0.5	0.9	0.2		0.1	0.1		0.1		0.1	0.1	0.1			0.1	0.1	0.1		
A1	0.4	0.8	1.4			0.4	0.1	0.1				0.3	0.3			0.3	0.2	0.2		
I-1	0.3		0.2			0.1		0	0		0.2		0			0.1		0		
I-2	0.4	0.6	0.3	0.1			0.1		0		0	0.2				0	0.1			

Point	1,3,5-Trimethylbenzene( $\mu\text{g m}^{-3}$ )					2-Ethyltoluene ( $\mu\text{g m}^{-3}$ )					1,2,4-Trimethylbenzene ( $\mu\text{g m}^{-3}$ )					N-Decane ( $\mu\text{g m}^{-3}$ )				
	P1	P2	P3	P4	P5	P1	P2	P3	P4	P5	P1	P2	P3	P4	P5	P1	P2	P3	P4	P5
1	0.1					0					0.1	0.7	0.1	0.1		0.4		0		
2	0.1				0	0.1	0		0	0.1	0.2	0.4		0.2	0	0.1	0.1		0.2	0.1
3	0.1					0	0				0.5	0.5	0.1	0		0.3	0.1	0.1		
4	0.2	0		0	0.1	0.2	0	0		0.1	0.6	0.8	0.1	0.3	0.5	3.4	0.2	0.1	0.4	0.9
5							0					0.7					0.2	0		
6		0				0	0	0	0	0	0	0.5	0.2	0.3	0.1		0.3	0.3	0	0.1
7	0.2	0.2	0			0	0.1	0	0	0	0.2	0.7	0.3	0.2	0.1	0.9	0.3	0.6	0	
9							0					0.3			0		0			
10	0.2					0	0	0			0.3	0.4	1.1	0		1.7	0.1	0.1		
11		0.3	0.2	0.1	0.1	0	0.3	0.5	0.1	0.1	0	1.6	1.8	0.7	0.4		2.3	5.6	0.8	0.6
12		0.1	0.1	0			0.1	0.2	0	0		0.6	0.6	0.4	0		0.5	1.5	0.5	0
13		0.1	0.1	0	0	0.3	0.2	0.1	0	0		0.9	0.6	0.3	0.2		0.5	0.9	0.1	0
14	0.1					0.1	0	0			0	0.4	0	0	0	0.1	0.2	0.1		
15	0.1					0		0			0		0.1	0.1		0.3		0.2		
16	0.1	0.6	0.2	0.1	0	0.1	0.7	0.7	0.2	0	0.3	1.8	1.7	0.8	0.3	1.2	3.8	5.1	1.6	0.5
17	0	0.2	0			0	0.1	0	0		0.2	0.7	0.3	0.2	0	0.1	1.3	0.4	0.1	
18			0.1	0				0.1	0	0			0	0.3	0			5.6	0.7	0
19		0.1	0				0.1	0		0		0.6	0.3	0.1	0		0.3	0.4		
20	0.1		0			0.1	0	0			0.2	0.2	0.4	0.2		0.2	0.1	0.5	0	
22							0	0				0.4	0.2	0			0.1	0.2		
23	0.3					0	0	0			0	0.4	0.1	0.2		1.3	0.1	0.1		
24	0.2		0	0		0		0	0		0.3		0.3	0.2		0.2		0.6	0.4	
25	0.2	0.1	0			0	0.1	0			0.5	0.7	0.1	0.2	0	0.4	0.4	0.2	0.1	
26	0.2					0	0	0			0.4	0.4	0.1	0.1	0	0.2	0.1	0.2	0.2	
29						0.3		0		0			0.1	0.4	0			0.2	0.1	
30	0.2	0.1				0	0	0			0.2	0.4	0.1	0.1		0.2	0.2	0.2	0.1	
32								0					0.1	0.1				0.5		
33	0.1					0					0.1			0.2		0.3			0	
34	0.2	0				0	0	0			0.3	0.6	0.1	0.1		0.4	0.4	0.3		
35							0.1	0				0.6	0	0	0		0.3	0	0	
36	0.2	0			0	0	0			0	0.5	0.4	0	0	0	0.1	0.2	0		
37	0.2					0	0				0.6	0.4	0.1	0.1		0.2	0.1	0.1		
39	0.1	0				0	0	0	0		0.1	0.5	0.1	0.2		0	0.3	0.1	0	
42							0		0			0.5	0	0			0.2	0.2	0.1	
43	0.4					0	0.1	0			0.5	0.5	0.1	0	0	0.4	0.4	0.2	0	
44	0.5	0.1		0	0	0.1	0.1	0	0	0	0.6	0.6	0.1	0.4	0.1	0.3	0.1	0.1	0.1	
45	0.2		0			0.1	0	0		0	0.3	0.4	0.2	0.3		0.6	0.2	0.3	0	
46							0.1	0				0.5	0.1		0		0.2	0.1		
47	0.1					0		0			0.2	0.4	0	0.2	0	0.2	0.1		0	
48							0			0		0.4	0	0.1	0		0.1	0		
49	0.2					0.1	0	0	0	0	0	0.5	0.1	0.3	0	1.1	0.4	0.1	0	
50							0		0			0.6	0.1	0.2			0.2	0		
53	0.2		0			0		0.1	0		0		0.3	0.2		0.7		0.4	0	
54	0.3	0				0.1	0				0	0.6	0	0.1		0.7	0.2	0.1		
55	0.1					0	0	0			0.1	0.4	0.2	0.3		0.1	0.1			
A1	0.2		0.1			0.1	0	0.1			0.1	0.6	0.6			0.6	0.2	0.6		
I-1	0.2		0			0		0			0.2		0.1	0.1		1.2		0.2		
I-2	0					0	0				0.1	0.5		0		0.2	0.3		0	

Point	1,3-Diethylbenzene ( $\mu\text{g m}^{-3}$ )					1,4-Diethylbenzene ( $\mu\text{g m}^{-3}$ )				
	P 1	P 2	P 3	P 4	P 5	P 1	P 2	P 3	P 4	P 5
1			0			0		0		
2							0		0	
3						0	0	0		
4	0.1		0	0	0.1	0.6	0.1	0	0.1	0.1
5					0.7		0.1			
6						0	0.1	0.2		
7			0			0.2	0.2	0.6		
9										
10	0.2		0.1			0.2	0	3.2		
11		0.4	0.2	0	0.1		3.7	0.6	0.3	0.1
12			0				0.1	0.2		
13	0	0.1			0	0	0.2	0.1		
14						0	0			
15	0.4					0.6		0.3		
16	0.1	0.5	0.2	0.1		0.1	4.2	0.7	0.4	
17		0.6	0.1			0.1	1.4			
18			0.4					0.5		
19			0				0.1	0.1		
20	0.7		0			0	0	0.7	0.1	
22			0				0	0.1		
23	0.1					0.1	0	0.6		
24			0			0.2		0.1		
25	0	0			0.1	0.2	0.2			0.1
26						0.1		0		
29			0.3			0		0.7		
30	0					0.1	0	0.1		
32										
33	0					0				
34						0.1	0.1	0.1		
35		0					0.1			
36						0	0.1	0		
37						0	0	0		
39	0					0.1	0.1	0		
42			0				0.1	0		
43	0.1					0.4	0.1	0.2		
44	0.3	0.1	0			0.3	0.1	0.1		
45	0					0.1	0.2	0.1	0	
46							0.1	0.2		
47				0		0.1	0.1		0.1	
48					2		0.1			
49	0	0				0.2	0.1			
50		0					0.1			
53	0.1					0.1				
54	0.1	0.1				0.3	0.1			
55						0.1		0.8		
A1	0.1	0	0.1			0.1	0.1	0.1		
I-1						0.1				
I-2							0.1			

### **4.3 The Effects of Petrochemical Complex and Petroleum Refinery on Aliaga Atmosphere**

Pollution maps of BTEX are plotted as Figure 4.2 for period 1, Figure 4.3 for period 2, Figure 4.4 for period 3, Figure 4.5 for period 4 and Figure 4.6 for period 5. In all figures, higher BTEX levels are shown near petroleum and petrochemical industries. The effects of petrochemical industry on Aliğa atmosphere depended on wind directions. In period 1, the south and south-south west of Aliğa were polluted by these industries due to air movements over the area from north-north easterly directions. Likewise, the south and south-south west of Aliğa was affected from same wind directions in period 2. In addition, relatively high levels of BTEX in the north of Aliğa was found due to southerly wind direction. In Helvacı village at south, due to winds from north west and north-north west and topographical conditions, the pollutants from petrochemical industry might have reached. In period 3, the south and south west of Aliğa were polluted by petroleum and petrochemical industries due to winds from north and north-north east. In period 4, there is no significant effect of these industries on ambient air of Aliğa compared to other periods. In period 5, generally due to south-south easterly wind direction, north-north west of Aliaga was influenced by industrial activities. Especially, when focused on toluene and benzene, south west of the town was polluted due to winds from north east.

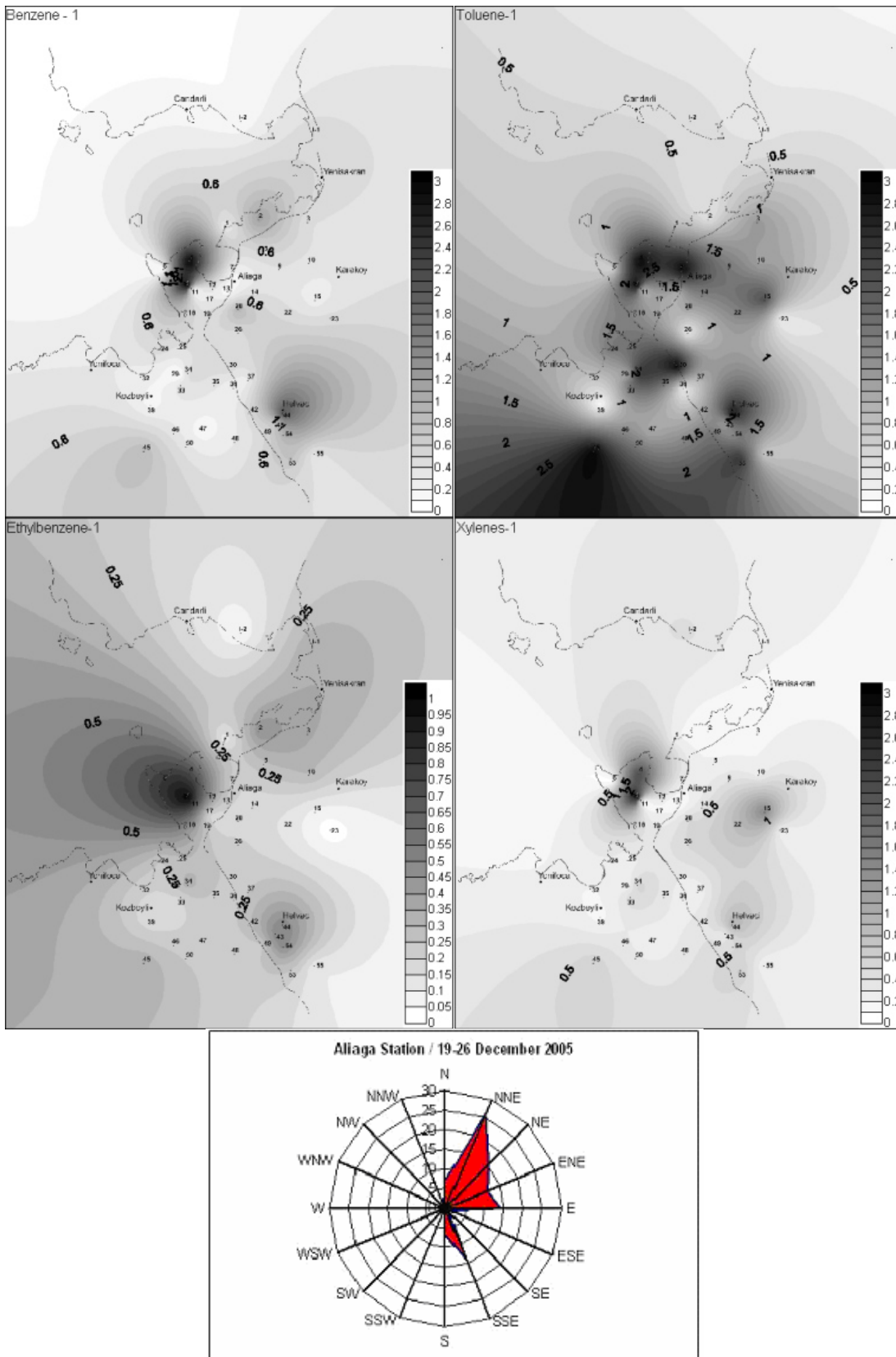


Figure 4.2. Pollution maps of BTEX for Period 1

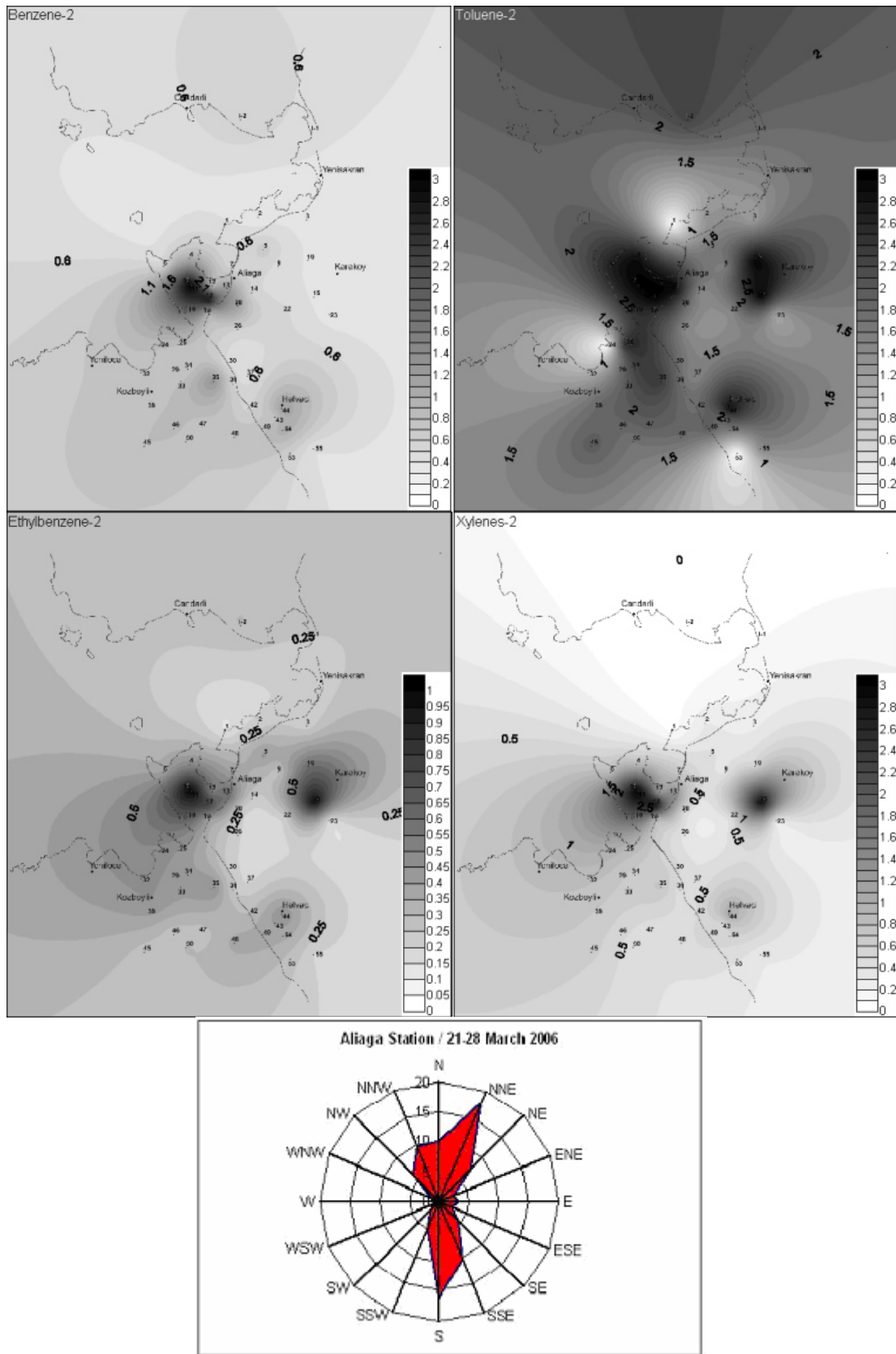


Figure 4.3 Pollution maps of BTEX for Period 2

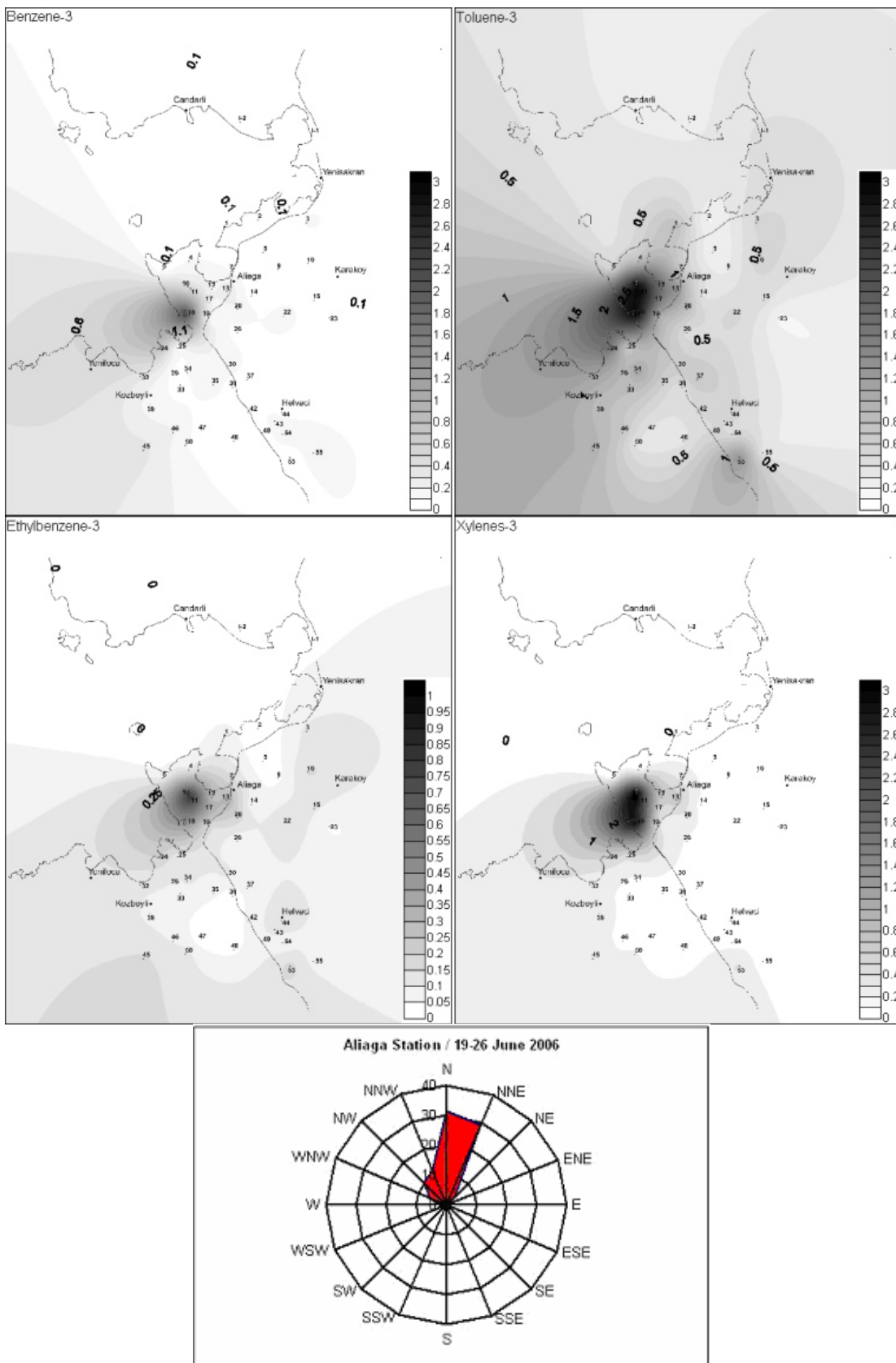


Figure 4.4 Pollution maps of BTEX for Period 3

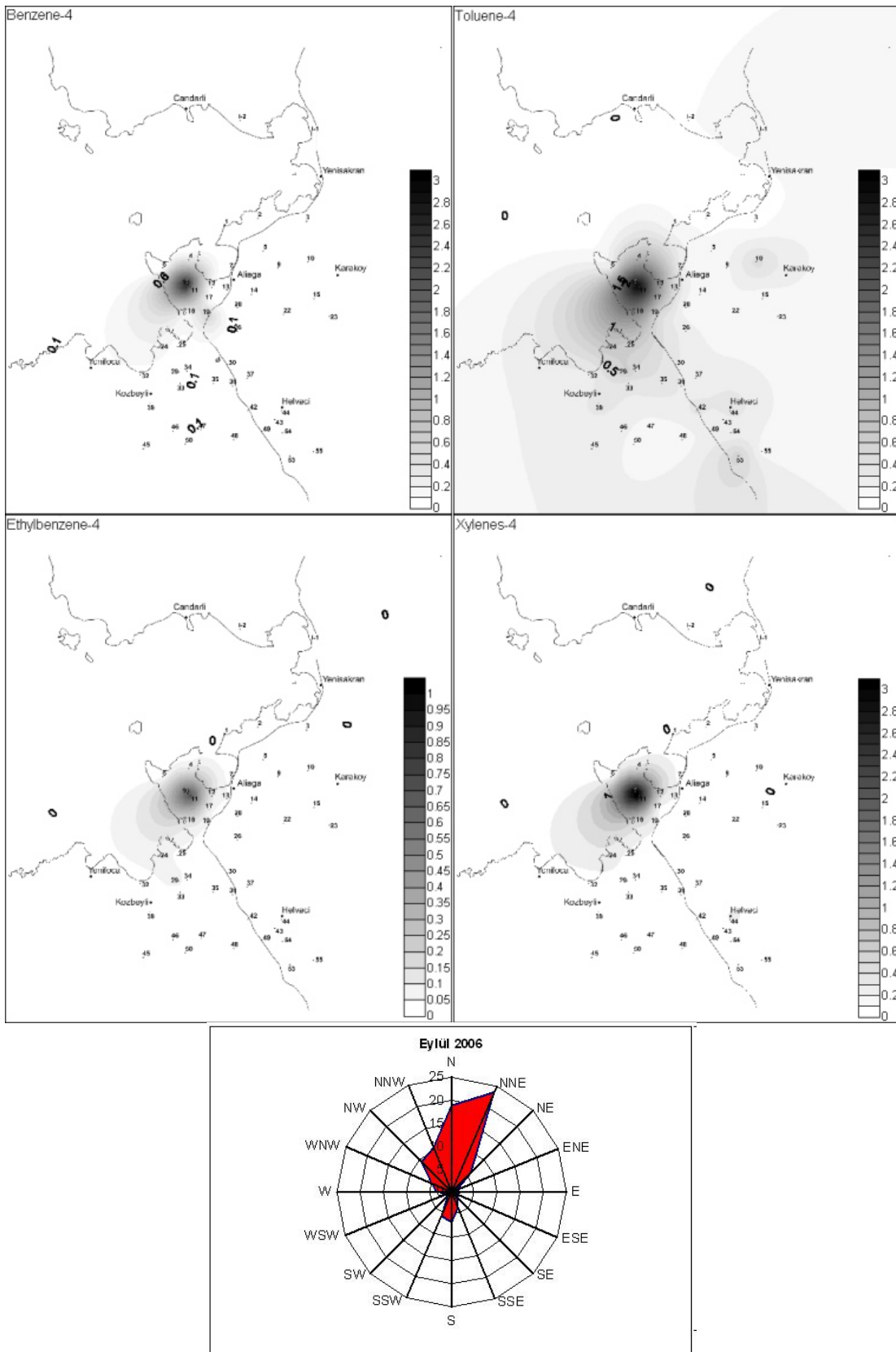


Figure 4.5 Pollution maps of BTEX for Period 4



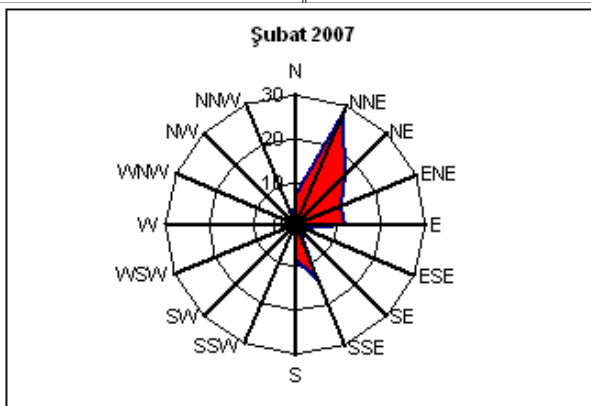
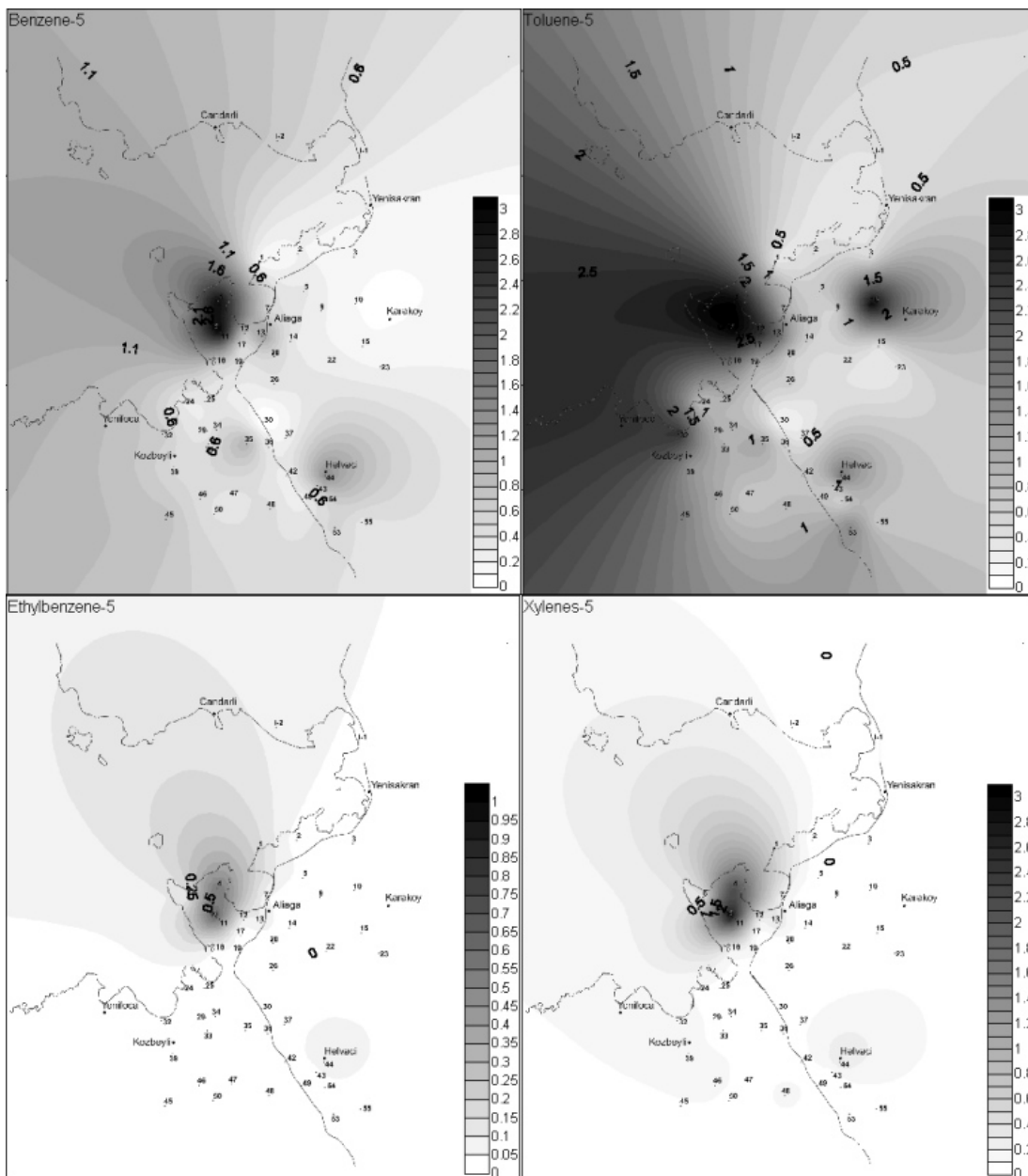


Figure 4.6 Pollution maps of BTEX for Period 5

#### 4.4 Seasonal Variations

The seasonal variation of BTEX concentrations is illustrated in Figure 4.7. Seasonal trends can be addressed by the seasonal characteristics of the prevailing meteorology, variations in the source strength and, most importantly, the availability of OH radicals due to intense insolation that take care of the removal process of the VOC species from the atmosphere (Hoque et al., 2008)

The levels of BTEX were relatively higher in winter as compared to summer periods. The cause of low levels of BTEX in summer might be because of the effects of higher temperatures and sunlight. These increase higher chemical removal reaction rates (Ho et al., 2004). Therefore the winter BTEX concentrations were higher than those in summer. In addition, temperature inversion, and lower mixing heights are more common in winter months and they restrict dilution of the pollutants. Thus in the winter months the pollutants generally show a higher level of concentration (Hoque et al., 2008).

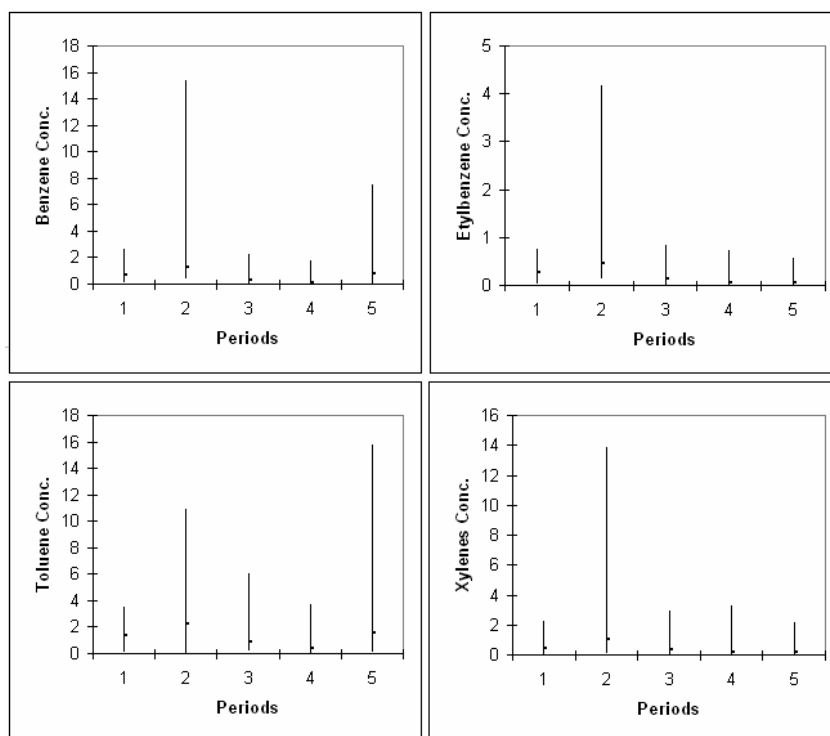


Figure 4.7 Seasonal variation of BTEX concentrations at five periods

#### 4.5 BTEX Ratios

Concentration ratios of BTEX compounds were calculated for the sampling periods. The ratio between benzene, toluene, ethylbenzene and xylenes (*m,p*-xylene + *o*-xylene) concentrations based on the normalization by minimum level (in this study ethylbenzene) were found. The average BTEX ratios were **2.5:5.3:1.0:1.5** for 1. period, **2.7:4.9:1.0:2.2** for 2. period, **2.0:6.7:1.0:2.5** for 3. period, **2.5:8.3:1.0:3.6** for 4. period and **13.0:25.9:1.0:3.3** for 5. period. The different ratios have possibly reflected impacts of different VOC sources in the area between periods, random changes in source strengths and perhaps both.

#### 4.6 T/B Ratios

Besides the BTEX ratios based on ethylbenzene, also the toluene to benzene (T/B) concentration ratios were determined to discuss the possible sources of VOCs. Toluene to benzene ratio has been commonly used as an indicator of traffic emissions (Dincer et al., 2006). In a study by Lee et al., (2002), T/B ratio increases with increasing traffic volume, industrial emissions and other urban sources in denser areas. For example a T/B ratio of 2.0 was reported from studies on vehicle exhaust (Scheff & Wadden, 1993). T/B ratios were found as 2.1 for 1. period; 1.8 for 2. period; 3.4 for 3. period; 3.3 for 4. period and 2.0 for 5. period. In winter (period 1, 2 and 5) vehicle exhaust was the main source of VOCs. However, it is clear that industrial activities also affected the air pollution as source of VOCs especially during 3 and 4 th periods.

In a sample taken from inside of petroleum refinery (point 16), the average concentration of benzene for all periods was  $21.05 \mu\text{g m}^{-3}$ , the average concentration of toluene for all periods was  $7.43 \mu\text{g m}^{-3}$  and the T/B ratio was 0.35. This low B/T ratio is because of high emissions of benzene from the petroleum refinery.

Pollution maps of T/B ratios were plotted as Figure 4.8 for period 1, Figure 4.9 for period 2, Figure 4.10 for period 3, Figure 4.11 for period 4 and Figure 4.12 for period

5. In all periods, T/B ratios were about 2-2.5 at main road of Aliğa which is more likely due to the effects of traffic. In addition, some points originating from different sources are notable in these maps. Especially the main industrial locations contribute to increased T/B ratios according to these maps.

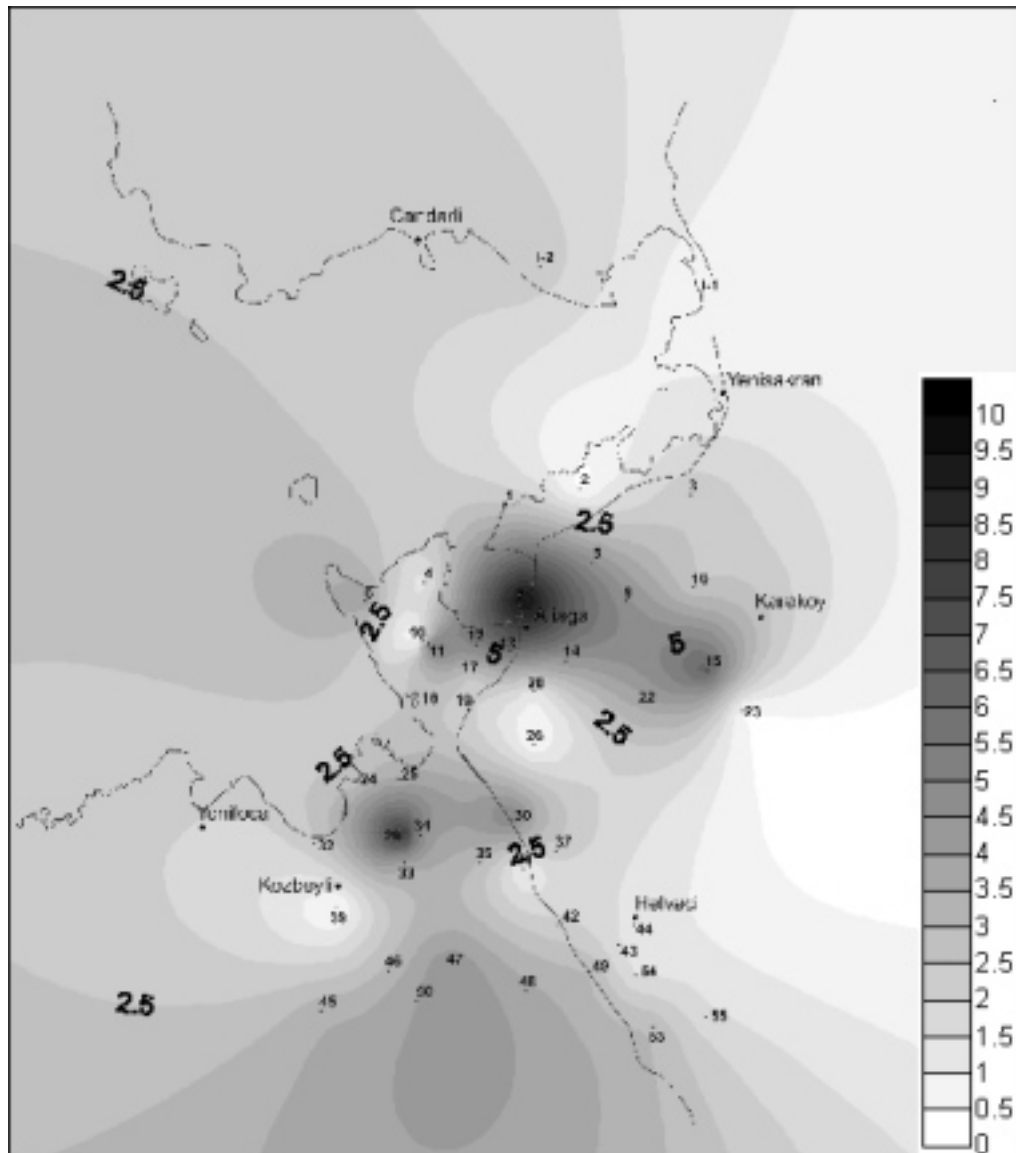


Figure 4.8 T/B ratios at period 1

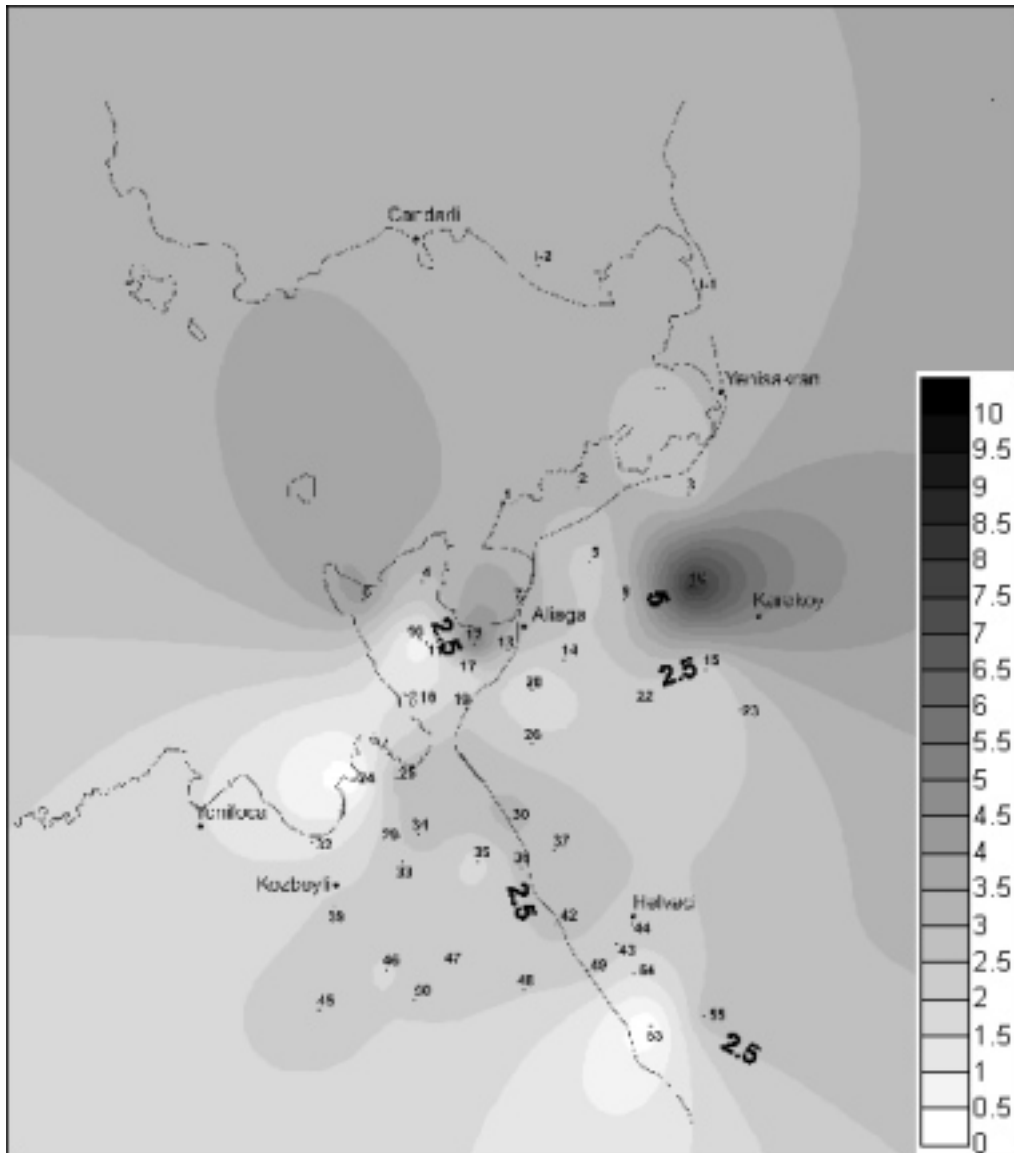


Figure 4.9 T/B ratios at period 2

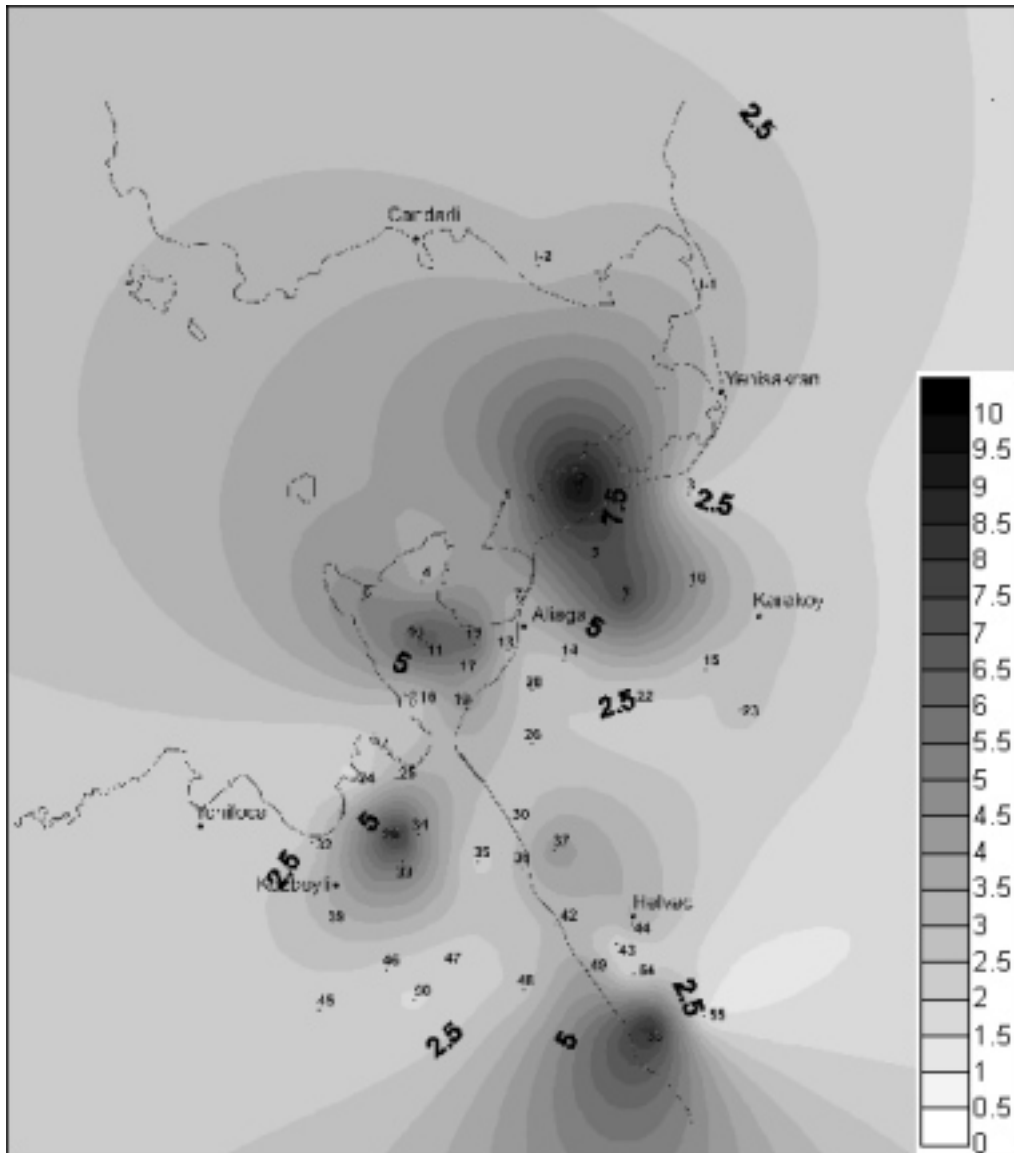


Figure 4.10 T/B ratios at period 3

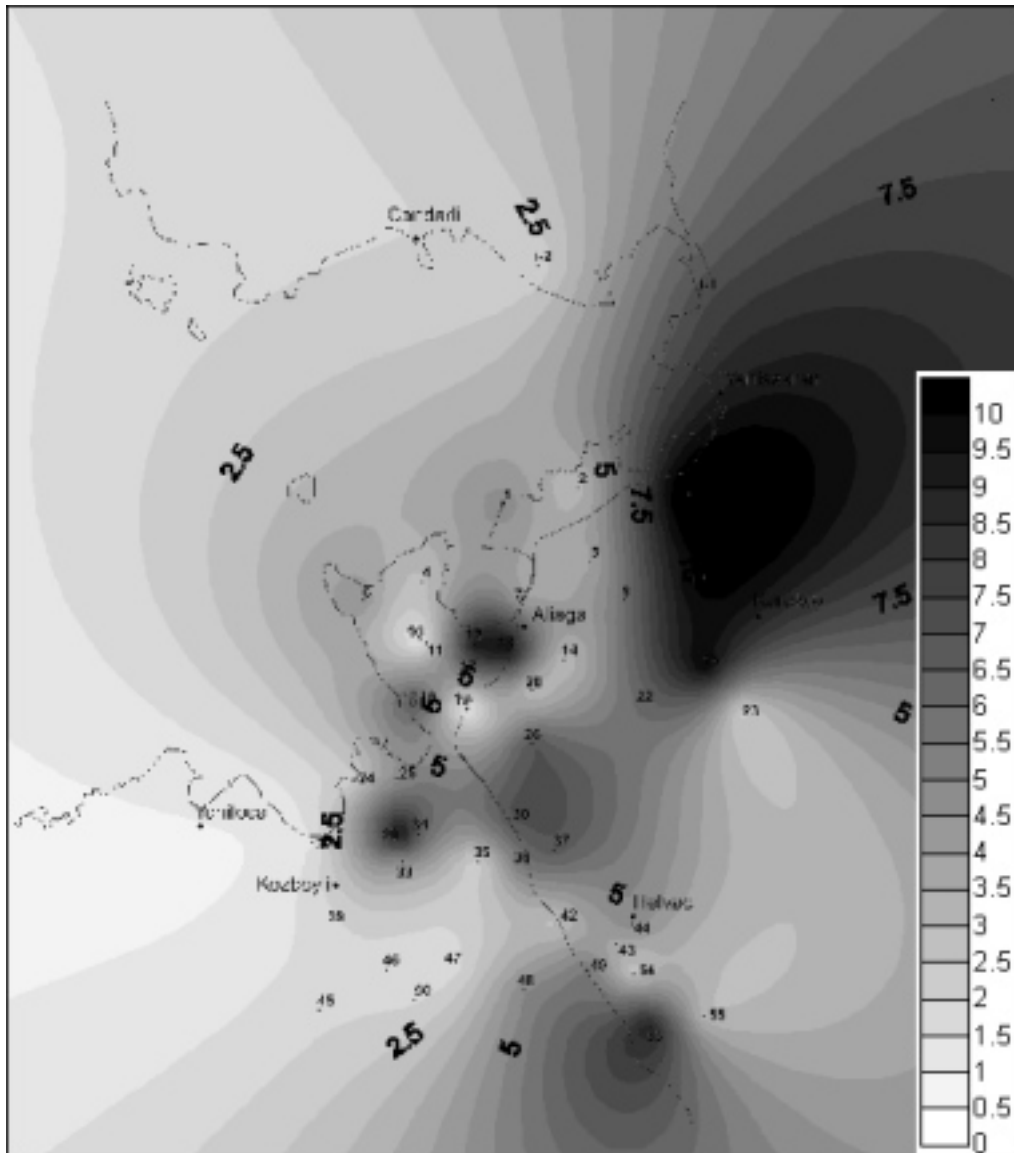


Figure 4.11 T/B ratios at period 4

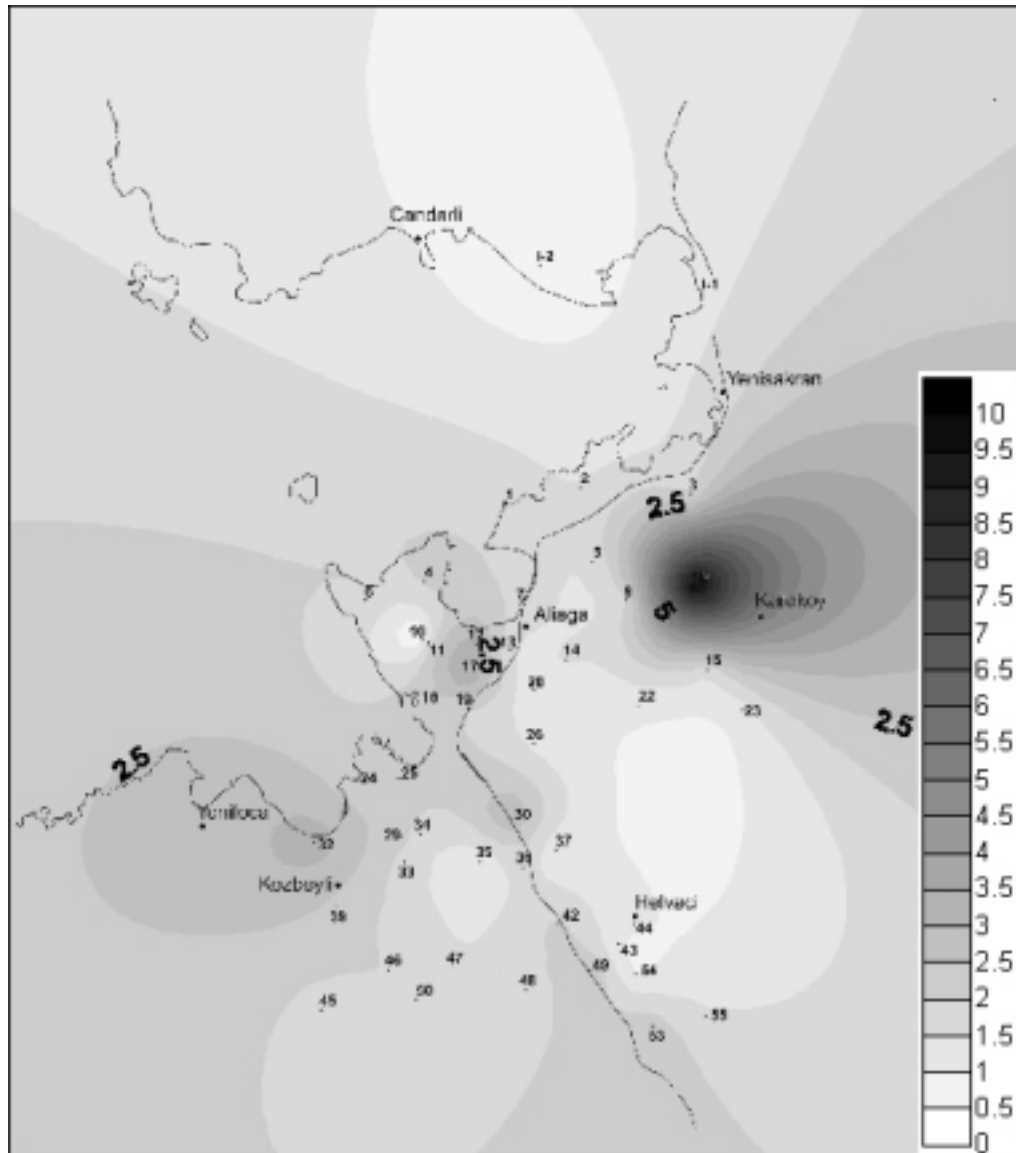


Figure 4.12 T/B ratios at period 5

#### 4.7 BTEX Correlations

As shown in Table 4.3, in order to identify the relationship between benzene, toluene, ethylbenzene, m,p-xylene and o-xylene and determine possible sources of these compounds, the correlation analysis was applied. Relatively good correlations between the BTEX compounds were obtained for the study periods except period 1. There were strong correlations among BTEX, suggesting a common source for these compounds. In period 1, poor correlations of BTEX were identified and it shows the presence of different sources for benzene and toluene. In all periods, ethylbenzene



and xylenes were well correlated with each other, suggesting that they came from the same sources.

Table 4.3 Summary of BTEX correlation coefficients (r) for all periods

	Benzene	Toluene	Ethylbenzene	m,p-xylene	o-xylene
<b><i>1.period</i></b>					
Benzene	1.00	-	-	-	-
Toluene	0.42	1.00	-	-	-
Ethylbenzene	0.66	0.43	1.00	-	-
m,p-xylene	0.57	0.52	0.44	1.00	-
o-xylene	0.80	0.55	0.82	0.88	1.00
<b><i>2.period</i></b>					
Benzene	1.00	-	-	-	-
Toluene	0.86	1.00	-	-	-
Ethylbenzene	0.99	0.92	1.00	-	-
m,p-xylene	0.99	0.91	0.98	1.00	-
o-xylene	0.99	0.92	0.99	1.00	1.00
<b><i>3.period</i></b>					
Benzene	1.00	-	-	-	-
Toluene	0.89	1.00	-	-	-
Ethylbenzene	0.58	0.83	1.00	-	-
m,p-xylene	0.77	0.95	0.92	1.00	-
o-xylene	0.88	0.98	0.82	0.97	1.00
<b><i>4.period</i></b>					
Benzene	1.00	-	-	-	-
Toluene	0.88	1.00	-	-	-
Ethylbenzene	0.93	0.96	1.00	-	-
m,p-xylene	0.94	0.94	0.99	1.00	-
o-xylene	0.93	0.95	0.99	0.99	1.00
<b><i>5.period</i></b>					
Benzene	1.00	-	-	-	-
Toluene	0.95	1.00	-	-	-
Ethylbenzene	0.91	0.88	1.00	-	-
m,p-xylene	0.94	0.91	0.99	1.00	-
o-xylene	0.88	0.88	0.99	0.99	1.00

#### 4.8 Health Risks at Aliaga Region

Benzene is a known carcinogen and continuous exposure to  $1 \mu\text{g m}^{-3}$  produces a lifetime risk of  $2.2 \times 10^{-6} - 7.8 \times 10^{-6}$  for leukaemia (EPA, 2002). It means that if an individual were to continuously breathe air containing benzene at the range of 1.3 to  $4.5 \mu\text{g m}^{-3}$  averaging  $1 \mu\text{g m}^{-3}$  over his or her entire lifetime, that person would theoretically have no more than a one-in-a-hundred thousand increased chance of developing cancer as a direct result of continuously breathing air containing this chemical. Usually,  $5 \mu\text{g m}^{-3}$  is considered as a practical limit (ENDS, 1996). Benzene levels in excess of this limit found at petrochemical industry and refinery and maximum value measured in this study was  $37.05 \mu\text{g m}^{-3}$ . Thus it is concluded that this may present a significant hazard to workers in these workplaces. Generally, there was no significant cancer risk due to benzene in the urban area of Aliaga.

Some different VOCs such as formaldehyde, chloroform, 1,4-dichlorobenzene, acetaldehyde and naphthalene also have cancer risks. Due to the lack of adequate data for these compounds, their risk factors could not have been investigated. The risk factors of these compounds should be investigated by further studies. Also, the human health effects other than carcinogenesis should be studied with suitable methods in future studies.

## CHAPTER 5

### CONCLUSIONS

This study was performed to investigate the concentration levels of VOCs, especially BTEX, in Aliaga urban and industrialization region. A sampling program was conducted between December 2005 and February 2007. Ambient air samples were collected using stainless steel sorbent tubes packed with Chromosorb 106 adsorbent. Ambient concentrations obtained from the experimental studies were evaluated by comparing them to the values reported in the literature.

Although active samplers have the advantage of being able to collect a precise volume of air in a short time, using them to survey a large number of points simultaneously is difficult mainly because of the lack of electricity at many points in the field. In this study, passive samplers were used because of the advantages of producing inexpensively, using to investigate many sampling points simultaneously and locating emission sources in a particular area.

Twenty-three VOCs were detected and quantified in Aliaga region for five periods. Styrene was the most abundant volatile organic compound, followed by 2-methylhexane and toluene with an average of  $2.10 \mu\text{g m}^{-3}$ ,  $1.65 \mu\text{g m}^{-3}$  and  $1.44 \mu\text{g m}^{-3}$  in the Aliaga region. In general, styrene levels were unexpectedly high, in fact the highest among all VOCs measured. Especially, in period 3, levels of styrene were extremely high and they increased the average styrene concentrations for all periods. According to previous studies in this region, levels of styrene were not found as high. In further studies, styrene levels should be investigated and discussed for a final decision about this compound.

Maximum average concentration of BTEX ( $4.86 \pm 6.88 \mu\text{g m}^{-3}$ ) was found in period 2 while minimum average concentration of BTEX ( $0.82 \pm 1.51 \mu\text{g m}^{-3}$ ) in period 4. Toluene was found to be the most abundant species varying from 45–60% of the total BTEX at different periods followed by benzene (16–30%).

Average concentrations of BTEX in winter periods were higher than those measured in summer periods. This is because of the effects of higher temperatures and sunlight on reactions that destroy the BTEX compounds in the air in summer. It is known that the reaction rates for such chemical removal are higher for such reactions at higher temperatures and strong insolation. In addition, temperature inversion and low mixing heights restrict dispersion of the pollutants and they are more frequent in winter. That might be the reason VOC levels were generally higher in the winter measurements than those in summer.

The highest VOC concentrations were measured at the sampling sites near petrochemical complex and refinery. There has been a relationship between high VOCs in the ambient air of Aliaga town and the wind directions bringing in pollutants from the emissions of petrochemical plant and refinery. Generally, the south and south west of Aliaga were affected by these industries due to air movements over the area from northerly directions.

Average BTEX ratios were calculated to compare the VOCs measured at the five sampling periods. Normalized over the ethylbenzene, benzene:toluene:ethylbenzene (=1):xylene ratios on the average BTEX values were 2.5:5.3:1.0:1.5 for 1. period, 2.7:4.9:1.0:2.2 for 2. period, 2.0:6.7:1.0:2.5 for 3. period, 2.5:8.3:1.0:3.6 for 4. period and 13.0:25.9:1.0:3.3 for 5. period. The different ratios reflected that changing sources were effective on the VOC concentrations of these sites between periods. At one time traffic and at another industrial activities might have been more important.

In addition to BTEX ratios, toluene to benzene (T/B) ratios were studied to identify the possible sources of VOCs. From studies elsewhere scientists put forth a T/B ratio of 2.0 is due to emissions from vehicles in traffic (Scheff & Wadden, 1993). In Aliaga T/B ratios were 2.1 for 1. period; 1.8 for 2. period; 3.4 for 3. period; 3.3 for 4. period and 2.0 for 5. period. It was noted that at wintertime (periods 1, 2 and 5) vehicular exhaust was the main source of VOCs. However, industrial activities were affecting the air pollution with VOCs in summer. Also geographical

distribution was important in Aliaga. In a sample taken from inside of petroleum refinery, the average concentration of benzene was  $21.05 \mu\text{g m}^{-3}$ , the average concentration of toluene was  $7.43 \mu\text{g m}^{-3}$  thus a T/B ratio as low as 0.35 was calculated. This low T/B ratio shows high emissions of benzene from petroleum refinery.

In order to identify the relationship between benzene, toluene, ethylbenzene, m,p-xylene and o-xylene and determine possible sources of these compounds, correlations between the compounds were calculated. Relatively good correlations between BTEX compounds were obtained in periods except for period 1. Good correlations showed a common source of these compounds. In period 1, poorer correlations of BTEX were identified and it shows the change of source composition for benzene and toluene.

The inhalation cancer risks of benzene from ambient air were also evaluated and in urban area a significant cancer risk was not found. However benzene levels were higher than  $5 \mu\text{g m}^{-3}$  in petrochemical and refinery region and there was a risk for people who worked in these industries and lived in these areas.

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