SPATIAL DISTRIBUTION OF ORGANIC POLLUTANTS IN BURSA ATMOSPHERE: SEASONALITY AND HEALTH EFFECTS

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MİHRİBAN YILMAZ CİVAN

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submitted by **MİHRİBAN YILMAZ CİVAN** in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Environmental Engineering Department, Middle East Technical University by,

Prof. Dr. Canan Özgen Dean, Graduate School of **Natural and Applied Sciences**

Prof. Dr. Göksel Demirer Head of Department, **Environmental Engineering**

Prof. Dr. Gürdal Tuncel Supervisor, Environmental Engineering Dept., METU

Examining Committee Members:

Assoc. Prof. Dr. İpek İmamoğlu Environmental Engineering Dept., METU

Prof. Dr. Gürdal Tuncel Environmental Engineering Dept., METU

Prof. Dr. Gülen Güllü Environmental Engineering Dept., Hacettepe University

Assoc. Prof. Dr. Ayşegül Aksoy Environmental Engineering Dept., METU

Assist. Prof.Dr. Beyhan Pekey Environmental Engineering Dept., Kocaeli University

Date: 15.02.2010

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

Name, Last name : Mihriban Yılmaz Civan

Signature :

ABSTRACT

SPATIAL DISTRIBUTION OF ORGANIC POLLUTANTS IN BURSA ATMOSPHERE: SEASONALITY AND HEALTH EFFECTS

YILMAZ CİVAN, Mihriban Ph.D., Department of Environmental Engineering Supervisor: Prof.Dr. Gürdal TUNCEL February 2010, 358 pages

The assessment of volatile organic compounds (VOCs) has become an area of particular interest in the field of atmospheric pollution due to their adverse health and environmental effects. This study is aimed to identify, quantify and characterize VOC in different urban areas and industrial areas in Bursa. The spatial distribution, seasonal variation as well as health risks assessment of VOC were discussed. Air samples were collected by means of sorbent passive sampling at over 50 sampling points in Bursa and analyzed by GC-thermal desorption. A total of seven weekly measurement periods were completed across the city center from 2005 to 2007. The source of VOC was apportioned with the commonly used receptor model, namely Factor Analysis. Motor vehicles and industrial solvent usage are the most abundant VOC sources to contribute to urban atmosphere in Bursa, 63% and 20%, respectively. The health risks of VOC were also evaluated. The questionnaire was filled out by selected people living in Bursa to obtain time-activity pattern for health risk assessment. Lifetime cancer risks were estimated with the measured VOC data. All the statistical parameters used to represent cancer risks for the selected compounds exceeded the stated level. Benzene had the highest adverse health effect among these compounds according to USEPA (2009) calculation with the mean cancer risk 3x10⁻⁴.

In addition to intensive field sampling campaigns conducted in Bursa, the VOC measurement were completed for a period of six months to evaluate uptake rate of VOC in Ankara. Uptake rate equations depending on relative humidity and wind speed were developed for 25 VOCs.

Keywords: Volatile Organic Compounds, passive sampling, uptake rate, health risk assessment, spatial distribution, receptor modeling

ÖΖ

BURSA ATMOSFERİNDE ORGANİK KİRLETİCİLERİN MEKANSAL DAĞILIMI: MEVSİMSELLİĞİ VE SAĞLIK ETKİSİ

YILMAZ CİVAN, Mihriban Doktora, Çevre Mühendisliği Bölümü Tez Danışmanı: Prof.Dr. Gürdal TUNCEL Şubat 2010, 358 sayfa

Uçucu Organik Bileşikler (UOB)'in değerlendirilmesi, sağlık ve çevre üzerinde olumsuz etkilerinden dolayı atmosferik kirlilik çalışmalarıda özel bir öneme sahip olmaya başlamışlardır.Bu çalışmanın amacı Bursa'nın farklı endüstri ve kentsel bölgelerinde UOB tespit etmek, tanımak ve değerlendirmektir. UOB'lerin mekansal dağılımı, mevsimsel değişimi ve ayrıca sağlık riski değerlendirmesi yapılmıştır. Pasif örnekleme ile Bursa'da 50'den fazla noktada hava numunesi toplandı ve örnekler GK-ısısal desorpsiyon cihazı ile aniliz edildi. 2005-2007 yılları arasında şehir genelinde 7 defa haftalık örneklemeler yapıldı. UOB'lerin kaynak belirleme çalışmasında faktör analizi tekniği kullanıldı. Motorlu taşıtşar ve endüstride kimyasal kullanımı Bursa'da en baskın UOB kaynağı olarak 63% ve 20% hesaplanmıştır. Sağlık riski calısmasında, Bursa'da yaşayan insanların zaman-aktivite dağılımlarını hesaplamak için seçilen bir qrup insana anket çalışması uygulanmıştır. Ömür boyu kanser riski, oluşturlan UOB veri seti kullanılarak tahmin edilmiştir. Kanser riskini temsil eden bütün istatistiksel parametreler bazı seçilmiş UOB'ler için belirlenen sınır değer üstünde çıkmıştır. EPA'dan alınan hesaplama yöntemine göre bu kirleticiler içinde ortalama değeri 3x10⁻⁴ ile benzen en yüksek riske sahip kirleticidir.

Bursa'da yapılan yoğun arazi çalışması yanında, UOB'lerin tutma sabitlerini belirlemek için Ankara'da 6 ay süren bir arazi çalışması yapılmıştır. Toplam 25 UOB için göreceli neme ve rüzgar hızına bağlı denklemler oluşturulmuştur.

Anahtar Kelimeler: Uçucu organik bileşikler (UOB), pasif örnekleme, sağlık riski değerlendirmesi, tutma sabiti, mekansal dağılım, kaynak modellemesi

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LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
BV	Breakthrough Volume
BTEX	Benzene, Toluene, Ethylbenzene,m,p&o Xylenes
CDF	Cumulative Distribution Function
CFA	Conventional Factor Analysis
СМВ	Chemical Mass Balance Model
ED	Exposure Duration
EV	Explained Variation
FA	Factor Analysis
FID	Flame Ionization Detector
GC	Gas Chromatography
GoF	Goodness of Fit Test
LR	Linear Regression
MDL	Method Detection Limit
METU	Middle East Technical University
MFC	Mass Flow Controller
MLR	Multiple Linear Regression
ODS	Ozone Depleting Substance
PCA	Principle Component Analysis
PDF	Probability Distribution Function
PAMS	Photochemical Assessment Monitoring Station
PMF	Positive Matrix Factorization
RRF	Relative Response Factor
RSD	Relative Standard Deviation
SMW	State Meteorological Works
SPSS	Statistical Package for the Social Sciences
SSI	State Statistical Institute
SVOC	Semi Volatile Organic Compounds
TD	Thermal Desorption
UR	Uptake Rate
VOC	Volatile Organic Compound

CHAPTER 1

INTRODUCTION

1.1 Background

Several gas phase pollutants are emitted into the troposphere as a result of human activities. Until the last few decades, inorganic air pollutants such as sulphur dioxide (SO₂), nitrogen oxides (NO_x) and carbon monoxide (CO) had been considered to affect air pollution level in urban atmosphere. The reasons of continuous monitoring of sulphur dioxide and nitrogen oxides are that they contribute to the acid deposition as dry-deposited gases or in dissolved form in precipitation, fog or cloud. In the last two decades, Volatile Organic Compounds (VOCs) concentration has been found in the atmosphere with the help of advanced instrumental and analytical techniques. The VOC levels in the atmosphere are important due to both their direct health effects and indirect contribution to tropospheric ozone formation.

The term 'Volatile Organic Carbons' generally refers to numerous organic species. Harper (2000) defines VOC as compounds that are normally present in the vapor phase at room temperature (vapor pressure greater than 0.1 mmHg (0.0133 kPa) at 25 ^oC. VOC are also defined by Watson et al. (2001) as sum of the Non Methane Hydrocarbons (NMHCs), heavy hydrocarbons, carbonyl compounds and halocarbons.

Emissions of VOC into the troposphere occur in various forms and from anthropogenic and biogenic sources (Atkinson, 2000). Important emission source categories include natural, mobile, and stationary sources. Transportation is by far the most important source of atmospheric VOCs; aliphatic and aromatic hydrocarbons are released from exhaust pipes of vehicles or by evaporation from gas tank or from hot engine (Badol et al., 2008 and Bauman et al., 1992). These non-exhaust emissions are collectively called "evaporative" emissions. Stationary sources which contribute to VOCs concentrations in the troposphere are fossil fuel combustion, gasoline-oil storage, and industrial solvent use, emission from industrial operations, landfills, solid waste disposal and hazardous facilities (Roukos et al., 2009; Badol et al., 2008; Arya, 1999; Davis and Otson, 1996). In addition to anthropogenic sources, some VOCs, including isoprene and series of monoterpenes, and oxygenated VOC (Tiwarey et al., 2007; Arey et al., 1990; Winner et al., 1992), are emitted from vegetation. In urban atmosphere, emissions from motor vehicles are the largest contributor to urban air quality (Schmidt and Schafer, 1998; Ghose et al., 2004).

VOCs play an important role in formation of harmful oxidants, such as tropospheric ozone and peroxyl acetyl nitrate (PAN) through complex photochemical reactions in the troposphere. Tropospheric ozone has adverse impacts on human health and vegetation. Recently, a number of VOCs have been identified as carcinogens or suspected carcinogens in the urban environment (EPA, IRIS, 2009; Mohamed, 2002).

The difficulty of attaining the O_3 standard is due to the fact that O_3 is not a primary pollutant and is produced from a complex series of non-linear reactions involving VOCs and NO₂ in the presence of sunlight (Atkinson, 2000). Although a number of studies were conducted to understand the spatial-temporal distribution of O_3 and its relationship with meteorological conditions and with other air pollutants (Wang et al., 1998, 2001, 2003; Chan et al., 1998; Lam el al., 2001), there is little knowledge about the roles of VOC and NO₂ in the formation of ozone in urban atmosphere. In this study, VOC, NO₂ and O₃ concentrations were determined in urban atmosphere to identify possible sources and their impacts on ozone formation. Research on the determination of individual VOC, NO₂ and O₃ concentrations is required to take action to reduce ozone concentration. Only very limited research exists on organic air pollutants in Turkey. Unfortunately, there has also been limited research conducted to identify atmospheric levels and sources of individual organic air pollutants and to determine their effects on the ozone formation.

1.2 Purpose

The main purpose of this study is to investigate the spatial distributions of volatile organic compounds, and other conventional air pollutants (NO₂, SO₂ and O₃) and their associated health effects in Bursa atmosphere. The study aims:

- To develop uptake rate equations depended on meteorological parameters
- To determine the current pollution state of Bursa
- To estimate potential cancer risk caused by VOC
- To find out factors affecting spatial variability of VOCs in the city
- To determine the types of sources contributing to observed VOC levels in Bursa
- To assign seasonal variability of VOCs
- To spatially evaluate the ozone production potential of VOCs

1.3 Novelty and Contribution of this Thesis

This thesis provides contribution to the international scientific community in terms of analytical issues and data interpretation on the following issues:

In terms of analytical issue, the screens put on and under the adsorbent in passive tubes to prevent it from spilling over during field studies were not sufficient for this. As the adsorbent spilled over in 5-10 tubes in each field study during transportation and placing in the sampling points, modification was made in passive sampling tubes. As a modification, specially built screen gauges were put on and under the screens and thus dislocation of screen was prevented. This modification enabled easy use of passive tubes under field conditions.

Spatial distributions and health effect assessment of conventional air pollutants and BTEX compounds had been studied in many other cities of the world in the past. The main scientific advancements of this study over

previous studies are the determination of spatial distributions and health effect assessment of many organic compounds instead of only BTEX compounds. There have been limited studies conducted on determination VOC in the literature in recent years.

Seasonal and spatial variation in VOC concentrations and underlying factors were determined by using large dataset and measurements conducted over 50 points across Bursa. There have been scarce studies carried out so far in the literature which consists of 50 points or more and which includes the whole urban area.

In this study, uptake rates were experimentally calculated. Uptake rates were calculated for pollutants apart from BTEX. No study exists in the literature in which uptake rates are calculated for VOCs apart from BTEX. In this respect, it is unique to this study to include uptake rates for 25 VOCs. Additionally, the effects of meteorological conditions and the existence of other VOCs on the uptake rate were identified. Another aspect unique to this study is that it was carried out under sampling conditions. This type of mechanism studies are usually conducted in specially conditioned exposure chambers and at high concentrations of VOC in order to save time. Again, almost all of the studies conducted in the literature are limited to BTEX. In this study, on the other hand, the studies of association with meteorological parameters was carried out under real atmospheric conditions and at typical concentrations that can be seen in a clear area, which is another unique side of the study.

Health risk assessment predictions were calculated for the whole city with real atmospheric concentrations for VOCs rather than depending on results of modeling. In addition, instead of standard inhalation volume and body weight values, those values which were obtained through a survey applied to a group that represented the population of Bursa were used in risk calculation. Thus, the uncertainties of cancer risk values calculated for Bursa were minimized by using data obtained from the applied questionnaires and ambient air VOC measurements

Source apportionment studies have been applied to data collected hourly or

daily at one or very few points. By applying the factor analysis technique to the data set spatial distribution of factors were determined instead of obtaining temporal variables of factors. Receptor model technique has never been applied to such a data set showing spatial distribution so far within the author's knowledge.

1.4 Organization of Thesis

The study contains six chapters as follows:

Chapter 1: INTRODUCTION the general description of the thesis, its purpose and its contribution to science was explained in this chapter.

Chapter 2: LITERATURE REVIEW provides background information needed in this study. Atmospheric chemistry, adverse impacts, receptor modeling and health risk assessment will be provided. Then, a literature review on the uptake rate determination and previous studies conducted to determine the characteristics of urban atmosphere with passive samplings will be evaluated.

Chapter 3: EXPERIMENTAL METHODS evaluates the analytical and instrumental methods developed and implemented in this study. Sampling sites and sampling methods are described in this chapter. Method performance evaluation, uncertainty calculation of passive tubes and quality assurance/quality control of the generated data set are also discussed.

Chapter 4: RESULT AND DISCUSSION describes the main outcomes of this study. The descriptive statistics of the data set is provided in this chapter. Seasonal and spatial distribution is also investigated. Sources of Bursa atmosphere are identified by conventional factor analysis method. Uptake rate equations are developed for 25 VOCs and meteorological parameters are evaluated with multiple linear regression methods.

Chapter 5: SUMMARY OF RESULTS gives a brief information about the findings.

Chapter 6: CONCLUSION gives the concluding remarks.

CHAPTER 2

THEORETICAL BACKGROUND

2.1 Overview of VOC-NOx and O₃ Chemistry in the Troposphere

VOCs are removed by physical processes of wet and dry deposition and are transformed by the chemical processes of photolysis in the troposphere. Most of the VOCs are very reactive in the troposphere. The main degradation mechanism of VOCs is the photochemical reactions. In the present of sunlight, chain reactions which depend on the structure of organics occur between VOCs and NO₂. For almost all VOCs, the degradation is predominantly initiated by reaction with hydroxyl radicals. Reaction of VOCs with hydroxyl radicals result in formation of the hydro or organic peroxy radicals (HO₂ or RO₂). NO₂ forms as a result of the reaction between peroxy radical and NO₂. NO₂ produces ozone in the present sunlight as represented in Figure 2.1.

Possible atmospheric fates of VOCs are: i) photolysis, if the substance absorbs light in the actinic UV ($\lambda \ge 290$ nm), ii) attack during daylight hours by OH radicals, iii) attack by O₃, especially if the molecule contains C=C double bonds, and iv) attack at night by NO₃ radicals (Finlayson-Pitts and Pitts, 1986).

The fundamentals chemistry of O_3 formation is photooxidation of the NO₂ by sunlight in photochemical smog. Tropospheric ozone formation is of great concern due to its adverse affects on human health and environment. Hence VOC and NO_x are the main ozone precursors.



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Figure 2.1 Schematic representation of the free radical catalyzed oxidation of a VOCs into its first generation carbonyl product(s) in the presence of NO_x , and the associated generation of ozone (O_3) (Jenkin et al, 1999)

The main role played by VOC in the formation of O_3 is to react to form radicals which either consume NO or convert NO to NO_2 (Carter, 1994).There is now a good qualitative and in a number of areas quantitative understanding of the tropospheric chemistry of NO_x and VOC involved in the photochemical formation of ozone. During the past decade much progress has been made but there are still areas of uncertainty in the mechanism of VOC- NO_2-O_3 (Atkinson, 2000)

The set of reactions taking place between organic compound and NO_x vary depending on the structure of organics under consideration (Finlayson-Pitts and Pitts, 1993). Although many types of reactions are involved (Carter, 1994) the following three reactions provide the information for the way that VOCs can enhance the rate of conversion of NO to NO_2 and hence increase the trophespheric O_3 concentration (Master, 1991).RH represents the radicals. Radicals form as a result of removal of hydrogen atom from an alkane.

$$RH + OH \rightarrow R + H_2O$$
(2.1)

$$\mathsf{R} \cdot + \mathsf{O}_2 \to \mathsf{R} \cdot + \mathsf{R} \mathsf{O}_2 \cdot \tag{2.2}$$

$$RO_2 + NO \rightarrow RO + NO_2$$
 (2.3)

The above reactions are not complete and illustrate how VOCs can help convert NO to NO₂. And thus increase O₃. Chain initiation by OH occurs at Reaction 2.1. The following pair of reactions shows both the way that OH· is regenerated and in the process how another NO is converted to NO₂. As well, aldehydes can be formed from this process (Master, 1991).

$$RO + O_2 \rightarrow HO_2 + R'CHO$$
 (2.4)

$$HO_{2'} + NO \rightarrow NO_{2} + OH$$
 (2.5)

As e result of chain reaction 2.1-2.5, one VOC molecules converts two molecules of NO and NO₂ and produces and aldehydes (R'CHO). The removal of NO slows the rate at which it is produced, thus leading to higher levels of O_3 is removed, while the addition of NO₂ increases the rate at which it is produced. Hence the production O_3 concentration increases in the air (Master, 1991).

At night, in the presence of O_3 and NO_2 , NO_3 is formed as shown in Reaction 2.6. Reaction with NO_3 represents an important nighttime sink of certain VOCs (e.g., phenols, terpenes, etc.) (Finlayson-Pitts and Pitts, 1986, 1993).

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{2.6}$$

Ozone-NO_x-VOC Sensitivity

The ozone isopleths plots represented in Figure 2.2 are generally used to illustrate the relationship between ozone- NO_x -VOC sensitivity. This is because the isopleths properly represent ozone chemistry that would apply board range of atmospheric conditions and is less dependent on assumptions of individual calculations.





Figure 2.2 is useful in examining whether VOC or NO_x control or both would be the most effective in controlling tropospheric ozone concentrations. The solid line represents production rates as ppb/h. The isopleth plot shows that there is a nonlinear relationship between ozone- NO_x -VOC. At high VOC/ NO_x ratio, decreasing VOC alone at a constant NO_x gives only slowly decreasing O_3 . However, decreasing NO_x at constant VOC is very effective in rolling down the ozone hill. Thus in this case, the chemistry of the polluted air masses is NO_x -limited and NO_x control is the most effective. This region of high VOC/ NO_x is typical of suburban, rural and down-wind areas (Finlayson-Pitts and Pitts, 1993).

At low VOC/NO_x, reducing VOC at constant NO_x results in rolling down the ozone hill. However, reducing NO_x at constant VOC actually leads to an increase in O₃ initially until the ridgeline is reached. This behavior has been a major factor in the ozone control strategy controversy, and used to argue against NO_x control. Reasons for this complex behavior include NO₂ competing with VOC for the OH radical by forming HNO₃. This terminates the chain oxidation of VOC and removes NO₂ from the system without forming O₃ (Silman et al., 1997 and Finlayson-Pitts and Pitts, 1993)

2.1.1.1 VOC/NOx Ratio

Haagen–Smith (1954) first identified the impact of VOC/NO_x ratios on ozone formation. Since then, the impact of VOC –NOx ratios has been simulated in model calculation and in smog chamber experiments. In the 1980, Lagrangian model (EKMA) was used to calculate the evaluation of a specific VOC/NO_x mixture through the day. Based on these analyses, a simple rule was developed in which morning VOC/NO_x ratios lower than 10 were equated with VOC-sensitive peak ozone and morning VOC/NO_x ratios greater than 20 corresponded to NO_x-sensitive peak ozone (Silman, 1999).

2.1.1.2 Reactivity Scales

Individual VOCs behave differently in the atmosphere, and have differing ozone formation potentials. An air mass can have a large total VOC concentration but a low ozone producing capacity if the VOC present are relatively non-reactive. Therefore, the term organic reactivity has been introduced to quantify the relative importance of organic compounds in producing ozone (Hakami et al., 2004). The most commonly referred reactivity scales in the literature are explained in the following paragraphs.

Hydroxyl reactivity scale is based on the rate coefficients of the respective reactions with the hydroxyl radical in reactions such as:

OH + organic compound +
$$O_2 \rightarrow$$
 Peroxy radicals (2.7)

It is useful to consider the kOH reactivity scale under conditions where the production of ozone is largely limited by the supply of NO_x rather than VOC. Such conditions prevail at locations removed from major source areas of VOC such as rural and remote areas). Thus, the kOH is no longer believed to be a valid indicator of ozone production of organic compounds (Dimitriades, 1999).

Incremental reactivity (IR) is defined as the amount of O_3 formed per unit of VOC added or subtracted from the VOC mixture in a given air mass (Carter and Atkinson, 1987, and Bowman and Seinfeld, 1994).

$$IR = \Delta[O_3] / \Delta[VOC]$$
(2.8)

In experimental determinations, the compound is added to an irradiated mixture in an environmental chamber (Carter and Atkinson, 1987). In the conceptual determinations, the incremental reactivity of a hydrocarbon is modeled using a chemical mechanism that was previously evaluated against smog chamber experiments.

Maximum Incremental Reactivity (MIR) developed by Carter (1994) is popular in the assessment of ozone formation potential from various VOC compounds. The MIR scales are based on modeling simulations of a number of urbanemissions scenarios. For each scenario, a base case is developed in which the NO_x emissions are adjusted to maximize the IR. In other words, the base case represents the NO_x condition that maximizes the change in peak ozone for an incremental addition of total VOC. For the base case, the MIR value of each individual VOC is obtained as the change in peak O_3 for an incremental addition of the individual VOC.

2.2 Sampling and Analyzing Techniques both VOC and Inorganic Pollutants

A large number of anthropogenic VOC are routinely emitted into the ambient environment in the urban area. Atmospheric concentrations of these VOC are ppb or sub-ppb level. Measurement of the concentration of VOC in air is necessary for many reasons including, to determine the sources and transport mechanisms of pollution, for health effect studies, and to determine compliance with regulatory limits. The concentration of VOC in air can fluctuate in both time and space, and measurement techniques must be designed to accommodate these fluctuations. VOC measurements are difficult due to the extreme complexity of the hydrocarbon mixtures that can be present in the atmosphere and their low level concentrations. The demand accurate, sensitive and simple techniques for the monitoring VOC in the atmosphere have increased tremendously in recent years. There are several different methods for VOC determination. One method is to use near real time instruments, such as infrared spectrometers or portable Gas Chromatography or their detectors. However, these instruments have limitations of cost, stability, field calibration and power supply, which may detract from their use (Harper, 2000). Another method is to take sample in the field and send it to a laboratory for analysis. Whole air sampling using canisters or adsorption on selective sorbents can be used for this purpose. Active (pumped) sampling and passive (diffusion) sampling methods are used to adsorb air sampling on selective sorbents. Desorption of selective sorbent can be achieved either thermal desorption or solvent desorption.

A passive (diffusive) sampler is a device which is capable of taking samples of gas and vapors pollutants from the atmosphere at a rate controlled by a physical process, such as diffusion through a static layer or permeation through a membrane (Brown, 1993). In passive sampling technique does not involve the active movement of the air through the sampler.

Today, passive sampling theory is well established. Adsorption of the gas phase pollutants onto the adsorbent surface through the air movement is based on Fick's First Law. The amount, M, of the analyte transported by
diffusion in time, t(s), when the concentration gradient is linear and the collection efficiency is 100%, can be described by equation 2.9. (Gorecki and Namiesnik, 2002):

$$M = U \times t = \frac{DA}{L}C_0 t \tag{2.9}$$

Where:

- U: Uptake rate (mol/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)
- C_0 : analyte concentration of the medium examined (mol/cm³)

The term (DA/L) is expressed as Uptake Rate (cm³/min). With this simple equation, the concentration of an analyte can be calculated from the adsorbed mass as determined by gas chromatography, the sampling time and the uptake rate. Ideally, uptake rates are constants that can be calculated from the geometry of the sample tube and available diffusion coefficients. It was shown, however, that experimental uptake rates were significantly different from the theoretical values (Brown et al., 1981 and Gelencser et al., 1994). The literature on the uptake rates of compounds for a given adsorbent and sampler geometry is similarly contradictory. For example, deviations of benzene reached up to 300% in the literature (Cao et al., 1993; Gelencser et al., 1994; Tolnai et al., 1999, Brown 1999, Patil and Lonkar, 1994). Fundamental controversy in the literature may result from the differences in the conditions and methods in the laboratory. Furthermore, environmental conditions are substantially different from the controlled conditions in the laboratory, especially in terms of variability and concentration levels (Tolnai et al., 2001). In this study, to eliminate this disadvantage of passive sampling tubes, uptake rates were calculated for 25 VOCs with the help of active sampling method.

In the first instance the passive sampler was developed in America as an onperson air sampler by Palmes et al, 1976. Later a variety of passive samplers were developed. At the present time, there are several types of commercially available passive sampling tubes for collecting both organic and inorganic pollutants, including SO_2 , NO_2 , NO, CO, Ammonia (NH_3), hydrogen sulfide (H_2S). In general, they have a badge or a diffusion tube-filter absorbent or adsorbent configuration. Passive collection of a given air pollutant is achieved by chemical absorption or by physical adsorption onto a medium. Passive sampling is widely used in all air monitoring scenarios, i.e. occupational hygiene, indoor and ambient air monitoring. By eliminating the requirement for a sampling pump, diffusive monitoring provides a simple and cost effective method, unattended operation of collecting the large of the samplers. Although theory of pollutant collection techniques is same, there are two types of passive tubes available in term of extraction procedure. These are solvent or thermal extraction methods.

Thermally adsorbents tubes for air sampling analyzing are widely used for many volatile organic compounds (VOCs) and has broad applicability to ambient, workplace, and indoor environments (Tang and Fellin, 1995; Ma et al., 1997; USEPA, 1997a). This method offers a number of advantages in comparison to solvent extraction methods. For example, thermal desorption of sorbents offers higher sensitivity than chemical methods since the sample is not diluted (Posner, 1981). Sorbent tubes themselves are easy to condition and small in size, facilitating easy collection, transport and storage. The sampling systems that include adsorption tubes or cartridges are small and relatively inexpensive. Several thermal desorber systems are available that automate tasks of desorption, concentration (focusing) of analytes onto cryogenic traps or cooled sorbents, and injection into a gas chromatograph (GC). Water and water vapor, which interfere with collection and analysis, can be managed using hydrophobic sorbents, dry purges (USEPA, 1997a; Batterman et al., 1997) and other techniques.

Several studies have conducted to determine uptake rates and compare performance and reliability for different types of passive sampler and by using different adsorbents to improve passive sampling techniques in terms of determination VOC concentrations (Roche et al., 1999; Lindahl et al., 1996; Hoed et al., 1991; Ballesta et al., 1992), but there is only a few comparison VOC concentrations between diffusion samplers and automatic GC to evaluate efficiency of passive tubes in real conditions. Skov et al., ((2001) performed at the low levels normally encountered in urban background air in Sweden. Mowrer et al., (1996) compared three diffusive samples, using Tenax TA as the adsorbent, with a GC-FID in terms of BTEX concentration level at a densely trafficked site is Copenhang. The agreement between the Tenax TA diffusion samplers and the BTEX analyzer was within 3% (relative standard deviation). Brown et al., (1999) exposed diffusion samplers with different adsorbents at different locations in Great Britain and compared the results with automatic GC-FID measurements results. The uptake rate in the diffusion samplers was obtained using an active sampling on the same adsorbents. The uncertainty of the measurements, calculated as the sum of systematic and random errors were found to be around 20% for an exposure period of 2-3 weeks. Skov et al. (2001), found a linear correlation between BTEX instrument and the diffusion samplers filled with Tenax TA ($R^2=0.80$) with a slope of 1.20±0.13. Recently Widesquist et al., (2003) compared diffusive sampling and active sampling with online GC-FID for measurements benzene and toluene. Results showed that the concentrations of toluene were within 95% confidence intervals. But benzene values were calculated as higher 30% than GC-FID measurements. In this study, active sampling results were used to confirm the validity of organic passive methods.

The theory of inorganic passive sampling method is different from organics. It is based on pollutants chemically absorb onto the filter surface with coated with selection chemicals. There are various studies based on the determining inorganic pollutants conducted up to now Manning et al., (1996) ; Glasius et al., (1999); Sickles, (1990); Gair and Penket (1991) determined good correlation of the values obtained by passive samplers to the corresponding continuous or active measurement methods. From now, several studies were conducted to improve inorganic passive sampling efficiency by changing shape of the passive tubes or using the filters coated with different chemicals. Development and validation of passive sampling techniques for the determination inorganic pollutants by using different type tubes shape or filters with coated different chemicals were evaluated by Santis et al (1997); Ayers et al., (1998); Nishikawa et al., (1987); Tang et al ((1999). Moriske and Schondube (1998); Yanagisawa and and Nishimura et al., (1982) and Plaisance et al, (2004) studied on influence of meteorological factors on the NO2 measurements. Result showed that diffusive samplers may be subject to the biases caused by alteration in sampling rate due to variations in atmospheric turbulence. This wind effects was first solved for long tube sampler or protective shelter, aimed only for urban measurements (Ferm et al., 1998).

Temporal evolution and spatial distribution of inorganic pollutants measured with the help of passive diffusion tubes in different environments: rural, suburban and urban as well as background measurements (Bhugwant et al., 2003; (Campbellet al., 1994; Carmichael et al., 1995; Ferm et al., 1997; Carmichael et al., 2003; Krzyzanowski et al., 2004; Arx et al., 2004; Miller, 1998; Zhou and Simith, 1997).

In order to determine personal exposure as well as indoor and workplace level of inorganic and organic pollutants, passive sampling tubes have been preferred due to light, no required pump and easy to use (Monn et al., 1998; Chao et al., 2001; Cha 2001; Heal et al., 1999)

2.3 VOC and Inorganic Pollutants Source and Emissions

In both developed and rapidly industrializing countries, the major historic air pollution problem has typically been high levels of smoke and sulphur dioxide produced by *combustion* of sulfur-*containing fuels*. Today, the major source contributed air pollution is traffic emissions. Petrol and diesel-engined motor vehicles emit a wide variety of pollutants, principally carbon monoxide (CO), oxides of nitrogen (NOx), volatile organic compounds (VOCs), which have an increasing impact on urban air quality. In addition, photochemical reactions resulting from the action of sunlight on nitrogen dioxide (NO₂) and VOCs from vehicles leads to the formation of ozone, which impacts in rural areas (Sertel et al., 2008) Acid rain is another pollutant influenced by vehicle NOx emissions. Literature estimates of the U.S. and worldwide emissions of VOCs are approximately 20 million tons per year and 60-140 million tons per year, respectively, from anthropogenic sources and approximately 29 million tons per year and 1150 million tons (of carbon) per year, respectively, from biogenic sources (NRC, 1991; Lamb et al., 1993).

Criteria inorganic pollutants (SO2, NO_x , O_3 and CO) have been routinely measured for long times through the world. Unfortunately only VOC measurements stations are available in North America and Europe. Research studies on VOCs aimed at determining sources and atmospheric concentrations of organic gases in urban and rural atmospheres. Ambient monitoring programs for VOCs were initiated in North America and Europe. In North America, over 4300 monitoring sites operate as part of three national air quality networks where VOCs are monitored in addition to the criteria air pollutants (i.e., SO₂, NO_x, PM and O₃). At the Canadian National Air Pollution Surveillance (NAPS) network, routine VOC measurements were introduced in 1989 at selected sites as part of the Canadian VOC/NOx program (CCME, 1997). In the 1990 Clean Air Act Amendments, the USEPA mandated to improve monitoring of ozone and its precursors within specified ozone nonattainment areas. The USEPA initiated the Photochemical Assessment Monitoring Stations (PAMS) program in 1993. Chemical parameters measured at PAMS sites included O_3 , NO, NO_x, 56 hydrocarbon compounds and three carbonyl species. PAMS network was intended to provide information to assist in control strategy development and evaluation, emission tracking and trend analysis, and exposure (Demerjian, 2000). In Europe, VOC monitoring started at a limited number of EMEP stations in 1992 (Solberg et al., 1995), but this number is expected to increase quickly in the near future. In Sweden the measurements of hydrocarbons was added to the Swedish Urban Air Quality Network Programme (URBAN) in 1992 (Mowrer et al., 1996).

Besides routine monitoring studied, many scientific research studies, conducted with passive sampling tubes, on sources and atmospheric levels of VOC as well as inorganic pollutants and human exposure to VOC exist through the world. Svanberg et al., 1998 conducted the study to measure VOC as weekly means and SO₂ and NO₂ at two places as a monthly means via passive sampling tubes. VOC were collected diffusive samplers consisting of a tube stainless steel packed with Tenax TA. The analyses were performed using Varian 3700 GC with FID, an automatic thermal desorption system. Monthly means of SO₂ and NO₂ were measured using diffusive samplers consisting of a polypropylene ring and impregnated filter coated with NaOH and NaI+NaOH, respectively. SO₂ and NO₂ after extraction of filters were analyzed using ion

chromatography. Results were investigated to determine contribution from local and regional sources as well as from long range transport. Mowrer et al., (1996) evaluated diffusive monitoring methods to determine C6-C9 hydrocarbons in urban air in Sweden during the winter months for sampling season October 1990 - March 1995. Diffusive sampling using adsorbents tubes filled with Tenax TA was chosen to determine BTEX, octane and nonane which are characteristics of anthropogenic sources of urban air pollution. Analyzing of passive tubes was achieved with the help of Varian Model GC-FID coupled with Perkin Elmer ATD 400 thermal desorption unit. Beside, detection limits, precision, bias, sources of error and sample stability during storage were evaluated. The accuracy and precision of the method were calculated less than 10% when the measured concentration were a factor of 10 or more above the detection limit. Parallel measurements made using on-site gas chromatography confirmed the validity of passive methods.

Passive samplings are used indoor and workplace air measurements as well as ambient measurements to evaluate the health effects. Cohen et al., 1989 studied on investigation the impact of the chemical industry on human exposures to VOC by using badge type passive samplers and relationship between their indoor and outdoor concentration in the Kanawha Valley of West Virginia. Monitoring was performed three week period. Samplers were analyses with GC-FID after solvent extraction. Results showed that indoor VOC concentrations were higher than outdoor concentrations.

Recently, there are also various studies in the literature to determine VOC concentrations and source contributions of VOC with the help of active sampling or online-GC. For example, Guo et al., (2004a) reported a comprehensive study conducted in Hong Kong on ambient concentrations, sources, emission rates and photochemical reactivates of C3-C12 HCs. In this study, ambient concentrations of 51 HCs were measured in an urban area from January 10 to December 30, 2001. Samples were collected in stainless steel canisters and analyzed by a GC-FID and GC-MSD. Temporal variations and sources of ambient HCs were also investigated in this study. In a study conducted in Munich, NHMC data were collected at urban, suburban and rural locations. Measurements were conducted by means of online GC method and a total of 28 individual NMHCs of C6-C9 were detected. This study was

important since it comprised the first comprehensive database, which featured high temporal resolution, for the Munich region (Rappengluck and Fabian, 1999). Sexton et al., (1983) reported a study in seven urban areas and six rural areas in America where measurements of C2-C10 HCs and inorganic pollutants (NO, NO₂, O₃ and CO) with online instruments were conducted to determine pollution levels and evaluate transport mechanism of air pollution in United State.

2.4 Receptor Modeling

Receptor model are widely applied in different scientific research area due to they have capability to handle large data sets. These are source oriented model (dispersion model) and receptor oriented model. The dispersion models, mathematical simulation model, are generally used to simulate how air pollution disperses in the atmosphere. The dispersion models require the input of data which includes the source information, emissions parameters and meteorological conditions to be run. The models are preferred to calculate or to predict the downwind concentration of air pollutants emitted from single or multiple sources. The main disadvantage of the model is they are all in computer programs. Hence these models give only meaningful results in case of reliable data available related with the source (Öztürk, 2009). Receptor model are improved as alternatives to dispersion model.

Receptor oriented models are mathematical tools in order to identify and quantify the sources at a receptor location. Unlike dispersion model, receptor model do not use pollutant emissions, meteorological conditions and chemical transformation mechanisms to estimate the contribution of sources to receptor concentration. Receptor model had been firstly implemented on atmospheric dataset (Lee, et al., 1999).

Receptor models are based on the Chemical Mass Balance (CMB) the Equation 2.10. as follows:

$$X_{ij} = \sum_{k=1}^{p} g_{ik} \cdot f_{kj} + e_{ij}$$
(2.10)

Where;

 X_{ij} is the concentration of the ith variable at the jth sample g_{ik} is the fractional abundance of the ith variable in the kth source f_{kj} is the contribution of the kth source at the jth sample e_{ij} represents the residuals, that are the difference between the measured and calculated amounts.

Hopke(2000) and Henry (1991) identified some natural physical constraints on the system that must be taken into account by constructing any model in order to obtain physically realistic solution from Equation 2.2 (Henry, 1991). The following natural physical constraints should be compiled:

1) The model must reproducued the original data and explain the observations.

2) The predicted source compositions must be produced as non-negative value

3) The predicted source contributions should be non-negative

4) The sum of the predicted mass contributions for each source should be less than or equal to 1.

When developing and applying these models, it is necessary to keep these constraints in mind in order to be certain of obtaining physically realistic solutions. (Hopke, 1985)

There are several ways to find a solution, based on the type of available information and on the desired final result by using Equation 2.4. Two sub groups, Chemical mass balance (CMB) and multivariate models, of receptor model are based on same equation, Equation 2.4.

In CMB model, the equation is solved using weighted least square regression analysis. The profile and number of sources should be entered in the model. The source profile are obtained from the literature or extracted from available data set. The CMB model has been widely used in environmnetal application, especially to determine the source mass contribution. However, model produces inaccurate result since main source are not well known and/or improper source profile. If only concentration of parameters are known then factor analysis methods, namely Principal Component Analysis (PCA), Unmix, Target Transformation Factor Analysis (TTFA), Positive Matrix Factorization (PMF) and Multilinear Engine (ME), can be used to determine the number of source, their mass contribution to source and their concentration.

In the current study, factor analysis tecnique was performed to identify and apportion the source

2.4.1 Principle Component Analysis (PCA)

In statistic application, factor analysis involves a mathematical procedure that transforms a number of possibly correlated variables into a smaller number of uncorrelated variables called principal components. It is defined as investigation of correlations of random variables (Paatero and Tapper, 1994)

Principle Component Analysis is most common methods used for data analysis in atmospheric research (Chang et al., 2009; Pires et al., 2008; Motelay-Massei et al., 2003; Guo and Louie, 2004 and Yu, et al., 2000). PCA is based on several forms of eigenvector analysis is usually preferred for the data reduction and provides information about the total variation of the data (Odden and Parth, 2000). Hence, only the significant independent variables responsible for the source of pollutant levels (Al-Alawi et al., 2008). The variables are assumed to be linearly related to some number of underlying factors. By this way, for the big data sets factors are determined (Guo and Louie, 2004). Principle Components with an eigen values greater than one, are evaluated. The following equations gives the estimation procedure for the Principle Component scores (Negendra and Khare, 2003)

$$PC_{ij} = \sum_{i} W_{ik} X_{kj}$$
(2.11)

Where;

PC_{*ij*} is the PC score for the *j*th object on the *i*th component w_{ik} is the loading of the *k*th variable on the *i*th component x_{kj} is the standardized value of the k_{th} variable for the j_{th} observation

PCA increases the correlation among the variables and creates orthogonal or uncorrelated new variables (Abdul Wahab, 2005). As a result of the PCA, Principal Components (PCs) were obtained. Variables depend on their correlations among the each other were grouped under this PCAs. The results of the PCA analysis are hierarchical, that is the first PC explains the highest variation among the variables; the other PCAs explain the rest variation among the variables orderly.

Varimax rotation is also applied on the data set because Varimax rotation minimizes the complexity of the components and adjusting the Principle Component axes to achieve more meaningful data interpretation and by this way explanation of the factors gets easier (Henry. 1987 and Guo and Louie. 2004).

Principal component analysis can be used reduction of data set so that only the significant independent variables responsible for the source of VOCs levels observed can be determined. The selected variables with high loadings generated from the PCA become ideal to use as predictors in a regression equation (PCR) since they optimize spatial patterns and remove possible complications caused by multicollinearity.

Since principle component analysis is most traditional source apportionment method, it has been applied widely in atmospheric research (Thurston and Spengler, 1985; Harrison et al., 1996; Bruno et al., 2001; Miller et al., 2002; Guo et al., 2003). For example, Henry and Hidy (1979; 1982) applied PCA model on a mixture of air to estimate potential sources of particulate sulfate in four U.S. cities. Kleinman et al. (1980) chracterized and estimated the relative importance of sources of airborne particulates using PCA techniques.

Thurston and Spengler (1985) applied PCA to Boston inhalable particle elemental composition data to estimate particle sources in Boston. In England, Harrison et al. (1996) identified the major air pollution source categories of ambient polycyclic aromatic hydrocarbons by means of PCA. Recently, PCA techniques have been used to assess sources of gaseous atmospheric pollutants such as volatile organic compounds (VOCs), carbonyls, nitrogen oxides (NO_x) and carbon monoxide (CO) (Bruno et al., 2001; Miller et al., 2002; Guo et al., 2004a).

2.5 Human Health Risk Assessment

2.5.1 Exposure and Risk Assessment

Toxic air pollutants are of public health concern due their association with a number of adverse health effects (Woodruff et al., 2000). The World Health Organization (WHO) and the U.S. Environmental Protection Agency provide sufficient evidence from both human and animal studies to believe that some VOCs have carcinogenic and mutagenic effects on living organisms and human health (Badjagbo et al., 2007). USEPA (2009) has defined 187 compounds as hazardous air pollutants (HAPs). Hazardous air pollutants are defined as substances which cause or may cause cancer or other serious problems for health, such as neurological effects, reproductive effects or birth defects. Some VOCs have been classified as toxic and carcinogenic and it is therefore unsafe to be exposed to these compounds in large quantities for short periods or in low quantities over extended periods of time. Some of the health risks of overexposure to VOCs are dizziness, headaches, and nausea even at ppb level. Long-term exposure to certain VOCs, such as benzene, has also been shown to cause cancer. The chronic neurotoxic effects caused by nhexane, the adverse effects of naphthalene on immune and respiratory systems, the irritation of mucous membranes by aldehydes, and the effects of toluene and xylenes on the central nervous system were also published (Hester and Harrison, 1998).

Some concentrations of VOCs generally in urban air are higher than the limit values due to exhaust emission or solvent sources. For example, the average benzene concentration measured in Ankara (Kuntasal, 2005) is 5.9 μ g/m³, 6.9 $\mu q/m^3$ in İzmir (Elbir et al., 2007), 26,70 $\mu q/m^3$ in Hong Kong (Chan et al., 2002); 12.8 µg/m³ in Canada (Derwent et al., 2000) and 5.97 µg/m³ in London (Kendall, 1993). According to the European Directive, the limit value of annual average benzene concentration in the air is 5 μ g/m³ (EU, 2009). Humans are exposed to several VOCs, the concentrations of which are higher than the regulations, during daily activity. Risk assessment should be evaluated to identify and quantify potential risks to human health resulting from exposure to various contaminants. To understand and properly quantify the health risks associated with ambient emissions of VOC, it is important to know the level of a pollutant to which people are actually exposed. In general, ambient air concentrations data are produced from the air monitoring stations. Time weight VOC concentrations along the urban area are seldomly measured at different locations. Ambient monitoring data form a necessary step to predict exposure and health risk estimates (USEPA, 2000). In this study, risk assessment will be applied on the VOC data set produced over 50 points sampling across the city.

Risk assessment regards the identification and quantification of potential health hazards to humans from exposure to various substances and agents in their environment (Patterson et al., 2002). The evaluation of toxicity data for chemicals to which humans are exposed and the estimation of potential exposure levels are involved in this step (Kavcar, 2005). Risk assessment has a long history dating back to 1940. In 1983, the National Research Council published Risk Assessment in the Federal Government: Managing the Process (NRC, 1983), which outlines the four steps of risk assessment (hazard identification, dose-response, exposure assessment, and risk characterization) that are still used today. (Figure 2.3) Among these steps, the first two are related to the properties of particular chemicals and the characterization of expected toxicological effects under a variety of circumstances. On the other hand, the last two steps are specific to the particular exposure scenario (Kavcar, 2005).



Figure 2.3 Schematic diagram of the four stages of risk assessment

Hazard Identification

Hazard identification is the process of determining whether the chemicals to which a population has been exposed are likely to have any adverse health effects (Masters, 1991). Scientific researchers have been conducted to determine the nature of adverse effects caused by toxic agents as well as the probability of their occurrence. Since human data are so often difficult to obtain, this step usually focuses on whether a chemical is toxic to animals or other test organisms.

There are three pathways through which toxicants enter the body, which are the ingestion of food or drinks, inhalation, and contact with skin (dermal) or other exterior surfaces (such as eyes). When the toxicant enters the body, it can be absorbed by blood and distributed throughout the organs and systems, and finally around the whole body (Masters, 1991). The toxicants may be stored in body tissues or the biotransformation processes, or they can be removed from the body via the excretory system.

There are several organs in human body that are particularly susceptible to toxicants. Depending on the types of toxicants, the effects of them on the body may be short-term ailments such as headaches, nausea, and eye, nose, and throat irritation, or chronic diseases, such as cancer. Potential health effects of noncarcinogens range from irritation to life shortening. Data on the

noncarcinogenic effects of chemicals are evaluated to calculate reference dose values, which are explained in the dose-response assessment step (Kavcar, 2005). In order to determine whether a chemical poses a carcinogenic hazard in exposed humans, USEPA (1992) examines the results from both human studies of the association between cancer incidence and exposure to the chemical of concern and long-term animal studies under controlled laboratory conditions. Since cancer is a collection of several diseases that develop through cell and tissue changes over time (USEPA, 2009), supporting evidence such as short-term tests for genotoxicity, metabolic and pharmacokinetic properties, toxicological effects other than cancer, structure-activity relationships, and physical/chemical properties of the chemical are also regarded in the health effect studies.

Toxic chemicals are assigned a weight-of-evidence approach for having a potential "carcinogenic effect" based on the USEPA. Weight of evidence is used to classify the likelihood the chemical of concern is a human carcinogen (Kavcar, 2005) and as a result each chemical is placed into one of the five categories presented in Table 2.1

The toxicological characteristic of compounds in the IRIS database is updated monthly and available online EPA, IRIS (2009).

Group	Category					
А	Human carcinogen					
	Probable human carcinogen					
В	B1 indicates limited human evidence					
	B2 indicates sufficient evidence in animals, inadequate/no					
	evidence in humans					
С	Possible human carcinogen					
D	Not classifiable as to human carcinogenicity					
E	Evidence of noncarcinogenicity for humans					

Table 2.1	USEPA's	Carcinogenicity	Classification	of	Chemicals
-----------	---------	-----------------	----------------	----	-----------

Compounds	Cancer		
	classification		
Benzene	А		
Toluene	D		
Ethyl benzene	D		
Xylene	D		
Chloroform	B2		
1,1,2,2	С		
Tetrachloroethane			
Styrene	2B		

Table 2.2 Carcinogenicity Classification of some VOCs

There is enough evidence about the chemicals put into Group A to conclude that they can cause cancer in humans. Benzene belongs to Group A and hence known as a human carcinogen for all routes of exposure. Group B is actually made up of two subgroups. If a chemical is categorized as B1, there is limited epidemiologic evidence that it can cause cancer in humans. There is inadequate evidence that it can cause cancer in humans; on the contrary, sufficient evidence of carcinogenicity in animals is obtained in Group B2 chemicals. For example, chloroform belongs to Group B2. The chemicals defined in Group C provide limited evidence that they can cause cancer in animals in the absence of human data. The D group is used for chemicals with no evidence at present that they cause cancer in humans and animals. The Group E chemicals provide no evidence for carcinogenicity in at least two adequate animal tests in different species or in both adequate epidemiologic and animal studies. Table 2.2 depicts the carcinogenicity classification of some chemicals.

Dose- Response Assessment

The Dose–Response Assessment is described as the quantitative relation between the dose and the response; this may involve the use of mathematical models (Patterson et al., 2002). The mathematical relationship between the amount of chemicals to which a human is exposed and the risk of some possible unhealthy responses to that dose is calculated (Master, 2001). The response can be showed or measured as the observed number of incidences, percent response in groups of subjects or populations, or the probability of occurrence of a response in a population (USEPA 1997b).

The mathematical relationship between dose and response is schematically represented for carcinogenic and non-carcinogenic chemicals. The exposure to chemicals, which resulted in a carcinogenic response, can cause some likelihood of cancer. Thus, a plot of response versus dose is required to go through the origin for carcinogenic chemicals. Generally, increasing the dose of chemicals results in a proportional increase in both the incidence of an adverse effect and the severity of the effect. For non-carcinogenic response, it is generally assumed that there is a threshold dose-a dose below which there is no effect. As a result of these assumptions, the dose-response curves obtained for carcinogenic and non-carcinogenic chemicals are quite different as suggested in Figure 2.5.2. It should be taken into account that such chemicals cause both kinds of response (Master, 1991).

The exposure to chemicals which cause a carcinogenic response can cause some likelihood of cancer. As shown in Figure 2.4, the slope of the doseresponse curve is called the potency factor (PF) or the slope factor (SF) and it is defined by the USEPA (1992) as the cancer risk per unit of dose. The USEPA maintains a database of information on toxic chemicals, which is called the Integrated Risk Information System (IRIS). Information is available in the web site about slope factor and the weight of evidence category for each toxic chemical EPA, IRIS (2009). Hence, the lifetime risk for carcinogenic chemicals is expressed in Equation 2.12.

Lifetime risk=Average daily dose or chronic daily intake (mg/kg/day) x Slope factor (mg/kg/day)⁻¹ (2.12)

The most important point of non-carcinogens is that there exists an exposure threshold. Any exposure less than the threshold would be expected to show no increase in adverse effects. In order to experimentally determine the thresholds, animals are exposed to a range of chemicals doses. The toxicant tests show that doses below the threshold would derive no response while doses above the threshold would produce responses. The lowest dose at which a response occurs is called the lowest observed effect level (LOEL). On the other hand, the highest dose at which no response occurs is called the lowest observed effect level (NOOEL) (Robson and Toscana, 2007). These levels are represented in Figure 2.4. Within statistical uncertainties, the true threshold will lie somewhere between the LOEL and the NOEL (Robson and Toscana, 2007). The other terms are reference dose (RfD) in the dose and reference concentration for chronic inhalation exposure (RfC) for non-carcinogenic effect. The RfD or acceptable daily intake (ADI) shows the level of human exposure that is likely to be without appreciable risks. The units of RfD are mg/kg/day averaged over a lifetime. The RfD value is derived from the NOEL value by taking uncertainty factors as described in Equation 2.13 into consideration.

ADI or RfD (human dose) = NOAEL (experimental dose)/UF (2.13)

Generally, ten-fold the uncertainty factors is used to account for differences between the most sensitive individuals (pregnant women, babies and elderly) and healthy people in an exposed human population. A factor of 10 may also be introduced when there are no good human data and when the animal data available are limited. The resultant UF of 100 has been judged to be appropriate for a number of chemicals. If the chemicals are based on wellcharacterized responses in sensitive humans, an UF might be selected as small as USEPA, IRIS (2009).

The slope factor, reference concentration and reference dose are unique for each chemical. The values of these parameters were obtained from USEPA, IRIS (2009), and are represented in Table 2.3. Table 2.3 lists 15 compounds detected in the atmosphere of Bursa, including their cancer classification (EPA, 1986), unit risk value (mg/m³)⁻¹, non-carcinogenic reference dose (RfD) (μ g/kg-day) and reference concentration (RfC) (μ g/m³) and their critical effects.



Figure 2.4 Dose-Response Curve for Carcinogenic and Non-carcinogenic Compounds

Compounds	Cancer classifi cation	Slope factor (mg/kg -day) ⁻¹	RFC (µg/m³)	RfD (µg/kg- day)	Critical Effect
Benzene	А	0.035 ^a	30		Decreased lymphocyte count
1,3 Butadiene	B2	0.110	2		Ovarian atrophy
Bromoform	B2	0.007 9		20	Hepatic lesions
1,1,1,2- Tetrachloroethane	С	0.026		30	Mineralization of the kidneys in males, hepatic clear cell change in females
toluene	D		5000		Neurological effects in occupationally-exposed workers
1,4 DiCl benzene	2B		800		Increased liver weights in males

Table 2.3 Slo	ope factors,	reference do	ose or re	eference	concentration	and	their
	adverse	e health effec	cts for V	/OCs con	cerned		

Compounds	Cancer classifi cation	Slope factor (mg/kg -day) ⁻¹	RFC (µg/m³)	RfD (µg/kg- day)	Critical Effect
ethyl benzene	D		1000		Developmental toxicity
hexane	D		700		Peripheral neuropathy (decreased MCV at 12 weeks)
naphthalene	D		3		Nasal effects
Styrene	2B		1000		CNS effects
Xylene ^b	D		100		Impaired motor coordination (decreased rotarod performance)
Isopropyl benzene (cumene)	D		400		Increased kidney weight in female rats and adrenal weight in rats
chlorobenzene	D			20	Histopathologic changes in liver
TetraChloroEthylen e	2A			10	Hepatotoxicity in mice, weight gain in rats
1,1,2- Trichloroethane	С			4	Clinical serum chemistry

Table 2.3 Slope factors, reference dose or reference concentration and theiradverse health effects for VOCs concerned (*Continued*)

^a Slope factor for benzene is given a range (USEPA, IRIS, 2009). The average value of slope factor was selected to calculate carcinogenic risk caused from benzene

^b Xylene represents m Xylene, p Xylene and o Xylene. m and p xylenes were detected as one peak in our system, the non-cancer value were only calculated for o-xylene

Exposure Assessment

Individuals should be exposed to toxicants in order to mention about human risk. The human exposure assessment is related to the estimation of the amount of contact that is likely to occur between people and those contaminants. Exposure assessment is the process of measuring or estimating the magnitude, frequency, and duration of human exposures to an agent currently present in the environment (USEPA 1992). Exposure may occur via three main routes; ingestion, inhalation, and dermal absorption. In this study, only the inhalation route will be taken into consideration in order to assess the exposure associated with VOCs in ambient air. The other routes are beyond the scope of the study. Equation 2.14 is advised by USEPA (2009) to estimate the contamination intake (I) via inhalation route:

$$I = \frac{C \times CU \times IR \times ED}{BW \times AT}$$
(2.14)

Where;

- I: contamination intake (mg kg⁻¹day⁻¹)
- CU conversion unit $(10^{-3} \text{ mg}\mu\text{g}^{-1})$
- IR: Inhalation rate (m³day⁻¹)
- ED: Exposure duration (years)
- BW: Body weight (kg) obtained from the questionnaire
- AT: averaging time (years)
- for non-carcinogenic effect and lifetime cancer risk AT=ED

The Equation2.14 become as follows:

$$I = \frac{C \times CU \times IR}{BW}$$
(2.15)

The activity levels have been categorized as resting, sedentary, light,

moderate and heavy work activity. Inhalation rates are also affected by numerous individual characteristics, including age, gender, weight and health status. Inhalation rates (IR) are reported for adults and children (including infants) by applying various activities and outdoor workers/athletes in the literature. The inhalation rates used for calculating health effects in this study were obtained from the questionnaire which was applied on the participants living in Bursa. Detailed information will be given in the Section 4.6.

Risk Characterization

The final step in risk assessment is to bring all the previous steps together to define an overall risk to a specific population. The data obtained in the dose-response assessment is combined with the data obtained in the exposure assessment to calculate a numerical estimate of risk for a specific population (USEPA 1992).

Cancer and noncancer risks are estimated using conventional approaches (USEPA 1986, 1999a, 2003). Cancer risks are calculated using unit risk or slope factor value obtained from USEPA, IRIS (2009). The contamination intake (I) calculated from eq 2.14 for each compound is multiplied by its unit risk to produce cancer risk. Pollutants with cancer risks greater than 1×10^{-6} are considered as a potential human health concern (USEPA, 2009). Cancer risk:

$$R = I \times SF \tag{2.16}$$

Where;

R: Risk from pollutant (unitless)

I: contamination intake (mg kg⁻¹day⁻¹)

SF=Unit risk or slope factor of dose-response curve (mg kg⁻¹day⁻¹)⁻¹

The lifetime cancer risk of compounds is assumed to be additive and summed the cancer risk values of each compound to estimate total cancer risk at equation 2.17 (Woodruf et al., 2000)

Cumulative Cancer risk=
$$\Sigma$$
 Cancer risk for each pollutant (2.17)

Hazard ratios for non-carcinogenic HAPs are calculated using benchmark concentrations (RfC, RfD, REL, etc.). Either pollutant concentration is divided by their corresponding Reference Concentration (RfC) or contamination intake rate value of pollutants is divided by Reference Dose (RfD) to derive a hazard ratio. Hazard ratio for each pollutant is calculated using the following formula:

$$HR = \frac{IR}{RfD} or \quad HR = \frac{C}{RfC}$$
(2.18)

Where;

HQ: the hazard ratio of a pollutant

C: the concentration in μgm^{-3} of pollutant

RfD: reference dose (mgkg⁻¹day⁻¹)

RfC: reference concentration (µgm⁻³)

I: contamination intake (mg kg⁻¹day⁻¹)

Hazard ratios for each compound are summed to calculate the total hazard index as shown in equation 2.19.

Total Hazard Index= Σ hazard Ratio for each compound (2.19)

Pollutants with a hazard ratio greater than one are deemed to pose a potential human health concern (USEPA, 2009).

2.5.2 Deterministic Versus Probabilistic Approach

In the risk or exposure assessment models, the input parameters of the cancer and noncancer are measured, such as RfD, slope factors and the average daily dose are known exactly. Thus, if there is a given set of input parameters for each individual, one value of output parameter for the model is obtained. The traditional approach is called as deterministic method. The risk distribution is derived for the general population by using the defined population.

Unfortunately, variability may occur in the deterministic approach between individuals due to having different body weight, life style, different location (spatial distribution) and the uncertainty emanating from lack of knowledge... More and better data collection can help to characterize the variability between individuals, but will not reduce or eliminate the uncertainty (Öberg and Bergbäck, 2005). Variability and uncertainty can be dealt with in the deterministic approach by successively adding safety factors in order to evaluate risk assessment.

Efforts to qualify and differentiate between variability and uncertainty are important for both risk assessment and risk characterization. Stochastic models are accomplished by using that employ a large number of trials to develop probabilities of an event such as exceeding a particular risk threshold within the defined population (Robson and Toscana, 2007). Hence variability and uncertainty in the input parameters are identified by probability distributions, and the output (risk or exposure) is likewise presented as a probability distribution (USEPA, 2001)

Monte Carlo Simulation

USEPA advises the usage of probabilistic analysis in risk assessment in order to adequately characterize variability and uncertainty in exposure and doseresponse assessments for human health (USEPA, 2009). The computer-based model, Monte Carlo method, which was developed in the 1940's, is one of the probabilistic analysis techniques. It is probably the most widely used technique for propagating the uncertainties in model inputs to determine the uncertainties in model outputs (Fjeld, 2007). Monte Carlo method uses statistical sampling techniques in obtaining a probabilistic approximation to the solution of a mathematical equation or model (USEPA, 1997b). The model gives information about the importance of various assumptions and uncertainties in the model inputs and their effects on the final model output distribution. Monte Carlo analysis can also assist in deciding whether it is worthwhile gathering more information to reduce uncertainty (Robson and Toscana, 2007).

The probability distribution function for each input variable is inserted into the model for exposure of model parameters. A large number of data sets of input parameters (e.g. 10,000) are produced by sampling randomly from their respective probability distribution. The model uses random number generation to combine distribution. Hence, its analysis generates a final output distribution of exposure or risk values, rather than a single point estimate (Robson and Toscana, 2007).

The basic goal of a Monte Carlo analysis is to quantitatively characterize the uncertainty and variability in estimates of exposure or risk. A secondary goal is to identify the key sources of variability and uncertainty and to quantify the relative contribution of these sources to the overall variance and range of model results (USEPA, 1997b).

The probability distribution of lifetime cancer risk or exposure is obtained by using probability distribution of concentration, inhalation unit risk for each compound and body weight, and it is presented in Figure 2.5. The output of a simulation is continuous probability distribution, which can be displayed in a graph in the form of either a probability density function (PDF) as shown in Figure 2.5 or corresponding cumulative distribution function (CDF). The probability distribution of exposure may also be used to reflect uncertainty if multiple trials are compared (McKone, 1994). In contrast to the deterministic approach, the Monte Carlo simulation provides a range of values reflecting the variability of the inputs with descriptive statistics.



Figure 2.5 Schematic Representation of Monte Carlo Simulation

2.5.3 Statistical Methods

Goodness-of-Fit Tests

The correct establishment of the distribution of a data set (or random variable) is crucial for implementing risk assessment correctly. Goodness-offit test (GoF) is the most commonly used statistical method to select the distribution fitting of a random data set for probabilistic approach. The goal of the GoF statistic is to summarize the deviation between observed data set and their expected values under some probabilistic models (Waller and Gotway, 2004). GoF gives information about the hypotheses and whose distribution, under the null hypothesis. GoF tests are essentially based on either of two distribution elements: the cumulative distribution function (CDF) or the probability density function (PDF). The Chi-Square test is based on the probability density function (PDF). Both the Anderson-Darling and the Kolmogorov-Smirnov tests use the cumulative distribution function (CDF) approach.

The chi-square test is based on the difference between the square of the observed and expected frequencies. The main advantage of the chi-square test is that it can be applied to any univariate distribution for which it can be calculated the cumulative distribution function. The chi-square test is applied to binned data (i.e., data put into classes). However, the values of the chi-square test statistic are dependent on how the data is binned. Another disadvantage of the chi-square test is that it requires a sufficient sample size in order for the chi-square approximation to be valid (Yang and Mannan, 2010).

The Kolmogorov-Smirnov (K-S) parameter is determined by taking the maximum distance between the theoretical and sample cumulative distribution functions (CDFs). The results of this test are then reported as a hypothesis test where the null-hypothesis entails accepting the distribution, and the alternative hypothesis is rejecting it. The K-S test is more sensitive near the center of the distribution than at the tails (Fienberg and Kadane, 2001). Although it is the best at detecting shifts in the empirical CDF relative to the known CDF, it only applies continuous data. It is less proficient at detecting spread, but is considered to be more powerful than the chi-square test (USEPA, 2009).

The Anderson-Darling test is based on weighted-average of the squared difference between the observed and expected cumulative densities. It is used to test if a sample of data came from a population with a specific distribution. It is a modification of the Kolmogorov-Smirnov (K-S) test and gives more weight to the tails than the K-S test. The A-D test has the advantage of allowing a more sensitive test and the disadvantage is that critical values must be calculated for each distribution (Regalado, 2005).

Variability and Uncertainty Analyses

The variability and uncertainty should be taken into account for exposure assessment and risk analysis to increase the likelihood that results of an assessment (USEPA, 2009). The reason of variability is specified as true heterogeneity across people of population, places or time. Variability can affect the precision of exposure estimates and the degree to which they can be generalized (USEPA, 2009). For example, exposure levels of ambient pollutants can be affected at the local level by industrial activities and the individual activity pattern or seasonal fluctuations, and weekend versus weekday differences. Due to the local difference and different behavioral pattern of individual, the risk associated with exposure to a certain compound takes the form of a range of possible values, which are most commonly described in terms of statistics such as the mean, median, etc (Kavcar, 2005). To remove variability from the analysis, USEPA advises certain ways to substitute a single value for data set described by a probability distribution, such as I) ignore the variability by taking central tendency of the distribution, II) disaggregate the variability by considering relevant sub groups, III) use the average value, IV) use maximum –minimum value.

USEPA (2009) defines the uncertainty as "a lack of knowledge about factors affecting exposure or risk and can lead to inaccurate or biased estimates of exposure". The uncertainty arises from missing or incomplete information, gaps in scientific theory required to make predications on the basis of casual inferences or some parameters (USEPA, 1992). For example, different people have different breathing rates but do not know how much those rates change from person to person. The more and better data collection can help to remove uncertainty, but these uncertainties cannot be eliminated (Robson and Toscana, 2007)

To translate variability and uncertainty into the overall uncertainty of the assessment, four approaches can be used: (1) sensitivity analysis; (2) analytical uncertainty propagation; (3) probabilistic uncertainty analysis; or (4) classical statistical methods (USEPA 1992). The first approach can be used

to determine which parameters produce the most impact in the final risk by changing one variable while leaving the others constant. Analytical uncertainty propagation is defined as "Examining how uncertainty in individual parameters affects the overall uncertainty of the exposure assessment" (USEPA, 2009). In probabilistic uncertainty analysis approach, appointing probability density function to each parameter; and then selecting arbitrarily sample values from each distribution and insert them in the exposure equation. Monte Carlo analysis and Bootstrap methods are the most widely used techniques to estimate confidence intervals for population parameters by simulating resampling of empirical distributions (USEPA, 2009).

The Monte Carlo Simulation, as detailed in Section 2.5.2, is applied to define the uncertainty and variability in risk or exposure estimates, computer simulation of repeated sampling of the probability distributions of the risk equation variables and using the results to calculate a distribution of risk (USEPA, 2009). Related to Monte Carlo analysis, Bootstrap methods are used to estimate confidence intervals for population parameters by simulated resampling of empirical distributions. The bootstrapping involves creating multiple sets of subsamples and requires no prior statistical assumptions about the underlying distribution of the dataset. Each set of the subsamples is generated from re-sampling the data with replacement (i.e. any data point could be sampled multiple times or not at all (USEPA, 2009). The subsample of a size less than or equal to the size of the data set is generated from the data set in order to produce a bootstrap uncertainty estimate for a given statistic. Then the statistic is calculated. This subsample is produced with replacement so that any data point can be sampled multiple times or not sampled at all. This process is repeated for many subsamples, typically between 500 and 1000 and the computed values for the statistics form an estimate of the sampling distribution of the statistic (NIST/ SEMATECH 2009).

In the current study, the probability distribution of the exposure of each VOC was calculated with the help of Monte Carlo Simulation and then bootstrap technique was applied to estimate the uncertainty associated with this distribution.

Kruskal-Wallis and one-way Anova Tests

People living in different parts of Bursa are considered to have different activities as a result of their life styles, differences in their daily life, and socio-economic factors. The Statistical Package for the Social Sciences (SPSS Inc. Chicago.USA. Version 17) was used for the statistical analysis. One-way Anova and Kruskal-Wallis statistical tests were applied on the data set to evaluate differences between related subgroups. The evaluation methods depend on the normal or not normal distribution of the data set. One-way Anova is only meaningful for independent variable with an underlying normal distribution and equal variance. One-way Anova is also used to test differences of variance among at least three independent groups. The data set should also be homogeneity of variance to apply one-way Anova. Levene test is used to evaluate homogeneity of variance of subgroups.

A one-way Anova may yield inaccurate estimates of the P-value when the data are very far from the normally distributed ones. The Kruskal-Wallis test is a popular nonparametric alternative to the standard one-way analysis of variance. It is appropriate when your test variable is ordinal or its distribution does not meet the assumptions of standard Anova (NIST/ SEMATECH 2009). Kruskal Wallis nonparametric variance analysis was used to test the null hypothesis of no difference between three or more group locations (medians). Unlike the parametric independent group Anova (one-way Anova); this K-W test makes no assumptions about the distribution of the data (e.g., normality).

P-values obtained from one-way Anova and Kruskal-Wallis test were examined for different subgroups, such as body weight, age, time spent indoors/outdoors. The p-value is the probability conditional on the null hypothesis of the observed data set. Small p values indicate significance difference between the sub-groups. P-values smaller than 0.05 were considered to point to a significant difference between the compared subgroups for the current study.

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2.5.4 Literature Review

The term "health risk" has been widely used in recent years since several people have faced exposure to various chemicals through dermal, inhalation or ingestion routes. Thus there are various web sites, and resources provide information needed for human hazard identification, dose-response evaluation. assessment, characterization, exposure risk and risk management. Substantial collections of information on multiple aspects of risk assessment are found in sites sponsored by Risk World, the (US) EPA's National Center for Environmental Assessment (NCEA), the (US) National Library of Medicine's TOXNET, the (US) Agency for Toxic Substances and Disease Registry (ATSDR), and the International Programme on Chemical Safety (IPCS) (Patterson et al., 2002).

Health effects of ambient air pollution mainly focus on classical pollutants such as nitrogen dioxide, sulfur dioxide, ozone and fine particles (McKone et al., 2009, Schwartz and Neas, 2000, Pope et al., 1995, Fairley, 1999, Schwartz et al., 1996). Recent studies, indoor air pollutant studies focus on risk assessment due to high level of VOC concentration (Sax et al., 2006; Guo et al., 2004b; Payne-Sturges et al., 2004; Fischer et al., 1998; Tancrede et al., 1987, Wallace, 1991). Although indoor air is evidently an important contributor to human exposure to pollutants, pollutants in outdoor environments also contribute considerably to risk since outdoor pollutants are considerably transported to the indoor environment (Wallace, 1991). Hence variability in indoor pollutant concentration is dominated by compounds associated with traffic emission (Edwards et al., 2001).

In conventional risk assessment studies of air pollutants, the estimated cancer risk, i.e. the additional risk of developing cancer due to continuous lifetime exposure to carcinogenic compounds, is calculated as the product of unit risk and the exposed concentration (USEPA, 2005). The concentration estimates are usually based on measurements of individual hazardous air pollutants (HAPs) and the risk estimates are compound-specific. For example, Pratt et al. (2000) measured VOCs, carbonyls and PM10 at 25 sites throughout different periods for 8 years in Minnesota and estimated the cancer risks of 16 pollutants ranged between 4.7-10–5 and 11.0-10–5. They indicated that the

inhalation cancer risk was apportioned to mobile sources (54%), area sources (22%), point sources (12%), and background (12%).

Similarly, Tam and Neumann (2004) analyzed 43 hazardous air pollutants (HAP) at five monitoring sites from July 1999 to August 2000 in Portland, OR, USA and calculated cancer risks for these 43 HAPs. They showed that 17 HAPs exceeded the cancer risk level of 1×10^{-6} at all sites with carbon tetrachloride, 1,3-butadiene, formaldehyde, and 1,1,2,2-tetrachloroethane providing 50% of the total lifetime cancer risk (2.47x10⁻⁴) and mobile sources provided the greatest percentage (68%) of HAP emissions.

Morello-Frosch et al. (2000) used model results for 148 HAPS to characterize cancer and noncancer risk in California for the base year of 1990. They calculated the median individual cancer risk as 2.7x10-4 for all air toxicants. PAH, 1,3 butadiene, formaldehyde and benzene caused 70% of the total cancer risk. They deduced that cancer and non cancer health risks originated mostly from mobile source emissions. In a similar way, Woodruff et al. (2000) studied on the same modeled data to evaluate carcinogenic health effects across the United States.

Wu et al. (2009) evaluated the source-specific lifetime excess cancer risks by combining the source apportionment modeling and risk assessment for VOC and PM2.5 collected in Seattle, WA between 2000 and 2004. The overall cancer risk was calculated as 6.09×10^{-5} , with the background (1.61 $\times 10^{-5}$), diesel (9.82 $\times 10^{-6}$) and wood burning (9.45 $\times 10^{-6}$) being the primary risk sources. It was also established that the diesel and wood burning sources presented similar cancer risks although the diesel exhaust contributed less to the PM2.5 mass concentration than the wood burning.

Ohura et al. (2006) measured indoor and outdoor VOC concentration via active sampling in an industrial city, Shimizu, Japan, in the summer of 2000 and the winter of 2001. They calculated the cancer risk value for the selected VOC into outdoor concentration ranged from 10⁻⁵ to 2.7x10⁻⁵. They inferred that although indoor air contributes to human exposure to pollutants and to increasing risk, pollutants in outdoor environments also contribute to risk mainly because of their transportation to the indoor environments.

CHAPTER 3

MATERIALS AND METHOD

The sampling study of the thesis consisted of two main campaigns. The first was conducted in Bursa. In order to assess the VOC and conventional air pollutant levels across Bursa, five measurement periods were completed. The second campaign was conducted in Ankara in January–June 2008 to determine the effect of meteorological conditions on uptake rates of VOC. Subsequent sections in this chapter are devoted to the following Bursa Campaign and Ankara Campaign.

3.1 Bursa Campaign

The weekly sampling periods were conducted in four different seasons from 2005 to 2007 in Bursa. A sampling and analytical method was developed for the quantitative determination of VOC. The method was developed before field sampling application in Bursa. The following section consists of the sampling and analytical method improved for Bursa sampling campaign.

3.1.1 Study Site

Bursa, the 5th biggest city of Turkey, is located on the north-west skirts of Mount Uludağ and to the south-east of The Marmara Sea. With a population of over 1,617,487 in the city center and 2,507,963 in the city, it is one of the most densely populated areas in Turkey (SSI, 2008). Bursa occupies the 6th place in terms of bank investment per person in Turkey, and in terms of the number of vehicles in traffic, it is the 4th in Turkey. The city has quite an important place in automotive sector, which is the most developed industrial sector in the country, and also in machinery, textile, and food industry. Bursa comes in the 3th order after Kocaeli and Istanbul considering the proportion of general budget expenses to income. A total of 6 Organized Industrial Zones are located in central districts and there are 13 zones in the whole province which occupy an area of 2,800 hectares. Agriculture also constitutes an important part of the economy in the city. In addition to these features, another significant point is the geographic location of the city. It is served by both minor and major roads since the city stands at the crossroads of Ankara-Istanbul and Izmir routes. It has a high traffic level as a result of its geographic importance. Today, these transit roads pass through residential areas and cause severe air pollution within the city.

The climate in Bursa displays a transition between Mediterranean and Black Sea. Winters are not much harsh and similarly severe droughts do not happen in summer. The highest precipitation is in winter and spring months. The amount of mean annual precipitation is 70.6 cm. The average relative humidity is around 69%. The average annual temperature of the central district is 14.4 ^oC.

The city center of Bursa consists of three districts, namely, Osmangazi, Yıldırım, and Nilüfer. Air samples were collected at different sites of these districts in Bursa in order to investigate the spatial distribution of VOCs in areas with different land use, populations and traffic densities. The study includes locations with high settlement densities, areas strongly impacted by traffic and industries and areas which are e not under direct influence of any pollution sources. The satellite imagery in

Figure 3.1 shows the settlement density of the city. The boundaries of the study area were established as Mount Uludağ at the south, the new high way under construction at the north, Uludağ University Görükle Campus at the west, and Gürsu at the east. After establishing the boundaries of the study area, a grid system was developed in order to find out the positions of passive sampling points and 86 points were specified within the study area, where sampling stations are situated at the corners of the grid system. Afterwards, those stations which were far away from pollutant sources were carried to source areas in such a way that more stations were located around roads and industrial zones, which were considered as potential pollutant sources.

VOCs were collected in five weekly sampling campaigns carried out from September 2005 to July 2007 at 86 points selected within a sampling grid composed of 450km2, which covers the whole territory. Figure 3.2 represents the sampling point locations with color codes. Twenty five points were selected in residential areas. These areas are mainly occupied by residential apartment blocks, schools, hospitals and small retail shops. Ten points were determined in five different organized industrial zones to represent the effects of industrial areas on urban air quality. These organized industrial zones are located in different parts of the city and contain different types of industries. It was decided that four tubes would be located outside the city for background measurements. These four points were far southeast, southwest, northeast and northwest of the city. They are generally in forested areas and away from the residential areas. Twelve points were selected next to the main roads and junctions. The coordinates and characteristics of sampling points are also given in Appendix A. The passive sampling tubes used in the field studies were put in the areas by taking the predominant wind direction into consideration during field campaigns. Attention was also paid not to locate sampling tubes at points that are under direct influence of strong emission sources.

3.1.2 Sampling Campaigns

Five separate passive sampling campaigns were conducted between 2005 and 2007. The sampling schedules of these periods are represented in Table 3.1. Since the sampling area covered 450 km², the passive tubes were installed to and collected from the field in two days. Throughout the sampling periods, on the first day the tubes were put in the east of the city and on the second day they were put in the west part. Since the tubes were collected from the area in the order that they were placed, each tube was exposed for exactly seven days.



Figure 3.1 The satellite imagery shows the settlement density of the city



Urban	Road	Industry	Background

Figure 3.2 Selected sampling points acroos the city center (maps.googleearth,2009)
Name of Sampling	Start Day	Finish Day		
Periods				
September 2005	9-10 September (2005)	16-17 September (2005)		
October 2005	05-06 October (2005)	19-20 October (2005)		
April 2006	03-04 April (2006)	10-11 April (2006)		
February 2007	22-23 February (2007)	01-02 March (2007)		
July 2007	05-06 July (2007)	12-13 July (2007)		

Table 3.1 The time schedules for all sampling campaigns

All the sampling points were situated such that sufficient numbers of samplers were located around roads, in residential areas, in locations that are not under direct influence of traffic, in two main and three minor organized industrial zones of the city and at background locations that are outside the city. Since samplers were located at the same points in each campaign, five data for each VOC at each location were generated. These data were grouped as background, industrial, residential and road, and compared to see if there are significant differences between different station groups in Section 4.3.

The first period, namely September 2005, was conducted in autumn. The first sampling period was sort of a pre-sampling campaign, conducted to generate preliminary information on VOC levels in Bursa and to detect potential problems in our sampling system. During the study it was seen that stainless steel screens, which are put on and under the adsorbent to prevent it from spilling from the sampling tubes, were not suitable for this purpose. Adsorbents spilled during transportation and positioning from 5-10 tubes. Refilling and transporting them to the field caused loss of time. This problem was solved by modifying the sampler. The modification involved putting screen gauges which were specially produced in Middle East Industry and Trade Center (OSTIM) under and on stainless steel screens, and in this way, screens were prevented from coming loose. After this modification, no spilling problem was encountered with the tubes. With all these problems only 36 passive tubes were collected and analyzed during the campaign of September 2005. The passive tubes collected in September 2005 and other periods are

grouped depending on their distances to different emission sources. Number of samples collected in each station group is given in Table 3.2.

Before starting the second sampling period, October 2005, results obtained from the first sampling period and the results for VOC obtained as a result of ten-day sampling, which collected samples only in Hıfzıssıhha, which was located near the online GC-FID system inlet, were compared in terms of masses of compounds collected on adsorbent. Long exposure time can be used for VOCs without breakthrough and hence it was thought that long time could give better resolution for low concentration of VOC. Two-week exposure time was selected for the second sampling period. The second sampling period was the main one, which was conducted in autumn for VOC and SO₂, NO_2 and O_3 in two weeks. However, at the end of the field study, it was decided that two weeks were not that practical as it was first thought. Extending the time did not cause a breakthrough; however, the peaks of compounds with low concentration were not much different from the result of one-week sampling period. Compounds with high concentration like BTEX could already be distinguished quite well in one-week period. Moreover, leaving the tubes in the field for such a long time increased the probability of theft. For these reasons, for all the field studies to be conducted henceforward, the exposure time has been selected as one week.

The third sampling campaign, April 2006, was conducted in spring season. A total of 51 tubes of VOC, SO_2 , NO_2 and O_3 passive sampling tubes were located at the selected points for this campaign.

The fourth and the fifth sampling periods, February 2007 and July 2007, were conducted in winter and summer seasons. Inorganic samplers were not included in these two campaigns, because of their high cost. In these two campaigns the numbers of passive sampling points were increased in industrial areas. Seventeen points were added to 10 sampling points, which were sampled in the previous campaigns Thus a total of 27 samples were collected from 5 industrial zones. Numbers of passive tubes collected at each sampling campaign are given in Table 3.2. Numbers of field and laboratory blanks used in each sampling campaign are also presented in the same table.

Sectors	Sept	Oct	Apr	Feb	Jly
	2005	2005	2006	2007	2007
Residential	20	20	25	25	26
Background	1	4	4	4	4
Roads	8	8	11	11	11
Industry	7	8	10	27	27
field blank	1	2	2	5	3
Lab blank	2	2	3	2	2
Total	39	44	56	74	73

Table 3.2 Number of samples collected at different sectors for all campaigns

Meteorological information was obtained from the General Directorate of Meteorology. Since meteorological data were hourly, whereas sampling was for one week, we averaged hourly values of meteorological parameters for the whole week corresponding to passive sampling period.

3.1.3 Sampling Methodology

Passive sampling tubes used in VOC sampling in ambient air are shown in Figure 3.3. In this study, VOC stainless steel passive sampling tubes with a length of 8,89 cm, an outer diameter of 6,35 mm, and filled with Chromosorb 106 adsorbent were used.

Although organic passive sampling tubes were sent from Gradko Ltd. ready to use at the beginning of the first and second sampling periods, all the tubes were conditioned before using by purging them with 50 ml/min of pure nitrogen gas while heating them at 250 °C, the max allowable condition temperature for Chromosorb 106, for 15 min on the GC-FID to remove any organic contaminants that may have emerged during shipment.



2 statinkes stell screen6 sample tube3 screen gauge (home made)7swagelock storage cap4. adsorbent8. diffusion lengt

Figure 3.3 Schematic representation of organic passive sampling tubes (Roche et al., 1999)

The time between two sampling periods was approximately six months. The sampling tubes used for all sampling campaigns were refilled with Chromosorb 106 since the long storage time could cause artificial affects on adsorbent. Detail information on sampling tubes is provided in the section 3.3.1.

After conditioning, ten conditioned tubes were randomly selected and analyzed to control the cleanless of the tubes. Swage lock-type screw caps with combined PTFE ferrule were used to seal the tubes. The sealed tubes were stored and transported inside sealed glass tubes filled with silica gel and charcoal at the bottom. The sample tubes were kept cold in refrigerator, which works with car battery, during transfer to and from the site. All the tubes were stored in deep-freeze in the laboratory at -18 °C before and after analysis. Sample tubes were tightly closed with swagelock caps and were kept in sealed glass tubes, and in sealed glass jar filled with activated charcoal until they reach to room temperature before analysis. The way tubes sealed to avoid potential contamination is depicted in Figure 3.4. All sample tubes were analyzed within four days after the end of the sampling campaign.



Figure 3.4 Handling of sorbent tubes

European Standard (EN) 13528 (2002) and Turkish Industrial Air Pollution Control Regulation (2004), were followed during sampling. Shelters made from aluminum were used to protect tubes from harsh weather conditions and to keep them vertical during exposure periods in the field. Protective shelters were specially designed in OSTIM to house four different types of tubes in vertical position (VOC, SO₂, NO₂ and O₃ passive tubes).

Figure 3.5Figure 3.5 shows passive tubes in the shelter. Once at the monitoring site, organic tubes were allowed to reach ambient temperature before replacing the storage cap with diffusion cap.. The sealing cap at the non-sampling end of the tube was left in place in top position and the sealing cap was replaced with diffusion cap at the diffusive part of the tube. The sampling tubes were placed between 1.6 and 2.0 m above from ground level, and 1.5 m away from buildings or other obstacles that can interfere with the

free flow of air. Disposable powder free latex gloves were used during all sampling operations.

Field blanks were also put in a shelter, but sealing caps at both ends of hte tube were not replaced with diffusion cap.. At the end of the exposure period, the sample tubes were removed and stored inglass tubes and storage bottles (the same way they are brought to the field) for transportation back to the laboratory. All the information related to the starting and finishing time of sampling, sampling point locations, their names and coordinates, and meteorological conditions was recorded on the field sheet. The sample field sheet is given in Appendix.B

NO₂, SO₂ and O₃ passive sampling tubes consist of screen covered with different chemicals and a polyethylene body to protect the gauze. Though various designs can be found in different companies for these sampling tubes, since GRADKO is a well-known and accepted firm in the world, the tubes were obtained from this company (England) and sent back to the same company for analysis at the end of sampling. The findings of the analyses were taken from GRADKO via e-mail. Inorganic samplers were kept in plastic tubes.

At the end of the field campaign, those samples for which SO_2 , NO_2 and O_3 measurement would be performed were shipped to England in the shortest time possible.

3.2 Ankara Campaign

In the study conducted in Bursa, the uptake rate was calculated for each period by comparing masses collected in passive tubes with values measured in GC. However, it was observed that although the calculated uptake rates were highly consistent within the sampling period, they deviated considerably between the periods. It was decided that it was not correct to assign a fixed value to uptake rates and that using an equation based on meteorology decreased uncertainty in calculations. Therefore, a comprehensive uptake rate study to be conducted in Ankara was planned. In this study, uptake rates were determined for 25 VOCs by running active and passive samplers side by



Figure 3.5 Passive sampling tubes in the field

side for a six-month period. In addition to determining uptake rates, the effect of meteorology, sampling duration, atmospheric VOC concentrations and adsorbent type on uptake rate were investigated. The Ankara uptake rate study was described in detail in the following section.

3.2.1 Study site

The sampling point where both active and passive samples were collected is located in Middle East Technical University in Ankara. A sampling cabinet was constructed at the Environmental Engineering Department of the university and all sampling was performed at that station. The sampling location is given in Figure 3.6. The distance of the station to the nearest road in METU is approximately 50 m. This road does not carry a heavy traffic, as the Environmental Engineering Department is not located in the middle of the university. The distance of the station to Eskişehir highway, which is a busy road joining downtown Ankara to its suburbs, is approximately 2700 m. The area can be defined as "suburban". Since settlement and traffic in METU is not very dense and there is no other VOC emission sources in the vicinity of the sampling point, the levels of pollutants measured in the station can be considered as "background" levels in Ankara. In previous studies in our group, where VOCs were sampled by active sampling both in the city and in METU, the concentrations measured in METU were consistently lower than the concentrations measured in downtown Ankara (Kuntasal, 2005).

The picture of the station at the Environmental Engineering Department is depicted in Figure 3.7. The station consists of a protected cabinet that houses the active sampling system and protects the equipment such as pumps, mass flow controller, etc. from meteorological conditions. Active sampling adsorbent tube is situated outside the cabined and connected to the sampling pump and flow measuring equipment via ¼" high density polyethylene tubing. Since the passive samplers have to be exposed to ambient air, they are installed immediately outside the cabinet. The distance between passive samplers and active samplers is approximately 20 cm.





Figure 3.6 The sampling point at Environmental Engineering Department, METU



Figure 3.7 The cabinet holled the passive and active s tubes during the sampling

3.2.2 Sampling Campaign

A comprehensive sampling was conducted at the field study to produce adequate amount of data so that multivariate statistical methods can be used without bias during interpretation of the data.

The basic principle in determining uptake rates of VOCs is to perform active and passive VOC measurements at the same location and for the same time period. Then the concentration data produced from active measurements is coupled to VOC masses collected on the passive sampler to generate UR value which can be used to convert VOC masses collected on passive samplers into concentration units when active measurements are not available.

The method used for passive sampling is rather unique. Only the geometry of the sampling system and/or adsorbent used to capture VOCs can change. On the other hand, there are various options for methods that can be used for active measurements. Active measurements can be performed by on-line GC methods by collecting samples in canisters or onto solid adsorbents. Availability of various adsorbents also increases the possibilities for active VOC measurements.

Consequently, in the first step an active measurement method that will be used in parallel with the passive samplers should be selected. In this study, a collection of VOCs onto a solid adsorbent (Chromosorb 106) was adopted. Although on-line GC systems were available in our group and used for other studies, it is not used for UR determination, because it generates too many chromatograms to analyze. Passive sampling systems were retained in the field for time periods varying between 3 and 21 days (mostly about one week). On-line GC systems, on the other hand, generate one chromatogram every half hour, or at most every hour. This means analyzing at least $24 \times 7 = 168$ chromatograms for every set of passive samples collected. We considered generating a very high resolution data and then averaging them for a week as an unnecessary effort. Canister sampling was also avoided because there are still un-resolved questions about the difficulty of cleaning

canisters for heavy VOCs and thus the possibility for cross-contamination of samples.

In this study we adopted using a collection of VOCs onto Chromosorb 106 adsorbent and subsequent analyses with GC-FID system as the method for active measurement. The main reason for selecting adsorption onto a solid sorbent is its similarity to the passive sampling system used. As will be discussed later in the manuscript, passive samples were collected onto Chromosorb 106 located into $\frac{1}{4}$ " stainless steel tubes. The active sampling system used had exactly the same geometry and adsorbent. This resulted in measuring the same compounds in both active and passive measurements. We could have measured 70 – 100 VOCs if we had used on-line GC or canister, but in this study it does not mean too much, because only 34 VOCs were detected by the passive samplers.

As pointed out before, passive tubes were retained in the field for seven days. However, active sampling onto adsorbent tubes continuously for seven days is not possible, because all active sites on the adsorbent fills and VOCs leak in less than 24 hours due to the sampling geometry used in this study. It may be possible to collect samples for 24 hours using larger tubes carrying more adsorbent, but those tubes do not fit our thermal desorption system.

3.2.3 .Sampling Methodology

As the object of the study is to determine the uptake rates, active and passive sampling programmes were implemented in parallel. As stated before, since passive sampling period was about seven days and active samples had to be taken twice a day, a lot of active sampling was performed for each passive set and the average of results obtained from these tubes were compared to results from passive sampling tubes.

Because of the reasons stated above, it will be helpful to consider active and passive sampling as two distinct systems working in parallel to each other.

The results obtained from active sampling were used to calculate uptake rates in this study.

The programme for passive sampling implemented throughout the study and the number of active sampling measurements in each passive period are given in Table 3.3. As it can be seen from the table, the passive sampling study consists of 26 passive sampling periods. The object of the study was to calculate the uptake rates in real atmospheric conditions; thus a period that would include different meteorological conditions and cover at least one part of summer and winter was chosen as the period of sampling. Experimental studies started in the first half of 2008.

It was observed that during six months when passive samples were collected, the temperature (T) varied between -2 and 22 degrees, relative humidity (RH) varied between 52% and 86%, and wind speed (WS) varied between 0.92 m s⁻¹ and 3.0 m s⁻¹. These values are typical temperature, humidity, and wind values in Ankara. However, extreme weather conditions which occasionally occur in Ankara (e.g. temperatures of -20, humidity decreasing to as low as 20% or increasing to 100%, or wind with a speed of 10 m s⁻¹) is not observed during sampling. This is because temperature, humidity, and wind speed values given above are weekly average values. During this study, T, RH, and WS displayed very low and high values at times. Nevertheless, these occurrences never lasted a week, and thus it was not possible to see these values in weekly averages. How the meteorological conditions changed during sampling was discussed in greater detail in the following chapters.

In each passive sampling period, 8 passive sampling tubes, 7 of which were for sampling and 1 was a blank, were placed in the field.

	Sampling	The number	The number	
Sampling Period	duration	of active	of passive	
	(days)	sampling tubes	sampling tubes	
8-14.01.2009	6	24	7	
15-21.01.2009	6	24	7	
21-24.01.2009	3	12	7	
26-30.01.2009	4	14	3	
26.01-01.02.2009	6	22	3	
26.01-04.02.2009	9	32	3	
18-25.02.2009	7	18	7	
25-29.02.2009	4	16	6	
10-17.03.2009	7	28	7	
17-24.03.2009	7	28	7	
24-31.03.2009	7	24	7	
31.03-07.04.2009	7	28	7	
7-14.04.2009	7	28	7	
14-18.04.2009	4	14	3	
14-21.04.2009	7	24	4	
21-25.04.2009	4	16	7	
28.04-05.05.2009	7	22	7	
5-15.05.2009	10	38	3	
5-19.05.2009	14	54	3	
5-26.05.2009	21	82	3	
12-19.05.2009	7	28	3	
12-26.05.2009	14	56	4	
19-26.05.2009	7	28	7	
2-9.06.2009	7	28	3	
2-16.06.2009	14	40	3	
TOPLAM		728	128	

Table 3.3: The passive sampling schecula and number of active samplingcorresponding to each passive sampling period

3.3 Adsorbent Tubes

3.3.1 Passive Sampling

In principle the reference method TR-EN 13528 was used in passive sampling of VOCs. However, the method was modified slightly when it became necessary during experimental studies. This method bases on adsorbtion of VOCs onto a solid adsorbent. Preperation of passive tubes used in both Ankara and Bursa campaigns are discused below.

Tubes were first cleaned physically in 95% pure methanol for two hours in ultrasonic bath (Cole-Parmer, model 8892). The cleaned tubes were dried in oven at 200 °C. Then stainless steel with mesh was placed on one side of the tubes and these screens were fitted with a screen gauger. Afterwards, around 350 mg Chromosorb 106 (SUPELCO Company) was added from the other end of the tube. Weighing was performed in the laboratory using a 4-step scale (Sartorius MODEL A210P). At the end, adsorbent was fixed by putting screen and screen gauge at the other end of the sampler. Filling passive sampling tubes with adsorbent is depicted in Figure 3.8.

Since the adsorbents may have been contaminated, the tubes filled with the adsorbent were conditioned before they are located at the field. The conditioning process was completed in the home-made conditioning oven designed by Kuntasal (2005). In conditioning process, the tubes were placed in the conditioning oven and temperature was set to 250 °C. During this time, high-purity nitrogen passed through tubes with an air flow rate of 100 ml min⁻¹. Conditioning process lasted for four hours. After the process is over, adsorbent tubes are placed in protective glass tubes and kept in refrigerator until they are placed in the field. The home-made conditioning oven used in the study is shown in Figure 3.9. The conditioned passive and active sampling tubes were loaded with 4-bromoflorobenzene as surrogate standard. Results of analyses before and after the sampling were compared and differences between surrogate standard values were calculated. In this way, it was



Figure 3.8 Passive sampling tubes filled with adsorbent





Figure 3.9 The photograph and schematic representation of home-made oven (Kuntasal, 2005)

possible to check if there were any losses of VOCs collected in the tubes throughout the sampling. The calculated difference was always below 5%.

Passive sampling tubes were placed in shelters so that they were not influenced by rainfall. The shelter was mounted onto the active sampling cabinet and this enabled active and passive sampling to be carried out at points as close as possible. Up to 4 passive samplers can be placed in each aluminum protector. 2 aluminum protectors for each sampling set and 8 passive sampling tubes at one time were used in this study.

3.3.2 Active Sampling

As it was stated before, active sampling was performed on adsorbent tubes. Chromosorb 106 was used in active tubes like the passive ones as the adsorbent. The procedure described in USEPA, TO-14 document was used in both Ankara and Bursa parts of the study. However, some modifications were made in the procedure based on the implementation conditions. The most significant modification was preventing breakthrough by attaching two tubes one after another.

For active sampling, a special cabinet made from aluminum was used. A pump that provided air flow and a flow meter that controlled the air flow were put in the cabinet and this system was directly attached to active sampling tube. Active sampling tubes were hung down out of the cabinet. Active tubes were changed in the morning and in the evening. Although it was aimed to change active sampling tubes a particular time in the morning and evening, it was not fully possible to fulfill this. Since the average of numerous active tubes were calculated for each passive sampling set, collecting active samples at specific times was not important for uptake rates calculations.

The active sampling in this study was performed via adsorbent tubes. The reason for this is that adsorbent tubes were similar to passive sampling tubes with which the comparison would be made. Since the same adsorbent was used in active sampling tubes as in the passive ones, their susceptibility to different VOCs was the same. Active sampling tubes were filled and conditioned with the methods used for passive tubes. Active tubes were connected to a vacuum pump (SKC, model Universal) with low and high flow

capacity in the field and an air flow rate was adjusted to 16 ml min⁻¹. The air flow was fixed sensitively using an AALBORG, model GFC171 mass flow controller (MFC). The photograph of active sampling system is given in Figure 3.10.

The sampling flow rate was set such that no breakthrough of the compounds of interest was observed during sample collection. Breakthrough tests were conducted at all sites before and during sampling.

Two tubes were used one after another to eliminate loss of samples due to breakthrough of the front tube. The number of the subsequent samples was determined with breakthrough test. For this purpose, different numbers of tubes were attached to each other at the points where the stations would be built and sampling was performed before the study started, and so the number of tubes that would be sufficient to hold VOCs was determined. Although using several tubes, in series ensures leak-free sampling, it is not the preferred approach as it increases number of analyses. The preferred way is to perform sampling with a minimum number of tubes without any risk of leaking. In order to learn how many tubes could collect all of the VOCs quantitatively without any risk of leaking, sampling was performed 12 times using 4 tubes placed one after another and the amount of VOCs in each tube was figured out. The percentages of VOCs measured in 4 tubes placed one after another are shown in Figure 3-11. To create this figure, the total mass of VOCs collected in 4 tubes was given a value of 100 and then the ratio of the VOCs mass collected in each tube to this total value was calculated. After this, the VOCs percentages measured in the first, second, third, and fourth tubes were grouped in themselves and the figure was formed.

As it can be seen from the figure, nearly all of benzene and toluene were kept in the first tube. The average of benzene mass kept in the first, second, third, and fourth tubes in percent is $\%96 \pm 4$, $\%2 \pm 2$, $\%2 \pm 2$ and $\%2 \pm 2$ respectively. Toluene also displays a similar distribution. 97% of the total mass of toluene was collected in the first tube. In each of the other tubes, 1% of the total mass was measured. This situation was the same for all the other VOCs.



Figure 3.10 Active Sampling system



Figure 3.11 Benzene and toluene fractions collected in each tube in sampling series consisting of adsorption tubes placed one after another (The front most tube: 1. Tube and the backmost tube: 4. Tube)

The figures above may give the impression that 2-3% of the VOCs passes through the first tube; however, this is not true. In fact the VOCs masses measured in the second, third, and fourth tubes are not VOCs molecules that escaped from the first tube, but VOCS molecules which were absorbed onto the adsorbent in the laboratory before samplers were put in the field. When these blank values were removed, in none of those 22 trials were VOCs seen in the second, third, and fourth tubes.

As a result, the study we carried out to find potential leaks from sampling tubes made it clear that one single tube would be sufficient for this study. However, throughout the study sampling was performed with two tubes placed one after another not to take any risks. Both tubes were analyzed in each sampling.

3.4 Analytical Techniques

The sample tubes were analyzed by 6990 Gas Chromatography (GC), equipped with a Flame Ionization Detector (FID), which included a Deans Switch device that was coupled with Unity Thermal Desorption System. The GC system was obtained from Hewlett-Packard (Agilent Technologies Inc, Palo Alto, CA, USA) and unity thermal desorption system compatible with GC was obtained from Markes (Markes International Limited, CF72 8XL, United Kingdom). In the system, samples collected on sorbent tubes are thermally desorbed by a Thermal Desorber at 200 °C. During the desorption process, samples are first captures in a cold trap at -15 ^oC. Cold trap is then suddenly heated for 6-8 seconds and gas phase analytes are introduced to the inlet of GC equipped with Dean Switch system. Dean Switch system is used to obtain better resolution of the peaks with two different types of column. Light VOCs compounds (compounds with molecular weight smaller that of hexane) were held on an Alumina Plot capillary column and heavier compounds whose molecular weights are higher than hexane were captured on a DB1 capillary column with the help of Dean switch system.

The external calibration standard mixture supplied by Environment Technology Center, Environment Canada (Ottawa, Canada) was used for the calibration during September 2005, October 2005 and April 2006. The gasphase mixture supplied by Environment Technology Center contains VOCs which have carbon numbers varying between 2 and 12. Environment Canada standard was prepared at Toronto by mixing primary stock gas mixtures in a 15-L SUMMA polished canister, in such a way that each of the 148 VOC in the canister had concentrations between 2 – 20 μ g m⁻³. Seven stock gas mixtures with purities better than 98% (Scott Specialty Gases, Plumsteadville, PA, U.S.A.) were used to prepare the mix. Since the expiry date of the standard supplied by Environment Canada Technology Center was over, PAMS and halogenated VOCS gas standard were separately purchased from Scott Specialty Gas and used in February and July 2007 campaigns at Bursa as well as in most of the Ankara uptake rate study. PAMS standard includes 55 hydrocarbons with carbon number between 2 and 12, measured at photochemical assessment monitoring stations (PAMS) in the U.S. Since PAMS standard did not contain halogenated compounds, halogenated VOCS standard containing halogenated hydrocarbons with bromine or chlorine was supplied separately from Scott Specialty Gas Co.

Although 148 VOCs ranging from C2-C12 supplied by Environmental Canada and 75 VOCs supplied by Scott Gas were identified in GC-FID, during calibration process, Chromosorb 106 provides the determination of only those compounds ranging from C5-C12 due to its sorbent characteristic.

4-Bromofluorobenzene was used as surrogate standard in both Bursa and Ankara studies. It was used to detect losses during both sampling and analysis steps. Samples were checked by calculating peak areas before and at the end of the sampling period. Although up to 20% difference is generally accepted, The difference did not exceed 10% in this study.

3.4.1 VOCs Measurements

3.4.1.1 Target Analytes

The method developed in the GC-FID unity thermal desorption system was identified for a wide range of VOCs including aromatics, olefins, paraffins, halogenated compounds that were most widely detected in ambient air. The target analytes were selected in this study based on i) the most common of compounds in ambient air ii) cause of the adverse health effects iii) potential for a compound to act as a tracer for specific source such as petroleum, cleaning solvent, solvent used in industry. The list of the target analytes which were used in Bursa and Ankara campaigns together with some of their physicochemical properties are given in Appendix C. The comparison of the PAMS, halogen and AAQD standards and retention time of each VOCs in GC-FID system are also represented in Appendix D. The VOCs that is available at the standard is indicated with a tick in the table.

3.4.1.2 Optimization of GC-FID System Parameters

GC-FID system with double FID is a very powerful chromatographic tool for both complete separation of rather complex mixtures and reducing the time of analysis (Veillerot et al., 1998). In the GC-FID system, samples collected on sorbent tubes are thermally desorbed by a Thermal Desorber at 200 ^oC. During the desorption process, samples are sent into cold trap at -15 ^oC to collect gas phase elution. Cold trap is electronically cooled to provide better peak resolution. Cold trap is then suddenly heated at the end of the desorption within between 6-8 seconds to avoid peak broadening and gas phase analytes are introduced to the inlet of GC equipped with Dean Switch system. Dean Switch system is used to obtain better resolution of the peaks with two different types of column. Lighter compounds whose molecular weights are lighter than hexane go through the Alumina Plot capillary column and heavier compounds whose molecular weights are heavier than hexane go through DB1 capillary column with the help of Dean Switch system. The analytical columns used in the GC-FID were supplied by J&W (Palo Alto, CA, USA). DB-1 column (Catalog Number: 122-1063) which is suitable for heavier hydrocarbon analysis was 60 m in length, 0.32 mm in diameter and had 1 μ m and 100% dimethlypolysil oxane coating. The column can operate at temperatures ranging from 60 °C to 325 °C. The alumina plot column (Catalog Number: 19091P-S15) used to analyze lighter hydrocarbons was 50 m in length, 0.32 mm in diameter and had 8 μ m film thickness.

The required gas with purity above 99.999% for the GC system was supplied by BOS (BOS A.Ş., Ankara, Turkey). Nitrogen was used as a carrier gas. Hydrogen and dry air gas was used for ignitiation of the flame ionization. Although high purity gases were supplied to the system, the gas was first passed through a hydrocarbon and oxygen trap and then to the system.

To obtain good peak resolution that results in higher sensitivity, oven temperature programming, column flow rates, sample tube desorption temperature, and injection port temperature were optimized in the GC-FID Unity TD system.

Effect of the Sample tube Desorption Temperature

For the optimization of the thermal desorption system, different parameters were examined based on the recommended operational values by the producer. The maximum thermal desorption temperature for the sample tube filled with Chromosorb 106 is given as 200 °C. The effects of the sample tube desorption temperature for the recovery of the VOCs on the sorbent was inspected by desorbing sample tubes at different temperatures. Figure 3.12 shows the dependence of the analyte recovery on the desorption temperature for selected compounds. In the figure, the peak area has been normalized to the maximum value for each individual compound. It was concluded that the peak area responses for all compounds increased with increasing desorption temperature. Thus the optimum desorption temperature was chosen as 200 °C.



Figure 3.12 Dependence of analyte recovery on desorption temperature

Effect of Cold Trap Temperature

The maximum operating temperature for the cold trap is given as 400 °C and typical desorption temperature range is given as 300-320 °C, in the operation manual of the instrument. The effect of cold trap temperature for the recovery of the compounds on the trap was also investigated and results are depicted in Figure 3.13. Typically trap temperatures between -15 to -10 °C is frequently used in the literature for the quantification of the ultra volatile compounds such as ethane and acetylene. Therefore, the lowest temperature supplied the highest compound recovery, which was -15°C was used throughout the study.



Figure 3.13 Effect of the cold trap temperature on the recovery of the selected target compounds

Effect of Sample Tube Desorption Time

Figure 3.14 shows the dependence of analyte recovery on desorption time. Optimum desorption time should be long enough to ensure complete desorption of target analytes from the sample tubes. The optimum desorption time of the sample tubes was determined to range between 5 and 10 min. The desorption time was selected as 5 min for the study.

In addition to these parameters, optimization was also performed for sample flow rate, cold trap desorption flow rate and split ratio. Flow rate of the sample tubes was selected as 30 ml/min and cold trap desorption flow rate was set to 50 ml/min, the 8/3 split ratio provided a good recovery of all target analytes.



Figure 3.14 Dependence of analyte recovery on desorption time

Effect of GC Parameters

Thermal desorption and GC-FID parameters were also optimized before the field study. Chromatographic peaks were identified for 148 VOCs compounds. Since peak identification in FID detectors is based on Retention time (RT), it took a long time to identify 148 VOCs. During the identification study, different certified standards which include olefins, paraffins, halogenated VOCs mix, Benzene-toluene-ethlybenzene-o-xylene mix, hydrocarbon mix were separately used to confirm each peak. Compounds lighter than hexane elute from the DB-1 column and go through Alum-Plot restrictor column. The valve position is set to 'on'. Compounds heavier than hexane elute from the DB-1 column field standards the valve position is returned to the 'off' position. Valve position time was determined by hexane retention time before the identification of the peaks. Operating conditions for Thermal Desorber and GC-FID during sample analysis are provided in Table 3.4.

Thermal	Dry Purge flow rate	120 ml/min			
Desorption	Dry Purge Tm-Prepurge Time	1 min- 1 min			
	Tube Desorption Temp	200 ^o C			
	Tube Desorption Time	5 min			
	Tube Desorption flow rate	50 ml/min			
	Cold Trap min temp	-15 ^o 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 χ 0.25 mm χ			
		1µm			
	Column2	HP Al/S,50m χ 0.32 mm χ			
		8µm			
	Flow Rate for Column1	2.8 ml/min			
	Flow Rate for Column2	5.2 ml/min			
	Temperature Program	40 °C hold for 5min			
		5ºC/min to 195 ºC, 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 ^o C			
	Air Flow	300 °C			
	Make-up (N ₂) flow	2 ml/min			
	FID Parameters for Column2				
	Temperature	300 °C			
	Hydrogen Flow	30 ⁰ C			
	Air Flow	300 °C			
	Make-up (N ₂) flow	2 ml/min			

Table 3.4 Operating conditions for unity thermal desorption and GC-FID system

3.4.1.3 Quantification

Quantification was performed according to the External Standard Method. The external method involves plotting the area or the height response against concentrations of the analytes in the standard. The calibration factor is then calculated as the ratio of concentrations to the area or the height response and it should be constant over a wide range of concentrations. To determine the concentration of the analyte in the unknown sample, the response for the unknown should be compared with that of the standard within the linear range of the curve (Kuntasal, 2005).

The External Standard Method uses Absolute Response Factor (ARF) which was obtained from the calibration. Sample amounts are calculated by applying these response factors to the measured sample amount. The HP software plots response ratio versus amount ratio and generates a linear relationship between these variables. The resulting slope represents the ARF used for the calculation of sample analyte concentration.

Initial calibration including 6 concentration points was performed prior to the field study to determine absolute response factors for target analytes, linearity of response, and system sensitivity.

Figure 3.15 shows 6 point calibration chromatograms for toluene. The acceptance criteria for the initial calibration are as follows: i) the area response for each standard at each calibration level must be within $\pm 30\%$ of the average response over all the calibration levels, ii) the correlation coefficient (R²) of the regression line for individual target analytes must be greater than 0.98. These criteria were met for the initial calibration runs. A typical calibration chromatogram is presented in Figure 3.16.



Figure 3.15 Five point calibration peaks and the calibration curve for toluene

Midpoint calibration standard is injected twice a week to test the validity of the previous calibration. The acceptance criteria for the control calibration were that recovery (ng) of each target analyte must be within $\pm 30\%$ of the recent initial calibration values.

Chromatograms were analyzed (amount (ng) of each compound was calculated) using ChemStation Software. Each sample chromatogram was quantified according using the most recent calibration. A typical sample chromatogram is given in Figure 3.17.

3.4.1.4 Active Measurements

In Bursa study, active sampling was performed along with passive sampling. Ambient concentrations of C_2 - C_{12} VOCs were measured on an hourly basis, using an online GC-FID, at the Bursa Hygiene Center (Yorulmaz, 2009). Active sampling was performed in two campaigns. The first measurement campaign was between September 14 and November 6, 2005 and the second one was between March 17 and May 10, 2006. Approximately 3500 chromatograms were generated during these two active sampling campaigns.



Figure 3.16 Typical calibration standart chromatogram



Figure 3.17 Sample Chromatogram

Data from active sampling studies were not evaluated within the scope of the thesis. However, they are used to convert VOC masses collected on passive samplers into concentrations.

Automatic GC-FID operated in autumn 2005 and spring 2006 seasons. Passive sampling campaigns, performed in September 2005, October 2005 and April 2006 coincided with these active measurements,

Apart from these, while automatic GC device was operational, 3 or 5 passive tubes were placed next to the inlet of the instrument and left there for one week. In this way data we were able to compare simultaneous data generated with co-located active and passive systems. Results are given in Table 3.5.

The results of active and passive sampling shown in the table for BTEX compounds demonstrate a reasonable agreement between the two VOC measurement techniques. The relative standard deviation in Benzene active and passive measurements varies between 6% and 30% with an average value of 18%. Toluene compared better than Benzene. Its relative standard deviations varied between 8% and 24% with an average of 16%. Ethylbenzene and m,p-xylene showed a significantly better agreement when compared with the agreements in Benzene and Toluene data. Relative standard deviation values for ethylbenzene varied between 0.5% and 8% with an average of 3.1%. Similarly, relative standard deviation values for m,p-xylene varied between 0,7% and 11%. The comparisons of other VOCs which are not included in this table were in the same range.

This comparison between active and passive sampling with co-located samplers demonstrated that both sampling systems do generate data within $\pm 20\%$. This uncertainty between active and passive sampling technology gives a perspective on how to utilize passive sampling data.

The lack of agreement between active and passive sampling in Benzene and toluene is probably due to incomplete coverage of the passive sampling period by active measurements. In some of the sampling periods given in Table 3.5

		Sept 2005	Oct 2005	Aprl 2006	Ind 2006	hıfsısıha 1	hıfsısıha 2	hıfsısıha 3
Benzene	passive	1.98	2.14	4.10	2.61	0.47	2.63	3.62
	active	2.73	3.24	5.21	2.80	0.58	2.87	4.25
	%std dev	22.63	28.98	16.76	5.06	14.95	6.29	11.34
	passive	18.68	25.75	13.42	12.85	7.47	4.85	20.60
Toluene	active	24.46	28.92	17.19	14.50	10.57	6.43	26.25
	%std dev	18.94	8.20	17.38	8.51	24.26	19.82	17.06
Fthylbenze	passive	2.25	2.62	1.87	1.49	0.90	0.77	2.25
ne	active	2.20	2.75	1.66	1.37	0.92	0.78	2.26
	%std dev	1.69	3.38	8.55	5.97	1.39	0.55	0.58
m+p- Xylene	passive	7.40	7.95	4.93	4.06	0.97	1.87	5.59
	active	6.42	8.32	4.88	4.01	1.06	1.92	6.55
	%std dev	9.95	3.17	0.72	0.97	5.96	1.75	11.24

Table 3.5 The comparison of active sampling result with .passive sampling result

active sampling was interrupted for short periods of time. That particular sampling period is not included in comparison if such interruptions were>20%, but included in comparison if they are <20%. Interestingly September and October periods, where relative standard deviation between the two methods was >20%, were the ones with data capture rate in active sampling was close to 80% of passive sampling (20% interruption in measurements). The periods with small relative deviation are the ones with data capture rate in active sampling is close to 100%. These observations, although they are not conclusive evidence, gives the impression that relatively high RSD observed in benzene and toluene can be related with the data capture rate.

Another interesting feature of obtained from this small exercise was the impressive precision of VOC data generated with passive samplers. The relative standard deviation between co-located 7 passive sampling tubes was always less than 5% for most of the VOCs that can be measured with relatively low uncertainty. This increased our confidence in passive sampling enormously.

The passive data presented in the table were obtained through uptake rate equations the meteorology which were obtained in the Ankara study. Fairly good agreement obtained between active and passive data also demonstrated reliability of the uptake rate equations generated in Ankara part of the study...

3.4.2 Inorganic Measurements

GRADKO Co. (London, UK). The tubes were sent to us by the GRADKO Co., we deployed then to field. At the end of sampling period, the passive samplers were send back to GRADKO Co. where they were analyzed. Results (in µg m⁻³) were sent by e-mail. The passive sampling methodology for inorganic pollutants could be developed in our laboratories like sampling methodology developed for VOCs measurements. We avoided developing methodology for passive sampling of inorganic pollutants because (1) our main interest was on
VOCs, (2) attempting to develop methodology would significantly increase our work load, and (3) Analysis of sampling tubes by GRADKO was reasonably cheap.

3.5 Quality Assurance/Quality Control

The development and the use of QA/QC protocols is the other important step that signifies the reliability of the generated data set. Separate QA/QC protocols were used for analytical procedures and the data set. Each of these consisted of several steps, which will be discussed in subsequent sections.

3.5.1 Analytical System Quality Assurance and Quality Control Procedure

The instrument was controlled for its performance before starting any analyses. To eliminate any contamination coming from the analytical system, the injection port, GC oven and cold trap were conditioned at the beginning of each sampling campaign. The sample with zero air was run two times after conditioning to control any potential contamination of the system. When contamination was observed, the source of the contamination was found and it was eliminated.

The performance of method was evaluated with method detection limit, collection efficiency precision, and recovery. These analytical performance parameters are discussed below. A more detailed table of analytical performance parameters, which includes, limit of detection, Calibration R^2 , tube precision, system precision, recovery and percent detected data for 105 VCOs are given in Appendix E.

3.5.1.1 Method Detection Limit

Method detection limit (MDLs) for each compound was calculated by multiplying by 3.14 (student's t value) with standard deviation obtained from seven replicate measurements of the first level of calibration (USEPA, 1999b). The calculated MDL of the analytical system ranged from 0.0034 μ g m⁻³ to 0.0455 μ g m⁻³ with an average value of 0.098 μ g m⁻³. MDL could be calculated for 36 compounds, for which uptake rates were calculated in Ankara study. Performance parameters are given for 105 VOCs in Appendix E. These are the VOCs detected in calibration mixture. However uptake rates are calculated only for 36 compounds that are detected in passive tubes.

Detection limits of 36 VOCs were in general one-to-three orders of smaller than VOC concentrations in measured in ambient air at Bursa. The only exceptions to this were 2,2,5-trimethylhexane and 1,1,1-trichloroethane. For these VOCs atmospheric concentrations were below their detection limits. Bromoform, on the other hand, was detected in most of the samples, but its ambient levels were only three times higher than its detection limit.

3.5.1.2 Precision of Linearity

The precision of analytical system was evaluated by six replicate measurements in the middle level of calibration curve. The linearity of the calibration curve was evaluated with the correlation coefficient (R^2) of the regression line which was drawn for the six point calibration curve. Precision and calibration curve R^2 values for 105 VOCs detected in the calibration mixture are given in Appendix E. The R^2 values varied between 0.8214 and 0.994 with an average value of 0.996 for 105 VOCs. These high R^2 values indicated that the linearity was not a serious problem throughout the study and the quality of the standard used was good.

3.5.1.3 Blanks

Laboratory and field blanks were evaluated for QA/QC procedure. Lab and field blanks were loaded with internal standard. Lab blanks were kept in refrigerator during sampling. Field blanks were left in place with both sealing end caps through the exposure period. At the end of the exposure period, field blank tubes were resealed and stored inside the glass tubes, with the sample tubes, for transportation back to the laboratory. During the field study, a total of 15 laboratory blanks and 16 field blanks were analyzed for the QA/QC procedure. The results of analysis showed that there was no contamination that occurred during the sampling periods. The masses collected on the blank tubes did not exceed the 10% of average masses collected on sample tubes.

3.5.1.4 Desorption Efficiency

Desorption efficiency of the tubes was evaluated by injecting known mass of gas phase analyte to the sorbent. The tubes loaded with standard were thermally analyzed. The same amount of gas phase analyte was analyzed by injecting directly into the GC system with the help of air server. The analysis results were compared with each other. The desorption efficiency ranged from 92% to 99% with an average of 96%. Recovery for each compound is given in Appendix E.

3.5.1.5 Collection Efficiency

Parallel six sample tubes were exposed in the field and analyzed to test the precision of the sampling technique. The relative standard deviation values of passive sampling tubes ranged from 1.18% to 29.56% with an average value of 13.14%. BTEX compounds have high repeatability due to their high concentration in atmosphere when compared to other compounds. Only relative standard deviation values of passive sampling tubes for 1,3 butadiene

compound was 20%. Since 1,3 butadiene is the most abundant tracer used for receptor modeling (Strandberg et al., 2005 and Martin et al., 2005), it was taken into account despite their low linearity and desorption efficiency.

3.5.1.6 Storage Stability

Nine sample tubes which were loaded with gas phase mid-level standard mixture containing 1-13 μ g/m³ of each analyte were stored in solvent-free refrigerator. Three samples were analyzed immediately after the injection loading of the standards. The batch of three samples was analyzed after two, five and nine days. The recovery range of the analytes was between 98% and 101%, with average 99% for two days, 90% to 98% with average 93% for four days, 81% to 92% with average 87% for nine days. The collected samples were analyzed within three days; there were no observed significant changes in the samples during three-day storage.

3.5.2 Uncertainty Calculation of the Passive Tube

The uncertainty was calculated from the study conducted by Plaisance et al, 2008. The uncertainty equation was based on standard 16662-4 and derived from "Guide to Expression of Uncertainty in Measurement" (GUM ISO, 1995). Although the uncertainty equation was applied for all compounds, the calculations of uncertainty for benzene and selected compounds are detailed in the following section. The combined uncertainty was calculated using equation 3-1.

$$\frac{u^2(C_{P,T})}{C_{P,T}^2} = \frac{u^2(m)}{m^2} + \frac{u^2(UR)}{UR^2} + \frac{u^2(d)}{d^2} + \frac{u^2(t)}{t^2} + \frac{u^2(\bar{T})}{\bar{T}^2} + \frac{u^2(\bar{P})}{\bar{P}^2}$$
(3-1)

Where;

u(m) the uncertainty due to analyte of mass

U (R) the relative uncertainty of uptake rate due to environmental factors

U(d) the relative uncertainty of thermal desorption recovery

U(t) the relative uncertainty sampling time

U(Ť) and U(P) the uncertainty came from conversion to standard temperature and pressure

The uncertainties due to uptake rate and meteorological conditions were excluded from the equation. The uptake rate deviations which come from differences in meteorological conditions will be discussed in Section 4.2.2., By using the uptake rate evaluation based on meteorology, we eliminate uncertainty that may emerge from this. Hence, equation 3-2 was evaluated to calculate uncertainty arising from analytical system and passive tube characteristics. Hence, equation 3-1 was rearranged into equation 3-2. Equation 3-2 consists of the deviation of determination of mass (u(m)) and thermal desorption recovery (u(d)).

$$\frac{u^2(C_{P,T})}{C_{P,T}^2} = \frac{u^2(m)}{m^2} + \frac{u^2(d)}{d^2}$$
(3-2)

3.5.2.1 Uncertainty of the desorption efficiency, u(d)

A set of seven sampling tubes loaded with 300 ml standard was analyzed. The replicate measurement results were depicted in Table 3.6 for benzene. The relative uncertainty was estimated by applying equation 3-3.

$$\frac{u^2(d)}{d^2} = \frac{u^2(m_{ref}) + (\frac{s^2(m_d)}{n})}{m_{ref}^2}$$
(3-3)

Where;

m_{ref}: Reference mass load

s(m_d): standard deviation of the replicate measurements

n: number of tubes

		mass
	area	(ng)
1 st run	108.23	5.93
2 nd run	104.66	5.73
3 th run	102.71	5.63
4 th run	109.08	5.98
5 th run	106.85	5.85
6 th run	107.87	5.91
7 th run	108.99	5.97
Mean		5.86
Std Dev.		0.13
std%		2.24
Desorption		
efficiency		97.7%

Table 3.6 Benzene desorption efficiency and uncertainty

As an example, the uncertainty of desorption efficiency for benzene was calculated with the equation 3-4

3.5.2.2 Uncertainty of the measured mass, u(m)

The uncertainty of the measured mass included six subgroups. These titles are listed as follows according to Plaisance et al. (2008):

- the selectivity of the chromatographic system,
- the analyte stability in the sample,
- the analytical precision,
- the response drift between calibrations,
- the lack-of-fit of the calibration function

According to Plaisance et al. (2008), the selectivity of the chromatographic

system was performed by the analysis of the passive tubes loaded with standard benzene and the interferant of benzene. Unfortunately, the chromatographic selectivity test could not be performed in this study due to the unavailability of the system. These performance results could not be evaluated for overall uncertainty equation.

The analyte stability of the tubes was performed for up to 9 days storage at -15 C⁰. The recovery range of the analytes were between 98% and 101%, with average 99% for two days, 90% to 98% with average 93% for four days, 81% to 92% with average 87% for nine days. The collected samples were analyzed within three days. There were no observed significant changes in the samples during the three-day storage. The uncertainty due to storage did not contribute to the overall uncertainty.

Analytical precision was evaluated by seven replicate measurements of the middle level of calibration curve and determined their standard deviation. The relative uncertainty coming from analytical repeatability was calculated from equation 3-5. Table 3.7 presents benzene replicate measurement results.

$$w_{ref}^2 = \frac{s^2(m_{rep})}{m_{rep}^2}$$
(3-5)

Where;

 $S(m_{rep})$: standard deviation of the replicate analysis m_{rep} : mean mass of the replicate analysis

According to Table 3.7, the relative uncertainty due to analytical repeatability was 1.35% for benzene.

The uncertainty due to analytical repeatability (w_{rep}) was calculated as 2.5%.

The calibration curve was prepared for each sampling period. The analyte area of the calibration mixture may be different between two successive calibrations. The difference causes uncertainty. The relative uncertainty due to different measurement values of standard mixture is calculated with the equation 3-6.

	Area	mass (ng)
1 st run	63.451	3.476
2 nd run	62.87	3.445
3 th run	62.58	3.428
4 th run	63.59	3.484
5 th run	65.16	3.570
6 th run	63.87	3.500
7 th run	62.99	3.451
Mean		3.479
Std		
Dev.		0.047
std%		1.349

Table 3.7 Analytical repeatability and standard deviation for benzene

$$w_d = \frac{|r_n - r_{n-1}|}{\sqrt{3} \times (\frac{r_n + r_{n-1}}{2})}$$
(3-6)

Where;

 $r_{n}:$ the peak area of the analyte at middle level calibration point of the second calibration curve

 $r_{n\mathchar`n\math$

The first calibration was performed at the beginning of the first sampling campaign. The second calibration was carried out 12 days after the first one. The second calibration curve was obtained for industrial sampling campaign. The relative uncertainty was also evaluated for the first and the last calibration curve. Table 3.8 represents the area value that resulted from three calibration curves and their uncertainties.

				w _d btw	w _d btw
	1 st	2 nd	Last	1 st and 2 nd	1 st and last
	calibration	calibration	calibration	calibration	calibration
	curve	curve	curve	curve	curve
pentane	3.95	3.82	3.52	0.0193	0.0664
benzene	3.,49	3.52	2.97	0.0049	0.0930
toluene	4.13	4.02	3.75	0.0155	0.0557
Ethylbenzene	5.39	5.13	5.03	0.0285	0.0399
m,p-xylene	10.53	10.59	9.87	0.0032	0.0374

Table 3.8 The area value belong the three calibration curve and their uncertainity value

The drift value between the first and the second calibration curve for benzene (w_d) was estimated as 0.49%.

The calibration equation was obtained by applying least square regression. The equation generated from the calibration curve was compared with the actual measured mass of analyte in order to evaluate lack-of-fit of the regression function. The uncertainty due to fit of the calibration line was calculated with the equation 3.7.

$$W_{F} = \frac{\frac{|m_{reg} - m_{cs}|}{m_{cs}}}{\sqrt{3}}$$
(3-7)

Where;

 m_{reg} : analyte mass of analyte calculated from the regression equation at middle level of the calibration standard

 $m_{cs}: \mbox{ analyte mass in calibration mixture at middle level }$

Table 3.9 illustrates the calibration equation, mass in the calibration mixture

and calculated mass according to calibration equation for selected compounds.

	100) ml	200) ml	300 ml		400 ml		500 ml	
	Std.	Mesr	Std.	Mesr	Std.	Mesr	Std.	Mesr	Std.	Mesr
	gas	WC3L	gas	West.	gas	MCSI.	gas	MCSI.	gas	MCSI.
Pentane	2.67	2.49	4.01	3.85	5.35	5.06	6.68	6.21	9.35	9.15
Benzene	1.16	1.15	2.32	2.06	3.48	3.16	4.64	4.47	5.80	5.11
Toluene	2.79	2.82	4.18	4.05	5.57	5.22	6.97	6.15	9.75	9.25
Ethylbnz	3.57	3.49	5.35	5.88	7.14	7.90	8.92	9.23	12.49	12.89
m&p-										
Xylene	3.51	3.25	7.02	6.88	10.52	9.54	14.03	13.88	17.54	16.55

Table 3.9 The mass of calculated based on calibration equation and measured

The w_f value was obtained 6.84% for benzene compound.

3.5.2.3 Combined uncertainty of the measured mass of analyte

The uncertainty due to analytical system and passive tubes were evaluated in this section. The overall uncertainty for compounds is given in Table 3.11. The total uncertainty of the related compounds was below the EN protocol requirement. These uptake rate deviations will be evaluated in Section 4.1.

$$\frac{u^2(m)}{m^2} = w_{rep}^2 + w_F^2 + w_d^2$$
(3-8)

The total uncertainty coming from analytical system was evaluated for selected compounds at Table 3.10.

The uncertainty due to analytical system and passive tubes were evaluated in this section. The overall uncertainty for compounds is depicted in Table 3.11. The total uncertainty of the related compounds was below the EN protocol

	W _f	W _d	Wrep	u(m)/m
n-Pentane	5.031	1.93	2.987	6.16
Benzene	6.840	0.49	2.541	7.31
Toluene	6.795	1.55	1.897	7.22
Ethylbenzene	6.120	2.85	1.874	7
m&p-Xylene	5.385	3.2	2.541	7.12

Table 3.10 The anaytical system uncertainity for selected compounds

(2002) requirement. These uptake rate deviations will be evaluated in Section4.1 in result section.

Compounds	$u^2(d)/d^2$	u ² (m)/m ²	$u^{2}(C_{P,T})/C^{2}_{P,T}$	$u(C_{P,T})/C_{P,T}$
n-Pentane	1.21	28.89	37.95	6.16
1,3-Butadiene	1.21	42.87	44.08	6.64
n-Hexane	1.1	31.45	41.85	6.47
Methylcyclopentane+				
2,4-Dimethylpentane	1.21	30.54	48.65	6.97
1,1,1-Tri-CI-Ethane	1.56	62.47	64.03	8.00
Benzene	1	53.44	54.44	7.38
Cyclohexane+Cyclohexene	1.1	49.54	50.64	7.12
2-Methylhexane	1.07	52.45	53.52	7.32
2,2,3-Trimethylbutane+				
2,3-Dimethylpentane	1.09	54.74	55.83	7.47
3-M-Hexane	1.05	49.78	50.83	7.13
2,2,4-Tri-M-Pentane	1.1	51.78	52.88	7.27

Table 3.11 Total uncertainity for all compounds

Compounds	$u^2(d)/d^2$	u ² (m)/m ²	$u^{2}(C_{P,T})/C^{2}_{P,T}$	$u(C_{P,T})/C_{P,T}$
n-Heptane+cis-3-Heptene	1	52.87	53.87	7.34
Methylcyclohexane	1.12	54.78	55.90	7.48
Toluene	1	52.13	53.13	7.29
2-M-Heptane	1.21	61.78	62.99	7.94
m+p-Chlorotoluene	1.21	62.74	63.95	8.00
Octane	1	49.98	50.98	7.14
2,2,5-Tri-M-Hexane+				
1,2,4-Tri-M-Cyclohexane	1.03	53.74	54.77	7.40
TetraChloroEthylene	1.15	56.87	58.02	7.62
Chlorobenzene	1.18	52.47	53.65	7.32
Ethylbenzene	1.01	49.02	50.03	7.07
Bromoform	1.14	58.78	59.92	7.74
m+p-Xylene	1	50.69	51.69	7.19
Styrene	1.02	49.85	50.87	7.13
o-xylene	1.01	54.85	55.86	7.47
n-Nonane	1.03	52.85	53.88	7.34
Isopropylbenzene	1.08	53.87	54.95	7.41
n-Probylbenzene	1	51.45	52.45	7.24
3-Ethyltoluene	1.11	53.74	54.85	7.41
4-Ethyltoluene	1.12	52.85	53.97	7.35
1,3,5-Tri-M-Benzene	1.11	55.74	56.85	7.54
2-Ethyltoluene	1.09	53.85	54.94	7.41
1,2,4-Tri-M-benzene	1.12	55.65	56.77	7.53
n-Decane	1.21	59.87	61.08	7.82
1,4-Di-Cl-Benzene	1.39	62.74	64.13	8.01
1,4-Di-E-Benzene	1.41	64.25	65.66	8.10
Naphthalene	1.37	69.87	71.24	8.44

Table 3.11 Total uncertainity for all compounds (Continued)

3.5.3 Data Set QA/QC Procedure

QA/QC procedure should also be applied both during data generation and after the completion of data generation. The main anomalies in the data, which refers to sudden unexpected strong increases or decreases in concentration of a particular VOC, could arise from peak-fitting during processing of chromatograms. The retention times of the peaks were very close, so it might be possible to confuse close peaks. However, it should also be pointed out that every increase or decrease in the concentrations of VOCs do not necessarily indicate an error in sampling and/or analysis. That very high number in the data set can be a real concentration. Consequently, in QA/QC of the data set, we are trying to differentiate faulty numbers from real concentrations.

The anomalies in the data set may also arise from problems during the sample collection in the field, laboratory analysis and integration of the data or due to meteorological anomalies or variations in source strength. These outliers may result in misleading information on the interpretation.

The QA/QC procedures applied after data generation are to assess the quality of the data and to eliminate any errors that can occur during data processing. If any anomaly was detected during application of QA/QC protocol,, Data is traced back performing same calculations backwards all the way to the chromatogram. If no source of possible error is found, that concentration value is assumed to be real.

The quality assurance/quality control (QA/QC) procedures used in Photochemical Assessment Monitoring Stations (PAMS) of the U.S.A. were followed for the VOCs data set. The QA/QC procedures used after data generation included the inspection of two different plots. Time series plots and scatter plot matrices were used to detect suspicious data points. Before handling the data, the outliers for individual species at each session were detected with the help of SPSS statistical software. The detection of outliers in data is the first step of determining anomalies. The term "outlier" is not formally defined. An outlier is simply an unusually extreme value for a variable, given the statistical model in use. The outlier detected with SPSS software was compared with time series and scatter plot results. The same outliers were identified as a result of three evaluation protocols.

Time series plots were drawn for each species. Time series plots were modified for passive sampling data set. It showed variation in the species concentration along with the location point instead of time. Time series plots were inspected for peaks in the concentrations. The peaks at certain points were detected for all periods. Figure 3.18 and Figure 3.18 show an example of time series plots drawn for benzene and toluene during all sessions. It is clearly seen from Figure 3.18 that there is a problem in the data measured at point 30 located in industrial areas. Benzene at this point was measured to be at a low level during winter and spring season and a high level during summer season. Analytical and sampling logbooks were inspected to see if there were any problems during the collection of these samples or during the analyses. There were no problems recorded in the logbooks. Thus, it was thought that high concentrations measured during summer sampling could be an additional source close to this point. If there could be additional sources at this point, it would be the effect concentrations of other VOCs that have similar sources with benzene. Toluene concentration was also high at the same sampling point, as depicted in Figure 3.19. Since both of these BTEX compounds have high concentrations at the same point, it is likely that this concentration is real and indicates a strong source close to that sampling point. Unfortunately, data sets produced in areas with different concentrations during passive sampling have too much diversity. The important point here is whether VOCs that were analyzed at the sampling point show similar variation from point to another.

The second test to detect suspicious data points was to investigate scatterplots graphs between VOCs. Scatter plots were drawn in the format of a correlation matrix. One or two outlier datum in the scatter-plot between two highly correlated VOCs is a suspicious datum (not necessarily wrong). Figure 3.20 shows a scatter plot matrix drawn for the selected compounds measured during summer campaign. Data that is marked indicate the points that do not match with other data in time series. Outliers found in this figure match well with the outliers found at the correlation matrix program and with the points found in time series plots.



Figure 3.18 Time series of benzene for all campaigns



Figure 3.19 Time series of toluene for all campaigns



Figure 3.20 Scatter plot of BTEX and TNMHC

The spatial distribution of the compounds was also evaluated to check if any problem occurred during sampling and analyzing procedures, as illustrated in Figure 3.21 A high level concentration was expected in the vicinity of the road, industrial areas and urban areas. Similarly, a low concentration was expected in remote areas. If different attitudes were observed in the pollution map, this point sampling chromatogram would be reevaluated for all compounds.



Figure 3.21 Spatial distribution of isopropylbenzene for winter sampling campaign

The point which was indicated with circle was normally expected to be a pollution area. However, VOC concentrations were low in this campaign. However, when investigated with other approaches used in QA/QC (scatter plots, time series etc) and when the chromatograms for these particular cases were reintegrated, it was concluded that the numbers are real and concentrations were low due to meteorology.

This multilayer approach in QA/QC of the generated data set was applied consistently in all sampling campaigns and proved very useful to trace errors in data entry or curve fitting.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Uptake Rates

Although passive samplers have been widely used as a cost-effective and reliable technique in measuring ambient pollutants, the main source of uncertainty in environmental applications of passive sampling is the use of uptake rates determined theoretically or in the laboratory or field (Tolnai et al., 2000). The experimental uptake rate depends on the strength of the analyte/sorbent interaction and meteorological condition. The theoretical uptake rate is calculated from the geometry of passive tube and diffusion coefficient of the compound. It was observed in the literature that experimental uptake rates were significantly different from the theoretical values (Brown et al., 1981 and Tolnai et al., 2001), For example, deviations of benzene reached up to 300% in the literature (Tolnai et al., 2001; Cao et al., 1993; Gelencser et al., 1994; Tolnai et al., 1999, Brown 1999, Patil and Lonkar, 1994). Fundamental discrepancy of uptake rates results in the literature may result from the differences in the conditions and methods in the laboratory. Furthermore, environmental conditions are substantially different from the controlled conditions in the laboratory, especially in terms of variability of meteorological conditions and concentration levels (Tolnai et al., 2001). Hence experimental uptake rate should be calculated under real atmospheric conditions. The sampling campaign conducted in Ankara was planned to comprehensively evaluate the uptake rates during six months.

Average uptake rates of VOCs measured in this study are depicted in Table 4.1. Average uptake rates vary between 0.33 ± 0.16 for methylcyclopentane + 2,4-dimethyl pentane and 0.70 ± 0.76 for t+c-1,3-dimethylcylohexane. This observed variability of uptake rates is due to different affinities of different VOCs to the adsorbent used.

Another point that attracts attention in the table is relatively high standard deviations of the URs, which indicates relatively high variability in the uptake rate values. However, it should be noted that the standard deviations given in the table are not the same as the standard deviations of replicate measurements and thus they are not a measure of the analytical uncertainty. The reason for relatively high standard deviation in the measured uptake rates of VOCs is the dependence of URs on large numbers of parameters. As will be discussed in the coming sections, calculated URs of VOCs depend on a number of meteorological and non-meteorological parameters, such as wind speed, relative humidity, and sampling period, etc. Since these parameters varied significantly during our sampling period, the calculated uptake rates responded to these variations. Actually, as pointed out in the section 2.2, uptake rates of VOCs calculated using parallel passive tubes do not show high standard deviations observed in Table 4.1. Actually, this variability is an indication of the need to investigate dependence of uptake rates on the meteorology and other factors and shows that the use of diffusion coefficients listed in the literature with Ficks law without paying attention to meteorology may lead to high uncertainty in passive measurements.

In subsequent sections, it is demonstrated that the best uptake rate is the one that is determined by regression analysis taking into account meteorological factors. In that sense the average uptake rates given in Table 4.1 are not the best ones to be used. However, the table is important, because there is no compilation of URs for so many VOCs in the literature.

The BTEX average uptake rates calculated in this study are compared with corresponding values reported in the literature in Table 4.2. The comparison is confined to BTEX compounds, because the uptake rates for other VOCs are scarce in the literature.

The uptake rate reported for benzene in the literature varies between 0.27 mL min⁻¹ and 0.68 mL min⁻¹, most of the data in the literature are accumulated in a small range between 0.4 and 0.5 mL min⁻¹. The uptake rate found in this study, which is 0.39, is almost in the same range. The uptake rate for toluene

	VOCs	Average URs (ml/min)
1	Methylcyclopentane+2,4-Dimethylpentane	0.33 ± 0.16
2	Benzene	0.39 ± 0.15
3	Cyclohexane+Cyclohexene	0.41 ± 0.18
4	2-Methylhexane	0.45 ± 0.15
5	2,2,3-Trimethylbutane+2,3-Dimethylpentane	0.51 ± 0.22
6	3-M-Hexane	0.41 ± 0.23
7	1-Heptene	0.44 ± 0.25
8	2,2,4-Tri-M-Pentane	0.41 ± 0.25
9	n-Heptane+cis-3-Heptene	0.45 ± 0.20
10	Methylcyclohexane	0.44 ± 0.20
11	Toluene	0.44 ± 0.13
12	2-M-Heptane	0.46 ± 0.20
13	m+p-Chlorotoluene	0.49 ± 0.19
14	4+3-M-Heptane	0.37 ± 0.16
15	t+c-1,3-Di-M-Cyclohexane	0.70 ± 0.76
16	Octane	0.45 ± 0.28
17	2,2,5-Tri-M-Hexane+1,2,4-Tri-M-Cyclohexane	0.53 ± 0.32
18	Ethylbenzene	0.39 ± 0.15
19	m+p-Xylene	0.40 ± 0.12
20	Styrene	0.37 ± 0.31
21	1-Nonene	0.37 ± 0.24
22	o-xylene	0.35 ± 0.11
23	n-Nonane	0.39 ± 0.19
24	Isopropylbenzene	0.61 ± 0.04
25	n-Propylbenzene	0.40 ± 0.19
26	3-Ethyltoluene	0.36 ± 0.13
27	4-Ethyltoluene	0.38 ± 0.16
28	1,3,5-Tri-M-Benzene	0.36 ± 0.09
29	2-Ethyltoluene	0.35 ± 0.13
30	1,2,4-Tri-M-benzene	0.41 ± 0.14
31	n-Decane	0.34 ± 0.17

in the literature varies between 0.32 mL min⁻¹ and 0.68 mL min⁻¹, with most of the values accumulated between 0.4 mL min⁻¹ and 0.5 mL min⁻¹. The average uptake rate calculated for toluene in this study is 0.44 mL min⁻¹, which agrees with most of the data in Table 4.2. For ethylbenzene, the uptake rate values reported in the literature varied between 0.44 and 0.55 mL min⁻¹. The uptake rate found in this study is 0.39 mL min⁻¹, which is slightly smaller than the values in Table 4.2. This small discrepancy may be due to smaller number of literature data available for ethylbenzene, compared to other BTEX compounds. The comparison of the average uptake rates calculated for m,pxylene and o-xylene in this study, with those reported in literature, are more or less similar to the comparison discussed for benzene and toluene.

Although the systematic study to determine VOCs uptake rates were performed in Ankara, uptake rate estimations, to a limited extend, were also performed during Bursa passive sampling study, which is discussed in different sections of this dissertation and in another passive sampling study, which is performed by our group at Aliağa, İzmir. Detailed information on passive sampling performed in Bursa is presented in the Experimental Section and will not be repeated here. In Izmir study, passive sampling was performed to determine how organic and inorganic pollutants are distributed around Aliağa industrial area. Passive sampling was one of the components in a fairly extensive TÜBİTAK (104Y276) project. In that study, passive samplers were deployed for four times in the years 2006 and 2007. In each passive sampling period, active measurements of VOCs were also performed using online GC at two locations. The purpose of using active measurements parallel with passive tubes was to determine the uptake rates of VOCs for the meteorological conditions prevailing at that time. Actually, the need to investigate the dependence of uptake rates on meteorology and other factors emerged during those two studies.

	Ankara										
	campaign	Mowrer	Nicholas	Roche	Hellen	ISO/DIS	HSF	Sokhi	Qury(a)	Qury(b)	Tolnai
Benzene	0.39	0.41	0.46	0.57	0.68	0.63	0.48-0.54	0.45-0.46	0.27	0.41	0.57-0.61
Toluene	0.44	0.45	0.52	0.51	0.62	0.56	0.52	0.43-0.55	0.32	0.44	0.42-0.49
Ethylbenzene	0.39	0.55	-	0.45	0.55	0.5	0.44	-	-	-	0.51-0.54
m+p-Xylene	0.40	0.55	-	0.43	0.53	0.47	0.48	0.47-0.50	0.44	0.42	0.41-0.58
o-Xylene	0.35	-	0.48	0.43	0.54	0.47	-	-	-	-	0.41-0.48

Table 4.2 Comparision of the BTEX average uptake rates calculated in this study with the literature

Mowrer et al., 1996, Nicholas et al., 2003, Roche et al., 1999, Hellen et al., 2002, ISO/DIS, 1998, HSF, 1995, Sokhi 1996, Qury 2006(a), Qury 2006(b), Tolnai et al., 2001 The BTEX uptake rates calculated in this study are compared with the uptake rates calculated during Bursa and Aliağa passive sampling campaigns in Figure 4.1. It is obvious in the figure that there are no substantial differences in the average uptake rates calculated in three studies. The URs calculated in this study are generally in good agreement with the URs calculated at Bursa. The URs calculated during Aliağa study are smaller than the other two. The only exception to this is observed in o-xylene, where UR calculated during Aliağa study is the highest among the three values.

The small differences observed between different URs can be attributed to different meteorological conditions that prevail during those studies. For example relatively small URs of BTEX compounds found during Aliağa study is probably due to higher average temperatures that occurred during sampling in Aliağa. As will be discussed in later sections, VOCs uptake rates are inversely related with the temperature. Thus, higher average temperatures in Aliağa results in lower URs for VOCs.

4.1.1 Dependence of Uptake Rates to Sampling Duration

Although there is no consensus on the dependence of passive sampling efficiency on sampling time, there is fair amount of literature which states that such a relation does exist and collection efficiency decreases beyond a threshold time (Langlois, 2008; Tolnai et al., 1999; Tolnai et al., 2001; Cardinal et al., 2005; Bruno et al., 2005), which is attributed to desorption of VOCs molecules that were initially adsorbed on the adsorbent after a certain sampling time. However, there is no agreement on what the threshold time is. Whatever the reason is and whatever the threshold sampling time is, if the efficiency of passive sampling decreases with time, then the uptake rates should also decrease in a parallel manner. We have decided to investigate this possibility of changing collection efficiency with time and designed an experiment accordingly. A large set of passive sampling tubes were collocated with active sampling tubes and sets of 5 - 7 of these tubes were taken at different times and analyzed along with active tubes. The sampling periods varied between 3 and 21 days. The results are depicted in Figure 4.2. Since it



Figure 4.1 Comparison of the BTEX average uptake rates with the previous studies performed in Bursa and Aliağa

was not practical to attempt to demonstrate this effect for all of the 34 VOCs, four VOCs were randomly selected and included in Figure 4.2. The behaviors of remaining VOCs were not significantly different.

As can be clearly seen in Figure 4.2, both uptake rates and concentrations of VOCs do decrease with time. Although the number of data points is small (26), the decrease is very obvious. The URs and concentrations do not change significantly in the first week or 10 days, but then starts to decrease. The decrease in VOCs concentrations and URs continued until we terminated the exercise in 21 days. No leveling off in the concentrations and URs was observed in 21 days of the exercise.

The mechanism for passive sampling is mainly based on molecular diffusion (Wideqvist et al., 2003). The masses of pollutants continue to accumlute into adsorbent until the build-up of an appreciable compounds concentrations into adsorbent (Tolnai et al., 2001) After a certain time, the masses into to adsorbent decrease due to desorption of the masses from the adsorbent. Hence behaviors of VOCs observed in this exercise suggest that the passive sampling time should be kept below 7 – 10 days. However, this is not observed in field applications in which sampling periods as long as 1 month are frequently used. Data generated in this study demonstrated that VOCs concentrations found as a result of sampling periods > 20 days may be a factor of 3 to 4 smaller than true VOCs concentrations in the atmosphere. Results of the passive sampling, which is becoming more and more widespread nowadays, should be viewed with this concern in mind

4.1.2 Relationship between Uptake Rates and Meteorological Parameters

In this section the relation between meteorological parameters and the uptake rates of VOCs is established. We also tried to demonstrate the margin of uncertainty in passive VOCs measurements when the meteorological parameters are not taken into account.



Figure 4.2 Relationship among the UR, concentration and sampling period

As briefly discussed in the experimental section, the studies towards understanding the dependence of uptake rate on meteorology parallel with active and passive sampling was performed for 6 months. During six months, sets of seven passive tubes were collocated with an active sampler every week. Thus, 26 sets of uptake rate data were collected. Since the samplingwas carried out between January and July, reasonable variation in the meteorological conditions prevailed during the study.

The uptake rate studies are generally performed in conditioning chambers where meteorological conditions are simulated and VOCs concentrations can be controlled. The study performed in this work has some advantages over the uptakes rates determined in conditioning oven. The most important advantage is that the uptakes are determined under natural conditions and under all possible natural combinations of meteorological parameters and concentrations. Another advantage is its relatively small cost. However, there are some disadvantages of our method against conditioning chamber studies as well. For example, in our approach, it is not possible to keep all the parameters constant and vary only one. The values of the meteorological parameters are the ones that naturally occur. Sometimes extreme meteorological conditions may not be observed. However, in conditioning chambers extreme meteorological conditions can be generated. With all these advantages and disadvantages, we believe that the determination of uptake rates under natural combination of meteorological parameters is the most important one because passive sampling in the field is not performed under laminar air flow and with the variation of only one of the parameters, after all.

The meteorological parameters included in this study are temperature (T), relative humidity (RH) and wind speed (WS). These are the parameters quoted as the most effective meteorological parameters on uptake rates (Namiesnik et al., 2005; Kumar and Viden, 2007; Ballach et al., 1999; Mowrer et al., 1996). The variation of these three parameters during our study is depicted in Figure 4.3. Temperature, relative humidity and wind speed varied between $-1^{\circ}C - +20^{\circ}C$, 50% - 86% and <1.0 m s⁻¹ – 3.0 m s⁻¹, respectively. However, it should be noted that these figures are weekly averages. Although the meteorological data obtained from the General

Directorate of Meteorology was hourly, they were averaged based on the passive sampling periods which were approximately one-week. Hourly T, RH and WS were sometimes significantly lower or higher than the average values shown in the figure. To illustrate this, hourly temperature data between January and July 2008 is given in Figure 4.3 (d). Although weekly average temperature varied between -1°C and +20°C, hourly temperatures lower than -10°C and higher than +30°C can be seen in the figure. Long-term monthly average temperatures, measured between 1975 and 2007, are also plotted in Figure 4.3 (d), to demonstrate how typical the temperatures measured during our study were for the region. It is fairly clear that temperatures measured during this work did not show large deviations from long term data obtained from Ankara Etimesgut meteorological station. The variation in relative humidity and wind speed were also similar to that observed in temperature.

The relationship between the VOCs uptake rates and temperature is given in Table 4.3. The first column in the table includes the VOCs, the second column includes the linear regression relationship between the UR and temperature, probability of chance correlation, the correlation coefficient between the uptake rates, and temperature and fractions of variance explained by temperature are given in columns, three, four and five, respectively. Bold numbers indicate statistically significant values.

Thirty-four VOCs measured in this study show negative relation with temperature. For four VOCs (2,2,3-thrimethylbutane+2,3-dimethylpentane, n-heptane+cis-3-heptene, 2-m-heptane and isopropylbenzene), the regression equation is statistically significant at 90% confidence interval. For five VOCs (cylohexane+cylohexene, m+p-chlorotoluene, n-nonane, npropylbenzene and n-decane) the regression relationship between their URs and temperature are statistically significant at 95% confidence interval and regression equation for the remaining 14 VOCs are statistically significant at 99% confidence interval. This discussion clearly demonstrates that uptake rates for 23 out of 34 VOCs show statistically significant negative relation with temperature. Although the remaining 11 VOCs also show negative relation with temperature, the regression equation is not statistically significant with confidence >90%.

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Figure 4.3 Meteorological parameters used in the study

Compounds	Regresion eqn.	Ρ	r	UR with Temp (%)
Methylcyclopentane +2,4-Dimethylpentane	UR=0.35-0.002xTE	0.17	0.42	3
Benzene	UR=0.50-0.012xTE	0.004	-0.66	44
Cyclohexane+cyclohexen e	UR=0.51-0.01xTE	0.037	-0.42	18
2-Methylhexane	UR=0.59-0.016xTE	0.001	-0.74	54.8
2,2,3-Trimethylbutane +2,3-Dimethylpentane	UR=0.58-0.010xTE	0.076	-0.38	14
3-M-Hexane	UR=0.48-0.006xTE	0.18	-0.28	8
1-Heptene	UR=0.48-0.003xTE	0.62	-0.11	1.3
2,2,4-Tri-M-Pentane	UR=0.54-0.014xTE	0.0087	-0.53	28
n-Heptane+cis-3- Heptene	UR=0.53-0.008xTE	0.093	-0.34	12
Methylcyclohexane	UR=0.56-0.013xTE	0.007	-0.53	29
Toluene	UR=0.54-0.014xTE	0.0001	-0.70	49
2-m-Heptane	UR=0.51-0.007xTE	0.092	-0.34	12
m+p-Chlorotoluene	UR=0.58-0.011xTE	0.014	-0.49	24
O-CI-Toluene +Di-Br-CI-Methane	UR=0.78-0.005xTE	0.73	-0.08	0.7
4+3-m-Heptane	UR=0.40-0.001xTE	0.72	-0.07	0.52
T+c-1,3-Di-M-Cyclohexane	UR=0.79-0.01xTE	0.45	-0.20	4.1
Octane	UR=0.48-0.006xTE	0.24	-0.24	6
2,2,5-tri-m-hexane +1,2,4-Tri-M-Cyclohexane	UR=0.64-0.009xTE	0.23	-0.26	7
Ethylbenzene	UR=0.48-0.012xTE	0.0003	-0.67	46
m+p-Xylene	UR=0.48-0.012xTE	0.0003	-0.68	46
Styrene	UR=0.50-0.019xTE	0.0015	-0.65	42
1-Nonene	UR=0.45-0.008xTE	0.16	-0.3	9
o-Xylene	UR=0.44-0.012xTE	0.00001	-0.73	54
n-Nonane	UR=0.45-0.009xTE	0.02	-0.45	21
Isopropylbenzene	UR=0.46+0.036xTE	0.071	-0.53	29
n-Probylbenzene	UR=0.46-0.009xTE	0.045	-0.42	18

Table 4.3 The relationship between uptake rates and temperature

				UR
	Regresion egn.	Р	r	with
Compounds	5			Temp.
				(%)
3-Ethyltoluene	UR=0.43-0.009xTE	0.0013	-0.62	38
4-Ethyltoluene	UR=0.47-0.012xTE	0.0003	-0.67	45
1,3,5-Tri-M-Benzene	UR=0.45-0.011xTE	0.0003	-0.67	45
2-Ethyltoluene	UR=0.45-0.012xTE	0.0003	-0.67	44
1,2,4-Tri-M-Benzene	UR=0.48-0.012xTE	0.001	-0.63	39
N-Decane	UR=0.40-0.008xTE	0.015	-0.49	24
Iso-Butylbenzene	UR=0.44+0.004xTE	0.55	0.13	2
1,2-Di-Cl-Benzene	UR=0.33+0.004xTE	0.56	-0.16	3

Table 4.3 The relationship between uptake rates and temperature (Continued)

The negative relation between VOCs uptake rates and temperature is also depicted in Figure 4.4. The negative relation between URs and temperature is also clear in the figure. One point worth noting is that the relation between URs and temperature is strong (statistically significant at >99% confidence interval) for the VOCs with well defined and relatively large (easy to integrate) peaks in the chromatogram. On the other hand, the relationship between UR and temperature is weak if the peak of that particular VOCs in the chromatogram is small and measured with relatively high analytical uncertainty. Although this may be a mere coincidence, it is also probable that the lack of statistically significant correlation between UR and temperature in 11 VOCs can be due to relatively high uncertainty in measurements of these trace species and the situation may change if larger numbers of data were to be used in the regression.

The relation between VOCs uptake rates and relative humidity is given in Table 4.4. The same relation is also depicted in Figure 4.5 for four selected VOCs for visual inspection. As it can be clearly observed in Table 4.4 and Figure 4.5, the relationship between the URs and the relative humidity is not as strong as the relationships between URs and temperature. However, URs of 19 out of 34 VOCs showed statistically significant relation with relative humidity with 90% or higher confidence.



Figure 4.4 The ralationship between temperature and uptake rates for selected compounds

Compounds	Degression equation	D		The explained % of UR
Compounds	Regression equation P		ſ	variance by RH (%)
Methylcyclopentane+2,4-Dimethylpentane	UR=0.095+0.0036xRH	0.17	0.27	7.6
Benzene	UR=-0.19+0.009xRH	0.005	0.54	29.6
Cyclohexane+Cyclohexene	UR=-0.22+0.0098xRH	0.02	0.46	21.3
2-Methylhexane	UR=-0.26+0.01xRH	0.005	0.55	30.98
2,2,3-Trimethylbutane+2,3-Dimethylpentane	UR=0.029+0.007xRH	0.11	0.33	11
3-M-Hexane	UR=0.20+0.003xRH	0.41	0.17	2.9
1-Heptene	UR=0.48-0.0002xRH	0.95	-0.01	0.019
2,2,4-Tri-M-Pentane	UR=0.22+0.003xRH	0.50	0.14	2.05
N-Heptane+cis-3-Heptene	UR=0.23+0.003xRH	0.39	0.17	3
Methylcyclohexane	UR=-0.14+0.008xRH	0.02	0.44	20
Toluene	UR=-0.25+0.01xRH	0.008	0.62	39
2-M-Heptane	UR=0.04+0.006xRH	0.082	0.35	12
M+p-Chlorotoluene	UR=0.20+0.004xRH	0.28	0.22	5
O-CI-Toluene+Di-Br-CI-Methane	UR=1.35-0.009xRH	0.43	-0.19	3.6
4+3-M-Heptane	UR=0.35+0.0005xRH	0.88	0.03	0.09
t+c-1,3-Di-M-Cyclohexane	UR=0.19+0.008xR	0.48	0.18	3.5
Octane	UR=0.24+0.003xRH	0.51	0.13	1.9

Table 4.4 Relationship between URs and Relative Humidity (RH) statistically meaningful relations are marked

Compounds	Regression equation	Р	r	The explained % of UR
				variance by RH (%)
2,2,5-Tri-M-Hexane+1,2,4-Tri-M-Cyclohexane	UR=0.59-0.0003xRH	0.96	-0.01	0.01
Ethylbenzene	UR=-0.11+0.008xRH	0.0078	0.52	26.9
M+p-Xylene	UR=-0.18+0.008xRH	0.0013	0.61	36.9
Styrene	UR=-0.087+0.007xRH	0.16	0.31	9.6
1-Nonene	UR=0.07+0.005xRH	0.31	0.21	4.5
O-Xylene	UR=-0.19+0.008xRH	0.0011	0.61	37.4
n-Nonane	UR=0.07+0.005xRH	0.19	0.27	7.3
Isopropylbenzene	UR=1.85-0.017xRH	0.21	-0.38	15
n-Probylbenzene	UR=-0.04+0.007xRH	0.06	0.38	15
3-Ethyltoluene	UR=-0.056+0.007xRH	0.013	0.49	24
4-Ethyltoluene	UR=-0.018+0.006xRH	0.0435	0.41	17
Tri-M-Benzene	UR=-0.18+0.008xRH	0.0013	0.61	37
2-Ethyltoluene	UR=-0.28+0.009xRH	0.0008	0.62	39
1,2,4-Tri-M-Benzene	UR=-0.18+0.009xRH	0.0036	0.56	32
n-Decane	UR=-0.05+0.006xRH	0.022	0.45	21
Iso-butylbenzene	UR=0.48-0.0003xRH	0.95	-0.01	0.017
1,2-Di-Cl-Benzene	UR=0.41-0.00088xRH	0.86	-0.04	0.20

Table 4.4. Relationship between URs and Relative Humidity (RH) statistically meaningful relations are marked (Continued)



Figure 4.5 Variation of uptake rates with relative humidity for selected compounds

Unlike the relation between UR and temperature, URs of all VOCs increased with increasing relative humidity. This probably is due to variation in the interaction between VOCs molecules and adsorbent.

The relationship between VOCs uptake rates and the wind speed is given in Table 4.5 and Figure 4.6. Although the relationship between UR and WS is not very strong, as in the case of relative humidity, uptake rates of 15 out of 34 showed statistically significant relation with wind speed with 90% or better confidence. As it can be seen in Table 4.5 and Figure 4.6, VOCs uptake rates increase with increasing wind speed.

Although data suggested a statistically significant correlation between UR and WS, there is one point that should be noted about this relationship. Ankara is a windless city. Hourly average wind speed recorded during our measurement period varied between 1.5 m s⁻¹ and 2.5 m s⁻¹. Approximately 57% of the recorded wind data were smaller than 1.0 m s⁻¹, which correspond to "calm" conditions in meteorology. Such low wind speed is typical for Ankara and is not specific to our sampling period. The average wind speed in Etimesgut meteorological station between 1975 and 2007, without including data <1.0 m s⁻¹ is approximately 2.0 m s⁻¹. The average wind speed calculated for our study period without including data < 1.0 m s⁻¹ is 2.1 m s⁻¹ (the average wind speed goes down to 1.3 m s⁻¹ when data <1.0 m s⁻¹ is included in the average). Because of general low wind speed in Ankara, it was not possible to study the effect of high winds on the uptake rate. However, although the variability in the wind speed was not high enough for a complete investigation of the dependence of UR on WS, even small variations in WS resulted in a statistically significant relation with URs of 15 VOCs.

The uptake rates of the 34 VOCs measured in this study showed a general decreasing trend with temperature and a weaker, but statistically significant increasing trend with increasing relative humidity and wind speed. These findings are in general agreement with limited data in the literature (Strandberg et al., 2005, Ballach et al., 1999; Cardinal et al., 2005)
				The	expla	ined
Compounds	Regression equation	Р	r	%	of	UR
				varia	nce by	y WS
Methylcyclopentane+2,4-Dimethylpentane	UR = 0.25 + 0.036 x WS	0.54	0.12		2	
Benzene	UR = 0.01 + 0.18 x WS	0.006	0.54		29	
Cyclohexane+cyclohexene	UR = 0.18 + 0.12 x WS	0.21	0.26		7	
2-Methylhexane	UR = 0.052 + 0.20 x WS	0.0096	0.52		28	
2,2,3-Trimethylbutane+2,3-Dimethylpentane	UR = 0.27 + 0.11 x WS	0.27	0.24		6	
3-m-Hexane	UR = 0.19 + 0.11 x WS	0.20	0.26		8	
1-Heptene	UR = 0.21 + 0.12 x WS	0.15	0.33		11	
2,2,4-Tri-M-Pentane	UR = -0.04 + 0.23 x WS	0.009	0.54		29	
N-Heptane+cis-3-Heptene	UR = 0.12 + 0.17 x WS	0.04	0.41		17	
Methylcyclohexane	UR = 0.052 + 0.19 x WS	0.02	0.46		21	
Toluene	UR = 0.06 + 0.18 x WS	0.01	0.50		25	
2-m-heptane	$UR = 0.32 + 0.06 \times WS$	0.43	0.16		3	
m+p-Chlorotoluene	UR = 0.38 + 0.05 x WS	0.54	0.13		2	
O-CI-Toluene+Di-Br-CI-Methane	$UR = -0.12 + 0.43 \times WS$	0.056	0.45		20	
4+3-M-Heptane	UR = 0.30 + 0.04 x WS	0.60	0.10		1	
t+c-1,3-Di-M-Cyclohexane	$UR = 0.64 + 0.036 \times WS$	0.85	0.05		0.2	
Octane	UR = 0.19 + 0.12 x WS	0.2	0.27		7	
2,2,5-Tri-m-Hexane+1,2,4-Tri-M-Cyclohexane	UR = 0.32 + 0.12 x WS	0.34	0.21		4	
Ethylbenzene	UR = 0.14 + 0.12 x WS	0.059	0.39		15	
m+p-Xylene	UR = 0.09 + 0.14 x WS	0.02	0.46		22	

Table 4.5 Relationship between URs and Wind Speed (WS) statistically meaningful relations are marked

Compounds	Degression equation	Р	r	The explained % of
compounds	Regression equation	P	I	UR variance by WS
m+p-Xylene	UR = 0.09 + 0.14 x WS	0.02	0.46	22
Styrene	$UR = 0.19 - 0.08 \times WS$	0.44	0.17	3
1-Nonene	UR = 0.14 + 0.12 x WS	0.24	0.25	7
o-Xylene	UR = 0.08 + 0.13 x WS	0.026	0.45	20
n-Nonane	UR = 0.15 + 0.11 x WS	0.14	0.30	9
Isopropylbenzene	UR = 0.28 + 0.16 x WS	0.44	0.25	6
n-Probylbenzene	UR = 0.12 + 0.14 x WS	0.07	0.38	15
3-Ethyltoluene	UR = 0.13 + 0.10 x WS	0.06	0.39	15
4-Ethyltoluene	UR = 0.07 + 0.14 x WS	0.02	0.47	22
Tri-M-Benzene	$UR = 0.12 + 0.11 \times WS$	0.06	0.32	15
2-Ethyltoluene	UR = 0.04 + 0.15 x WS	0.02	0.47	22
1,2,4-Tri-M-benzene	$UR = 0.23 + 0.07 \times WS$	0.29	0.22	5
n-Decane	$UR = 0.22 + 0.06 \times WS$	0.34	0.20	4
Iso-Butylbenzene	$UR = 0.61 - 0.07 \times WS$	0.46	-0.17	3
1,2-Di-Cl-Benzene	UR = 0.70 - 0.17 x WS	0.14	-0.38	15

Table 4.5. Relationship between URs and Wind Speed (WS) statistically meaningful relations are marked (Continued)



Figure 4.6 Variation of uptake rates with wind speed for selected compounds

The VOCs can be separated into three groups based on the relation between their uptake rates and meteorological parameters. The first group consisted of 10 VOCs including Methylcyclopentane+2,4-dimethylpentane, 3-m-hexane, 1-heptene, O-Cl-Toluene+Di-Br-Cl-Methane, 4+3-m-heptane, t+c-1,3-Di-M-Cyclohexane, Octane, 2,2,5-tri-m-hexane+1,2,4-tri-m-cyclohexane, Iso-butylbenzene, 1,2-di-cl-benzene. Uptake rates of these 10 VOCs do not show statistically significant correlation with the three meteorological parameters investigated in this study (temperature, relative humidity and wind speed).

Benzene, The second group consisted 2-methylhexane, of Cyclohexane+cyclohexene, methylcyclohexane, toluene, 2-m-heptane, ethylbenzene, 2,2,4-tri-m-pentane, n-Heptane+cis-3-Heptene, m+p-xylene, o-xylene, n-probylbenzene, 3-ethyltoluene, 4-ethyltoluene, 1,3,5-tri-mbenzene, 2-ethyltoluene, 1,2,4-tri-m-benzene, and n-decane. Uptake rates of these 18 VOCs showed statistically significant correlations with all three met parameters. Among these URs of n-decane, 1,2,4-tri-m-benzene and 2-mcyclohexane+cyclohexene heptane, showed statistically significant relationship with temperature and humidity > 90% confidence, but their correlation with wind speed was not statistically significant in the same confidence interval. These three VOCs are still included in the second group considering that the lack of correlation between UR and wind speed can be an artifact due to small variability in the wind speed during study period, as discussed previously in the manuscript.

The third group consisted of 6 VOCs including m+p-Chlorotoluene, styrene, n-Nonane, isopropylbenzene, cyclohexane+cyclohexene, 2,2,3-trimethylbutane+2,3-dimethylpentane. Uptake rates of these VOCs showed statistically significant correlation with temperature, but not with relative humidity and wind speed. Apparently uptake rates of these VOCs vary with temperature, but they are not sensitive to variations in humidity and wind speed.

Only a small fraction of the variance (between 2% and 24%) in uptake rates of group-1 VOCs are explained by temperature, wind speed and relative humidity. The same statement is also true for Group 3 VOCs, except for styrene and isopropylbenzene. Approximately 50% of the variance in the URs of these two compounds is explained by temperature.

Fractions of variances of URs of Group 2 VOCs with temperature, relative humidity and wind speed varies between 48% and 100%, except for n-heptane+cis-3-heptene, 2-m-heptane, for 27% and 32% of variances are explained, respectively, by the three meteorological parameters.

The important conclusion reached in this section is that for most of the VOCs, uptake rate is a function of meteorological parameters (temperature, RH and WS). The measurements of VOCs without taking into account this fact can lead to incorrect concentrations. The magnitude of this error is discussed in the coming sections.

4.1.3 Calculation of Uptake Rates by Using Multiple Linear Regression

It was clearly demonstrated in the previous section that uptake rates of most of the VOCs depend on meteorological parameters and thus these parameters should be taken into account in the field studies in determining uptake rates that are used to convert VOCs masses collected on passive samplers into concentrations. Then the next question is how to use meteorological parameters to calculate uptake rates of VOCs. The linear regression expressions given in Table 4.3, Table 4.4 and Table 4.5 cannot be used for this purpose, because they give the relation between the uptake rate and one of the met parameters. A relation that shows the dependence of URs to temperature, relative humidity and wind speed simultaneously is needed.

Such a relation for each VOCs is established by a multiple linear regression study where UR is used as a dependent variable and temperature, relative humidity and wind speed are used as independent variables. Once the multiple linear regression expressions are calculated for each VOCs, then uptake rates for a particular sampling campaign can be calculated by inserting temperature, humidity and wind speed data measured during the sampling period. Finally, the uptake rate value, which will be specific for that sampling period, can be used to calculate concentrations of VOCs. Please note that VOCs concentrations corresponding to the same VOCs mass on the sampler can be different at different samplings, if the meteorological parameters are not the same.

The regression equation for each VOCs calculated by the MLR study is given in Table 4.6 In the MLR study, meteorological parameters, particularly temperature and relative humidity was found to be auto-correlated. These two parameters were standardized using the methods developed by Berry and Feldman (1985) and Menard (1995) and standardized variables were used in the MLR. Standardization was performed by calculating averages of temperature and relative humidity values and subtracting each value from the average. These standardized temperature and wind speed are no longer auto-correlated.

Another point that should be noted in the table is that although 34 VOCs were measured in this study, regression equations are given for 25 of these compounds. This is because r^2 values for the regression equations calculated for 9 VOCs were not statistically significant at 90% confidence interval.

With the above discussion, it was clearly demonstrated that the uptake rates of VOCs do depend on meteorological parameters and this dependence should be taken into account in order to generate reliable data in passive measurements. However, it should be admitted that the measurements which are based on MLR approach explained in this section are more difficult than using of simple Ficks law or than using average uptake rates rather than calculating uptake rates each time using meteorological data at every measurement campaign. If the difference between concentrations calculated using Ficks law is not substantially different than concentrations calculated using MLR approach, then it may be feasible to use Ficks law and accept the slight error it produces. However, if the concentrations calculated by using these two approaches are significantly different from each other, then it may be worthwhile to calculate uptake rates in each campaign using the meteorological data and regression equations given in Table 4.6. Table 4.6 Multiple linear regression equations of the uptake rates depend on the meteorology by means of Relative Humidity (RH), Temperature (T) and Wind Speed (WS)

VOCs	Equations depend on the meteorology	R ²
Methylcyclopentane+2,4-Dimethylpentane	-0.048+0.006RH	0.265
Benzene	-0.519+0.008BN+0.173 WS	0.544
Cyclohexane+Cyclohexene	-0.74+0.013RH+0.154WS	0.417
2-Methylhexane	-0.661+0.011RH+0.191WS	0.534
2,2,3-Trimethylbutane+2,3-Dimethylpentane	-0.602+0.011RH+0.173WS	0.454
3-M-Hexane	-0.362+0.007RH.161WS	0.436
2,2,4-Tri-M-Pentane	-0.04+0.226WS	0.271
n-Heptane+cis-3-Heptene	0.257-0.01T+0.131WS	0.565
Methylcyclohexane	-0.482+0.009RH+0.183WS	0.380
Toluene	-0.572+0.01RH+0.165WS	0.616
2-Methyl-Heptane	-0.01+0.008RH	0.238
m+p Chlorotoluene	0.599-0.014T	0.388
2,2,5-Trimethylhexane	0.667-0.015T	0.220

Table 4.6 Multiple linear regression equations of the uptake rates depend on the meteorology by means of Relative Humidty (RH),Temperature (T) and Wind Speed (WS) (Continued)

VOCs	Equations depend on the meteorology	R ²
Ethylbenzene	-0.332+0.007RH+0.117WS	0.408
m,p-Xylene	-0.432+0.008RH+0.135WS	0.561
Styrene	0,506-0.019T	0.486
n-Nonene	0.479-0.011T	0.189
o-Xylene	-0.417+0.008RH+0.12 RH	0.566
n-Propilbenzene	-0.299+0.006BN+0.133WS	0.301
3-Ethyltoluene	-0.249+0.006RH+0.101WS	0.377
4-Ethyltoluene	0.468-0.011T	0.433
1,3,5 Trimethylbenzene	-0.376+0.008RH+0.103WS	0.495
2- Ethyltoluene	-0.547+0.009BN+0.14RH	0.571
1,2,4 Trimethylbenzene	0.486-0.011T	0.363
n-Decane	0.398-0.007T	0.234

To test the magnitude of the influence of meteorology on measured concentrations, we have selected one of our stations where passive sampling was performed at the Aliağa, İzmir as the test site. The concentrations of VOCs were calculated using three different methods by using the VOCs masses found on the passive sampler in that station in July 2006 sampling campaign. First, the concentrations were calculated using Ficks law, then they were calculated using average uptake rate for each VOCs found in this study, and finally UR for each VOCs were calculated using MLR approach by using regression equations given in Table 4.6 and temperature, relative humidity and wind speed measured at the same station during the campaign.

The results of this comparison exercise are given in Table 4.7 and variations of BTEX concentrations with approaches used are also depicted in Figure 4.7. The limitation of Ficks law can be clearly seen in Table 4.7. Concentrations of only 8 VOCs were found using Ficks law, because reliable diffusion coefficients were available only for these 8 species. Uptakes rates of 10 VOCs were also not measured using MLR approach, because r^2 values for these compounds for regression equations given in Table 4.6 were not statistically significant with >90% confidence. However, concentrations of these VOCs were calculated using average URs calculated in this study.

The most striking result of this exercise was the significant differences in concentrations found using different approaches. As can be seen in both Table 4.7 and Figure 4.7, the concentrations of VOCs calculated using MLR equations and met data for that sampling period and for that station are 30% higher than the corresponding concentrations found using average uptake rates and approximately 50% higher than the concentrations found using Ficks law. The concentrations of VOCs found by using average uptake rates of VOCs are only 10% - 20% higher than the concentrations found by using Ficks law.

This small exercise demonstrated the magnitude of differences in concentrations of VOCs calculated using different methods, with higher concentrations found in regression approach. The term "higher" in this sentence and in previous paragraph is misleading, because MLR equations given in Table 4.6 can result in lower concentrations than those found by

	Concentrations	Concentrations	Concentrations			
	calculated by using	calculated by	calculated by			
Compounds	URs via regression	using average	using URs via			
	(URs	Ficks Law			
	(µg m °)	(µg m⁻³)	(µg m⁻³)			
Methylcyclopentane+	0 4 0 4	0 5 2 5				
2,4 Dimethylpentane	0.090	0.525				
Benzene	10.319	6.745	4.477			
Cyclohexane+	0.010	1 270				
Cyclohexene	2.313	1.379				
2-Methylhexane	3.494	2.323				
2,2,3-						
Trimethylbutane+	0.675	0.434				
2,3-Dimethylpentane						
3-Methylhexane	3.522	2.741				
1-Heptene		0.268				
2,2,4-Tri-M-Pentane	0.57	0.589				
n-Heptane+cis-3-	1 / 17	1 07/				
Heptene	1.017	1.370				
Toluene	57.638	47.633	38.977			
2-M-Heptane	1.697	1.079				
m+p-Chlorotoluene	2.28	1.444	1.663			
o-CI-Toluene+di-br-	0.005	0.405				
cl-Methane	0.995	0.495				
4+3-M-Heptane		0.928				
t+c-1,3-Di-M-						
Cyclohexane		1.666				
t+c-1,4-Di-M-		0.0/1				
Cyclohexane		0.201				
Octane		1.401	1.645			

Table 4.7 VOCs concentrations calculated by using different URs for the same sampling tube

Compounds	Concentrations calculated by using URs via regression (µg m ⁻³)	Concentrations calculated by using average URs (µg m ⁻³)	Concentrations calculated by using URs via Ficks Law (µg m ⁻³)
2,2,5-Tri-M-Hexane+ 1,2,4-Tri-M-Cyclohexane	0.289	0.153	
Ethylbenzene	10.097	6.644	5.698
m+p-Xylene	30.713	19.203	18.489
Styrene	0.212	0.013	
1-Nonene		0.208	
o-Xylene	4.145	2.705	2.17
n-Nonane		0.371	
Isopropylbenzene		0.183	0.284
n-propylbenzene	0.533	0.363	
3-Ethyltoluene	3.701	2.592	
4-Ethyltoluene	1.912	1.475	
1.3.5-trimethylbenzene	1.36	0.833	
2-Ethyltoluene	1.43	0.801	
1.2.4-Trimethylbenzene	3.481	2.049	
n-Decane	2.771	1.727	
Iso-Butylbenzene		0.563	
1.2-di-cl-Benzene		0.41	

 Table 4.7 VOCs concentration calculated by using different Urs for the same sampling tube (*Continued*)



Figure 4.7 BTEX concentrations calculated by different methods

using Ficks law and average URs under a set of different meteorological conditions (such as lower relative humidity, lower wind speed and higher temperatures). Naturally, concentrations found by using Ficks law and average uptake rates would not be any different under different meteorological conditions.

4.1.4 Comparison of Two Different Adsorbents

Tenax and Chromosorb 106 are two adsorbents, which are frequently used in both active and passive sampling trains. In the past, these two adsorbents were frequently used in our group and probably they will also be frequently used in the future. Because of our frequent use of both adsorbents, a small exercise to test the efficiency of these two adsorbents is also added to this study.

For this, seven passive sampling tubes filled with Tenax and seven tubes filled

with Chromosorb 106 were collocated in our station and left there for one week. At the end of the one-week sampling period, tubes were collected and analyzed. This sampling was repeated twice in different weeks.

The VOCs masses in ng collected on Tenax and Chromosorb 106 are given in Table 4.8 and the Tenax/Chromosorb 106 mass ratio is depicted in Figure 4.8. Since the samplers were located side by side and the sampling period was exactly the same for both adsorbent types, the discussion of masses collected on samplers is not any different from the discussion of concentrations measured by both adsorbents and uptake rates calculated for each adsorbent

Both Table 4.8 and

Figure 4.8 demonstrate that both adsorbents collect VOCs measured in this study with equal efficiency. Better efficiency of Chromosorb 106 over Tenax for light hydrocarbons with 5 carbon numbers was reported in the literature (Cao and Hewit, 1993). In this study we were not able to detect hydrocarbons with 4 carbons. This can be either due low level of these VOCs in the atmosphere (poor detection limits of the GC-FID system used in this work, or can be due to low efficiency of both adsorbents. The efficiency of tenax and Chromosorb 106 were similar for the lightest VOCs, such as pentane and hexane, measured in this study.

Similar efficiencies and comparable reproducibility of both adsorbents suggest that tenax and Chromosorb 106 are equally good to be used in both passive and active sampling. We will continue to use either one depending on their availability and cost. Table 4.8 Comparision of the Tenax and Chromosorb 106

	WEE	K 1	WEEK 2			
	VOCs mass	VOCs mass	VOCs mass	VOCs mass		
Compounds	on Tenax (ng)	on C-106 (ng)	on Tenax (ng)	on C-106 (ng)		
n-Hexane	2.32	2.51	2.42	2.39		
t-3-M-2-Pentene	0.3	0.34	0.26	0.28		
2,3-Di-M-Pentane+1,2-Di-Cl-Ethane	0.25	0.25	0.35	0.28		
Benzene	4.75	3.14	3.89	3.45		
Cyclohexane+Cyclohexene	1.21	1.04	1.31	1.2		
2-Methylhexane	0.56	0.89	0.57	0.93		
3-M-Hexane	2.7	2.55		2.67		
1-Heptene	0.22	0.21	0.25	0.24		
2,2,4-Tri-M-Pentane	0.34	0.3	0.23	0.29		
n-Heptane+cis-3-Heptene	0.97	0.93	1	0.83		
C+t-1,3-Dichloropropene	0.29	0.46	0.37			
Methylcyclohexane	0.21	0.18	0.22			
2,2-Di-M-Hexane+2,5-Di-M-Hexane	0.34		0.28	0.21		

	WEEK 1	WEEK 2		WEEK 1
Compounds	VOCs mass	VOCs mass		VOCs mass
	on Tenax (ng)	on C-106 (ng)		on Tenax (ng)
2,4-Di-M-Hexane+1,1,2-Tri-Cl-Ethane	0.29		0.33	0.31
Toluene	15.56	17.87	24.35	28.43
2-m-heptane	1.04	0.81	1.01	0.99
m+P-Chlorotoluene	1.45	0.94		1.42
1-Octene	0.66	0.76	0.53	0.84
Octane	1.18	0.82	0.3	0.32
t-1,2-Di-M-Cyclohexane		0.17		0.36
Ethylbenzene	1.42	1.83	1.67	
m+p-Xylene	3.87	3.65	5.49	5.51
Styrene	1.56	1.55	1.71	1.91
1-Nonene	1.02	0.8		
o-Xylene	0.8	0.76	1.44	1.48
n-Nonane	1.26	0.65	1.49	0.81
n-Probylbenzene	0.23	0.22	0.22	0.24
3-Ethyltoluene	0.39	0.87	0.56	0.88

Table 4.8. Comparison of the Tenax and Chromosorb 106 (Continued)

	WEEK 1	WEEK 2		WEEK 1
Compounds	VOCs mass	VOCs mass		VOCs mass
	on Tenax (ng)	on C-106 (ng)		on Tenax (ng)
4-Ethyltoluene		0.61	0.72	0.68
1,3,5-Tri-M-Benzene	0.41	0.36	0.36	0.37
2-Ethyltoluene	0.2	0.29	0.31	0.42
1,2,4-Tri-M-Benzene	0.6	0.5	0.66	0.66
n-Decane	0.99	1.14	1.13	0.99
1,2,3-Tri-M-Benzene+p-Cymene			0.95	1.05
1,3-Di-E-Benzene		0.77		0.93
1,4-Di-E-Benzene		0.88		1.01
n-Butylbenzene		1.4		1.37
1-Undecene	15.83		9.12	5.82
Undecene	0.94	0.85	1.03	0.84
Naphthalene	0.52		0.69	0.7
Dodecene	4.27	3.88	4.14	4.59

Table 4.8. Comparison of the Tenax and Chromosorb 106 (Continued)



Figure 4.8 The ratio of the Tenax/C-106 adsorbents as a result of the parallel sampling

4.2 Spatial Distribution of VOCs in Bursa Atmosphere

4.2.1 General Features of Data

The VOCs were measured during five sampling periods at different seasons. Totally 334 sample tubes were collected and analzed to determine VOCs level and their distributions in Bursa atmosphere. Number of compounds detected in more than 50% of samples collected at all campaigns were approximately 64. Unfortunatally, only the concentrations could be calculated for 25 VOCs out of 64 target VOC due to lack of the uptake rates of other VOC in the literature. These 25 compounds were detected in more than 90% of the samples collected at all sites. Statistical features of the data set are given in Table 4.9. VOC data were generally fit by geomentric distribution, the median and minimum and maximum values of these 25 compounds are presented in the table. Chi-square test performad demonstrated that concentrations of VOCs measured in this study are log-normally dsitributed and represented best by median or geometric mean concentations.

On average, the most abundatan 20 species accounted for 85%, 84%, 81% and 89% of the total VOCs concentations during five sampling campaigns. The high cocnetrations of VOCs were detected around road and industrial areas. The seasonal and spatial distribution of VOCs concentations will be discussed in the following sections.

BTEX were most abundant species detected at all sampling points. Toluene is most abundant specie at all sites with a median cocnetartion ranging from 2 μ g m⁻³ at background site 120 μ g m⁻³ at industrial areas.

Organic compound measured in this study are collected under four groups, namely parrafins, olefin, aromatic and halogonated compounds. The top 20 species detected at all sites consist of 11 aromatic, 5 parafin, 4 olefin and 1 halogonated.

	September 05		October 05		April 06		February 07		July 07	
	median	Range	median	Range	median	Range	median	Range	median	Range
SO ₂			16.60	4.01-101.8	14.46	2.14-36.58				
NO ₂			33.80	4.18-75.98	48.24	1.13-82.45				
O ₃			29.44	2.19-55.13	29.13	5.14-126.24				
Pentane	0.47	0.21-3.07	0.20	0.06-1.14	0.52	0.13-2.87	0.97	0.3-1.98	0.48	0.18-4.30
1,3 Butadiene	0.17	BDL-0.69	0.27	0.0687	0.10	BDL-0.59	0.39	0.1-1.12	0.06	0.03-0.23
n-Hexane	0.32	BDL-4.77	0.39	0.05-1.70	0.57	0.18-1.29	0.66	BDL-2.79	0.53	BDL-72.75
Methylcyclopentane										
+2,4-Dimethylpentane	0.14	BDL-2.14	0.16	0.04-0.79	0.14	BDL-0.65	1.05	BDL-4.17	0.34	BDL-4.59
1,1,1-Tri-Cl-Ethane	0	BDL-0.03	0.00	BDL-1.03	0.00	BDL-0.33	0.00	BDL-0.77	0.00	BDL-11.0
Benzene	1.71	0.44-7.14	2.24	0.66-5.49	2.10	0.73-5.09	8.21	3.05-19.0	2.26	0.94-19.72
Cyclohexane+Cyclohexene	0.97	0-2.80	1.98	BDL-4.25	0.18	BDL-0.78	1.36	BDL-12.9	0.74	BDL-24.0
2-Methylhexane	1	0.19-2.57	0.00	BDL-1.97	0.38	0.05-1.82	0.73	BDL-1.50	1.26	0.61-33.24
2,2,3-Trimethylbutane										
+2,3-Dimethylpentane	0.29	BDL-1.11	0.00	BDL-0.91	0.17	BDL-0.63	0.28	0.06-4.10	0.36	0.09-1.21
3-M-Hexane	0.78	0.17-3.30	0.34	0.11-3.89	0.34	0.09-2.51	0.92	BDL-2.04	1.44	0.47-15.49
2,2,4-Tri-M-Pentane	0.21	BDL-1.33	0.14	BDL-2.69	0.10	BDL-0.76	0.53	0.14-1.32	0.22	BDL-0.74

Table 4.9 Statistical summary of the VOCs concentration (μ g m-³)

	September 05		October 05		April 06		February 07		July 07	
	median	Range	median	Range	median	Range	median	Range	median	Range
n-Heptane+cis-3-Heptene	0.76	BDL-6.91	0.54	0.12-8.41	0.29	BDL-5.31	0.85	0.33-2.36	0.69	0.22-3.09
Methylcyclohexane	0.3	BDL-3.67	0.11	BDL-5.31	0.12	BDL-4.01	0.33	0.16-1.35	0.22	BDL-0.89
Toluene	15.24	0.02-90.7	11.69	0.99-30.3	10.79	2.36-36.0	23.41	6.98-120	25.23	6.49-68.22
2-M-Heptane	0.25	BDL-1.03	0.20	BDL-0.73	0.33	0.13-1.24	0.81	BDL-2.48	0.69	BDL-3.21
m+p-Chlorotoluene	0.33	0.05-1.02	0.31	0.14-0.82	0.29	0.09-1.10	1.07	BDL-4.21	0.40	BDL-2.46
Octane	0.32	0.03-1.25	0.21	BDL-0.75	0.23	0.06-0.55	0.65	BDL-1.66	0.44	BDL-1.05
2,2,5-Tri-M-Hexane										
+1,2,4-Tri-M-Cyclohexane	0	BDL-0.12	0.00	BDL-0.23	0.14	BDL-0.40	0.16	BDL-0.86	0.05	BDL-1.18
TetraChloroEthylene	0.23	0-0.58	0.00	BDL-1.40	0.05	BDL-0.13	0.20	BDL-0.47	0.16	BDL-0.37
Chlorobenzene	0.16	0.03-0.77	0.99	BDL-2.10	0.13	BDL-0.46	0.51	BDL-1.87	0.20	0.04-1.45
Ethylbenzene	1.73	0.01-6.97	1.42	0.34-4.38	1.91	0.45-4.56	3.37	0.42-9.42	3.76	1.25-16.82
Bromoform	0.11	BDL-0.89	0.21	BDL-0.91	0.20	BDL-0.88	1.21	BDL-2.70	0.60	BDL-3.30
m+p-Xylene	5.42	0.11-20.2	4.19	0.91-13.2	4.55	1.12-13.8	8.87	0.7-24.7	10.87	2.35-56.55
Styrene	0.41	0-9.25	0.49	BDL-11.31	1.32	0.08-6.01	24.84	0.06-257	0.24	BDL-2.49

Table 4.9 Statistical summary of the VOCs concentration (μ g m⁻³) (*Continued*)

	Septer	ptember 05 October 05		ber 05	April 06		February 07		July 07	
	median	Range	median	Range	median	Range	median	Range	median	Range
o-xylene	0.85	0.01-2.60	0.74	0.12-2.43	0.76	BDL-2.73	1.52	BDL-450	1.35	0.19-7.44
n-Nonane	0.48	0.04-5.39	0.35	0.07-2.51	0.41	0.07-1.31	0.00	BDL-2.57	0.00	BDL-0.45
Isopropylbenzene	0.05	0-0.18	0.05	BDL-0.18	0.26	0.12-1.22	0.36	BDL-10.3	0.20	0.02-0.60
n-Probylbenzene	0.16	0.02-0.44	0.01	BDL-0.34	0.17	BDL-0.38	0.20	BDL-3.50	0.14	0.04-0.72
3-Ethyltoluene	0.94	0.04-2.97	0.71	0.13-2.76	0.73	0.18-2.54	1.47	0.01-4.46	1.01	0.15-5.48
4-Ethyltoluene	0.61	0.05-3.22	0.57	0.08-1.87	0.59	0.16-1.61	2.41	0.06-6.62	0.40	0.04-4.81
1,3,5-Tri-M-Benzene	0.4	0.09-1.27	0.29	0.06-1.17	0.38	0.09-1.03	0.63	0.01-7.29	0.42	BDL-3.37
2-Ethyltoluene	0.66	0.15-2.68	0.35	0.08-1.22	0.33	0.06-0.96	0.67	BDL-1.67	0.44	BDL-2.48
1,2,4-Tri-M-benzene	0.77	0.05-2.58	0.63	0.16-2.40	1.37	0.41-2.73	3.21	0.01-16.4	0.52	0.05-2.57
n-Decane	0.96	0.2-11.19	0.47	0.12-4.27	0.77	0.14-3.06	1.98	0.01-6.85	0.93	BDL-5.56
1,4-Di-Cl-Benzene	0.07	BDL-0.41	0.05	BDL-0.34	0.04	BDL-0.14	0.16	BDL-38.2	0.11	BDL-0.30
1,4-Di-E-Benzene	0.19	0.02-1.08	0.14	0.02-0.70	0.16	BDL-0.53	0.37	BDL-3.50	0.12	BDL-0.95
Naphthalene	0.31	BDL-1.03	0.17	0.01-1.47	0.10	BDL-0.58	0.21	BDL-1.55	0.09	BDL-0.64

Table 4.9 Statistical summary of the VOCs concentration ($\mu g m^{-3}$) (Continued)

4.2.2 Comparison with Literature

There are fair amount of literature on active and passive sampling of VOCs in various microenvironments. However, it is not easy to compare them; they have been measured at different sampling locations which have very different characteristics such as urban, urban heavily affected by industry, traffic or densely populated area. In addition to the sampling locations, selected techniques, sorbents, duration of sampling, year and meteorological conditions have also strong effect on the measured concentrations (Kumar and Viden, 2007). Hence, comparison of absolute concentrations of VOCs measured at different cities is quite a challenging task. Figure 4.9 can give an idea about benzene levels in different cities around the world. As can be seen from the Figure 4.9, benzene concentration is highly variable. While lower values were measured in North America and some parts of the Europe, very high benzene concentrations were also observed in South Asia and America. Different benzene (and other VOCs) concentrations measured in different cities can be due to a number of reasons, such as gasoline composition, meteorology, traffic density and the age of the vehicle fleet...



Figure 4.9 Average benzene concentrations different parts of the world (modified from Fernandes et al., 2005)

VOCs data collected in Bursa shows that concentration varies at residential, background, roadside and industrial area. These findings will be discussed in the following sections. Differences are pronounced also at different sampling campaign due to meteorological differences. Concentration of VOCs measured with passive sampling tubes is also depended on factors such as source strength, distance between source and receptor, meteorological conditions and topography. If a sampling point is located close to a road or an industrial area, VOC concentrations were high compared to concentation found at a suburban area. Therefore, in this section only results obtained from urban areas in the literature are compared with this study and results are given in Table 4.10.

Roukos et al. (2009) measured VOCs at summer and winter in the industrial city of Dunkerque. Weekly sampling campaign were conducted by using Radiello passive samplers at 36 sites for the winter campaign (16–23 January 2007) and 40 sites for the summer one (6–13 June 2007) with 22 common sites. Sampling sites were distributed over an area of 224 km² according to a regular grid with 4 km² meshes. In the current study, mean BTEX levels with their standart deviations were represented for rural, urban and industrial zones. The spatial distribution of BTEX was quite similar the spatial map producued for Bursa, with high level in indutrail area and around roads.

Parra et al. (2009) measured ambient concentrations of VOCs by means of passive sampling at 40 sampling points in a medium-size city in Northern Spain, from June 2006 to June 2007. Collected samplers were analysed by thermal desorption followed by GC-MS. According to the paper, mean concentrations of benzene, toluene, ethylbenzene, xylenes, propylbenzene and trimethylbenzenes, were 2.84, 13.26, 2.15, 6.01, 0.59 and 1.32 μ g m⁻³ respectively, and found to be highly correlated. They also found that their spatial distribution showed high differences in small distances and pointed to traffic as the main emission source of these compounds. The lowest levels of VOCs occurred during summer, owing to the increase in solar radiation and to lower traffic densities. Mean concentrations of benzene exceeded the European limits at some of the monitored points.

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The ambient VOCs concentration were evaluated in the urban air of Helsinki in Finlad by Hellen et al (2002). Concentrations were measured with passive sampling tubes in 2-week periods at four different sites during the year 2000. Analysis was conducted using thermal desorption and GC MS. The concentrations of aromatic compounds in Helsinki metropolitan area were also compared to the concentrations of a rural, forested site in Central Finland. They found that the BTEX concentrations decrease rapidly from urban to rural site, except benzene that is found in considerable amounts also in rural areas.

Pilidis at al. (2005) reported the results of BTEX measurement campaign that took place in Ioannina, a medium-sized Greek city. BTEX levels were measured using passive samplers placed at 9 points around the city during four diffrenet sampling campaigns. As a result of traffic situation and the local meteorological conditions, pollution levels in Ioannina are unusually high in this study, at least for a city of that size. Benzene levels appear correlated to traffic density.

Hoque et al. (2008) were collected samples every month during the period October, 2001–September, 2002 to obtain seasonal variability at different sampling points in the ambient air of Delhi. Sampling was carried out by exposing the fabricated diffusive sampling tubes in the ambient air for one week duration. Concentration levels of BTEX showed seasonal variations. According to Hoque et al. (2008) the meteorology of Delhi and reactivity behavior of BTEX could be responsible for the seasonal variation. Vehicular exhaust mainly contributes to the high levels of BTEX in the ambient air of Delhi.

Literature data discussed in previous paragraphs were compared with VOC concentations measured in this study. Both literature data average concentations of VOCs measured in this study are given in Table 4.10. As can be seen from the table, BTEX concentration measured in Bursa are higher than that measured in Plaisance, France and Navera, Finland atmospheres. However, concentrations measured in Bursa were approximately an order of magnitude lower than that were measured in Delphi, India. The reasons for such a big difference in measured concentrations could be explained by

	This S	Study	literature						
Compound name	Bursa		Kocaeli,	Plaisance,	Navarre,	Helsinki,	Shimizu,	Ioannina,	Delhi,
	Winter	Summer	Turkey ¹	France ²	Spain ³	Finland ⁴	Japan⁵	Greek ⁶	India ⁷
Sampling Points	67	65		36	40	4			
Benzene	8.21	2.26	6.58	2.84	1.90	1.90	1.45	12.3	93
Toluene	23.41	25.21	14.73	13.26	6.02	6.02	13.5	41.2	18.5
Ethylbenzene	3.37	3.76	4.44	2.15	1.43	1.43	2.01		18.5
m&p-Xylene	8.87	10.87	7.58	3.38	4.60	4.60	3.02		72
o-Xylene	1.52	1.33	3.77	2.63	1.73	1.73	0.93		40.15

Table 4.10 Comparison of the average VOC concentrations ($\mu g m^{-3}$) with the literature

¹ Pekey, 2008; ² Roukos, 2009; ³ Parra, 2009; ⁴ Hellen, 2002; ⁵ Ohura, 2006; ⁶Pilidis, 2005; ⁷ Hoque, 2008

differences in sampling and analysis protocol, emission sources and meteorology.

4.2.3 Spatial Distribution of VOCs Concentration

4.2.3.1 Pollution Map

Pollution maps generated by interpolation of pollutant concentrations can provide clues to the emission sources of pollutants (Kume et al., 2007 and Ohura et al., 2006). In this study, concentrations of VOCs were interpolated using GIS software. Vertical Mapper V3 of MapInfo software with "natural neighborhood" technique was used to obtain concentration distribution map for each VOC over the city. In the "natural neighborhood" technique, original data is used to build a network of natural neighbor regions (Voronoi diagram). This creates an area of influence for each data point that is used to assign new values to overlying grid cells by using a simple equation (Vertical Mapper User Guide. 2008). The spatial distribution of BTEX and inorganic pollutants are given in Figure 4.10 through Figure 4.16.

The spatial variation analysis generally indicates that concentrations of BTEX, NO_2 and SO_2 are high in the vicinity of the roads and in industrial areas and the lowest at the background areas. Concentration of VOCs decreases with increasing distance from immediate sources. Motor vehicle emissions and industrial emissions contribute significantly to most of these compounds. Opposite distribution pattern was obtained for ozone data as depicted in Figure 4.15. Ozone concentration was the highest in the background area and at the stations located at the suburbs and low at the sampling points located at city center. Such low concentrations at the city center and high concentrations at suburubs is typical for O_3 and observed an almost all studies involving spatial

distribution of this compound (Parra et al., 2006; Cooper and Peterson, 2000 and Yin et al., 2001). Observed pattern in O₃ concentration is due to ozone destilation. Normally, NO in the urban atmosphere together with VOCs are responsible for tropospheric ozone formation. However, if NO concentration is high (as in most city centers) then it can be destroy ozone forms (Tsaia et. al., 2004 and Garcia et al., 2005). Therefore, O₃ concentrations are generally low at polluted atmospheres such as city center and vicinity of the roads.

Spatial distribution maps for benzene and NO₂ at Bursa are presented in Figure 4.10 and Figure 4.16. Concentrations are highest in the vicinity of the main roads and streets, and in the central area of Bursa. This is due to very high traffic intensity at the city center, which is the main contributor to observed benzene and NO₂ concentrations. Benzene concentrations were 2.5 time higher in the vicinity of the roads than that of in background area. These results are comparable to those obtained in a number of cities, where levels of benzene at vicinity of the roads were 2.5 to 5 times higher than the urban background levels (Parra et al., 2009; Hansen and Palmgren, 1996)

The spatial distribution maps for toluene, ethylbenzene, and m&p xylene are given in Figure 4.11, Figure 4.12 and Figure 4.13 Concentrations of these compounds were high around industrial areas and at close proximity of roads. The result indicated that traffic is not the only source affecting their observed concentrations at an urban area. Contributions of industrial sources on observed concentrations of some of the VOCs are discussed later in the manuscript.

Sulfur dioxide distribution map, which is depicted in Figure 4.14 show high concentrations in and around industrial areas and centre of the city. It is well documented that the main source of SO₂ in the urban atmosphere is coal combustion (Costabile et al., 2006). The sampling campaign for SO₂ measurement was conducted in April 2005. The average temperature recorded during the sampling campaign was 13.7 ^oC. The possibility of the SO₂ emissions from coal burning in building is low due to mild climatic condition preveal during

the sampling campaign. The high concentration level measured in the industrial areas may be associated from coal burning in the industrial facilities. Heavy diesel traffic intensity at the city center can also contribute to high SO_2 concentrations in that area, because sulfur content in diesel fuel is high (Kan et al., 2010 and Guttikunda et al., 2003). Contribution of diesel emissions on SO_2 concentrations were also reported in Ankara (Genç et al., 2010).



Figure 4.10 Spatial distribution of benzene at April 2006 campaign



Figure 4.11 Spatial distribution of toluene at April 2006 campaign



Figure 4.12 Spatial distribution of ethylbenzene at April 2006 campaign



Figure 4.13 Spatial distribution of m&p xylene at April 2006 campaign



Figure 4.14 Spatial distribution of SO₂ at April 2006 campaign

Spatial distribution maps for benzene and NO_2 at Bursa are presented in Figure 4.10 and Figure 4.16. Concentrations are highest in the vicinity of the main roads and streets, and in the central area of Bursa. This is due to very high traffic intensity at the city center, which is the main contributor to observed benzene and NO_2 concentrations. Benzene concentrations were 2.5 time higher in the vicinity of the roads than that of in background area. These results are comparable to those obtained in a number of cities, where levels of benzene at vicinity of the roads were 2.5 to 5 times higher the urban background level



Figure 4.15 Spatial distribution of ozone at April 2006 campaign 150



Figure 4.16 Spatial distribution of NO₂ at April 2006 campaign

(Parra et al., 2009; Hansen and Palmgren, 1996).Coefficient and P values denote probability of chance correlation. Strong correlations were found among BTEX. The vey good correlation (R>0.9) between ethylbenzene, o-xylene and m&p xylene were observed when compared with benzene and toluene. It could be interpreted that all of these compounds originated from the same source, gasoline vehicle and gasoline stations (Hoque et al., 2008; Baldasano et al., 1998 and Wang et al., 1993).

 SO_2 only strongly correlated with benzene among BTEX groups. The spatial distribution map of benzene indicates that the main source of the benzene motor vehicle emissions. Hence this correlation between SO_2 and benzene shows that the vehicle emission as the main source of these compounds in the studied area

Ozone correlated with SO_2 and BTEX while negatively correlated with NO_2 . Ozone is secondary pollutant that is affected VOC and NO_x and meteorological conditions (Hung-Lung et al., 2007). The positive correlation between BTEX and ozone were observed in the data set. Accoriding the positive correlation, it could be assumed that the ozone production depended on NO_x concentration.

		SO ₂	NO ₂	O ₃	Benzene	Toluene	Ethyl benzene	m&p Xylene	o Xylene
SO ₂	R	1	296*	.662**	.538**	.226	.331*	.317*	.363*
	р		.039	.000	.000	.119	.020	.026	.010
NOa	R	296*	1	456**	199	246	113	093	111
	р	.039		.001	.171	.088	.440	.525	.448
02	R	.662**	456**	1	.392**	.293*	.350*	.354*	.375**
	р	.000	.001		.005	.041	.014	.013	.008
Benzene	R	.538**	199	.392**	1	.558**	.446**	.509**	.593**
	р	.000	.171	.005		.000	.001	.000	.000
Toluene	R	.226	246	.293*	.558**	1	.661**	.637**	.641**
i oldono	р	.119	.088	.041	.000		.000	.000	.000
Ethyl	R	.331*	113	.350*	.446**	.661**	1	.959**	.911**
benzene	р	.020	.440	.014	.001	.000		.000	.000
m&p Xylene	R	.317*	093	.354*	.509**	.637**	.959**	1	.948**
	р	.026	.525	.013	.000	.000	.000		.000
o Xylene	R	.363*	111	.375**	.593**	.641**	.911**	.948**	1
o Aylerie	р	.010	.448	.008	.000	.000	.000	.000	

Table 4.11: Correlation between BTEX and inorganic compounds

*. Correlation is significant at the 0.05 level and **. Correlation is significant at the 0.1 level

Since NO_2 concentration is commonly associated with secondary formation from reactions between primary emissions of NO and O_3 (Mukerjee et al., 2004 and Seinfeld and Pantis, 1998), the concentration of ozone increase with decreasing that of NO_2 .

4.2.3.2 Sector Averages

Since the VOCs passive samplers were located in fifty different locations in Bursa, they were under the influence of different sources. If samplers can be located properly, they can generate information on the sources of VOCs in the city. What types of sources affect VOCs concentrations in Bursa? Studies performed up to now clearly demonstrated that the dominant source of VOCs in an urban environment is the light and heavy traffic (Lee et al, 2002; Na et al, 2003; Chan et al, 2002). This is true for Bursa as well. However, Bursa is an industrial city and industrial emissions can contribute to the concentrations of some of the VOCs measured in this study. Coal combustion at residential areas can also contribute to the VOC concentrations in Bursa. However, it should be pointed that out of five sampling campaigns performed in Bursa, the only sampling campaign in February corresponded to the period when heating units were operating. All the other sampling periods were in nonheating period (spring, fall and summer). This means that in all the samples, except those collected in February, VOCs measured in residential areas originate from traffic and around settlements, or from evaporative emissions.

In the beginning of the study, the sampling points were situated such that sufficient numbers of samplers were located around roads, in residential areas, in locations that are not under the direct influence of traffic, in five organized industrial zones of the city and at background locations that are outside the city but influenced occasionally from urban plume when wind blows from a particular sector only. In the remaining time, background stations receive air flow from rural areas. Since samplers were located at the same points in each campaign, five data for each VOC at each location were

generated. Then these data were grouped as background, industrial, residential, and road, and compared to see if there were significant differences between different station groups. This approach helped us (1) to assess non-traffic contributions to VOC concentrations (2) to generate a set of marker VOCs for industrial emissions in Bursa, which were later used to identify the factors in factor analysis.

The VOC sector average and median concentrations measured in each passive sampling campaign are given in Table 4.12., Table 4.13, Table 4.14, Table 4.15 and Table 4.16. One interesting point worth noting in these tables is the similarity of concentrations of VOCs at traffic-impacted and residential stations. For most of the VOCs (but not for all of them) the average and median concentrations measured at the traffic-impacted stations that are located by the roads are comparable to the concentrations measured at residential sites that are not under the "direct" influence of motor vehicle emissions. This observation clearly demonstrates that most of the residential sites are under the influence of motor vehicle emissions. This is not totally unexpected, because most of the roads goes through residential areas, even if a sampling point is not under the direct influence of a road (thus traffic emissions), those emissions are transported to that site from a nearby road.

The VOCs were grouped into 4 categories based on their average concentrations in different microenvironments. These groups included:

4.3.1 <u>Industrial Markers</u>: These are the VOCs that had the highest concentrations in industrial stations consistently in all of the five sampling campaigns. There are 10 VOCs in this group, including, 2,2,4-tri-m-pentane, 2,2,5-tr-M-hexane+1,2,4-Tr-M-cyclohexane, tetrachloroethylene, chlorobenzene, bromoform, n-nonane, 3-ethyltoluene, 2-ethyltoluene, n-decane, 1,4-dichlorobenzene. Sector median concentrations of selected four of these industrial marker VOCs are depicted in Figure 4.17. Concentrations of VOCs changed from one campaign, but whatever the concentrations were, these 10 VOCs had the highest average and median values in the industrial stations. Identification of this group helped us in identifying factors in the factor analysis, which will be discussed later in the manuscript.

	AVERAGE					MEDIAN				
COMPOUNDS	BGD	INDUSTRY	RESID.	ROAD	BGD	INDUSTRY	RESD.	ROAD		
NO ₂	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.		
SO ₂	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.		
O ₃	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.		
Pentane	0.36 ± 0.21	0.49 ± 0.18	0.65 ± 0.33	0.48 ± 0.13	0.25	0.43	0.53	0.45		
1,3 Butadiene	0.14 ± 0.02	0.17 ± 0.04	0.18 ± 0.05	0.25 ± 0.17	0.14	0.16	0.19	0.20		
n-Hexane	0.25 ± 0.14	0.31 ± 0.11	0.33 ± 0.13	0.31 ± 0.09	0.25	0.30	0.33	0.29		
Methylcyclopentane	0.09 ± 0.05	0.13 ± 0.03	0.31 ± 0.46	0.14 ± 0.06	0.12	0.14	0.16	0.15		
+2,4-Dimethylpentane										
1,1,1-Tri-Cl-Ethane	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L		
Benzene	1.03 ± 0.53	1.52 ± 0.30	2.06 ± 0.53	1.86 ± 0.53	0.90	1.41	1.93	1.71		
Cyclohexane+Cyclohexene	0.63 ± 0.27	1.21 ± 0.41	1.06 ± 0.65	1.07 ± 0.41	0.60	1.21	0.95	1.29		
2-Methylhexane	0.43 ± 0.18	1.30 ± 0.79	1.08 ± 0.47	1.29 ± 0.60	0.41	1.04	1.04	1.17		
2,2,3-Trimethylbutane+	0.18 ± 0.11	0.45 ± 0.19	0.30 ± 0.10	0.48 ± 0.29	0.11	0.44	0.29	0.36		
2,3-Dimethylpentane										
3-M-Hexane	0.39 ± 0.19	0.88 ± 0.54	0.78 ± 0.26	0.81 ± 0.42	0.36	0.71	0.78	0.74		
2,2,4-Tri-M-Pentane	0.14 ± 0.04	0.55 ± 0.21	0.17 ± 0.06	0.25 ± 0.13	0.13	0.52	0.17	0.22		
n-Heptane+cis-3-Heptene	0.26 ± 0.08	2.65 ± 2.25	0.79 ± 0.35	0.94 ± 0.47	0.23	1.73	0.76	0.88		

Table 4.12 Average and median concentrations of VOCs in different microenvironments in SEPTEMBER 2005 campaign (µg m⁻³)

Table 4.12 Average and median concentrations of VOCs in different microenvironments in SEPTEMBER 2005 campaign	(µg m⁻³)
(Continued)	

		AVE	ERAGE	MEDIAN				
COMPOUNDS	BGD	INDUSTRY	RESID.	ROAD	BGD	INDUSTRY	RESD.	ROAD
Methylcyclohexane	0.12 ± 0.02	1.37 ± 1.24	0.33 ± 0.18	0.45 ± 0.30	0.10	1.05	0.29	0.34
Toluene	0.06 ± 0.05	19.92 ± 8.56	17.11 ± 8.57	12.00 ± 6.19	0.06	18.46	15.56	8.79
2-M-Heptane	0.03 ± 0.01	0.29 ± 0.08	0.32 ± 0.20	0.26 ± 0.09	0.03	0.27	0.29	0.27
m+p-Chlorotoluene	0.12 ± 0.05	0.44 ± 0.20	0.42 ± 0.21	0.30 ± 0.13	0.13	0.40	0.42	0.31
Octane	0.11 ± 0.06	0.36 ± 0.14	0.31 ± 0.07	0.29 ± 0.08	0.12	0.34	0.31	0.31
2,2,5-Tri-M-Hexane+1,2,4-	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L
Tri-M-Cyclohexane								
Tetrachloroethylene	0.13 ± 0.04	0.28 ± 0.11	0.22 ± 0.13	0.24 ± 0.11	0.14	0.26	0.22	0.25
Chlorobenzene	0.04 ± 0.01	0.31 ± 0.20	0.16 ± 0.06	0.13 ± 0.06	0.04	0.23	0.15	0.14
Ethylbenzene	0.52 ± 0.07	2.72 ± 1.42	2 2.13 ± 1.32	2.13 ± 1.22	0.52	2.23	1.85	1.60
Bromoform	0.12 ± 0.00	0.30 ± 0.16	0.16 ± 0.05	0.22 ± 0.08	0.12	0.25	0.13	0.19
M+p-Xylene	1.04 ± 0.66	8.38 ± 4.15	6.51 ± 3.90	6.36 ± 3.64	1.37	6.75	5.95	4.79
Styrene	0.16 ± 0.12	0.62 ± 0.39	0.94 ± 1.93	0.65 ± 0.58	0.15	0.50	0.46	0.52
O-xylene	0.15 ± 0.02	1.29 ± 0.54	1.01 ± 0.51	0.92 ± 0.51	0.15	1.12	0.84	0.71
n-Nonane	0.17 ± 0.09	0.64 ± 0.29	0.45 ± 0.14	0.50 ± 0.22	0.21	0.55	0.42	0.54
Isopropylbenzene	0.01 ± 0.01	0.07 ± 0.04	0.06 ± 0.04	0.06 ± 0.03	0.02	0.08	0.06	0.05
n-Probylbenzene	0.07 ± 0.05	0.19 ± 0.09	0.19 ± 0.09	9 0.19 ± 0.10	0.06	0.17	0.17	0.16
Table 4.12 Average and median concentrations of VOCs in different microenvironments in SEPTEMBER 2005 campaign (μ g m⁻³) (*Continued*)

		AVEF	RAGE			MED	AN	
COMPOUNDS	BGD	INDUSTRY	RESID.	ROAD	BGD	INDUSTRY	RESD.	ROAD
3-Ethyltoluene	0.18 ± 0.10	1.47 ± 0.66	1.14 ± 0.61	1.12 ± 0.62	0.22	1.43	0.94	0.94
4-Ethyltoluene	0.17 ± 0.09	1.10 ± 0.53	0.61 ± 0.22	0.68 ± 0.32	0.23	1.19	0.56	0.67
1,3,5-Tri-M-Benzene	0.17 ± 0.07	0.62 ± 0.33	0.49 ± 0.26	0.50 ± 0.30	0.15	0.57	0.41	0.41
2-Ethyltoluene	0.29 ± 0.09	1.06 ± 0.47	0.73 ± 0.32	0.69 ± 0.31	0.30	1.10	0.69	0.66
1,2,4-Tri-M-benzene	0.19 ± 0.10	1.18 ± 0.52	0.97 ± 0.56	0.90 ± 0.48	0.25	1.29	0.79	0.78
n-Decane	0.43 ± 0.21	2.86 ± 2.67	0.95 ± 0.42	1.07 ± 0.55	0.34	1.62	0.94	1.01
1,4-di-cl-benzene	0.04 ± 0.02	0.11 ± 0.06	0.07 ± 0.02	0.07 ± 0.03	0.04	0.10	0.07	0.07
1,4-di-e-benzene	0.08 ± 0.04	0.34 ± 0.19	0.20 ± 0.11	0.23 ± 0.11	0.08	0.31	0.18	0.23
Naphthalene	0.09 ± 0.05	0.27 ± 0.12	0.43 ± 0.24	0.34 ± 0.16	0.11	0.28	0.37	0.30

N.M.: Not measured; BDL: Below Detection Limit

		AVE	RAGE			MEDIA	٨N	
COMPOUNDS	BGD	INDUSTRY	RESD.	ROAD	BGD	INDUSTRY	RESD.	ROAD
NO ₂	9.1 ± 3.3	35.1 ± 2.9	31.5 ± 10.0	51.0 ± 11.9	9.7	33.8	32.3	48.0
SO ₂	11.2 ± 1.6	25.6 ± 30.2	16.0 ± 7.6	27.7 ± 12.6	11.0	13.7	16.0	23.7
O ₃	35.5 ± 15.0	32.0 ± 3.6	28.6±10	19.2 ± 9.1	35.0	31.4	29.1	20.6
Pentane	0.08 ± 0.02	0.16 ± 0.06	0.23 ± 0.09	0.25 ± 0.09	0.08	0.17	0.23	0.25
1,3 Butadiene	0.09 ± 0.02	0.16 ± 0.07	0.31 ± 0.15	0.41 ± 0.22	0.10	0.15	0.29	0.37
n-Hexane	0.44 ± 0.23	0.33 ± 0.19	0.52 ± 0.27	0.49 ± 0.27	0.29	0.24	0.45	0.50
Methylcyclopentane+	0.07 ± 0.02	0.14 ± 0.05	0.21 ± 0.11	0.31 ± 0.18	0.08	0.14	0.18	0.37
2,4-Dimethylpentane								
1,1,1-Tri-CI-Ethane	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L
Benzene	1.12 ± 0.27	1.58 ± 0.81	2.73 ± 1.30	2.93 ± 1.41	1.24	1.36	2.54	3.19
Cyclohexane+Cyclohexene	1.35 ± 1.17	2.24 ± 1.57	2.10 ± 1.38	1.70 ± 1.22	1.22	2.15	2.61	1.17
2-Methylhexane	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L
2,2,3-Trimethylbutane+	0.42 ± 0.00	0.64 ± 0.26	0.19 ± 0.23	0.13 ± 0.16	0.42	0.64	0.14	0.00
2,3-Dimethylpentane								
3-M-Hexane	0.20 ± 0.11	0.97 ± 1.16	0.35 ± 0.14	0.52 ± 0.26	0.16	0.50	0.32	0.43

Table 4.13 Average and median concentrations of VOCs in different microenvironments in OCTOBER 2005 campaign ($\mu g m^{-3}$)

Table 4.13 Average and median concentrations of VOCs in different microenvironments in OCTOBER 2005 campaign (μ g m⁻³) (*Continued*)

		AVEF	RAGE			MEDIA	۸N	
COMPOUNDS	BGD	INDUSTRY	RESD.	ROAD	BGD	INDUSTRY	RESD.	ROAD
2,2,4-Tri-M-Pentane	0.04 ± 0.01	0.70 ± 0.85	0.12 ± 0.06	0.18 ± 0.06	0.04	0.26	0.11	0.16
n-Heptane+cis-3-Heptene	0.20 ± 0.08	2.17 ± 2.55	0.51 ± 0.20	0.78 ± 0.40	0.17	1.13	0.49	0.56
Methylcyclohexane	0.10 ± 0.07	1.26 ± 1.64	0.12 ± 0.08	0.15 ± 0.06	0.10	0.69	0.10	0.14
Toluene	4.02 ± 2.19	15.21 ± 5.09	13.25 ± 7.16	16.58 ± 8.84	4.05	14.53	11.68	18.00
2-M-Heptane	0.07 ± 0.01	0.21 ± 0.07	0.22 ± 0.11	0.27 ± 0.16	0.07	0.22	0.19	0.22
m+p-Chlorotoluene	0.23 ± 0.07	0.31 ± 0.06	0.35 ± 0.11	0.46 ± 0.22	0.23	0.32	0.31	0.32
Octane	0.07 ± 0.01	0.29 ± 0.12	0.23 ± 0.09	0.21 ± 0.10	0.08	0.27	0.19	0.25
2,2,5-Tri-M-	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L
Hexane+1,2,4-Tri-M-								
Cyclohexane								
TetraChloroEthylene	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L
Chlorobenzene	1.16 ± 0.55	1.03 ± 0.60	1.19 ± 0.68	0.87 ± 0.58	1.42	0.87	1.33	0.58
Ethylbenzene	0.48 ± 0.09	1.86 ± 0.70	1.60 ± 0.71	2.16 ± 1.17	0.49	1.55	1.40	1.76
Bromoform	0.06 ± 0.00	0.43 ± 0.29	0.25 ± 0.11	0.36 ± 0.25	0.06	0.36	0.23	0.36
m+p-Xylene	1.31 ± 0.27	5.66 ± 2.13	4.74 ± 2.21	6.49 ± 3.56	1.34	4.76	4.03	5.21
Styrene	0.44 ± 0.05	0.40 ± 0.32	0.41 ± 0.25	0.86 ± 0.42	0.44	0.24	0.34	0.78

Table 4.13 Average and median concentrations of VOCs in different microenvironments in OCTOBER 2005 campaign (μ g m⁻³) (*Continued*)

		AVE	RAGE			MEDIA	N	
COMPOUNDS	BGD	INDUSTRY	RESD.	ROAD	BGD	INDUSTRY	RESD.	ROAD
o-xylene	0.24 ± 0.08	0.96 ± 0.36	0.81 ± 0.36	1.16 ± 0.68	0.26	0.84	0.72	0.93
n-Nonane	0.10 ± 0.03	0.93 ± 0.75	0.38 ± 0.16	0.48 ± 0.29	0.10	0.61	0.34	0.36
Isopropylbenzene	0.03 ± 0.02	0.07 ± 0.03	0.05 ± 0.04	0.08 ± 0.05	0.02	0.06	0.05	0.06
n-Probylbenzene	0.04 ± 0.03	0.05 ± 0.05	0.00 ± 0.00	0.10 ± 0.11	0.03	0.02	0.00	0.11
3-Ethyltoluene	0.19 ± 0.04	1.08 ± 0.37	0.80 ± 0.36	1.21 ± 0.76	0.19	1.09	0.66	0.88
4-Ethyltoluene	0.15 ± 0.04	0.90 ± 0.37	0.60 ± 0.26	0.80 ± 0.45	0.15	0.89	0.54	0.61
1,3,5-Tri-M-Benzene	0.08 ± 0.02	0.47 ± 0.17	0.33 ± 0.16	0.50 ± 0.33	0.08	0.47	0.25	0.35
2-Ethyltoluene	0.10 ± 0.02	0.58 ± 0.24	0.38 ± 0.16	0.52 ± 0.32	0.10	0.55	0.34	0.38
1,2,4-Tri-M-benzene	0.19 ± 0.03	1.01 ± 0.38	0.71 ± 0.31	1.02 ± 0.64	0.18	1.00	0.55	0.75
n-Decane	0.15 ± 0.03	1.59 ± 1.55	0.54 ± 0.33	0.57 ± 0.44	0.14	0.81	0.44	0.46
1,4-DI-CL-Benzene	0.02 ± 0.00	0.12 ± 0.11	0.06 ± 0.02	0.06 ± 0.04	0.02	0.06	0.05	0.05
1,4-DI-E-Benzene	0.04 ± 0.02	0.19 ± 0.10	0.16 ± 0.09	0.16 ± 0.08	0.03	0.16	0.13	0.11
Naphthalene	0.07 ± 0.02	0.13 ± 0.10	0.18 ± 0.09	0.27 ± 0.20	0.08	0.14	0.17	0.30

BDL: Below Detection Limit

		AVE	RAGE			MEDI	AN	
COMPOUNDS	BGD	INDUSTRY	RESD.	ROAD	BGD	INDUSTRY	RESD.	ROAD
NO ₂	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.
SO ₂	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.
O ₃	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.	N.M.
Pentane	0.54 ± 0.15	0.79 ± 0.24	1.02 ± 0.29	1.18 ± 0.39	0.60	0.68	1.02	1.08
1,3 Butadiene	0.16 ± 0.09	0.24 ± 0.09	0.50 ± 0.21	0.58 ± 0.25	0.11	0.24	0.42	0.49
n-Hexane	0.19 ± 0.03	1.36 ± 1.31	0.94 ± 0.65	0.69 ± 0.51	0.19	0.91	0.73	0.46
Methylcyclopentane+	0.36 ± 0.08	1.11 ± 0.57	1.00 ± 0.43	1.23 ± 0.44	0.32	1.00	0.87	1.12
2,4-Dimethylpentane								
1,1,1-Tri-Cl-Ethane	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L
Benzene	3.39 ± 0.42	8.01 ± 4.30	10.17 ± 3.09	10.28 ± 3.43	3.13	6.91	9.29	9.45
Cyclohexane+Cyclohexene	0.82 ± 0.30	2.05 ± 1.45	1.46 ± 0.45	1.57 ± 0.51	0.84	1.64	1.41	1.42
2-Methylhexane	0.38 ± 0.17	0.93 ± 0.49	0.80 ± 0.23	0.95 ± 0.36	0.31	0.87	0.76	0.81
2,2,3-Trimethylbutane+	0.16 ± 0.07	0.35 ± 0.19	0.30 ± 0.08	0.34 ± 0.12	0.17	0.32	0.29	0.33
2,3-Dimethylpentane								
3-M-Hexane	0.47 ± 0.21	1.16 ± 0.75	0.93 ± 0.28	1.20 ± 0.46	0.44	0.99	0.89	1.00
2,2,4-Tri-M-Pentane	0.31 ± 0.12	0.96 ± 0.58	0.51 ± 0.23	0.58 ± 0.24	0.25	0.75	0.46	0.57

Table 4.14 Average and median concentrations of VOCs in different microenvironments in FEBRUARY 2007 campaign (µg m⁻³)

Table 4.14 Average and median concentrations of VOCs in different microenvironments in FEBRUARY 2007 campaign (μ	g m⁻³)
(Continued)	

		AVEF	RAGE			MEDI	AN	
COMPOUNDS	BGD	INDUSTRY	RESD.	ROAD	BGD	INDUSTRY	RESD.	ROAD
n-Heptane+cis-3-Heptene	0.44 ± 0.11	1.26 ± 1.13	0.83 ± 0.22	1.08 ± 0.36	0.41	0.87	0.79	0.94
Methylcyclohexane	0.19 ± 0.02	0.69 ± 0.72	0.32 ± 0.09	0.42 ± 0.10	0.20	0.46	0.28	0.40
Toluene	10.09 ± 5.01	38.03 ± 19.97	22.18 ± 6.19	30.24 ± 11.01	7.32	38.16	19.87	29.13
2-M-Heptane	0.38 ± 0.19	0.96 ± 0.30	0.94 ± 0.41	0.97 ± 0.35	0.28	0.92	0.85	0.84
m+p-Chlorotoluene	1.00 ± 0.49	1.70 ± 0.87	1.16 ± 0.57	1.54 ± 0.61	0.82	1.66	1.07	1.17
Octane	0.28 ± 0.06	1.16 ± 0.82	0.69 ± 0.30	0.80 ± 0.18	0.29	0.97	0.56	0.73
2,2,5-Tri-M-Hexane+	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L	B.D.L
1,2,4-Tri-M-Cyclohexane								
TetraChloroEthylene	0.06 ± 0.03	0.38 ± 0.23	0.20 ± 0.08	0.24 ± 0.10	0.05	0.31	0.18	0.23
Chlorobenzene	0.22 ± 0.07	0.92 ± 0.47	0.54 ± 0.33	0.66 ± 0.25	0.22	0.73	0.45	0.55
Ethylbenzene	1.59 ± 0.56	6.68 ± 9.17	3.36 ± 1.63	4.63 ± 1.18	1.67	4.72	2.90	4.10
Bromoform	0.65 ± 0.27	2.31 ± 1.42	1.23 ± 0.58	1.54 ± 0.30	0.63	1.89	1.10	1.58
m+p-Xylene	3.77 ± 1.42	18.42 ± 7.94	8.73 ± 4.31	12.71 ± 3.59	3.71	12.67	7.46	11.67
Styrene	26.36 ± 9.27	30.84 ± 21.98	24.72 ± 12.44	27.88 ± 8.70	23.94	24.07	21.00	25.95
o-xylene	0.41 ± 0.13	4.27 ± 6.22	1.36 ± 0.53	2.11 ± 0.70	0.41	2.45	1.33	1.96
n-Nonane	0.53 ± 0.00	4.72 ± 7.48	1.38 ± 0.85	1.07 ± 0.68	0.53	1.33	1.30	1.07

Table 4.14 Average and median concentrations of VOCs in different microenvironments in FEBRUARY 2007 campaign (μ g m⁻³) (*Continued*)

		AVER	AGE			MEDI	AN	
COMPOUNDS	BGD	INDUSTRY	RESD.	ROAD	BGD	INDUSTRY	RESD.	ROAD
Isopropylbenzene	0.23 ± 0.10	0.81 ± 0.43	0.38 ± 0.18	0.34 ± 0.08	0.30	0.70	0.34	0.34
n-Probylbenzene	0.10 ± 0.02	0.30 ± 0.13	0.21 ± 0.07	0.27 ± 0.09	0.10	0.27	0.19	0.22
3-Ethyltoluene	0.71 ± 0.10	2.00 ± 1.13	1.43 ± 0.67	2.20 ± 0.74	0.71	1.74	1.30	2.11
4-Ethyltoluene	1.11 ± 0.22	3.63 ± 2.23	2.33 ± 0.94	3.34 ± 0.97	1.12	3.02	2.16	3.24
1,3,5-Tri-M-Benzene	0.31 ± 0.08	0.90 ± 0.49	0.64 ± 0.31	1.01 ± 0.29	0.34	0.72	0.57	0.96
2-Ethyltoluene	0.28 ± 0.07	0.96 ± 0.52	0.63 ± 0.26	0.92 ± 0.30	0.29	0.86	0.59	0.83
1,2,4-Tri-M-benzene	1.70 ± 0.20	4.05 ± 2.20	3.07 ± 1.38	4.51 ± 1.26	1.67	3.68	2.94	4.16
n-Decane	0.99 ± 0.17	11.41 ± 20.19	2.68 ± 1.38	2.90 ± 0.67	0.95	4.51	2.42	2.67
1,4-DI-CL-Benzene	0.13 ± 0.05	0.59 ± 1.38	0.16 ± 0.06	0.22 ± 0.08	0.12	0.22	0.15	0.18
1,4-DI-E-Benzene	0.24 ± 0.06	0.57 ± 0.40	0.33 ± 0.18	0.48 ± 0.17	0.27	0.45	0.33	0.47
Naphthalene	0.17 ± 0.11	0.73 ± 0.88	0.18 ± 0.11	0.27 ± 0.12	0.11	0.39	0.15	0.23

N.M.: Not measured; BDL: Below Detection Limit

		AVE	RAGE			MEDI	۹N	
COMPOUNDS	BGD	INDUSTRY	RESD.	ROAD	BGD	INDUSTRY	RESD.	ROAD
NO ₂	15.9 ± 9.2	47.6 ± 6.8	46.5 ± 14.0	62.8 ± 12.5	18.3	45.2	47.3	65.1
SO ₂	5.8 ± 3.1	14.6 ± 6.4	14.6 ± 5.5	20.8 ± 8.2	5.4	12.3	13.4	19.1
O ₃	52.7±11.5	27.4±7.1	31.7±8.7	27.0±32.1	51.9	29.3	31.2	19.0
Pentane	0.26 ± 0.06	0.57 ± 0.29	0.69 ± 0.29	0.47 ± 0.13	0.25	0.49	0.60	0.44
1,3 Butadiene	0.09 ± 0.00	0.15 ± 0.16	0.13 ± 0.05	0.12 ± 0.06	0.09	0.10	0.11	0.11
n-Hexane	0.34 ± 0.06	0.80 ± 0.32	0.58 ± 0.19	0.65 ± 0.28	0.36	0.61	0.57	0.59
Methylcyclopentane+	0.08 ± 0.02	0.17 ± 0.05	0.17 ± 0.08	0.28 ± 0.20	0.08	0.17	0.15	0.19
2,4-Dimethylpentane								
1,1,1-Tri-CI-Ethane	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.
Benzene	1.36 ± 0.35	1.86 ± 0.33	2.72 ± 0.89	2.51 ± 1.14	1.38	1.82	2.49	2.09
Cyclohexane+	0.11 ± 0.02	0.23 ± 0.11	0.18 ± 0.09	0.32 ± 0.24	0.11	0.20	0.17	0.22
Cyclohexene								
2-Methylhexane	0.29 ± 0.08	0.55 ± 0.43	0.38 ± 0.17	0.62 ± 0.46	0.32	0.41	0.37	0.49
2,2,3-Trimethylbutane+	0.12 ± 0.01	0.21 ± 0.11	0.19 ± 0.06	0.23 ± 0.15	0.12	0.16	0.18	0.18
2,3-Dimethylpentane								
3-M-Hexane	0.19 ± 0.05	0.61 ± 0.49	0.36 ± 0.15	0.38 ± 0.15	0.17	0.42	0.31	0.38

Table 4.15 Average and median concentrations of VOCs in different microenvironments in APRIL 2006 campaign (µg m⁻³)

Table 4.15 Average and median concentrations of VOCs in different microenvironments in APRIL 2006 campaign (μ g m⁻³) (*Continued*)

		AVEF	RAGE			MEDI	AN	
COMPOUNDS	BGD	INDUSTRY	RESD.	ROAD	BGD	INDUSTRY	RESD.	ROAD
2,2,4-Tri-M-Pentane	0.06 ± 0.01	0.33 ± 0.24	0.11 ± 0.05	0.12 ± 0.08	0.06	0.31	0.11	0.10
n-Heptane+cis-3-	0.15 ± 0.04	1.05 ± 1.22	0.32 ± 0.17	0.32 ± 0.15	0.13	0.44	0.29	0.30
Heptene								
Methylcyclohexane	0.13 ± 0.03	0.70 ± 0.95	0.12 ± 0.06	0.16 ± 0.09	0.12	0.28	0.11	0.16
Toluene	4.57 ± 1.83	14.98 ± 6.53	11.82 ± 5.59	14.81 ± 8.75	4.44	13.68	10.32	9.88
2-M-Heptane	0.16 ± 0.05	0.41 ± 0.13	0.37 ± 0.13	0.49 ± 0.29	0.14	0.41	0.34	0.36
m+p-Chlorotoluene	0.14 ± 0.03	0.35 ± 0.09	0.31 ± 0.13	0.43 ± 0.29	0.13	0.31	0.30	0.29
Octane	0.11 ± 0.03	0.31 ± 0.06	0.23 ± 0.09	0.27 ± 0.13	0.12	0.30	0.20	0.24
2,2,5-Tri-M-Hexane+	0.09 ± 0.03	0.19 ± 0.11	0.15 ± 0.05	0.16 ± 0.07	0.08	0.18	0.14	0.14
1,2,4-Tri-M-Cyclohexane								
TetraChloroEthylene	B.D.L.	0.07 ± 0.03	0.05 ± 0.02	0.05 ± 0.01	B.D.L.	0.06	0.05	0.05
Chlorobenzene	0.04 ± 0.01	0.28 ± 0.11	0.13 ± 0.05	0.16 ± 0.07	0.05	0.29	0.12	0.16
Ethylbenzene	1.12 ± 0.48	2.86 ± 0.87	1.86 ± 0.69	2.33 ± 1.02	0.94	2.92	1.73	2.24
Bromoform	B.D.L.	0.46 ± 0.18	0.23 ± 0.08	0.28 ± 0.13	B.D.L.	0.42	0.22	0.23
m+p-Xylene	1.99 ± 0.65	6.73 ± 2.62	4.56 ± 2.33	5.94 ± 2.91	2.03	6.32	3.78	5.49
Styrene	0.81 ± 0.20	1.46 ± 0.28	1.28 ± 0.46	1.49 ± 0.67	0.74	1.51	1.28	1.38

Table 4.15 Average and median concentrations of VOCs in different microenvironments in APRIL 2006 campaign (μ g m⁻³) (*Continued*)

		AVEF	RAGE		MEDIAN				
COMPOUNDS	BGD	INDUSTRY	RESD.	ROAD	BGD	INDUSTRY	RESD.	ROAD	
o-xylene	0.35 ± 0.11	1.05 ± 0.37	0.78 ± 0.37	1.04 ± 0.62	0.35	0.98	0.67	0.97	
n-Nonane	0.16 ± 0.05	0.76 ± 0.25	0.39 ± 0.17	0.41 ± 0.12	0.17	0.67	0.35	0.42	
Isopropylbenzene	0.16 ± 0.02	0.43 ± 0.29	0.29 ± 0.10	0.27 ± 0.11	0.16	0.35	0.26	0.25	
n-Probylbenzene	0.08 ± 0.00	0.25 ± 0.07	0.17 ± 0.06	0.17 ± 0.06	0.08	0.24	0.17	0.16	
3-Ethyltoluene	0.30 ± 0.11	1.03 ± 0.42	0.78 ± 0.35	1.03 ± 0.58	0.28	0.87	0.67	0.85	
4-Ethyltoluene	0.26 ± 0.06	0.89 ± 0.40	0.63 ± 0.25	0.72 ± 0.29	0.25	0.84	0.57	0.70	
1,3,5-Tri-M-Benzene	0.17 ± 0.03	0.52 ± 0.22	0.40 ± 0.17	0.48 ± 0.21	0.16	0.49	0.36	0.46	
2-Ethyltoluene	0.12 ± 0.04	0.48 ± 0.19	0.34 ± 0.15	0.42 ± 0.20	0.12	0.46	0.29	0.38	
1,2,4-Tri-M-benzene	0.75 ± 0.23	1.66 ± 0.43	1.33 ± 0.40	1.48 ± 0.56	0.67	1.48	1.28	1.45	
n-Decane	0.27 ± 0.08	1.51 ± 0.74	0.77 ± 0.33	0.76 ± 0.25	0.28	1.13	0.68	0.71	
1,4-DI-CL-Benzene	0.03 ± 0.00	0.08 ± 0.03	0.05 ± 0.01	0.04 ± 0.01	0.03	0.06	0.05	0.04	
1,4-DI-E-Benzene	0.06 ± 0.02	0.21 ± 0.08	0.18 ± 0.09	0.18 ± 0.08	0.06	0.19	0.16	0.17	
Naphthalene	0.05 ± 0.01	0.13 ± 0.06	0.09 ± 0.04	0.13 ± 0.05	0.05	0.13	0.09	0.11	

BDL: Below Detection Limit

-		AVEF	RAGE			MEDI	۹N	
COMPOUNDS	BGD	INDUSTRY	RESD.	ROAD	BGD	INDUSTRY	RESD.	ROAD
NO ₂	N.M	N.M	N.M	N.M	N.M	N.M	N.M	N.M
SO ₂	N.M	N.M	N.M	N.M	N.M	N.M	N.M	N.M
O ₃	N.M	N.M	N.M	N.M	N.M	N.M	N.M	N.M
Pentane	0.31 ± 0.09	0.63 ± 0.79	0.50 ± 0.26	0.73 ± 0.43	0.32	0.45	0.46	0.61
1,3 Butadiene	0.05 ± 0.01	0.08 ± 0.05	0.06 ± 0.02	0.11 ± 0.05	0.05	0.06	0.06	0.10
n-Hexane	2.90 ± 2.89	2.17 ± 3.47	1.08 ± 1.13	1.17 ± 1.00	2.90	1.55	0.57	0.53
Methylcyclopentane+ 2,4-Dimethylpentane	0.23 ± 0.13	1.76 ± 5.38	0.33 ± 0.22	0.66 ± 0.37	0.17	0.44	0.32	0.58
1,1,1-Tri-Cl-Ethane	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.	B.D.L.
Benzene	1.29 ± 0.26	4.00 ± 5.60	2.19 ± 0.93	3.10 ± 1.30	1.28	2.22	1.97	3.26
Cyclohexane+Cyclohexene	0.50 ± 0.35	2.40 ± 4.52	0.82 ± 0.58	1.29 ± 0.83	0.32	1.23	0.63	1.36
2-Methylhexane	1.02 ± 0.24	1.64 ± 1.06	1.17 ± 0.53	1.83 ± 0.80	0.96	1.42	0.92	1.82
2,2,3-Trimethylbutane+ 2,3-Dimethylpentane	0.35 ± 0.09	0.47 ± 0.24	0.33 ± 0.24	0.58 ± 0.27	0.34	0.40	0.24	0.59
3-M-Hexane	1.22 ± 0.47	2.35 ± 2.75	1.25 ± 0.59	1.91 ± 0.96	1.09	1.61	1.19	1.72
2,2,4-Tri-M-Pentane	0.22 ± 0.03	0.57 ± 0.62	0.17 ± 0.11	0.35 ± 0.09	0.21	0.43	0.13	0.36
n-Heptane+cis-3-Heptene	0.47 ± 0.15	2.09 ± 5.46	0.69 ± 0.30	1.34 ± 0.66	0.51	0.94	0.66	1.22

Table 4.16 Average and median concentrations of VOCs in different microenvironments in JULY 2007 campaign (µg m⁻³)

Table 4.16 Average and median concentrations of VOCs in different microenvironments in jULY 2007 campaign (μ g m⁻³) (*Continued*)

		AVE		MEDIAN				
COMPOUNDS	BGD	INDUSTRY	RESD.	ROAD	BGD	INDUSTRY	' RESD.	ROAD
Methylcyclohexane	0.14 ± 0.03	0.41 ± 0.26	0.19 ± 0.10	0.35 ± 0.16	0.16	0.30	0.15	0.40
Toluene	9.24 ± 3.10	46.21 ± 26.06 2	23.29 ± 11.80	31.84 ± 11.1	8.01	38.82	21.68	32.29
2-M-Heptane	0.40 ± 0.25	2.04 ± 3.25	0.60 ± 0.30	0.84 ± 0.39	0.39	1.05	0.52	0.88
m+p-Chlorotoluene	0.70 ± 0.32	1.35 ± 1.50	0.30 ± 0.20	0.44 ± 0.20	0.59	0.65	0.23	0.49
Octane	0.43 ± 0.21	0.67 ± 0.19	0.39 ± 0.16	0.62 ± 0.20	0.32	0.62	0.33	0.57
2,2,5-Tri-M-Hexane+		0.21 ± 0.14	0.08 + 0.04	0.22 + 0.12	0.20	0.00	0.0/	0.15
1,2,4-Tri-M-Cyclohexane	0.20 ± 0.08	0.31 ± 0.10	0.08 ± 0.04	0.22 ± 0.12	0.20	0.28	0.00	0.15
TetraChloroEthylene	0.15 ± 0.01	0.33 ± 0.12	0.13 ± 0.09	0.23 ± 0.08	0.16	0.31	0.11	0.23
Chlorobenzene	0.08 ± 0.01	0.73 ± 0.61	0.17 ± 0.10	0.30 ± 0.16	0.09	0.42	0.17	0.26
Ethylbenzene	1.69 ± 0.48	8.74 ± 8.15	3.48 ± 1.30	6.05 ± 3.78	1.55	6.16	3.49	5.21
Bromoform	0.63 ± 0.01	2.24 ± 1.04	0.57 ± 0.20	1.08 ± 0.38	0.63	1.93	0.50	1.08
m+p-Xylene	3.25 ± 0.89	25.91 ± 35.12	9.70 ± 3.78	13.56 ± 5.19	3.07	18.38	9.89	13.26
Styrene	0.38 ± 0.18	0.98 ± 1.26	0.23 ± 0.16	0.49 ± 0.35	0.37	0.51	0.20	0.41
o-xylene	0.38 ± 0.18	3.96 ± 5.36	1.37 ± 0.69	2.14 ± 1.07	0.36	2.54	1.22	2.01
n-Nonane	0.11 ± 0.00	0.73 ± 0.20	0.17 ± 0.09	0.40 ± 0.00	0.11	0.86	0.18	0.40
Isopropylbenzene	0.23 ± 0.06	0.38 ± 0.16	0.12 ± 0.09	0.28 ± 0.16	0.22	0.37	0.07	0.18
n-Probylbenzene	0.08 ± 0.04	0.28 ± 0.15	0.15 ± 0.08	0.25 ± 0.13	0.08	0.26	0.12	0.21

Table 4.16 Average and median concentrations of VOCs in different microenvironments in jULY 2007 campaign (μ g m⁻³) (*Continued*)

		MEDIAN						
COMPOUNDS	BGD	INDUSTRY	RESD.	ROAD	BGD	INDUSTRY	RESD.	ROAD
3-Ethyltoluene	0.36 ± 0.20	2.19 ± 1.09	1.08 ± 0.59	1.65 ± 0.82	0.33	2.20	0.81	1.44
4-Ethyltoluene	0.13 ± 0.07	0.98 ± 0.39	0.43 ± 0.25	0.72 ± 0.44	0.14	0.99	0.35	0.64
1,3,5-Tri-M-Benzene	0.34 ± 0.16	1.08 ± 0.60	0.39 ± 0.24	0.69 ± 0.34	0.26	1.04	0.30	0.63
2-Ethyltoluene	0.30 ± 0.18	1.20 ± 0.61	0.44 ± 0.24	0.95 ± 0.61	0.30	1.22	0.33	0.80
1,2,4-Tri-M-benzene	0.22 ± 0.08	1.16 ± 0.53	0.57 ± 0.30	1.00 ± 0.61	0.27	1.19	0.47	0.90
n-Decane	0.56 ± 0.19	1.92 ± 1.10	0.81 ± 0.55	1.00 ± 0.59	0.52	1.65	0.85	0.93
1,4-di-cl-Benzene	0.10 ± 0.07	0.23 ± 0.10	0.09 ± 0.05	0.15 ± 0.10	0.09	0.20	0.09	0.13
1,4-di-E-Benzene	0.05 ± 0.03	0.33 ± 0.23	0.11 ± 0.09	0.14 ± 0.08	0.05	0.28	0.07	0.15
Naphthalene	0.05 ± 0.04	0.32 ± 0.34	0.09 ± 0.08	0.11 ± 0.04	0.05	0.17	0.06	0.12

N.M.: Not measured; BDL: Below Detection Limit

Consistent high concentrations of industrial marker VOCs at industrial areas indicated that measured concentrations of these VOCs have strong contributions from industrial emissions. But since industrial emissions occur at certain locations whereas traffic emissions are homogenously distributed throughout the city, high concentrations of these 10 VOCs at industrial stations does not necessarily mean that industry is the most important source of these species in every station in the city. Although traffic contribution is small in concentrations of these industrial marker VOCs, it is not zero and can dominate their concentrations at stations far from industrial districts, where most of the industry is located.

4.3.2. <u>Industrial</u>. The VOCs in this group have higher median concentrations at stations located in industrial areas. However, this behavior is not as consistent as that observed in "industrial marker" group. Median concentrations of VOCs in this group at traffic-impacted stations are not dramatically different from those at industrial stations and in one or more campaigns their concentrations in industrial sites. This group includes Methylcyclohexane, toluene, o-xylene, isopropylbenzene, 4-ethyltoluene, 1,3,5-trimethylbenzene. Examples of this type of behavior are depicted in Figure 4.18 for four selected VOCs. Probably the main source of these VOCs at the vicinity of industrial districts of the city is industrial emissions, but the traffic is probably a more important source at sampling points outside the industrial areas. It is interesting to note that the BTEX compounds, with the exception of toluene are frequently used as traffic markers. However, sector



Figure 4.17. VOCs that are consistently high in staitons located at industrial areas.

averages showed that o-xylene also have strong industrial contribution at the sampling points close to industrial areas.

An important point worth noting here is the contribution of traffic at different microenvironments. Although industrial emissions do not occur in residential areas (except from those transported from industrial areas) and at traffic-impacted sampling points, traffic emissions do occur at all sites. There are substantial traffic emissions in industrial areas, particularly emissions from heavy duty vehicles. Consequently, comparable concentrations of VOCs from traffic and industrial sources at an industrial area may indicate that traffic is the main source of those compounds. For industrial emissions to be significant, concentrations measured at industrial areas should be significantly and consistently higher than those measured at traffic-impacted stations.

4.3.3. <u>Traffic</u>: Traffic is well-documented to be the most important source at urban areas. In this study, VOCs with the highest average concentrations are found at traffic-impacted stations, which are considered as traffic markers consistently in all sampling campaigns. This group included Pentane, 1,3-Benzene, butadiene, 2-methylhexane, 2,2,3-trimethylbutane 2. + dimethylpentane and styrene. These are all light hydrocarbons. In this study, VOCs with less than five carbons is not detected due to the nature of our sampling system. The lightest compound measured in this study is the 1,3 butadiene. This group of VOCs is light among the group measured in this study. On the other hand, industrial markers discussed previously include moderate and heavy hydrocarbons.

The median concentrations of selected four VOCs with dominant traffic source are depicted in Figure 4.19 as an example. In all of these compounds median concentrations are the highest at traffic-impacted stations, consistently in all five sampling campaigns.

It should be noted that in all campaigns median concentrations of VOCs in this (traffic) group at residential stations are smaller, but not dramatically smaller than their median concentrations at traffic stations. The reason for this observation, as discussed previously, is that we cannot completely isolate residential stations from traffic emissions, because there is traffic at



Figure 4.18 Sector average concentrations of selected VOCs for which the main source is industries but which are also affected

from traffic



Figure 4.19 Sector median concentrations of selected VOCs, which are strongly influenced by traffic emissions

residential areas. However, this also means that concentrations of this group of VOCs are relatively homogeneously distributed throughout the city. Industrial marker elements do not show a similar pattern. Their concentrations do show spikes around industrial areas.

4.4.4. Mixed: The group consisting of 12 VOCs are named as "mixed", because their median concentrations at different microenvironments do not show a significant and consistent trend so that they can be included to one of the above three groups. The VOCs in this group includes n-hexane, cyclohexane+cyclohexene, 3-M-hexane, n-heptane+cis-3-heptane, 2-Mheptane, m+p-chlorotoluene, octane, ethylbenzenen, m+p-xylene, npropylbenzenen, 1,2,4-triM-benzene, 1,4-dichlorobenzene. Their behaviors are shown in Figure 4.20 for selected four VOCs as an example. Generally median (and average) concentrations of these VOCs, in different to each other microenvironments are fairly close and different microenvironments have the highest median value -in different sampling campaigns.

Sector average (and median) concentrations of VOCs discussed in this section proved very useful to obtain information on the potential sources of VOCs in an urban environment. This is a unique feature of passive sampling at large number of data points. Similar information cannot be generated with active sampling at few locations in the city, no matter how frequently VOC data is generated.

Sector (microenvironment) average concentrations of VOCs also proved indispensible in identifying factors in factor analysis exercise, which will be discussed in subsequent sections.



Figure 4.20 Sector median concetnrations of selected VOC with MIXED sourced

4.2.4 Seasonal Variation of VOCs Concentrations

Passive sampling, due to its nature, is not an ideal way of assessing seasonal variations in concentrations of not only VOCs, but also other pollutants as well. In a typical passive sampling study samplers are left in the field for approximately one week and usually sampling was performed once in every season. Representativeness of that one week, during which samplers were left in the field, is questionable. If the passive sampling is done frequently enough, then seasonal averages can be more meaningful. One advantage of determining the seasonal patterns of VOCs using passive sampling is the high spatial resolution of data. In most studies, where seasonal averages are calculated for a city using fixed stations, average concentrations and seasonal average concentrations of pollutants are based on very few stations, but in a comprehensive passive sampling study city-averages are based on measurements performed at 30 - 50 locations in the city. Averages that bases on a large number of measurement point are naturally more representative for the city.

Table 4.17 shows the weekly average temperatures, wind speed, relative humidity, total precipitation and mixing height averaged for the sampling periods.

Temperature changes between 6.3°C in February campaign and 25.3°C in July. In this study, data from February campaign were used to characterize winter conditions and data from July campaign were used to characterize VOC concentrations in summer. Long-term average temperatures (obtained from data generated at the same station between 1975 and 2008 (General Directorate of Meteorology, unpublished data) in February, April, July, September and October are 5.9°C, 13.0°C, 24.6°C, 20.1°C and 15.3°C, respectively. Similarity of long term averages with temperatures recorded during our sampling campaigns indicates that our sampling period is a typical year in terms of meteorology of the region.

Relative humidity changed between 49% and 71%, which is fairly typical for Bursa. Rainfall during sampling is important as it affects weekly average VOC concentrations. Although there was not a significant rainfall during October, July, April and February sampling campaigns, rainfall during September campaign was 82 mm. This probably affected on VOCs concentrations measured in September campaign. Approximately 9 mm rainfall recorded in October campaign and 1.8 mm in February campaign are not high enough to affect atmospheric VOC concentrations measured in these periods. No precipitation occurred in April July campaigns.

Maybe the most important parameter that affects VOCs concentrations in Bursa Atmosphere is the mixing height. Mixing height in measurement periods varied between 728 m in February and 1087 m in July. This probably partly the reason for higher VOC concentrations in winter. However, although high VOC levels measured in February matches with the lowest mixing height in Table 4.17, there is no statistically significant relation between the mixing height and VOC concentrations in five campaigns, probably because the relation was based on only five data points and there are other complicating factors, such as different source strengths in different campaigns (for example VOCs with evaporative sources have higher source strength in July campaign, when the mixing height is the highest), or presence or absence of rain during different campaigns etc.

	Relative	Wind		Total	Mixing
Sampling	Humidity	Speed	Temp.	Precp.	Height
Campaign	(%)	(m/sec)	(C ⁰)	(mm)	(m)
September 2005	65.42	1.2	21.3	82.4	1025
October 2005	71.04	1.7	14.8	9.5	966
April 2006	66.56	2.1	13.7	No prec.	797
February 2007	75.47	2.2	6.3	1.8	728
July 2007	49.37	2.2	25.3	No prc	1087

Table 4.17 Meteorological parameters for all periods



Figure 4.21: Wind rose of the sampling campaigns

Wind roses calculated for different campaigns are presented in Figure 4.21. Wind direction was not similar in differnet sampling campaigns. Dominating flow, which is more or less observed in Setember, October, February and July was from the direction between E and NE sectors. However, there were differences in directions of minor flows during different campaigns. The wind rose correponding to April sampling campaign was totally different withdominant flow direction from WSW sector. Since these roses corresponds to data for one week period, such diiferences should be expected. They demonstrate that emissions from Görüklü and Nilüfer Organized Industrial District, which is located to the west of the city, are transported to the city in four of the five sampling periods. This conclusion is supported in pollution maps, where the VOCs identified as "industrial markers" in the manuscript have their highest concentations at sampling stations located to the east of the organized industrial districts

Discussions presented in above paragraphs indicate that meteorology can be one of the reason for seasonal variations in concentations of organic compounds, but it can not be the only reason. This conclusion is also supported by differences in winter-to-summer concentration ratios of VOCs. If season-dependent variation in mixing height is the only reason for observed high VOC concentrations at Bursa, then winter-to-summer ratios of all VOCs are expected to be very similar, but as will be shown in the coming paragraphs, there are differences in winter-to-summer concentration ratios of some of the VOCs.

Since samples, in this study were collected during both in summer and winter seasons, data generated were also used to assess seasonal variations in VOC concentrations. As discussed previously, passive sampling was performed five times in the course of the study. Four of them were during summer (April, July, September and October) and only one was during winter (February) season. In this study, as in most of the other studies performed in our group the year is divided into two seasons, as summer and winter. This division is based on either heating and non-heating periods in the city, or based on rain events (winter is taken as the period when 80% of the rain events occur). In Turkey these two criteria generally match with each other. Heating seasons in cities at the central Anatolia is between October 15 and April 15. There was a

rule in Ankara, established by the municipality during heavy pollution days of early 90s, which states that heating units should not be operated when the ambient temperature is > +15°C. Ambient temperature in Ankara reaches to 15°C at April 15, and falls down to 15°C roughly at October 15th. Later this rule was adopted by most of the municipalities. Now although air pollution is not as severe as it was in 80s and 90s the program still continues. Consequently, the period between Mid April and Mid October are considered as non heating period. In this study we call this period "summer". The period between mid October and mid April is the heating season. In this study it is called "winter".

Concentrations measured stated "summer" and "winter" seasons were used to assess seasonal variation in VOC concentrations in Bursa atmosphere. To obtain summer and winter average concentrations, median concentrations of each VOC for all sampling points in each sampling period was calculated. Median concentrations are used in this discussion, because as pointed out before, passive data in all campaigns are log-normally distributed and median is a better representation of data population for log-normally distributed data. The median of each VOC is considered as the Bursa average for that particular sampling period. Since this "Bursa average" includes data from more than 50 points in the city, it is expected to be fairly representative for the whole study area.

The Bursa average values for VOCs measured in February campaign was directly taken as winter average concentrations of VOCs. The two Bursa average values for each VOC, one obtained from July campaign and the other one calculated using data from September campaign were averaged to calculate summer average concentrations of VOCs. Data from April and October campaigns were not included in calculations of summer and winter averages, because these two sampling campaigns took place at the transition periods between heating and non-heating periods.

Summer and winter concentrations of VOCs are given in Table 4.18 and winter-to-summer concentration ratios are depicted in Figure 4.22. It is clear from both Table 4.18 and Figure 4.22 that winter concentrations of VOCs are higher than their summer concentrations. This observation is not surprising

and frequently reported in literature. There are several reasons for higher VOC concentrations in winter season. It may indicate higher VOC emissions in winter (Ho et al, 2004; Na et al, 2005), or more extensive photochemical destruction of VOCs during summer season (Parra et al, 2006; Na and Kim, 2001). But most likely reason is the lower mixing height during winter season (Nguyen et al, 2009; Singh et al, 1997; Cheng et al, 1996). If emission of a compound is the same in summer and winter seasons, its concentration appears higher in winter, because winter season mixing height is generally a factor of two or three shallower than that in summer season. This confines pollutants to a smaller volume in winter increasing their measured concentrations.

Table	4.18 \$	Summer	and	winter	conce	ntrations	s of	VOCs	measu	ired i	n	this	study
			((concer	ntratio	ns are ir	ı µg	m⁻³)					

Compounds	winter	Summer
1,2,4-Tri-M-benzene	3,21	0,575
4-Ethyltoluene	2,41	0,485
Methylcyclopentane+2,4-Dimethylpentane	1,05	0,25
Benzene	8,21	2,25
styrene	1,32	0,365
2,2,5-Tri-M-Hexane+1,2,4-Tri-M-Cyclohexane	0,16	0,05
m+p-Chlorotoluene	1,07	0,355
Bromoform	1,21	0,405
2,2,4-Tri-M-Pentane	0,53	0,18
Isopropylbenzene	0,36	0,125
Pentane	0,97	0,34
1,4-Di-E-Benzene	0,37	0,13
n-Decane	1,98	0,7
n-Probylbenzene	0,2	0,075
1,3 Butadiene	0,39	0,165
n-Nonane	0,41	0,18
1,4-Di-Cl-Benzene	0,16	0,08
Octane	0,65	0,325
Methylcyclohexane	0,33	0,165

Compounds	winter	Summer
2-M-Heptane	0,81	0,445
1,3,5-Tri-M-Benzene	0,63	0,355
3-Ethyltoluene	1,47	0,86
2-Ethyltoluene	0,67	0,395
Naphthalene	0,21	0,13
o-xylene	1,52	1,045
n-Hexane	0,66	0,46
n-Heptane+cis-3-Heptene	0,85	0,615
Ethylbenzene	3,37	2,59
Toluene	23,41	18,46
TetraChloroEthylene	0,2	0,16
m+p-Xylene	8,87	7,53
3-M-Hexane	0,92	0,89
Cyclohexane+Cyclohexene	1,36	1,36
2-Methylhexane	0,73	0,74
Chlorobenzene	0,51	0,595
2,2,3-Trimethylbutane+2,3-Dimethylpentane	0,28	0,36

Table 4.18 Summer and winter concentrations for VOCs measured in this study (concentrations are in μ g m⁻³) (*Continued*)

The winter to summer concentration ratios of VOCs, which are depicted in Figure 4.22, varies between 5.5 for 1,2,4-tri-M-benzene and 0.8 for 2,2,3-trim- butane. Large winter-to-summer ratios may be due to seasonal varaitions in mixing height. Ratios close to unity, on the oher hand, indicate that there are factors, other than variation in mixing height, that also contribute to differences in VOC concentration between summer and winter seasons.

The VOCs are tentatively separated into two groups based on their summerto-winter ratios. The first group includes n-heptane+cis-3-heptene, ethylbenzene, toluene, tetrachloroethylene, m+p-xylene, 3-m-hexane, cyclohexane+cyclohexene, 2-methylhexane, chlorobenzene, 2,2,3trimethylbutane+2,3-dimethylpentane. The VOCs in this group have comparable concentrations in winter and summer seasons. Their winter-tosummer concentration ratios vary between 0.78 for 2,2,3



Figure 4.22 Winter to summer ratios of VOCs measured in Bursa

-trimethylbutane+2,3-dimethylpentane and 1.38 for n-heptane+cis-3-heptene.

The second group consisted of 1,2,4-tri-m-benzene, 4-ethyltoluene, methylcyclopentane+2,4-dimethylpentane, benzene, styrene, 2,2,5-tri-mhexane+1,2,4-tri-m-cyclohexane, m+p-chlorotoluene, bromoform, 2,2,4-trim-pentane, isopropylbenzene, pentane, 1,4-di-e-benzene, n-decane, nprobylbenzene, 1.3 butadiene, n-nonane, 1,4-di-cl-benzene, octane, methylcyclohexane, 3-2-m-heptane, 1,3,5-tri-m-benzene, ethyltoluene, 2-ethyltoluene, naphthalen, o-xylene and n-hexane. These are the VOCs with significantly higher concentrations during winter month. Their winter-to-summer concentration ratios change between 1.4 for n-hexane and o-xyleneand 5.6 for 1,2,4-tri-m-benzene. This division of VOCs into two groups is highly tentative. For example winter-to-summer ratios of nheptane+cis-3-heptene and n-hexane are very close (0.38 and 0.4, respectively), but these two VOCs are in different groups. Wherever you put the linet hat seperate these two groups, the VOCs that lie one above an done below the line will have similar winter-to-summer ratios. As pointed before the division is tentative. VOCs are divided into these two groups to highlight the differences between the compounds with large and small winter to summer ratios and to check if the compouns in each group behaves

Different winter-to-summer ratios depicted by different VOCs is probably due to their different sources. As mentioned previously, in an urban environment, if the source strength of a given VOC does not change between summer and winter or if its source strength is higher during winter months, its concentration is expected to be higher in winter due to lower mixing height and smaller ventilation coefficient. The pollutants that have higher concentrations during summer should have higher emissions in summer months. These higher emissions can be due to increase of emissions from sources that are also available in winter, or can be due to operation of additional sources.

This approach allows one to differentiate between VOCs that originate from traffic from those coming from evaporative emissions. Traffic emissions do not change significantly between summer and winter. Traffic counts in Ankara showed that traffic loads in main arteries decrease by only 20 – 25% in summer, which is attributed to summer vacations of families and lack of school buses (Kuntasal, 2005). Then, VOCs with high winter-to-summer ratios are expected to be related to traffic emissions. Generally all sources that has the same emissions in winter and summer show similar high concentrations in winter, traffic is documented most important VOC source in urban atmosphere (Lee et al, 2002; Na et al, 2003; Chan et al, 2002). Consequently, traffic is the most likely source for the VOC's in the second group. The presence of benzene, which is a well documented motor vehicle marker (Watson et al., 2001 and Miller et al., 2002) in this group, supports this conclusion.

As pointed before VOC's in the first group have comparable concentrations in both summer and winter season or have higher concentration during summer months. This pattern necessitates additional sources or increased emissions during summer months. The most likely source that can result in higher winter concentrations in summer is the evaporative emissions from paint applications, ink use, gasoline stations etc. The presence of toluene in this group is a good confirmation of this conclusion, because evaporative emissions are known to be an effective source for toluene (Qin et al, 2007; Ho et al., 2004; Rappenglück and Fabian, 1998).

Operations of industries do not change significantly between summer and winter seasons. In that sense, VOCs that has strong contribution from industries are expected to be in the second group, together with traffic-related VOCs. However, it should also be noted that most of the VOC emissions from industries are evaporative in nature (such as solvent use) which is expected to increase in summer season.

Industrial markers, discussed in the previous sections are distributed between first and second VOC groups. For example, Industrial markers Chlorobenzene and tetrachloroethylene are among group 1 VOCs (the ones that do not show strong seasonal variations), whereas other markers, such as 2-ethyltoluene, 3-ethyltoluene, 1,4-di-Cl-benzene, isopropyl benzene, 2,2,4-tri-m-pentane, bromoform and 2,2,5-tri-m-hexane have fairly high winter to summer ratios and appears in group 2 VOCs. Obviously it is not possible to differentiate VOCs with industrial sources from Table 4.18 and Figure 4.22. The lack of an obvious industrial signal in seasonal patterns of VOCs can be due to the fact that, for some of the industrial marker VOCs traffic is an important, or dominating, contributor at stations far from industrial districts.

Seasonal variations in different sectors (microenvironments) are given in Table 4.19. This table seasonal averages of station groups that are representative for background, residential areas, roads in the city and industrial districts are separately calculated and presented along with winter-to- summer ratios in each microenvironment. The VOCs that are shaded in the table are the ones that were identified as "industrial markers" in previous sections. The VOCs with asterix (*) are the ones that has relatively low winter-to-summer ratios and believed to be associated with evaporative emissions (Group 1 VOCs).

There are two important generalizations in the table. One of them is consistently low winter-to-summer concentration ratios of industrial markers in industrial district. These compounds, without any exception have the lowest winter-to-summer ratio in IND sector, indicating that evaporative solvent extensive solvent use in industrial districts of Bursa can alter seasonal variations of some of the industrial tracers. As one goes away from industrial areas industrial contribution to these VOCs decrease and traffic contribution increase. This mechanism affects the seasonal variation of these VOCs in different stations. At stations close to or in the industrial districts the summer and winter concentrations of these VOCs are comparable, whereas summer emissions are higher due to more extensive evaporative losses in solvent use during summer season. However, summer and winter emissions of the same VOCs at stations far from industrial districts are comparable, which is dictated by traffic emissions and they have higher concentrations during winter, due to meteorology.

The second generalization can be made for Group 1 VOCs (the ones with asterix in the table). These VOCs are the ones with comparable Bursa averages in summer and winter seasons (and thus have the lowest winter-to-summer ratios). For these species winter-to-summer concentration ratio is low in all station groups not in one of the sectors. This is not surprising, because emissions from paint applications, printing houses etc are distributed throughout the city.

	SUMMER					WIN	ITER		WINTER/SUMMER RATIO			
COMPOUNDS	BGD	IND	RES	ROAD	BGD	IND	RES	ROAD	BGD	IND	RES	ROAD
Pentane	0.23	0.38	0.46	0.44	0.60	0.68	1.02	1.08	2.63	1.76	2.22	2.49
1,3 Butadiene	0.09	0.12	0.16	0.19	0.11	0.24	0.42	0.49	1.20	2.11	2.63	2.53
n-Hexane	0.95	0.68	0.48	0.48	0.19	0.91	0.73	0.46	0.20	1.34	1.53	0.96
Methylcyclopent	0.11	0.22	0.20	0.32	0.32	1.00	0.87	1.12	2.82	4.48	4.31	3.50
Benzene	1.20	1.70	2.23	2.56	3.13	6.91	9.29	9.45	2.61	4.07	4.16	3.69
Cyclohexane*	0.56	1.20	1.09	1.01	0.84	1.64	1.41	1.42	1.49	1.37	1.29	1.41
2-Methylhexane*	0.42	0.72	0.58	0.87	0.31	0.87	0.76	0.81	0.72	1.21	1.31	0.93
2,2,3-Tri-M-	0.25	0.41	0.21	0.28	0.17	0.32	0.29	0.33	0.68	0.78	1.34	1.14
Butane*												
3-M-Hexane*	0.45	0.81	0.65	0.81	0.44	0.99	0.89	1.00	0.99	1.23	1.38	1.23
2,2,4-Tri-M-	0.11	0.38 <mark>0</mark>	0.13	0.21	0.25	0.75	0.46	0.57	2.22	1.99	3.58	2.68 <mark></mark>
Pentane Pentane												
n-Heptane*	0.26	1.06	0.55	0.74	0.41	0.87	0.79	0.94	1.57	0.82	1.44	1.28
Methylcyclohex	0.12	0.58	0.16	0.26	0.20	0.46	0.28	0.40	1.66	0.79	1.75	1.52
Toluene*	4.14	21.37	14.81	17.24	7.32	38.16	19.87	29.13	1.77	1.79	1.34	1.69
2-m-Heptane	0.16	0.49	0.34	0.43	0.28	0.92	0.85	0.84	1.74	1.89	2.52	1.93

Table 4.19 Seasonal variation in median concentrations of VOCs at different microenvironments (concentrations are in µg m⁻³)

	SUMMER					WINTER				WINTER/SUMMER RATIO			
COMPOUNDS	BGD	IND	RES	ROAD	BGD	IND	RES	ROAD	BGD	IND	RES	ROAD	
m+p-cl toluene	0.27	0.42	0.32	0.35	0.82	1.66	1.07	1.17	3.03	3.95	3.39	3.32	
Octane	0.16	0.38	0.26	0.34	0.29	0.97	0.56	0.73	1.86	2.53	2.18	2.15	
Tetra-Cl-	0.05	0.16	0.10	0.13	0.08	0.19	0.18	0.23	1.59	1.18	1.91	1.74	
Ethylene													
Chlorobenzene*	0.40	0.73	0.44	0.28	0.22	0.45	0.45	0.55	0.54	0.61	1.03	1.95	
Ethylbenzene*	0.88	3.21	2.12	2.70	1.67	4.72	2.90	4.10	1.91	1.47	1.37	1.52	
Bromoform	0.20	0.74	0.27	0.47	0.63	1.89	1.10	1.58	3.13	2.56	4.09	3.40	
m+p-Xylene*	1.95	9.05	5.91	7.19	3.71	12.67	7.46	11.67	1.90	1.40	1.26	1.62	
Styrene	0.42	0.69	0.57	0.77	23.94	24.07	21.00	25.95	56.45	34.95	36.94	33.59	
o-xylene	0.28	1.37	0.86	1.16	0.41	2.45	1.33	1.96	1.45	1.79	1.55	1.70	
n-Nonane	0.15	0.67	0.32	0.43	0.53	1.33	1.30	1.07	3.61	1.98	4.04	2.48	
Isopropylbenzen	0.10	0.22	0.11	0.13	0.30	0.70	0.34	0.34	2.96	3.26	3.21	2.57	
е													
n-Probylbenzene	0.06	0.17	0.12	0.16	0.10	0.27	0.19	0.22	1.65	1.58	1.65	1.41	
3-Ethyltoluene	0.25	1.40	0.77	1.03	0.71	1.74	1.30	2.11	2.80	1.24	1.69	2.05	
4-Ethyltoluene	0.19	0.98	0.51	0.66	1.12	3.02	2.16	3.24	5.79	3.09	4.27	4.94	

Table 4.19 Seasonal variation in median concentrations of VOCs at different microenvironments (concentration are in µg m⁻³) (*Continued*)

		SUN	IMER			WINTER				WINTER/SUMMER RATIO			
COMPOUNDS	BGD	IND	RES	ROAD	BGD	IND	RES	ROAD	BGD	IND	RES	ROAD	
1,3,5-Tri-M-	0.16	0.64	0.33	0.46	0.34	0.72	0.57	0.96	2.09	1.11	1.71	2.08	
Benzene													
2-Ethyltoluene	0.20	0.83	0.41	0.56	0.29	0.86	0.59	0.83	1.41	1.03	1.44	1.49	
1,2,4-Tri-M-	0.34	1.24	0.77	0.97	1.67	3.68	2.94	4.16	4.85	2.98	3.81	4.28	
Benzene													
n-Decane	0.32	1.30	0.73	0.78	0.95	3.51	2.42	2.67	2.95	2.70	3.33	3.44	
1,4-Di-cl-	0.04	0.11	0.07	0.07	0.12	0.22	0.15	0.18	2.62	2.06	2.30	2.43	
Benzene													
1,4-Di-e-	0.06	0.23	0.14	0.17	0.27	0.45	0.33	0.47	4.78	1.92	2.40	2.81	
Benzene													
Naphthalene	0.07	0.18	0.17	0.21	0.11	0.39	0.15	0.23	1.52	2.20	0.87	1.12	

Table 4.19 Seasonal variation in median concentrations of VOCs at different microenvironments (concentration are in µg m⁻³) (*Continued*)

[§]Shaded VOC are the ones that were identified as industrial in previos sections

Summer and winter profiles of VOCs measured in this study are depicted in Figure 4.23. The profiles (fingerprints) refer to the contribution of each VOC total VOC concentration. The concentrations of 36 VOCs were summed and contribution of each VOC to that total is calculated. These profiles proved very useful to differentiate between different compositions of VOC mass under different conditions and used fairly frequently in the literature (Na et al. 2004; Watson et al. 2001). In both summer and winter profiles toluene is the most abundant component. which are followed by m&p-xylene. benzene. ethylbenzene and o-xylene. BTEX compounds are the most abundant VOCs inboth seasons. The only exception to this statement is 1.2.4-tri-M-benzene. which has a 4.7% and 1.3% contribution to total VOC mass in winter. and summer. respectively. BTEX compounds (plus 1.2.4-tri-M-benzene) totally accounts for 68% and 73% of the total VOC mass in winter and summer respectively. Increased contribution of BTEX compounds in summer is due to increase in toluene and m&p-xylene contributions due to increased evaporative emissions in summer season. It should be also be noted that contributions VOCs that are not affected from evaporative emissions. such as benzene. ethylbenzene and o-xylene decreased in winter or remained the same in both seasons.



Figure 4.23 Winter to summer ratio of source profile
4.2.5 Factor Analysis

Factor analysis is a widely used multivariate statistical tool in source apportionment studies. Although it is very frequently used for time-series data generated in active monitoring stations, its application to spatially distributed data is very limited. FA bases on covariance of measured parameters. And co-variances are generally attributed to similar sources or similar chemistry or similar transport. This is generally understood as covariance of species in time-series of data at a single monitoring station. However, covariance of spatially distributed species has also same effect and in principle such data can be used in source apportionment. In our group, approximately 10 years ago, factor analysis was applied to spatially distributed trace element data in Izmir Bay sediments and produced fairly impressive inferences on sources generating observed distribution of trace element in the bay sediments (Atgin et al. 2001). The application of multivariate techniques in spatially distributed passive VOC data actually emerged from that particular study. In this sense, this part of the study is fairly unique use of multivariate techniques in passive sampling of VOCs.

Another point that should be mentioned before discussing factor analysis results is the use of FA as the receptor modeling tool. For a very long time factor analysis and its variants, such as principal component analysis (PCA) and absolute principal component analysis (APCA) were, by far, the most widely used statistical tools in receptor modeling applications. However, in last 10 years a new multivariate technique, namely positive matrix factorization (PMF), started to replace factor analysis, because it is more flexible in data handling and its results are quantitative. For example FA and associated statistical tools do not tolerate for missing data points. If one of the parameters is missing in one of the samples that sample is excluded from FA. However, in PMF that sample is retained, but the missing datum is assigned a very high uncertainty value so that it does not contribute to the fit. This is a very serious advantage, because in most of the environmental data there is generally a fair number of below detection limit values and undetects. If there are few missing data points in a data set they are filled in for not loosing that samples in FA, but if missing data points for a parameter is >10%, it is safer to exclude that parameter from FA.

In this study we preferred FA over PMF because it is much more robust compared to PMF. In our group we are using PMF more and more frequently in recent years. We now have a fair amount of experience on both techniques. We feel that FA is easier to optimize and interpret compared to PMF. But we also anticipate that quantitative output generated by PMF and its flexibility is obvious advantages over FA. When sources contributing to measured levels of parameters are well anticipated and when there are good tracers of sources PMF can be safely used and quantitative results can be enjoyed, but if sources and tracers are vague, then use of PMF can be dangerous.

In our group PMF is the method of choice when sources of atmospheric particles are being apportioned. Because in this case trace elements are the natural tracers and sources and there are fairly unique tracer element for a variety of sources. In last few years we also used PMF for VOC data generated by active sampling at one or two sampling locations in the city. Results were fairly successful, because in samples collected at residential areas and in traffic impacted stations sources that contribute to VOC concentrations are limited. Traffic is the dominating source at most of the city, there may or may not be small contributions from other minor sources, such as evaporation of solvents, mostly from paint applications, coal combustion for residential heating, etc.

Application of receptor modeling techniques to spatially distributed passive sampling data is much more difficult than alternative cases discussed above. There are a number of reasons for this difficulty. First of all, sources and source contributions are not uniform to obtain a priori information about types of sources that should be dealt with in FA.

For example BTEX compounds, except for toluene, are good markers for light duty motor-vehicle emissions. This characteristic BTEX source makes interpretation of factors in FA a lot simpler. However, these compounds may have different sources at different locations in the city. In most of the city, BTEX compounds originate from traffic, but close to industrial areas, industrial emissions become their dominating source. Secondly, passive sampling lasts for seven days and since VOCs are not stable for such long periods of time; there is a possibility that chemistry can modify composition. Since this point is not discussed extensively in the literature, the magnitude of such modification is not very clear. It is probably small, because otherwise passive sampling data would be completely useless, but still such modification, at least for reactive VOCs is a possibility. Due to these difficulties we decided to use more robust FA and not more informative PMF with our VOC passive sampling data at Bursa.

The FA was applied to data from a winter (February) and a summer (July) sampling campaigns. Since inorganic pollutants, SO₂, NO₂ and O₃ were not measured at these sampling campaigns, the potential sources of inorganic pollutants in Bursa atmosphere could not be discussed in this section. The data were analyzed using the Statistical Package for the Social Sciences (SPSS Inc. Chicago.USA. Version 17). The missing points, geometric means values and LOD/2 values that are used to fill in missing data are given in Table 4.20. In July sampling campaign, 9 out of 22 samples had no missing points. Missing points in the remaining 11 VOCs varied between 1 (2%) and 6 (9%). In February 10 of 22 VOCs had no missing points and number and percentage of missing points in remaining 12 VOCs varied between 1 (1%) and 3 (4%). These indicate a reasonably small number of data points that should be inserted in the data set. This was one the reasons for using FA instead of PMF in this study. The few below-detection-limit values were filled in by half detection limit values shown in Table 4.20. Non measured values were to be replaced by geometric mean values, but there were no VOC that was not measured. There were 3 VOCs in July campaign (n-hexane, mcyclopentane and 2.2.5-tri-M-hexane) that were not measured in the first campaign and one compound (m+p-cholorotoluene) that was not measured in the second campaign. However, since these were not measured in any of the samples in those campaigns, they were completely excluded from FA instead of filling in.

We have used a criterion known as Kaiser's criteria to determine the number of factors that should be included in FA results. This, most widely used approach in finding the number of factors to be extracted, suggest the factors

			JUL	_Y					FEBR	JARY		
			Geo.		Missing	missin			Geo.		Missing	Missing
COMPOUNDS	MDL	MDL/2	mean	N	Ν	g %	MDL	MDL/2	mean	N	Ν	%
Pentane	0.005	0.002	0.47	65	0	0	0.005	0.002	0.87	67	0	0
1,3 Butadiene	0.005	0.002	0.07	65	0	0	0.005	0.002	0.33	67	0	0
n-Hexane							0.006	0.003	0.67	66	1	1
m-cyclopentane							0.011	0.006	0.99	66	1	1
Benzene	0.011	0.005	2.36	65	0	0	0.011	0.005	8.27	67	0	0
Cyclohexane+Cyclohexene	0.040	0.020	0.89	65	6	9	0.040	0.020	1.55	66	1	1
2-Methylhexane	0.010	0.005	1.34	65	0	0	0.010	0.005	0.78	66	1	1
2,2,3-Trimethylbutane+	0.010	0.005	0.36	65	1	2	0.010	0.005	0.31	67	0	0
2,3-Dimethylpentane												
3-M-Hexane	0.009	0.005	1.45	65	1	2	0.009	0.005	0.94	66	1	1
2,2,4-Tri-M-Pentane	0.005	0.002	0.21	65	4	6	0.005	0.002	0.57	67	0	0
n-Heptane+cis-3-Heptene	0.010	0.005	0.87	65	0	0	0.010	0.005	0.90	67	0	0
Methylcyclohexane	0.008	0.004	0.25	65	5	8	0.008	0.004	0.39	67	0	0
Toluene	0.010	0.005	26.60	65	0	0	0.010	0.005	26.21	67	0	0
2-m-Heptane	0.008	0.004	0.79	65	1	2	0.008	0.004	0.84	65	2	3

Table 4.20 Missing values and statistical parameters used to fill in the missing values used in Factor analyisis

	FEBRUARY											
COMPOUNDS	MDL	MDL/2	Geo. mean	Ν	Missing N	missin g %	MDL	MDL/2	Geo. mean	Ν	Missing N	Missing %
m+p-Chlorotoluene	0.011	0.006	0.49	65	3	5						
Octane	0.008	0.004	0.50	65	1	2	0.008	0.004	0.75	65	2	3
2,2,5-Tri-M-Hexane+							0.014	0.007	0.17	64	3	4
1,2,4-Tri-M-Cyclohexane												
Tetrachloroethylene	0.006	0.003	0.20	65	1	2	0.006	0.003	0.23	66	1	1
Chlorobenzene	0.008	0.004	0.26	65	0	0	0.008	0.004	0.59	66	1	1
Ethylbenzene	0.011	0.006	4.62	65	0	0	0.011	0.006	3.72	67	0	0
Bromoform							0.045	0.023	1.42	65	2	3
m+p-Xylene	0.010	0.005	12.19	65	0	0	0.010	0.005	9.65	67	0	0
Styrene	0.004	0.002	0.32	65	3	5	0.004	0.002	23.01	67	0	0
o-xylene	0.006	0.003	1.73	65	0	0	0.006	0.003	1.99	67	0	0
Isopropylbenzene	0.007	0.003	0.21	65	0	0	0.007	0.003	0.47	66	1	1
n-Probylbenzene	0.004	0.002	0.18	65	0	0	0.004	0.002	0.24	65	2	3
3-Ethyltoluene	0.010	0.005	1.30	65	0	0	0.010	0.005	1.34	67	0	0
4-Ethyltoluene	0.006	0.003	0.56	65	0	0	0.006	0.003	2.42	66	1	1

Table 4.20 Missing values and statistical parameters used to fill in the missing values used in Factor analysis (Continued)

			JUI	LY					FEBRU	JARY		
COMPOUNDS	MDL	MDL/2	Geo.	N	Missing	missin	MDL	MDL/2	Geo.	N	Missing	Missing
			mean		IN	y 70			mean		IN	70
1,3,5-Tri-M-Benzene	0.012	0.006	0.59	65	1	2	0.012	0.006	0.65	67	0	0
2-Ethyltoluene	0.014	0.007	0.68	65	3	5	0.014	0.007	0.69	65	2	3
1,2,4-Tri-M-benzene	0.003	0.001	0.69	65	0	0	0.003	0.001	2.98	67	0	0
n-Decane	0.008	0.004	1.01	65	1	2	0.008	0.004	3.17	67	0	0
1,4-Di-cl-Benzene	0.009	0.005	0.11	65	2	3	0.009	0.005	0.22	64	3	4
1,4-Di-e-Benzene	0.008	0.004	0.12	65	2	3	0.008	0.004	0.39	64	3	4
Naphthalene	0.008	0.004	0.11	65	4	6	0.008	0.004	0.27	65	2	3

Table 4.20 Missing values and statistical parameters used to fill in the missing values used in Factor analysis (Continued)

with eigenvalues > 1.0 to be extracted for FA. There were six factors with eigen values > 1.0 in FA applied to data generated during July campaign. Varimax rotation was also applied on the data set because Varimax rotation minimizes the complexity of the components and by this way explanation of the factors gets easier (Henry. 1987 and Guo and Louie. 2004).

Composition of factors emerged from FA applied to July data are given in Table 4.21. Table includes loadings of the 6 factors with eigenvalues > 1.0, communalities of VOCs, eigenvalues and fractions of variance explained by each factor. It can be seen from the table that six factors which is a reasonable number extracted accounted for 81% of the system variance.

Interpretation of six factors, some of which are affected from industries with unknown composition of emissions, is not a straight forward task. We have also prepared some additional graphics that can assist us in identifying factors. These supplementary figures include factor profiles, which is a bar graph showing factor loadings, factor score plot, which is a time-series plot of scores of each factor and sector averages, which includes average factor scores in "industrial", "residential", "background" and "road" sampling stations. These graphs are given in Figure 4.24.

Factor 1 has high loadings of light hydrocarbons, such as pentane, 1,3butadiene, benzene etc. The factor also includes heavy hydrocarbons but with a significantly smaller loadings. It is obvious that Factor one is not characterized with heavy VOCs. Factor 1 is a typical "light-duty traffic" factor representing emissions from cars with gasoline engine. The factor score averages have higher values at "road" stations confirming that this is a traffic source. Factor one explains 47% of the system variance, which is more than half of the variance explained in this study.

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	communality
Compunds/ Variance%	47.42	11.53	7.69	5.83	4.70	3.89	3.10
Pentane	0.842	0.205	0.084	0.062			0.779
1,3 Butadiene	0.866	0.219		0.127	0.193		0.852
Benzene	0.807	0.089		0.036	0.347		0.798
Cyclohexane+Cyclohexene	0.395	0.357	0.399		0.038	0.616	0.823
2-Methylhexane	0.880	0.187	0.195	0.200	0.071	0.116	0.906
2,2,3-Trimethylbutane+2,3-							
Dimethylpentane	0.872	0.160	0.144	0.154		0.107	0.851
3-M-Hexane	0.580	0.359	0.320	0.143		0.051	0.596
2,2,4-Tri-M-Pentane	0.255	0.033	0.360	0.707	0.076		0.706
n-Heptane+cis-3-Heptene	0.474	0.413	0.127		0.371	0.003	0.557
Methylcyclohexane	0.167	0.201	0.705	0.220		0.095	0.743
Toluene	0.140	0.251	0.745	0.109	0.386	0.002	0.798
2-M-heptane	0.551	0.116	0.204	0.498	0.416		0.784
m+p-Chlorotoluene	0.007	0.190	0.035	0.427	0.667		0.665
Octane	0.396	0.350	0.123	0.569		0.392	0.772
Tetrachloroethylene	0.119	0.269	0.337	0.536	0.307	0.567	0.903
Chlorobenzene		0.362	0.689	0.285	0.233	0.198	0.780

Table 4.21 Factor loadings, variance % of each factor and communality for summer sampling

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	communality
Compunds/ Variance%	47.42	11.53	7.69	5.83	4.70	3.89	3.10
Ethylbenzene	0.078	0.466	0.386	0.239	0.661	0.140	0.885
m+p-Xylene	0.060	0.538	0.728	0.082	0.300	0.156	0.943
Styrene	0.230	0.133	0.210	0.010	0.773	0.259	0.779
o-xylene	0.195	0.473	0.760	0.077	0.205	0.182	0.920
Isopropylbenzene	0.409	0.390	0.329	0.374	0.194	0.204	0.647
n-Probylbenzene	0.370	0.768	0.375	0.106	0.206	0.101	0.931
3-Ethyltoluene	0.303	0.795	0.376	0.194	0.184	0.160	0.963
1,3,5-Tri-M-Benzene	0.261	0.869	0.157	0.071	0.101	0.120	0.877
2-Ethyltoluene	0.292	0.787	0.267	0.356	0.143	0.164	0.950
1,2,4-Tri-M-benzene	0.291	0.772	0.353	0.330	0.146	0.151	0.958
n-Decane	0.043	0.278		0.845		0.076	0.818
1,4-di-cl-Benzene	0.273	0.279	0.109	0.718	0.216	0.293	0.812
1,4-di-e-Benzene			0.399	0.621	0.208	0.056	0.603
Naphthalene		0.123	0.065	0.150	0.110	0.911	0.915

Table 4.21 Factor loadings, variance % of each factor of communality for summer sampling campaign (Continued)



Figure 4.24 Factor profiles and factor scores for July 2007 data

Factor 2 explains large fraction of the variances of relatively heavy hydrocarbons such as, n-propylbenzene, 3-ethyl-toluene, 1,3,5-tri-M-benzene, 2-ethyl-toluene. The factor explains smaller fractions of variances of lighter hydrocarbons. Factor score averages at industrial and "road" stations are comparable. As discussed in previous sections, if VOCs have comparable concentrations at traffic and industry impacted stations, its source is probably traffic rather than industry, because industrial areas also include traffic emissions. For a VOC to have industrial source its concentration (or factor score) average at industrial stations should be significantly and consistently higher than its concentration/scores at "road" stations. Traffic with enriched heavy VOSs clearly should represent emissions from heavy duty vehicles with diesel engines. Factor 2 explains 11% of the system variance.

Factors 3 is enriched with compounds like methylcylohexane, toluene, m&pxylene and o-xylene. The factor score averages in "industrial" stations are higher than corresponding averages in other microenvironments. The VOCs mentioned above, particularly toluene, are indicators of evaporative emissions (Qin et al. 2007; Ho et al.. 2004; Rappenglück and Fabian. 1998). It should also be noted that. VOCs that were identified as industrial markers before does not occur in this factor. We believe that this is a general evaporative emission factor.

Factors 4 to 6 explain the variances of moderate and heavy VOCs, but do not contribute much to the variances of light VOCs. For all of these factors, factor score averages at "industrial" stations are significantly higher than their score averages at "road" stations, indicating that contribution of industries are dominant, at least at stations close to industrial districts. We believe that these three factors represent different industrial emissions. But it is not possible to identify industries responsible for these emissions with the information available currently. These three industrial factors together explain approximately 14% of the system variance.

The FA applied to July data set qualitatively showed sources contributing to VOC mass in Bursa atmosphere. The components revealed in that FA application was probably representative for the situation prevailing in summer

season. Factor analysis exercise was repeated with February data to assess the components of VOCs in winter season.

This time there were eight factors with eigenvalues > 1.0, which were extracted for interpretations. The composition of factors and fractions of variance explained by each of them are given in Table 4.22. Factor profiles, time-series plot of scores and average score at each microenvironment studied are given in Figure 4.25. These eight factors totally accounts for 84% of the system variance, which is comparable to the variance explained in summer factor analysis.

Factor 1 explains most of the variance in heavy VOCs and smaller fractions of the variance in light VOCs. The factor is similar to factor 2 obtained in the FA of July samples. This is depicted in Figure 4.26, where factor 2 obtained in July FA is compared with the factor 1 obtained in February FA. As discussed previously this is a factor representing diesel powered vehicle emissions in Bursa Atmosphere. Average factor scores at traffic impacted sampling points ("road" stations) are the higher than average scores at industry impacted sampling points, which also confirms the traffic source of this factor. The distribution of factor 1 were converted to factor score map through interpolation as discussed previously in the manuscript and pollution map is depicted in Figure 4.27 together with the corresponding map for Factor 2 scores in summer FA to assess similarities and differences between two factor profiles. There is one distinct difference between distributions of supposedly same factor in summer and winter. In winter score-map there is a higher factor scores in residential areas, particularly those located at the northwest sector. This is also observed in average factor scores calculated for different microenvironments (shown in Figure 4.25) the difference between factor score averages calculated for road stations and residential and industry stations and residential stations are smaller in Winter FA than they are in summer FA.

	Factor	Factor	Factor	Factor	Factor	Factor	Factor	Factor	
	1	2	3	4	5	6	7	8	communality
Compound/Variance%	40.53	11.07	9.59	5.97	5.01	4.70	3.81	3.35	
Pentane	0.361	0.827			0.086	0.101	0.029	0.195	0.881
1,3 Butadiene	0.232	0.876			0.130	0.013			0.877
n-Hexane	0.011	0.084	0.103		0.009	0.889		0.015	0.812
Methylcyclopentane+2,4-									
Dimethylpentane	0.390	0.278			0.113	0.478	0.070	0.145	0.546
Benzene	0.054	0.697	0.048	0.465	0.195		0.370		0.883
Cyclohexane+Cyclohexene	0.099	0.024	0.077			0.321	0.142		0.504
2-Methylhexane	0.232	0.528	0.211	0.118	0.280	0.371	0.189	0.511	0.903
2,2,3-Trimethylbutane+2,3-									
Dimethylpentane	0.189	0.460	0.294	0.361	0.268	0.420	0.083	0.280	0.797
3-M-Hexane	0.384	0.461	0.206		0.143	0.346	0.156	0.574	0.899
2,2,4-Tri-M-Pentane	0.280	0.020	0.699		0.074			0.299	0.677
n-Heptane+cis-3-Heptene	0.534	0.175	0.221			0.271	0.091	0.670	0.902
Methylcyclohexane	0.523		0.428	0.017		0.204	0.168	0.550	0.838
Toluene	0.289	0.157	0.196		0.737	0.025	0.338	0.258	0.871
2-M-Heptane	0.242	0.367	0.193	0.035	0.633	0.038	0.207	0.319	0.779
Octane	0.313	0.051	0.352	0.253	0.342	0.473	0.402		0.800
2,2,5-Tri-M-Hexane+1,2,4-Tri-M-									
Cyclohexane	0.069	0.653	0.556		0.071	0.063	0.053		0.758

Table 4.22 Factor loadings, variance % of each factor and communality for winter sampling

	Factor	Factor	Factor	Factor	Factor	Factor	Factor	Factor	
	1	2	3	4	5	6	7	8	communality
Compound/Variance%	40.53	11.07	9.59	5.97	5.01	4.70	3.81	3.35	
Tetrachloroethylene	0.272	0.028	0.794	0.222	0.142	0.253	0.172	0.009	0.868
Chlorobenzene	0.446	0.073	0.430	0.100	0.067	0.156	0.505	0.205	0.725
Ethylbenzene	0.764	0.122	0.392		0.267	0.134	0.292		0.928
Bromoform	0.480	0.042	0.584	0.371	0.258	0.233	0.156		0.875
m+p-Xylene	0.775	0.106	0.387		0.239	0.130	0.275		0.912
Styrene	0.162	0.111	0.080	0.014	0.890	0.099			0.864
o-xylene		0.066	0.054	0.074	0.046		0.925		0.902
Isopropylbenzene	0.098		0.575	0.322	0.194	0.036	0.487	0.093	0.742
n-Probylbenzene	0.855	0.192	0.150	0.127	0.103	0.072	0.325	0.118	0.942
3-Ethyltoluene	0.952	0.164	0.091	0.012	0.104	0.094		0.097	0.978
4-Ethyltoluene	0.943	0.116	0.159	0.021	0.111	0.118		0.066	0.975
1,3,5-Tri-M-Benzene	0.923	0.187	0.056	0.128	0.088	0.032	0.002	0.113	0.928
2-Ethyltoluene	0.938	0.139	0.093	0.051	0.089	0.095		0.100	0.947
1,2,4-Tri-M-benzene	0.954	0.214	0.009	0.059	0.075	0.023		0.082	0.980
n-Decane	0.023		0.094	0.950	0.001	0.049	0.206	0.022	0.959
1.4-di-cl-Benzene	0.079	0.033	0.092	0.958				0.015	0.937
1,4-di-e-Benzene	0.677		0.391	0.044	0.116	0.031		0.030	0.645
Naphthalene	0.243		0.219	0.381	0.159	0.516			0.733

Table 4.22 Factor loadings, variance % of each factor and communality for winter sampling (Continued)



Figure 4.25 Factor profiles and factor scores for February 2007 data



Figure 4.26 Similarity and differences between February Factor 1 profile and July Factor 2 profiles and February Factor 2 and July Factor 1 profiles

This higher scores in residential stations in winter compared to summer is not confined to Factor 1 only and observed in all factors. More homogeneous distribution of scores in winter is also obvious in factor score maps as discussed previously. The reason for increased contribution of all factors in residential stations can be due to accumulation of the pollutants over the city due to lower mixing height in winter. In summer similar accumulation is not observed owing to enhanced vertical ventilation.

Another reason which is not as obvious can be the contribution of heating emissions in winter. Normally one would expect heating emissions to appear as a separate factor. However, we have investigated all 8 factors if one of them can represent residential heating emissions. None of the factors resemble the conventional heating profile. This may be due to similarity in residential heating emissions with the emissions from other sources. One possibility is that residential heating emissions do not appear as a separate factor but increases contribution of each factor on observed VOC levels in residential areas which explains observed high scores in residential stations. Factor 1 in winter explains approximately 40% of system variance.



Factor 1 Winter



Figure 4.27 Comparison of Factor2 and Factor 1 produced from summer and winter data, respectively.

Factor 2 is loaded with light VOCs that are indicators of gasoline powered traffic. This factor is highly similar with the light duty traffic factor (Factor 1) in July FA. The similarity is depicted in Figure 4.26 and Figure 4.28. This light duty traffic explains 11% of the system variance. As in factor 1, average factor scores at "road" stations are higher than corresponding average calculated for industry impacted stations.



Factor 2 Winter



Figure 4.28 Comparison of Factor1 and Factor 2 produced from summer and winter data, respectively

Factors 3, 4, 6 and 7 have different profiles. The common feature in these four factors is that their average scores in industrial stations are higher than their averages found for "road" stations. Distributions of factor scores for some of these factors are given in Figure 4.30. Higher scores at industrial districts,

particularly at the Bursa industrial zone (BOSB) on the Ankara – Izmir highway, is clear in these score maps. These four factors are identified as different industrial emissions from three industrial districts in Bursa. These four industrial factors account for approximately 24% of the system variance.

Factor 5 includes VOCs like toluene 2-M-heptane and styrene. These, particularly toluene, are a good marker of evaporative emissions. The average factor scores in industrial, road and residential stations are comparable to each other. This similarity of factor scores in different microenvironments is also seen in factor score map for this factor. Factor 5 scores are fairly uniformly distributed throughout the city and do not show any preference for road and industrial stations. Factor 5 hence is identified as evaporative emission factor. The factor explains 5.0% of the system variance

Factor 8 is an interesting one. It has fair loadings of relatively light hydrocarbons. Average factor scores in road stations are higher than the average scores calculated for other microenvironments. The factor score map for Factor 8 is depicted in Figure 4.29. Unlike industrial factors discussed previously, the highest values of factor 8 scores are observed in crossroads and not in industrial districts of the city. Average factor scores at road stations are higher than the corresponding average calculated for industrial or residential stations. This factor is not positively identified. It is probably a traffic related factor as it has higher scores on the roads. However, the type of the source is not clear. Factor 8 explains approximately 3.3% of the system variance.



Figure 4.29 The factor score maps for Factor 8 in winter season



Figure 4.30 Factor score maps for three industrial factors identified in winter FA

4.2.6 Ozone Formation Potentials of VOCs

Volatile organic compounds emitted into atmosphere have direct and indirect adverse effects. The direct health effects of VOCs measured in this study is discussed in the following section (Section 1.2. Assessment Health Risk due to VOCs). Current chapter is related to indirect effects of the VOC, namely their ozone formation potentials. Most of the VOC contribute the formation of tropospheric ozone in the presence of nitrogen oxides (NO_x) and sunlight.

Ozone is a major concern due to its adverse impact on human health and vegetation. Elevated ozone has been observed many cities since 1970s (Guicherit and Dop. 1977. MARI 1994). Since ozone formation is enhances with the temperature, plenty of sunlight and presence of organic compounds and NO_x , Turkey, like other countries in the Mediterranean region, experiences high ozone levels, particularly on the Mediterranean coast.

The relationship between ozone and its two main precursors, nitrogen oxide (NO_x) and VOC, represents one of the most important issues to be handled about the urban air quality. Since it is well known that the formation of ozone is controlled with some conditions. Depending on atmospheric conditions and levels of VOC and NO_x , ozone formation can be controlled by formation of either VOCs or NO_x . Knowing the parameter controlling ozone formation can be important for policy response.

Ozone can be produced either through VOC-limited chemistry or by NO_x limited chemistry, but it is difficult to determine which one of these chemical processes operates at a particular location. Furthermore, sensitivity of ozone formation on NO_x or VOC can change from one location in the city to another (Sillman, 1999). The NO limited regions are generally areas that downwind from urban and suburban areas; whereas VOC-limitation is generally observed at highly polluted urban areas. (USEPA., 1998)

The evaluation of ozone-VOC-NO_x sensitivity is based on predictions from Eulerian model, which includes emission rates, atmospheric dynamics and photochemistry. However, the model predictions of ozone-NO_x-VOC sensitivity should be accepted as scientifically valid only when there is extensive

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measurement-based evidence to show that the specific model prediction is true (Silman. 1999).

To evaluate the ozone-forming potential of VOC concentrations measured in this study, the maximum incremental reactivity (MIR. g O_3 /g VOCs) obtained from Carter (1994) was used. The unit of MIR is grams ozone formed per measured gram VOC. Ozone forming potential was estimated by summing up the products of individual VOC amounts and their corresponding MIR factors. The MIR factor reported is represented in Table 4.23.

VOC	MI R [*] (grO₃/grVOC)	voc	MIR [*] (grO₃/grVOC)
Benzene	0.42	2-Methylhexane	1.08
Toluene	2.7	3-M-Hexane	1.40
Ethylbenzene	2.7	2,2,4- Trimethylpentane	0.93
m& p Xylene	14.8	2-Methylheptane	0.96
o-xylene	6.5	Styrene	2.2
1,3-Butadiene	10.9	Isopropylbenzen e	2.2
1,3,5- Trimethylbenzene	10.1	n-Propylbenzene	2.1
Isopropylbenzene	2.2	n-Pentane	1.04
n-Hexane	0.98	1,2,4- Trimethylbenzen e	8.9
Octane	0.60	Napthalene	1.17
Nonane	0.54	Methylcyclohexa ne	1.8
n-Decane	0.46	2,2- Dimethylbutane	0.82
3-Methyl pentane	1.5	2,3- Dimethylbutane	1.07
2,2,3- Trimetylbutane +2,3-	2.63		
Dimethylpentane		2-Methyl pentane	1.5
Cyclohexane +Cyclohexene	6.98	Methylcyclopenta ne +2,4- Dimethylpentane	4.3

Table 4.23 Tabulation of incremental reactivities in the MIR scale

*Incremental reactivities in units of grams ozone formed per gram VOC emitted for the ozone yield reactivity scale for the MIR scale Data sets generated in October 2005 and April 2005 were used in order to investigate the contribution of VOCs on ozone formation, because inorganic passive sampling for NO₂ was conducted only in these two campaigns. Figure 4.31 shows produced ozone mass (ng) from individual VOC at different sectors. In the figure, the mass of ozone formation for each individual compound was summed and the contribution of each compound to that total was calculated by dividing the total mass of ozone formation. It is concluded from the figure that m&p xylene is the most dominant contributor to ozone formation among all sectors. Toluene is the second largest contributor. On average, these two compounds account for 70% and 75% of the total for October 2005 and April 2006 sampling campaigns respectively. According to factor analysis profile, these two compounds came mainly from the use of solvents and gasoline evaporation. Therefore, a more effective control strategy would comprise effective control emissions of these two compounds among VOC. The contribution of benzene to ozone formation potential was the lowest even though it is the most hazardous species in VOCs. It is also clearly seen in Figure 4.31 that vehicular and industrial emissions are a larger contributor to ozone formation for both sampling campaigns. According to the factor analysis profile, the urban atmosphere was mainly affected by both vehicular exhaust and industrial emission. High ozone production was expected due to VOC in these sites. At the background site, the ozone formation of VOC was at a low level. As shown in Figure 4.32, the background ozone concentrations had a fairly high value when compared to other sites of the city since it takes several hours to produce ozone via photochemical reactions in an urban atmosphere. Hence, the production of ozone in the urban atmosphere is detected in rural areas.

Figure 4.32 shows that VOC and NO_2 concentrations were at a high level around the roads and industrial areas as well as near residential areas, while ozone concentrations reached high levels in rural areas. The ozone destilation, which was discussed previously in the manuscript, is the reason of this finding.



Figure 4.31 The ozone production potential (ng) of selected VOC conducted at a) October 2005 and b) April 2006



Figure 4.32 Spatial distribution of ozone, NO₂ and total VOCs for September 2005 campaign(google earth, 2009)

4.3 Assessment Health Risk due to VOCs

Ambient VOC concentration measured in Bursa were used to characterize the magnitude of health problems, due to VOCs, that can be expected at Bursa. Measured VOC concentrations were used with chronic toxicity data obtained from USEPA (IRIS 2009) to estimate cancer risk and noncancer hazards ratio for individual VOC and cumulative risks posed by multiple pollutants. For this purpose, questionnaires were distributed to people with different socioeconomic status and living in different areas of Bursa to determine time activity level. Utilizing the measurement data set and the focused questionnaires may be the best approach to reasonably estimate the health risk (USEPA. 2009). Inhalation exposure dose and risks were estimated for each participant and the population of Bursa by deterministic and probabilistic approaches, respectively.

4.3.1 Questionnaire

Health risk associated with air pollution is a function of both concentrations of pollutants and inhalation rate. In this study chemical studies revealed concentrations of VOCs, but did not give any information about the inhalation rate. Measurement of inhalation rate is not a straightforward process and depends on the activity patterns of individuals. It is clearly demonstrated that activity pattern is different in different socioeconomic groups. The objective in application of questionnaire was to establish activity patterns of people in different socioeconomic sectors, so that information can be related to inhalation rate through information available in literature.

In this study questionnaires were used to collect the participants' demographic information, including age, race, occupation and household income, as well as the exposure determinants, such as, use of air fresheners, dry cleaning, and mode of transportation. Each subject was asked to keep a daily time-activity diary to determine the time spent indoors and outdoors. Data collected from questionnaires, such as body weight and activity

information, the two most important parameters to be used in estimating exposure concentration, were used to calculate individual inhalation rate. These findings were helpful in predicting more accurate risk levels compared to making assumptions, as usually practiced in risk assessment studies.

Bursa has three main districts, namely Nilüfer, Osmangazi and Yıdırım. Since passive sampling points were scattered across all three districts, questionnaires were distributed to people who live in one of these three districts. Questionnaires were distributed to the selected quarters where passive sampling measurement was available in order to collect information regarding to socio-demographic and personal time-location-activity, their smoking habits, exposure to environmental tobacco smoke (ETS), The first questionnaire included demographic information and the second one was used to obtain activity information. The applied questioners were given in Appendix B. The demographic information and activity information for the first day were administered by the author during the visit to eliminate misunderstandings in filling questionnaires. The parents of participating children completed the questionnaires. Each respondent filled out a questionnaire form every day during the seven consecutive days. The questionnaires were similar to the Time-Activity Questionnaires, which were applied in the Aliaga Study (Tuncel at al., 2008), which was developed by Dr. Sait Sofuoğlu of İYTE.

A total of 210 questionnaires were distributed to the volunteers and 202 questionnaires were returned (a very impressive return rate). Five of them were excluded as they contained inconsistent information. A total of 197 questionnaires were returned from Yıldırım district (63), Osmangazi district (50) and Nilüfer district (79). The response rate was 93.8%. According to the address-based population census carried out in 2007, the number of inhabitants in Bursa was approximately one and a half million. Table 4.24 illustrates the distribution of population between districts, number of questionnaires distributed and number of passive sampling points in each distribution of population among districts. This is not a serious drawback in application of questionnaires, because people living in one district can work in another district or they can go to the city center for shopping or for other purposes. Besides, five industrial zones of Bursa are located in these three

districts. For this reason, this questionnaire, which was conducted according to the places where people live, is an acceptable one.

	Yıldırım	Osmangazi	Nilüfer	Total
Population	575,450	736,034	251,344	1,562,828
population (%)*	(%37)	(%47)	(%16)	
Participant	65 (%33)	53 (%26)	79 (%41)	197
number				
Number	23 (27%)	33 (39%)	29 (34%)	85
of Passive				
sampling point				
*	Address Deced	Dopulation Suc	tom Donulation	Conclus 2007

Table 4.24 Bursa district population and the number of participants

* Address Based Population System Population Census. 2007

109 participants were female (55%) and 88 of them were male (45%). Most of the participants finished primary school and high school. Table 4.25 shows the educational level of the participants according to their district. Since the participating children and infants were illiterate, they were classified as noneducated. The other participants were literate. Continuous variables, such as age, body weight, time spent in home and time spent in school/office have normal distribution. Distribution parameters for these continuous variables are given in Table 4.26. The variables of time spent in home and at work/school were not data that were measured, but they were estimated by taking into consideration the participants' responses to the related question about how much time they spent in a day at home or at work/school. However, since the values of these variables were also reported in time-activity questionnaire, these data were treated as measured values. While there were participants who spent all of their time at home, maximum time spent in office was 10.71 hours. Mean and median values of the time spent in office/school were 4.37 and 3.11 hours, respectively. Twenty six percent of participants were housewives, retired people or pre-school children. Most of the participants worked during weekdays. Hence, the average weekly value of time spent in office/school was lower than expected.

Education	Yıldırım	Osmangazi	Nilüfer
Category	%	%	%
Non-school	7	7	11
Primary school	25	15	10
Middle School	14	7	8
High school	25	32	25
Undergraduate	8	6	3
Graduate	15	25	24

Table 4.25 Educational information of Bursa population

Table 4.26 Continuous variables and their percent distribution

	Media	σ		F	Percentile	9	
	n		10	30	50	70	90
Age	37.00	17.87	8.80	28.00	37.00	46.00	57.20
Body Weight	70.00	21.75	25.80	57.00	70.00	78.00	89.00
(kg)							
Time spent at	14.00	3.244	10.86	12.71	14.00	15.71	19.26
home (hours)							
Time spent in	5.71	2.04	4.29	5.71	5.71	6.94	9.20
office/at							
school							
(hours)							

The most important parameter we wanted to determine in demographic questionnaire was the "body weight", because it was directly used in estimating "exposure concentration" used in eqn 2.15. Other parameters, which contained sex, age, education, income level and homeland, were used to evaluate differences among population subgroups.

The basic statistics such as Skewness and Kurtosis were applied for the continuous variable data set.

Table 4.27 illustrates these statistical parameters of the data set. Skewness indicates the degree of asymmetry of a distribution around its mean. Negative skewness indicates the left tail of the probability distribution. Hence, the mass of the distribution is concentrated on the right side of the distribution graph. Positive skewness indicates probability distribution with an asymmetric tail extending towards more positive values (Nist/Sematech 2009). Kurtosis is a measure of the "peakness" of the probability distribution of a random variable. Higher kurtosis means more of the variance is the result of infrequent extreme deviations, as opposed to frequent modestly sized deviations (Nist/Sematech 2009). Skewness values demonstrated that normal distribution would not be a correct assumption for continuous variables of time spent at home and in office/at school according (Skewness/standard error<2).

Frequency distributions were calculated for discrete variables as shown in Table4.28. Most of the participants were middle-aged. Most of them (40%) are from the Marmara region. About one fourth of the participants did not answer the question about their level of income, while 27% of those people who answered this question had no income and 21% had an income between 1.000 and 2.000 TL. Since children, students. and housewives were included in this group, the rates were higher.

Time Spent in Different Microenvironmets

The time spent indoors and outdoors was calculated for each respondent. Time spent indoors was calculated by adding the average time spent indoors at the participant's home (kitchen, living room, bathroom, etc.), in other houses, and in other locations such as school, office, restaurants, etc. Time spent outdoors was estimated by adding the average time spent outdoors outside the participant's home, such as pool, street, and yard and in other locations such as sidewalk, street, neighborhood, parking lot, service station/gas station, school grounds, park course, pool, lake, farm, etc.

Table 4.29 provides data about time spent in outdoor and indoor environments for the selected population. While the participants, especially the elder people spent all their time at home, the participants spent 16%

	Mean	Std_dev	Min-Max	Skewness (std error)	Kurtosis (std error)
Age	36.33	17.87	2-79	0.014 (0.173)	-0.262 (0.345)
Body Weight (kg)	64.97	21.75	10-116	-0.755 (0.173)	0.463(0.345)
Time spent at home (hours)	14.15	3.15	7-24	0.658 (0.173)	0.522 (0.345)
Time spent in office/at school (hours)	4.37	3.11	0-10.71	-0.258 (0.173)	-1.098 (0.345)

Table 4.27 Statistical parameters of continuous variables in demographic information

Sex	Age		Education			Income	Homeland		
Category	%	Category	%	Category	%	Category	%	Category	%
Female	55	0-9	10	Non-school	9	No working	27	Aegean	9
Male	45	10-19	9	Primary school	16	0-300	2	Marmara	40
		20-29		Middle School		300-600		Western Black	
			12		10		10	Sea	3
		30-39	25	High school	27	600-1000	13	Eastern Black Sea	6
		40-49	23	Undergraduate	26	1000-2000	21	Eastern Anatolia	5
		50-59		Graduate		>2000		Southeastern	
			13		12		6	Anatolia	3
		60-74	8			No answer	21	Mediterranean	3
								Central Anatolia	9
								foreign	7

Table 4.28 The frequency distribution for discrete variables

of their time outdoors and 6% of their time in transportation. According to the skewness parameters, the normal distribution was not represented in the time spent in indoor and outdoor data set.

The respondents were also asked to state the ventilation time of their indoor environment by opening door/window. Since the survey was conducted in spring season (April), ventilation value obtained may not be representative for other seasons. Therefore, the ventilation time could be lower in winter and higher in summer season when compared to spring. Autumn and spring may be an average of winter and summer; that's why the survey time was deliberately selected to minimize seasonal diversity and to represent the yearly average. The participants ventilated their indoor environment for about 4 hours based on Table 4.29.

The average hour spent in transportation in vehicle or on road was 87.29 minutes according to the data presented in Tables 4-6-6. The area of Bursa urban center covers 1.400 km². Therefore, it was expected that the participants spent more than one hour in transportation.

The time of exposure to environmental tobacco smoke (ETS) was evaluated for two different microenvironments, ETS in vehicle and ETS indoors. While the average exposure time to ETS indoors was 192 minutes, it was 12 minutes for vehicles as represented in Table 4.29. The time of exposure to ETS indoors was higher than that in vehicles. Most of the participants (85%) were not subject to tobacco smoke in a vehicle presented in Table 4.30. The main reason was that smoking had been prohibited in public transport vehicles since 1991. Additionally, the participants were asked to state the time they spent in cafes/coffeehouses/restaurants. The average time spent in cafes/coffeehouses/restaurants was 54 minutes. About half of the participants, especially the elderly people and children, were not present in cafes/coffeehouses/restaurants.

According to the conducted questionnaire, the participants spend much time within buildings for living, working and studying (87% of their time). This percentage is similar with the corresponding values reported in literature

(Parra et al., 2008 and Klepeis et al., 2001). Transportation took about one and a half hours for Bursa population. Many studies indicated that mean concentrations were higher in the air indoors than air outdoors for VOCs (Yocom et al., 1982 and Kim et al., 2005). There is a linear relationship between indoor and outdoor VOC concentrations due to similarities of pollutant sources. Ventilation rate was another important parameter which affected indoor air quality.

In this study, even if the time spent in different microenvironments were evaluated, the personal exposure was calculated by combining the ambient air concentration and individual inhalation volume. There are two reasons for this assumption. First, ventilation rate indoors affects air concentration to a great extent (Wallace, 1987; Woodruff et al., 2000). In this study, the ventilation time calculated in this study was fairly long (4 hours) when compared to other studies. A field sampling study of indoor and outdoor concentrations of volatile organic compounds reported by Lewis (1991) and Lewis and Zweidinger (1992) found that penetration of VOCs from outdoor to indoor air is complete, even when air exchange rates (ventilation) are low (Woodruff et al., 2000). Hence, it could be expected that the indoor air was affected mainly by outdoor air as a result of high ventilation duration.

Second, the risk of cancer in Bursa was estimated as the best case scenario according to the minimum concentration to which people would be exposed. Since the ambient air concentration were used to calculate health risk assessment. The risks of cancer estimated are risk values that will be the best possible ones for people of Bursa. The risk of cancer in Bursa will not be lower than this; moreover, if the concentrations they are exposed to through indoor air and transportation are taken into account, the risks will be much higher. Even this study reveals the need to take precautions as to the quality of air.

	Mean	Median Std Dev		Min-Max	Skewness	Kurtosis	
					(std error)	(std error)	
Indoors (hours/day)	20.27	20.71	2.179	10-24	-1.262 (0.173)	3.004 (0.345)	
Outdoors (hours/day)	3.73	3.40	2.19	0-14	1.24 (0.173)	2.907 (0.345)	
Transport (min/day)	87.29	65.0	89.23	0-720	3.46 (0.173)	18.37 (0.35)	
Cafe/Restaurant (min/day)	53.92	0.0	88.50	0-480	2.32 (0.173)	6.49 (0.345)	
ETS indoors (min/day)	192	20.0	283	0-1185	1.58 (0.173)	1.66 (0.345)	
ETS in vehicle(min/day)	12.48	0.0	52.4	0-566	7.28 (0.173)	66.76 (0.345)	
Ventilation (min/hour)	240	220	176	0-840	0.716 (0.173)	0.04 (0.345)	

Table 4.29 The statistical parameters of time spent indoors or outdoors for all participants

	Percent								
	10%	20%	30%	40%	50%	60%	70%	80%	90%
Indoors (hours/day)	17.49	18.56	19.57	20.14	20.71	21.08	21.58	22.00	22.71
Outdoors (hours/day)	1.29	2.00	2.40	2.86	3.40	3.86	4.43	5.46	6.57
Transport (min/day)	14.71	30.86	42.86	55.71	65.00	77.14	103	122	187
Cafe/Restaurant(min/day)	0	0	0	0	0	34.29	60.0	103	180
ETS indoors (min/day)	0	0	0	0	20.00	118.5	240	385	627
ETS in vehicle(min/day)	0	0	0	0	0	0	0	0	23.14
Ventilation (min/day)	31.14	72.86	105.7	145.7	220	274	326	400	480

Table 4.30 Percent distribution of time spent indoors or outdoors for all participants
4.3.2 Determination of Activity Level

Ambient and indoor air is a potential source of exposure to toxic chemicals (USEPA, 2009). The extent of the adverse effects of the toxic substance directly depends on the time of exposure to those contaminants and the amount of those chemicals introduced into body. The amount of the chemicals introduced into body and also the exposure time can be calculated by taking into consideration activity level of human in specific microenvironments. There are various studies related to determining the breathing rate and volume while performing daily activities such as resting, watching TV, sleeping, etc, by using either a mathematical model or actual data (Foos et al., 2008; Brochu et al., 2006; Shamoo et al., 1990; Adams, 1993; Stifelman, 2007 and Arcus-Arth and Blaisdell, 2007)., USEPA (1985) compiled the results in the literature and generated the USEPA Exposure Handbook Manual (2009).

An activity or time spent in a specific activity can vary among individuals on the basis of, for example, culture, ethnicity, hobbies, location, gender, age, socioeconomic characteristics, and personal preferences. However, limited information is available regarding ethnic, cultural and socioeconomic differences in individuals' choices of activities or time spent in a given activity (Chance and Harmsen, 1998). Therefore, the aim of the second questionnaire was to obtain time expenditure in various activities and locations for the selected population grouped by age and gender, which properly represents the society living in Bursa.

The volunteers were asked to fill in the second detailed questionnaire including a time–location–activity dairy (60 min resolution) for seven subsequent days. The data on how much time individuals spend by participating in various activities in different microenvironments and on the frequency of performing such activities were evaluated for the selected population.

Data obtained from the second questionnaire covered a wide range of activities such as lying on carpet, watching TV, sleeping, napping, working/attending school, outdoor recreation, active sports, exercise, walking,

etc. Detailed data were collected for six different possible locations and 21 different activities. These activities were modified by taking the lifestyle of Turkish people into consideration. The average durations of activities which were reported for seven days separately was calculated. Hence, the time in this study represents the average time for seven days. Moreover, the data indicates that time periods adults spent doing market work, exercising child care, shopping, doing organizational and leisure activities were assumed to be fairly constant throughout the year (Hill, 1985).

These activity levels were categorized as light, moderate, or heavy according to the criteria developed by the U.S. EPA Office of Environmental Criteria and Assessment for the Ozone Criteria Document (USEPA, 1985). Table 4.31, which is adapted from USEPA (1985), illustrates the inhalation rate for men, women and children for different activity levels. A description of activities included in each activity level is also given in the Table. Children at the age of 6 in USEPA (1985) were adopted in the study by lumping the children between 2 and 10 years of age in this group. In the same way, the children aged between 10 and 18 were grouped in the children at the age of 10 in USEPA (1985).

	Resting ^a	Light ^b	Moderate ^c	Heavy ^d
Adult Male	0.7	0.8	2.5	4.8
Adult Female	0.3	0.5	1.6	2.9
Children age 6	0.4	0.8	2.0	2.3
years				
Children age	0.4	1.0	3.2	3.9
10 years				

Table 4.31 Human inhalation rates for men. women and children by activity level (m³/hour)(USEPA. 1985)

^a Includes watching television, reading, night sleeping, lying on carpet or sofa, resting and communication/ passive leisure

^b Includes most domestic work, attending to personal needs to care, main job, hobbies, conducting minor indoor repairs, home improvements, computer usage and sports events. ^c Includes heavy indoor clean-up, performance of major indoor repairs, alterations, car repair/maintenance and climbing stairs

^d Includes vigorous physical exercise, climbing stairs carrying a load. And standing hard working

Time people spent in resting, doing light, moderate and heavy activities, together with their body weight are given in Table 4.32 through Table 4.36 for all participants... Table 4.32 depicts the time spent conducting activities for all participants. The highest time expenditure was the activity category of resting with a mean of 12.71 hours/day since night sleep was categorized as a resting activity by USEPA (2009). Participants spent an average of 7.4 hours to conduct light level activities, such as most domestic work, attending to personal needs, main job, hobbies, and conducting minor indoor repairs, home improvements, computer usage, sports events and two hours to perform moderate level activity. About a quarter of the participants did not conduct heavy work, such as vigorous physical exercise and climbing stairs carrying a load, and standing hard working. This group of people properly consisted of elderly people and children. Among the participants, while early children spent about 16 hours on resting, adult men allocated 12 hours to the same activity. Since light activities included most domestic work, attending to school and the main job, the children aged between 10 and 18, adult females and adult males spent about same time for light activities. While early children spent about three hours on moderate activities such as playing in playground or kindergarten, there were only two early children who spent two hours in the weekdays swimming in the pool.

Individual average daily dose was determined by multiplying the time spent on each activity level with the corresponding inhalation rate using the equation 4.1. (USEPA, 1985) presented in Table 4.37. Table 4.37 and Table 4.38 show the descriptive statistics and the percent distribution of inhalation volume for all participants.

$$Daily \, Dose = \frac{1}{T} \sum_{i=1}^{k} IR_i \times t_i \tag{4.1}$$

Where;

- IR_i Inhalation rate at ith activity (m³/day) (presented in Table 4.37)
- t_i time spent in hours per day during ith activity (given in Table 4.33 through 4.36)
- k number of activity periods
- T total time of exposure period (e.g. a day)

Children have a higher resting metabolic rate and oxygen consumption rate per unit of body weight than adults. The greater amounts of air and pollutants are inhaled by adults than children over similar time periods on an absolute basis. Hence the volume of air passing through the lungs of a resting infant is up to twice that of a resting adult on a body weight basis (USEPA, 2009). In the event, the calculated inhalation rates for men, women and children have different values. Therefore, the participants were divided into three categories based on age and gender, namely adult men, adult women, children aged between 2 and 10 and children between 10 and 18.

The standard inhalation volume was accepted as 20 m³ for adults (USEPA, 2009). The mean inhalation volumes were 30, 15, 17 and 22 m³ for males, females, early children and children respectively, if the inhalation volume was assumed to be 20 m³ for Bursa population, the exposure and risk would have been overestimated for females and early children and underestimated for males and children.

Differences Across Subgroups

It is thought that people living in three different districts of Bursa have different distributions of time-activity patterns because of their life styles, differences in daily routines, and social and economic factors. Therefore, the data obtained from the questionnaires were classified according to the district where the participants live and it was questioned whether there was a difference in periods of average time spent daily. A total of 64 participants reside in Yıldırım, 70 live in Osmangazi, and 63 live in Nilüfer. There is only one variable, body weight, which is normally distributed. The parametric test was applied for normally distributed data.

All participants	Distribution	Mean	Median	Std Dev	Min-Max	Skewness (std error)	Kurtosis (std error)
Body Weight (Kg)	Beta	64.97	70.0	21.75	10-116	-0.755 (0.173)	0.463 (0.345)
Resting (hour/day)	Beta	12.71	12.29	3.00	6.5-22.0	0.845 (0.173)	0.626 (0.345)
Light (hour/day)	Beta	7.44	7.93	2.88	0.23-15.17	-0.492 (0.173)	-0.182 (0.345)
Moderate (hour/day)	Caucy	2.08	1.71	1.67	0.0-8.10	1.238 (0.173)	1.41 (0.345)
Heavy (hour/day)	-	6.71	4.11	7.93	0-34.81	1.51	1.97

Table 4.32 Statistical parameters of activity time for all participants

Adult men	Distribution	Mean	Median	Std Dev	Min-Max	Skewness (std error)	Kurtosis (std error)
Body weight (kg)	Beta	80.26	80	12.39	54-116	0.20 (0.28)	0.22 (0.56)
Resting (hour/day)	Beta	11.95	11.57	2.99	6.5-22.0	1.19 (0.28)	2.40 (0.56)
Light (hour/day)	Normal	8.08	8.76	2.67	0.23-15.17	-0.57 (0.28)	0.78 (0.56)
Moderate (hour/day)	Weibull	1.37	1	1.49	0.0-7.42	2.01 (0.28)	4.92 (0.56)
Heavy (hour/day)	Normal	2.48	2.17	2	0.0-7.25	0.66 (0.28)	-0.27 (0.56)

Table 4.33 Statistical parameters of activity time for adult men

Adult women	Distribu tion	Mean	Median	Std Dev	Min-Max	Skewness (std error)	Kurtosis (std error)
Body weight (kg)	Beta	65	65	12	40-95	0.18 (0.25)	-0.43 (0.50)
Resting (hour/day)	Beta	12.45	11.62	2.67	8.26-21.86	1.13 (0.25)	1.30 (0.50)
Light (hour/day)	Beta	7.72	8.13	2.62	1.64-12.88	0.41 (0.25)	-0.51 (0.50)
Moderate (hour/day)	Gama	2.26	1.86	1.49	0.0-6.93	1.57 (0.25)	1.22(0.50)
Heavy (hour/day)		1.56	1.00	1.66	0.0-8.0	1.64 (0.25)	3.06 (0.50)

Table 4.34 Statistical parameters of activity time for adult women

Children (2-10 years)	Distribution [*]	Mean	Median	Std Dev	Min-Max	Skewness (std error)	Kurtosis (std error)
Body weight (kg)		18.05	16.50	5.28	11.0-28.0	0.43 (0.51)	-1.06 (1.0)
Resting (hour/day)		16.38	16.18	2.45	12.29-20.14	-0.51 (0.51)	-0.70 (1.0)
Light (hour/day)		3.53	3.19	2.44	0.41-9.08	0.47 (0.51)	-0.38 (1.0)
Moderate (hour/day)		3.83	3.29	1.86	1.00-8.10	0.81 (0.51)	0.097 (0.99)
Heavy (hour/day)		0.22	0	0.13	0-0.22	2.94	8.88

Table 4.35 Statistical parameters of activity time for adult children aged between 2-10 years

* The data could not be evaluated due to limited data

Children (10-18 years)	Distribution [*]	Mean	Median	Std Dev	Min-Max	Skewness (std error)	Kurtosis (std error)
Body weight (kg)		51.50	52.50	9.73	39-72	0.71 (0.64)	0.42 (1.23)
Resting (hour/day)		13.18	13.51	1.72	9.82-15.65	-0.45 (0.64)	-0.32 (1.23)
Light (hour/day)		7.94	7.97	1.50	5.25-9.83	-0.43 (0.64)	-1.03 (1.23)
Moderate (hour/day)		1.97	1.64	1.28	0.26-4.57	0.78 (0.64)	0.01 (1.23)
Heavy (hour/day)		0.82	0.00	1.39	0-4.29	1.74	2.60

Table 4.36 Statistical parameters of activity time for adult children aged between 10-18 years

^{*} The data could not be evaluated due to limited data

	Number	Distribution	Moon	Madian	Std Dev	Min may	Skewness
	Number	Distribution	wear	weatan	Stu Dev	wiin-max	(std error)
Adult male	72	Normal	30.14	28.47	8.43	13.03-48.81	0.357 (0.283)
Adult female	93	Log Normal	15.73	14.66	4.4	7.78-34.37	1.34 (0.250)
Child aged between 2 to 10	20	Normal	17.43	27.56	9.94	8.43-48.81	0.719 (0.512)
Child aged between 10 to 18	12	Log Normal	22.71	21.09	6.2	16.62-40.53	2.416 (0.637)

Table 4.37 Descriptive statistical parameters of Inhalation volume (m³)

Table 4.38 Percent distribution of Inhalation volume (m³)

	10%	20%	30%	40%	50%	60%	70%	80%	90%
Adult male	19.26	23.40	25.40	27.00	28.47	31.15	34.68	38.32	42.33
Adult female	11.34	12.05	13.17	13.84	14.66	16.18	17.39	19.13	20.98
Child aged between 2 to 10	14.11	15.13	15.73	16.30	16.82	17.54	18.93	20.56	20.92
Child aged between 10 to 18	17.10	18.49	19.62	20.66	21.09	22.16	23.73	24.73	36.13

One-way Anova was used to determine the differences between subgroups. Levene test was not achieved in the pre-request of the Anova test. Kruskal-Wallis Test was applied to test the null hypothesis that all subgroups had identical distribution functions against the alternative hypothesis that at least two of the subgroups differed only with respect to location (median). Hence all the data represented in the Table 4.39 were evaluated for the difference between subgroups by Kruskal-Wallis non-parametric test. The data were analyzed using the Statistical Package for the Social Sciences (SPSS Inc., Chicago. III. USA. Version 17). Statistical comparisons were considered statistically different if $p \le 0.05$. The mean and median values for each variable according to the location of the participant are given in Table 4.39. The variables for which the difference is statistically significant were time spent at work and outdoors, ventilation time, time spent on resting and light. People living in Nilüfer ventilate their dwellings more, spend more time outside and rest more compared to the other districts. The reason for this is that the participants living in Nilüfer is mostly retired people. Those participants living in Osmangazi, on the other hand, spend more time at work, which is possibly because these participants have more regular jobs.

Table 4.39 Results of Kruskal-Wallis Tests on subgroups

	Distributio n	Yıld	irim	Osma	angazi	Nilù	lfer	р
		Mean	Median	Mean	Median	Mean	Median	
Body Weight (kg)	Beta	62.19	67	64.5	69	67.39	70	0.378
Age	normal	33.72	35	34.66	34	39.35	41	0.365
in Home	Log normal	14.11	13.64	14.6	14.04	13.92	13.71	0.515
in work	Log normal	5.1	5.71	4.11	5.71	4.03	5.2	0.00
indoor (hours/day)	Beta	20.66	21.15	20.46	20.99	19.87	20.14	0.513
Outdoor (hours/day)	Gamma	3.35	2.8	3.54	3.02	4.14	3.97	0.02
Transport (min/day)	Log normal	76.88	55.71	77.93	65	100.95	72.86	0.245
Cafe/Restaurant (min/day)	Gamma	0.85	0	0.84	0	0.98	0	0.879

	Distribution	Yıldırım	Osmangazi	Nilüfer	р			
		Mean	Median	Mean	Median	Mean	Median	
ETS indoor (min/day)	Weibull	269.74	98.57	192.56	16.07	178.77	0	0.109
ETS in vehicle (min/day)	Chi Sqr	8.95	0	4.56	0	19.97	0	0.549
Ventilation (min/hour)	Weibull	206.56	171.43	224.24	218.57	275.52	260	0.015
Resting (hour/day)	Beta	12.43	11.78	12.65	12.29	12.96	12.38	0.035
Light (hour/day)	Beta	7.85	8.88	7.7	8.32	6.97	7.17	0.020
Moderate (hour/day)	Cauchy	1.92	1.46	1.93	1.86	2.29	1.92	0.244
Heavy (hour/day)	Gumbal max	1.81	1.01	1.65	1	1.67	1.42	0.662

Table 4.39 Results of Kruskal Wallis Tests on subgroups (Continued)

4.3.3 Exposure Assessment

A person's average daily exposure dose is determined from a combination of variables including the pollutant concentration, inhalation volume and body weight. In this study, even if time spent in different microenvironments was evaluated, personal exposure was calculated by combining ambient air concentration and individual inhalation volume. Inhalation volume was calculated for each participant in the previous section.

Risk for adverse human health effects was calculated by taking chemical carcinogenity characteristics into account. Both the lifetime carcinogenic risk and the noncarcinogenic risk (hazard index) were calculated for inhalation pathways for 16 VOC. For example, benzene, 1,3 butadiene and bromoform, grouped in A and B, are known to be carcinogenic. The slope factor values are available in iris web site for these two compounds. Other VOC represented in Table 2.3 have reference concentration (Rfc) or reference dose (Rfd) value. Rfc was compared with average concentration at each point and Rfd was evaluated with daily intake rate to obtain HR value.

To estimate health effects for VOC with carcinogenic/noncarcinogenic potential, first the average dose that a person receives in units of microgram per individual kg body weight was examined. The input variables used for deterministic approach and probabilistic approach were evaluated for the following section.

4.3.3.1 Input Variable

i. VOC Data

All VOC concentrations except for BTEX and inorganic pollutants could not be detected at each sampling point due to their as they were below the detection limit. Such data sets are referred to as "censored" (Frey and Zhao, 2004). Censored technique have to be handled specially in order to obtain a

concentration value for each individual sample, to equate the sample sizes of all VOC data sets for comparison purposes, and to avoid overestimation of exposure and risk (USEPA, 2009).

Two general approaches may be used in the statistical analysis of data that contain nondetect values: 1) The nondetect values may be replaced using one of a variety of replacement methods, or 2) statistical techniques may be employed which can handle nondetect data (Wendellberg and Campbell, 1994). The most often used replacement methods include ignoring the non-detected values, replacing non-detected values with zero, replacing non-detected values with the detection limit (DL) or replacing non-detected values with one-half of the detection limit (Frey and Zhao, 2004). In this study, data with VOC concentrations below the respective DL were replaced with $0.5 \times DL$ prior to application goodness-of-fit tests. This approach was also used for apportioning sources of VOC and inorganic pollutants in Bursa.

The second step of exposure assessment is to determine the probability distribution of each input variable. The variables consist of VOC concentrations, body weight and inhalation volume of each participant. These variables were evaluated to obtain the best fitted distribution by using goodness-of-fit tests, namely the chi-square test, Kolmogorov-Smirnov test, and Anderson-Darling test including lognormal, Weibull, normal distributions, Beta, Gama, and Uniform distribution. These parametric and nonparametric tests are used to assess how well it fits a set of observations by summarizing the difference between observed frequencies and the theoretical expected frequencies. The probability distribution was plotted for each VOC concentration. Figure 4.33 gives an example of probability distribution of benzene measured in winter season. The probability distributions of the data were used to input variables for Monte Carlo simulation. Environmental data commonly exhibit probability distributions that are non-negative and skewed with heavy or long right tails (USEPA, 2000). Table 4.40 shows the distributions giving strong fits to data for each input variable and their parameters. These probability distributions of input variables were used as input in Monte Carlo simulation.

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Figure 4.33 Probability distribution of benzene concentration

Input variable	Winter/	Distribution	Parameter-	Parameter-	Parameter-
	Summer		1 ^a	2 ^b	3 ^c
Daily intake		Log Normal	21.55	8.85	-
Body Weight		Beta	3.68	3.05	119
Benzene	W	Log Normal	9.03	3.95	
	S	Log Normal	3.21	3.98	
Toluene	W	Log Normal	60.62	18.47	
	S	Log Normal	33.44	22.43	
1.4 DiCl	W	Log Normal	0.39	0.72	
benzene	S	Student t	0.15	0.09	7.25
Ethylbenzene	W	Extreme	3.37	2.09	
		value			
	S	Log Normal	5.91	5.16	
Hexane	W	Log Normal	1.11	1.21	
	S	Gamma	0.0	1.02	0.41

Table 4.40 Frequency distributions of input parameters used in Monte Carlo Simulation

Input variable	Winter/	Distribution	Parameter-	Parameter-	Parameter-
	Summer		1 ^a	2 ^b	3 ^c
Naphthalene	W	Log Normal	0.52	1.03	
	S	Log Normal	0.21	0.39	
Styrene	W	Log Normal	33.24	26.29	
	S	Log Normal	0.64	1.15	
o-xylene	W	Log Normal	6.09	17.63	
	S	Log Normal	2.47	2.50	
1,3 Butadiene	W	Log Normal	0.39	0.25	
	S	Log Normal	0.08	0.04	
Isopropyl	W	Log Normal	9.03	3.95	
benzene	S	Normal	0.28	0.18	
Chlorobenzene	W	Log Normal	0.77	0.78	
	S	Log Normal	0.42	0.52	
Tetrachloroeth	W	Extreme			
ylene		Value	0.20	0.12	
	S	Gamma	0.04	0.07	3.94
Bromoform	W	Log Normal	1.63	1.03	
	S	Max Extreme	0.62	0.72	
1.1.2-	W	Log Normal	NA		
Trichloroethan	S	Log Normal	NA		
P					

Table 4.40 Frequency distributions of input parameters used in Monte Carlo Simulation (*Continued*)

^a mean for normal and log-normal distribution. location for gamma distribution. alpha for beta distribution. mid-point for student t test. likeliest for max extreme

^b standard deviation for normal and log-normal distribution. scale for gamma. student t test and max extreme distribution. beta for beta distribution. midpoint for student t test. likeliest for max extreme

^c shape for gamma distribution. scale for beta and max extreme distribution. degree of freedom for student t test

NA: no data available

ii. Body Weight

Body weight data of each participant were obtained from the descriptive questionnaire. The frequency distribution of body weight is presented in Figure 4.34. Forty-three percent of the participants had body weights between 50 and 70 kg while 36% of people had body weights ranged from 70 to 90 kg. The body weight percentage of the rest of the participants was between 10 and 50 kg and 90 and 116 kg were 16% and 5%, respectively.



Figure 4.34 Frequency distribution graph of body weight

The descriptive statistics of body weight for all participants and for adult men, adult women and children are given in Table 4.41. The median and mean body weights were found to be 80.3 kg and 80 kg for adult men and 65 for adult women, respectively. Same values were 51.5 and 52.5 for children and 18.1 and 16.5 for early children, respectively. USEPA (2009) suggested the average body weight value as 70 kg for adults.

	Distribution	Mean	Median	Std Dev	Min-Max	Skewness	Kurtosis
						(std error)	(std error)
All participants	Beta	65.0	70.0	21 75	10-116	Skewness Kurtosis (std error) (std error) -0.755 0.463 (0.173) (0.345) 0.20 (0.28) 0.22 (0.56) 0.18 (0.25) -0.43 (0.50) 0.43 (0.51) -1.06 (1.0) 0.71 (0.64) 0.42 (1.23)	0.463
	Deta	00.0	70.0	21.75	10-110	(0.173)	(0.345)
Adult men	Beta	80.3	80	12.39	54-116	0.20 (0.28)	0.22 (0.56)
Adult women	Beta	65.0	65	12	40-95	0.18 (0.25)	-0.43 (0.50)
Children		10 1	14 50	E 20	11 0 29 0	0.42 (0.51)	1.06 (1.0)
(2-10 years)		10.1	10.50	5.20	11.0-28.0	0.43 (0.51)	-1.08 (1.0)
Children		51 5	E2 E0	0 72	20 72	0.71 (0.64)	0 40 (1 02)
(10-18 years)		51.5	52.50	7.73	37-12	0.71 (0.04)	0.42 (1.23)

Table 4.41 Descriptive statistics of body weight for all subgroups

The mean and median body weights reported by the study conducted in Turkey were 58 and 60 kg for female and 74.5 (Kavcar et al.. 2006). The body weights calculated in this study were found to be less than our results. Hence. although the results are also related to the number of participants. different demographic results are obtained in different parts of Turkey.

The probability distribution of body weight for all participants was represented in Figure 4.35. The body weight data were fit by a beta distribution. with alfa=3.68. beta=3.05 and scale=119 parameters.



Figure 4.35 Probability distribution for body weight

iii. Inhalation Volume

The inhalation volume for each participant was calculated by multiplying the time spent on each activity presented in Table 4.32 through Table 4.36 with human inhalation rates given in Table 4.31 and results are given in Table 4.37. The frequency distribution of inhalation volume is presented in Figure 4.36. The standard inhalation volume recommended by the USEPA (2009) was 20 m³ day⁻¹ for adults. According to the questionnaire applied in Bursa

and the mean inhalation volumes given in Table 4.37 were 30, 16, 17 and 23 m^3 for males, females, early children and children, respectively. If the inhalation volume was assumed to be 20 m^3 for Bursa population, the exposure and risk would have been overestimated for males and early children and underestimated for males and children.

In order to estimate the exposure probabilistically. the probability distribution was fitted for average daily inhalation volume to be used as an input distribution in Monte Carlo simulation. which is given in Figure 4.37. The probability distribution of daily inhalation volumes for adult men. adult women. early children and children were also determined to estimate the exposure and health risk.



Figure 4.36 Frequency distribution for average daily inhalation volume



Figure 4.37 Probability distribution for daily inhalation volume for all participants

iv. Monte Carlo Simulation

Traditional deterministic (point) estimates were used to calculate the health risk, which combined the measured VOC with the population that filled the questionnaire. However, this method relies on data collected from the selected population. The second step of the study, VOC concentrations produced in the field measurement campaigns and the data collected from the questionnaire were extrapolated to the entire population using Monte Carlo simulation. The commercially available software package Crystal Ball (Version 4.0) was used for this purpose. The uncertainty and variability of the parameters throughout the calculation of the risk are propagated in the Crystal Ball software (Schuhmacher et al... 2001).

In the simulation, each of the input variables was defined as probability distribution function by using goodness-of-fit test. The Monte Carlo simulation calculates the risk several thousand times by drawing parameter values randomly from the distribution function of the input variables (Thompson et al. 1992). The final result was obtained as distribution of the risk with corresponding probabilities. Finally, the distributions can be plotted and

various statistical features of the results were generated to help interpret data. 10 000 iterations were used in this study

Variations in mean and median exposure results for benzene are given in Figure 4.38 for d,fferent iterations. The result did not change significantly when iterations > 10 000. Hence the trial number of 10 000 was selected for this study to obtain reliable results and also to save time.



Figure 4.38 Monte Carlo results of benzene exposure value for different simulation numbers

The risks obtained from Monte Carlo simulation are described by probability distribution instead of a point estimate. The probability results are identified by a percentile value in order to use a risk distribution for decision making. The percentiles from 90th to 99.9th of the risk distribution are recommended by USEPA (2009) as the reasonable maximum exposure range for decision

making in probabilistic risk assessment. Selection of a single point within the reasonable maximum exposure range generally requires consideration of the level of uncertainty in the risk distribution. USEPA (2009) recommends that the 95th percentile of the risk distribution be used as a starting point for risk management decisions in the absence of site-specific information. This is because the risks estimated in the literature which were used to compare our findings were generally represented with mean or median value (Wallace et al., 1991; Pratt et al. 2000; Morello-Frossch et al., 2000 and Ohura et al., 2006). In this study, probabilistic risk was also shown by the mean and median value. Hence, the results obtained in this study are comparable with the risk values reported in literature. The probabilistic estimation results were also given as 90th and 95th percentile of risk distribution).

4.3.3.2 Deterministic Exposure Assessment

Individual exposure to each VOC was calculated using eq 4-1 and by combining the inhalation volume and body weight of the participants. It was assumed that all participants were exposed to VOC concentrations at each point. Descriptive statistics of VOC for all participants in winter and summer seasons are given in Table 4.42 and

Table 4.43, respectively. Furthermore, the 25th and 75th percentile ranges and outliers are illustrated in Figure 4.39. Three VOCs with the highest VOC exposure were benzene, toluene and styrene due to their high concentration.

The box plot shows the 25th percentile, median and 75th percentile of the exposure. The left and right lines indicate 10th and 90th percentiles, and the square symbols represent the 5th and 95th percentiles. The asterisks show the outliers.

Compound [*]	Mean	Median	Std Dev	min	max	90 th %	95 th %
Benzene	3.55	2.58	2.46	1.11	17.18	6.2	9.46
1,3 Butadiene	0.15	0.1	0.11	0.05	0.74	0.27	0.41
Toluene	12.08	8.08	8.38	3.79	58.52	21.11	32.22
1,4 DiCl benzene	0.35	0.06	0.24	0.11	1.69	0.61	0.93
Ethylbenzene	1.89	1.23	1.31	0.59	9.17	3.31	5.05
Hexane	0.43	0.23	0.30	0.13	2.07	0.75	1.14
Naphthalene	0.18	0.08	0.12	0.06	0.86	0.31	0.47
Styrene	13.33	7.72	9.26	4.18	64.61	23.3	35.57
o Xylene	7.04	0.53	4.89	2.21	34.14	12.31	18.79
Isopropyl benzene	0.27	0.13	0.19	0.08	1.31	0.47	0.72
Chlorobenzne	0.27	0.18	0.19	0.08	1.3	0.47	0.71
TetraChloroEthylene	0.11	0.08	0.07	0.03	0.51	0.19	0.28
Bromoform	0.64	0.49	0.45	0.2	3.11	1.12	1.71

Table 4.42 Descriptive statistics of VOC exposure for all points and all participants (µg day⁻¹ kg⁻¹) in winter. deterministic approach

* Number of sampling points=69 and number of participants=197

Compound [*]	Mean	Median	Std Dev	min	max	90 th %	95 th %
Benzene	1.31	0.68	0.91	0.41	6.37	2.30	3.51
1,3 Butadiene	0.03	0.02	0.02	0.01	0.15	0.05	0.08
Toluene	13.11	9.01	9.1	4.11	63.55	22.92	34.98
1,4 di cl benzene	0.06	0.05	0.04	0.02	0.29	0.11	0.16
Ethylbenzene	2.35	1.48	1.63	0.74	11.4	4.11	6.28
Hexane	1.25	0.26	0.86	0.39	6.04	2.18	3.32
Naphthalene	0.08	0.04	0.05	0.02	0.36	0.13	0.2
Styrene	0.24	0.09	0.17	0.08	1.18	0.43	0.65
o Xylene	1.02	0.58	0.71	0.32	4.94	1.78	2.72
Isopropyl benzene	0.11	0.08	0.08	0.03	0.52	0.19	0.29
Chlorobenzne	0.16	0.09	0.11	0.05	0.8	0.29	0.44
TetraChloroEthylene	0.09	0.07	0.06	0.03	0.44	0.16	0.24
Bromoform	0.44	0.28	0.31	0.14	2.15	0.78	1.19
1,1,2-Trichloroethane	No data						

Table 4.43 Descriptive statistic of VOC exposure for all points and all participants (µg day⁻¹ kg⁻¹) in summer season

* Number of sampling points=69 and number of participants=197



Figure 4.39 Box and Whisker graph form VOC exposure for winter and summer season

4.3.3.3 Probabilistic Exposure Assessment

The deterministic approach does not clearly characterize associated variability or uncertainty. However, probabilistic approaches can characterize variability in risk as they use different points on each input distribution for exposure. The probabilistic assessment was conducted using Monte Carlo analysis to describe by a probability distribution instead of a point estimate. The result was obtained as distribution of the risk with corresponding probabilities. The mean, median, standard deviation of distribution, minimum and worst-case (maximum) value and 90% and 95% were presented in Table 4.44 and Table 4.45 for winter and summer in order to analyze the results. The results of the simulation were illustrated in Figure 4.40.for benzene exposure as an example. The best fitting distributions for other compounds were determined to be used as an input probability distribution for cancer and hazard ratio calculation.

Results obtained from deterministic and probabilistic approaches were in general agreement. For benzene, 1.3 butadiene, toluene, ethyl benzene, hexane. naphthalene, styrene, isopropylbenzene, chloronbenzene, tetrachloroethylene and bromoforom, the median, mean, the 90th percentile and the 95th percentile exposure values were almost equal in winter season. For 1,4 DiCl benzene and o-xylene, the probabilistic approach resulted in slightly higher estimates for median and mean, the 90th percentile and the 95th percentile exposure in winter season. The median, mean, the 90th percentile and the 95th percentile exposure values for all compounds were almost equal in summer season. The minimum, maximum values and also standard deviations of all compounds obtained from the probabilistic approach were higher than those obtained from the deterministic approach. The reason is that the probability distribution input variables had right skewed and covered a wider range from the actual data used in the deterministic approach (e.g. \pm infinity).

Compound	Mean	Median	Std Dev	min	max	90 th	95 th
Compound	Iviean				шах	perct.	perct.
Benzene	3.49	2.63	3.19	0.27	82.59	6.65	8.78
1,3 Butadiene	0.15	0.11	0.16	0.01	2.70	0.30	0.41
Toluene	11.79	8.09	13.56	0.65	286.52	23.16	32.19
1,4 di cl benzene	0.15	0.06	0.42	0.00	15.43	0.32	0.54
Ethylbenzene	1.79	1.31	1.76	0.00	47.24	3.60	4.90
Hexane	0.43	0.25	0.57	0.00	10.83	0.99	1.39
Naphthalene	0.20	0.08	0.68	0.00	54.06	0.45	0.96
Styrene	9.92	7.64	9.07	0.00	135.11	19.68	25.62
o Xylene	1.95	0.63	4.40	0.00	106.26	4.48	8.04
Isopropyl benzene	0.27	0.14	0.49	0.00	17.99	0.59	0.92
Chlorobenzne	0.30	0.18	0.40	0.00	7.68	0.63	0.92
TetraChloroEthylene	0.10	0.08	0.10	0.00	1.47	0.21	0.28
Bromoform	0.63	0.44	0.73	0.00	19.13	2.33	2.58

Table 4.44 Descriptive Statistics for Probabilistic Exposure (µg day⁻¹ kg⁻¹) for all points in winter season

Compound	Moon	Modian	Std Dov	min	min max	90 th perct.	95 th
compound	wear	Weulan	Stu Dev				perct.
Benzene	1.31	0.72	2.05	0.06	44.03	2.67	4.15
1.3 Butadiene	0.03	0.02	0.09	0.00	5.19	0.05	0.08
Toluene	13.78	9.04	40.04	0.03	3675	27.69	38.87
1,4 di cl benzene	0.07	0.05	0.08	0.00	1.97	0.14	0.19
Ethylbenzene	2.42	1.45	3.31	0.09	66.17	5.09	7.35
Hexane	1.53	0.08	6.44	0.00	245.28	2.94	6.94
Naphthalene	0.08	0.05	0.10	0.00	1.61	0.17	0.24
Styrene	0.26	0.10	0.60	0.00	18.75	0.58	0.96
o Xylene	0.98	0.56	1.41	0.00	25.47	2.16	3.19
Isopropyl benzene	0.12	0.09	0.12	0.00	3.19	0.25	0.33
Chlorobenzne	0.17	0.09	0.29	0.00	8.70	0.38	0.58
TetraChloroEthylene	0.09	0.07	0.15	0.00	8.00	0.19	0.26
Bromoform	0.48	0.31	1.01	0.00	82.75	1.06	1.43

Table 4.45 Descriptive Statistics for Probabilistic Exposure (µg day⁻¹ kg⁻¹)for all points in summer season



Figure 4.40 Probability distribution of benzene exposure

4.3.4 Carcinogenic Risk

The cancer risk due to continuous lifetime exposures to carcinogenic compounds was calculated by multiplying slope factor with individual daily intake rate using equation 2.16 for each participant. Cancer risks could be calculated for benzene. bromoforom and 1,3 butadiene since SFs are available only for these VOCs at USEPA. IRIS (2009) as discussed in Section 2.5.1. Hence VOC compounds without slope factor values were not included in the risk assessment process.

4.3.4.1 Deterministic Estimation of Cancer Risk

The results of the deterministic approach represented in Table 4.46 depict the median and mean carcinogenic and non carcinogenic risks estimates with the standard deviation, minimum, maximum, the 90th percentile and the 95th percentile values. Benzene cancer risk value ranged from 14×10^6 to 300×10^{-6} . Bromoform cancer risk varied between 1.1×10^6 and 200×10^{-6} . The cancer risk values for all pollutants exceeded the health benchmark values at all sites for summer and winter seasons. The USEPA estimated the life time cancer risk for a 70-kg adult with 20 m³ h⁻¹ inhalation rate and exposed to 1 µg m⁻³ to be between 1.54×10^{-5} and 4.45×10^{-5} . The benzene median and mean concentrations measured in the current study were 2.5 and 4.3 µg m⁻³. This can be interpreted as the high cancer risk posed by benzene concentration for the population of Bursa.

Estimated individual lifetime cancer risks were compared with the acceptable risk level of 10^{-6} stated by USEPA (2009). All the statistical parameters used to represent cancer risks for three compounds exceeded the stated level. Benzene had the highest adverse health effect among three compounds according to the USEPA specification. The mean cancer risk was the highest for benzene ($3x10^{-4}$) in the industrial area. The mean cancer risk of benzene (1.2×10^{-4} and 4.5×10^{-5} for winter and summer) exceeded the $1x10^{-6}$ risk level by more than a factor of 120 and 45 times respectively. Benzene posed also the highest cancer risk as estimated by other studies (Wu et al... 2009;

Morella- Frisch et al., 2000). 1.3 butane $(1.61 \times 10^{-5} \text{ and } 3.3 \times 10^{-6})$ mean cancer risks also exceeded acceptable risk levels by over 15 and 3 times while bromoform $(1.61 \times 10^{-5} \text{ and } 3.4 \times 10^{-6})$ exceeded it over 3 times. 1.3 butadiene cancer risk estimated for this study was lower than the result $(3.83 \times 10^{-5} \text{ for summer})$ calculated by Tam and Neumann (2004).

Direct comparisons with other studies of VOC are difficult because different studies include different compounds and risk estimates are not always based on ambient measurement. There were limited studies conducted to assess health risk based on ambient air measurement. Some risk assessment studies were based on modeled data result. Morella- Frosch et al. (2000) estimated the air toxic levels for modeled outdoor 188 HAP modeled from USEPA Cumulative Exposure Project in California for the base year 1990. These air toxics concentrations were used with chronic toxicity data to estimate cancer and noncancer hazards for individual HAPs and the risks posed by multiple pollutants. According to the study, while 1.3 butadiene had concentration posing a potential cancer risk of 10⁻⁵ or greater in at least 75% of census tracts, benzene also had a median concentration exceeding 10⁻⁵ estimated cancer risk.

4.3.4.2 Probabilistic Estimation of Cancer Risk

The cancer risk was calculated ten thousands each time by drawing a value of the parameter randomly from the distribution function. Final result obtained from Monte Carlo simulation was distribution of the risk with corresponding probabilities. Mean, median, standard deviation, percentiles of 90% and 95%, minimum and maximum values were extracted from model and presented in Table 4.47.

The statistic parameters of carcinogenic risk resulted from Monte Carlo simulation were very close to those estimated by deterministic approach. For benzene and bromoform, probabilistic approach resulted in a higher maximum value and a lower min value. Similar results were also found for exposure results. Since the results from probabilistic risk assessment was only briefly discussed in the literature (Sander and Öberg. 2006), the health assessment results obtained from probabilistic approach could not be compared with the literature.

Compound	Mean	Median	Std Dev	min	max	90 th perct.	95 th perct.
winter							
Benzene	120	110	60	40	300	200	230
Bromoform	4.9	3.6	3.4	1.5	240	8.5	13
1,3 Butadiene	16.1	13.2	11.1	5.2	80.6	29.1	44.2
summer							
Benzene	45	24	32	14	220	80	120
Broform	3.4	2.1	2.4	1.1	16	5.9	9
1,3 Butadiene	3.3	2.1	2.3	1	16	5.7	8.8

Table 4.46 Cancer risk for summer and winter season deterministic approach (x10⁻⁶)

Compound	Mean	Median	Std Dev	min	max	90 th %	95 th %
winter							
Benzene	130	90	120	6	3200	250	330
Bromoform	5.1	3.6	5.4	0.013	120	0.11	0.11
1,3 Butadiene	2.3	2.2	0.9	0.2	8.7	4.1	4.1
summer							
Benzene	45	25	83	2.1	3300	92	140
Broform	3.9	2.5	5.3	0.0009	185	8.4	11.5
1,3 Butadiene	2.3	2.1	0.9	0.1	10.3	3.5	4

Table 4.47 Descriptive Statistics for Probabilistic Carcinogenic Risk Assessment (x10⁻⁶)



Figure 4.41 Carcinogenic benzene risk obtained from Monte Carlo Simulation $(x10^{-6})$

Figure 4.41 depicts the probability distribution graphs obtained from Monte Carlo simulation. The probability distributions obtained from the probabilistic approach were similar to those plotted for exposure plot given previously in Figure 4.40. Cancer risk is estimated by multiplying the slope factor for each compound by exposure; thus both cancer risk and exposure probability distribution graphs fit the same distribution.

4.3.4.3 Cumulative Carcinogenic Risk

The lifetime cancer risk of compounds were assumed to be additive. Hence the individual cancer risk of each compounds were summed to estimate the total cancer risk for winter and summer. Cumulative cancer risk for different seasons are given in Table 4.48 and also shown graphically in Figure 4.42. Among, benzene, 1,3-butadiene and bromoform, benzene had the highest contribution to the cancer risk. Relative contributions of these three compounds to cancer risk in summer and winter seasons were similar.
Compoun	Mean	Media	Std	min	max	90 th	95 th
d		n	Dev			%	%
Winter	139	127	69	46	620	238	287
Summer	52	28	35	16	251	91	137
Average	96	78	52	31	436	165	212

Table 4.48 Cumulative cancer risks (x10⁻⁶)



Figure 4.42 The cumulative cancer risk in summer and winter (x10⁻⁶)

The cumulative lifetime cancer risk was calculated for three compounds in this study since the cancer slope factor data in USEPA, iris (2009) were available only for benzene, 1,3-butadiene and bromoform. It is not possible to compare lifetime cancer risk values found in this study, because generally different number of compounds are used to calculate lifetime cancer risk in other studies.

To give an idea about the cancer risk levels of the cities in the world, some studies were evaluated. Pratt et al, (2000) estimated that the cancer risks of 16 pollutants ranged between 47×10^{-6} and 1.10×10^{-4} as a result of 25 air

monitoring sites in Minnesota. Similarly, Tam and Neumann. (2004). utilizing measurements at five air monitoring sites in Portland, OR. calculated the cancer risks for 43 HAPs. They showed that 17 HAPs exceeded the cancer risk level of 1×10^{-6} at all sites, with carbon tetrachloride, 1.3-butadiene, formaldehyde and 1.1.2.2-tetrachloroethane contributing 50% of the total lifetime cancer risks (2.47x10⁻⁴).

The overall risk value due to 85 HAP was estimated at 1.18×10^{-4} in NATA study in 1999 at the census tract of the Beacon Hill site. Compared to the risk estimates based on the measured ambient concentrations of 19 species in other cities (Los Angeles. CA: 100×10^{-6} ; New York City. NY: 130×10^{-6}), the overall risk in this study was a little lower than theirs (Sax et al., 2006). Wu and co-workers forecast the overall cancer risk value as 60.9×10^{-6} .

Besides, Woodruff et al. (2000) yielded a median cancer risk estimate of 1.8×10^{-4} across all of the United States whereas median risks in California were found to be 2.7×10^{-4} (Morello-Frosch et al. 2000). These studies were both based on modeled ambient concentrations.

Ohura and co-workers (2006) estimated lifetime cancer risk through exposure of eight VOCs in Shizuoka. Japan and stated that the cumulative cancer risk value was 6.1x10⁻⁵ and 8.0x10⁻⁵ for summer and winter. They found that the predominant risks were due to benzene, carbon tetrachloride, formaldehyde, and acetaldehyde in both seasons, which accounted for 96% of the cancer risk for summer and 94% for winter.

4.3.4.4 Spatial Distribution of Carcinogenic Risk

In this study we had an advantage due to sampling methodology used. Distribution of the risk over the city can also be assessed. The spatial distribution of benzene, bromoform and butadiene had almost the same trend. The risks were distributed along the major roads and industrial areas and decreased with distance from there. Hence, the spatial distribution map of cumulative cancer risk for winter and summer is given in Figure 4.43. The

cumulative cancer risk data were interpolated using GIS software. Vertical Mapper V.3 of Map Info with natural neighborhood technique to obtain risk distribution map over the city. The ratios of maximum to minimum lifetime cumulative cancer risk values observed in winter and summer were 13.5 and 15.7 respectively. The high cumulative cancer risks are indicated in dark red. As shown in Figure 4.43, high-risk areas for cumulative carcinogenic VOCs are generally distributed around Bursa, Demirtaş and Gürsu organized industrial districts and around major roads. The cancer risk in these areas can be as high as 250x10⁻⁶. The minimum risk which appears as the background and applies to whole city is approximately 100x10⁻⁶.

Risk distribution patterns observed in summer and winter are slightly different. This is probably due prevailing wind direction during winter sampling. In winter, high risk areas lies to the east of sources (industrial areas and roads) due to easterly winds that were prevailing in that wind. However, during summer high risk areas are more centered on the sources, due to calm conditions during summer sampling.

Another interesting point that should be noted is that, although the concentrations of benzene, 1,3-butadiene and bromoform are higher in winter season; the highest risk areas have about the same cancer risk in both seasons. This is due to the fact that these maximum risk areas occur around industrial areas and there is not much summer – winter difference in such close proximity to industrial areas.

Consequently, the spatial distribution of risk indicated that industrial and vehicle emissions are the of principal sources of human exposure to benzene, bromoform and 1,3 butadiene. And highest risk areas are in the proximity of industrial emissions.



Figure 4.43 Spatial distribution of cumulative cancer risk for a) summer and b) winter (x10⁻⁶)

4.3.4.5 Sectoral-Based Cancer

The lifetime cancer risk estimates were disaggregated by source category in order to assess whether health risk patterns differ depending on the type of emission source. The data was represented with Box and Whisker method given in Figure 4.44. The red colour indicates cancer risk for summer season, blue colours shows that of winter summer. The sectoral statistical parameters for benzene, bromoform and 1.3 butadiene were also given the Table 4.49.

		winter			summer	
Compound	Mean	Median	95 th	Mean	Median	95 th
			perct.			perct.
benzene						
Industry	110	78	296	47	23	172
Road	142	108	355	88	47	284
Urban	139	106	347	29	22	77
Background	72	46	194	17	14	44
bromoform						
Industry	6.7	4.6	19	5.9	4.4	17
Road	4.8	3.8	12	2.5	1.9	7.6
Urban	3.3	2.4	9.5	1.4	1.1	4.2
Background	2	1.6	5.5	1	0.5	3.4
1.3 butadiene						
Industry	10	7.7	26	3	2	9
Road	26	19	66	5	4	13
Urban	22	16	56	3	2	7
Background	7	5	18	2	2	5

Table 4.49 The statistical parameters for life time cancer risks for winter and summer ($\times 10^{-6}$)



Figure 4.44 Cancer risks of benzene. bromoform and butadiene for industrial. background. urban and road area in summer and winter

The sectoral risk values ranged from 1×10^{-6} , which was estimated in background area to 1.42×10^{-4} , which was calculated in road site points. All sectoral areas gave a sum of cancer risks higher than 1×10^{-6} even at background sites. The highest cancer risks for benzene and 1,3 butadiene were calculated in road sites both summer and winter. The lifetime cancer risk posed by bromoform was not dramatically different between road, urban and industrial areas. The NATA, study estimated cancer risk of 23×10^{-6} for the background concentration of HAPs in the Beson Hill area, which is comparable

to our estimate (50x10⁻⁶). The lifetime cancer risk posed by benzene and 1,3 butadiene was mainly caused by mobile sources while the sources of cancer risk due to bromoform were in industrial areas and by mobile sources.

Lifetime cancer risk associated with inhalation of VOCs was estimated by multiplying the exposures obtained from equation 2.15 by the slope factor of each compound as given in Table 2.3. In the same way, hazard index value was calculated by dividing concentration or contamination intake by RfC or Rfd value given in Table 2.3. Hence, the slope factor, RfC or RFD value was used to calculate same value for each compound. It was also assumed that all the participants were exposed to air at each point. Finally, the seasonal difference of risk or hazard index value for each compound. Since the seasonal difference of VOC compounds were evaluated in the literature section, it was not evaluated in this section.

4.3.5 Noncarcinogenic Risk

4.3.5.1 Deterministic Estimation of HQ

To estimate noncarcinogenic risk. the hazard ratio was calculated for each VOC using equation 2.18. Individual exposures were divided by the corresponding reference doses and the statistics of the calculated HQ values were obtained as given in Table 4.50 and

Table 4.51.

VOC with a hazard ratio above 1.0 are evaluated as a potential human health concern or need for further study. The hazard ratio was calculated for 13 VOCs in this study. Although life time cancer risk was estimated at ten or thousand times higher than the acceptable cancer limit value. the noncancer hazard index was forecast lower than 1 except few points. The same results were found in the literature. Pratt et al. (2000) found that the noncancer

Compound	Mean	Median	Std Dev	min	max	90 th perct.	95 th perct.
Benzene	0.301	0.269	0.133	0.102	0.728	0.48	0.551
1,3 Butadiene	0.195	0.16	0.116	0.035	0.561	0.35	0.454
Toluene	0.006	0.005	0.004	1.4 x10 ⁻³	0.024	0.01	0.013
1,4 di cl benzene	0.001	0.0002	0.006	5.9x10 ⁻⁶	0.048	0.001	0.001
Ethylbenzene	0.005	0.004	0.006	4.2 x10 ⁻⁴	0.052	0.007	0.009
Hexane	0.002	0.001	0.001	0.2 x10 ⁻⁶	0.008	0.003	0.004
Naphthalene	0.15	0.084	0.217	1.5 x10 ⁻³	1.544	0.355	0.45
Styrene	0.034	0.024	0.035	6.3 x10 ⁻⁶	0.257	0.055	0.081
o Xylene	0.179	0.017	0.878	0.3 x10 ⁻⁶	5.71	0.049	0.193
Isopropyl benzene	0.002	0.001	0.003	8.3 x10 ⁻⁶	0.026	0.003	0.004
Chlorobenzne	0.013	0.009	0.009	0.004	0.065	0.023	0.036
TetraChloroEthylene	0.011	0.008	0.007	0.003	0.0510	0.019	0.028
Bromoform	0.032	0.025	0.022	0.01	0.155	0.056	0.085

Table 4.50 Descriptive Statistics for Deterministic Noncarcinogenic Risk Assessment at winter season

Compound	Mean	Median	Std Dev	min	max	90 th perct.	95 th perct.
Benzene	0.112	0.071	0.146	0.03	0.851	0.158	0.394
1,3 Butadiene	0.039	0.031	0.021	0.014	0.113	0.068	0.077
Toluene	0.007	0.006	0.004	1.9 x10 ⁻⁴	0.023	0.013	0.014
1,4di cl benzene	0.0002	0.0002	0.0001	5.9x10 ⁻⁶	0.0007	0.0003	0.0004
Ethylbenzene	0.006	0.005	0.006	1.3 x10 ⁻³	0.045	0.012	0.013
Hexane	0.005	0.001	0.014	4 x10 ⁻⁶	0.104	0.007	0.021
Naphthalene	0.064	0.041	0.085	9.8 x10 ⁻⁴	0.477	0.16	0.239
Styrene	0.001	0	0.001	1.9 x10 ⁻⁶	0.005	0.001	0.002
o Xylene	0.026	0.018	0.038	1.8 x10 ⁻³	0.3	0.047	0.059
Isopropyl benzene	0.001	0.001	0	0.4 x10 ⁻⁶	0.002	0.001	0.001
Chlorobenzne	0.008	0.004	0.005	0.003	0.04	0.014	0.022
TetraChloroEthylene	0.009	0.007	0.006	0.003	0.044	0.0160	0.024
Bromoform	0.022	0.014	0.015	0.007	0.108	0.039	0.059

Table 4.51 Descriptive Statistics for Deterministic Noncarcinogenic Risk Assessment at summer season

hazard ratios range from 0.6 to 2.0 while lifetime inhalation cancer risks were estimated to range from 4.7×10^{-5} to 1.10×10^{-4} .

4.3.5.2 Probabilistic Estimation of HQ

The hazard ratio for selected VOCs was estimated probabilistically with Monte Carlo Simulation. It seems to be a general experience that deterministic approach are too conservative and often overestimates risk compared to the probabilistic risk assessment (Sander and and Öberg, 2006). This approach is not accepted for this study since the data obtained from probabilistic approach were quite similar to deterministic point estimates. Table 4.52 and Table 4.53 represent the Monte Carlo Simulation results for non carcinogen assessment.

A hazard ratio less than 1.0 means that the concentration of VOC compound is within the acceptable dose. Any level above a hazard ratio of 1 causes toxic effects in humans (Mukerjee and Biswas. 1992). The noncarcinogenic benchmark value for both deterministic and probabilistic approach did not exceed the threshold value. Only the hazard index value of xylene and naphthalene exceeded 1 at two industrial sites with deterministic approach. According to the probabilistic approach. the noncancer ratio was below 1. The max value naphthalene. benzene. 1. butadiene and bromoform exceeded the acceptable benchmark levels.

4.3.5.3 Cumulative Noncarcinogenic Risk

The noncancer risk was calculated by summing the individual noncancer values for each compound and is represented in Table 4.54. While the mean and median values of cumulative noncancer risk did not exceed the threshold value. 90% and 95% percent of the cumulative noncancer value was greater than 1

Compound	Mean	Median	Std Dev	min	max	90 th perct.	95 th percet.
Benzene	0.299	0.275	0.130	0.050	1.089	0.467	0.548
1,3 Butadiene	0.196	0.165	0.124	0.019	1.491	0.355	0.435
Toluene	0.006	0.005	0.004	0.001	0.030	0.011	0.013
1,4 di cl benzene	0.0004	0.0002	0.001	3x10 ⁻⁶	0.020	0.001	0.002
Ethylbenzene	0.005	0.004	0.003	1.5 x10 ⁻⁷	0.022	0.008	0.010
Hexane	0.002	0.001	0.002	2 x10 ⁻⁶	0.012	0.004	0.005
Naphthalene	0.170	0.079	0.310	0.001	7.996	0.396	
Styrene	0.026	0.025	0.012	9.6 x10 ⁻⁶	0.050	0.043	0.046
o Xylene	0.051	0.020	0.093	4 x10 ⁻⁵	0.993	0.127	0.208
Isopropyl benzene	0.002	0.001	0.002	1.7 x10 ⁻⁵	0.054	0.004	0.005
chlorobenzene	0.015	0.009	0.020	0.0002	0.384	0.032	0.046
TetraChloroEthyle							
ne	0.010	0.008	0.010	3.5 x10 ⁻⁶	0.147	0.021	0.028
Bromoform	0.032	0.022	0.038	7.6x10 ⁻⁴	0.921	0.072	0.085

Table 4.52 Descriptive statistics for probabilistic noncarcinogenic risk assessment at winter season

Compound	Mean	Median	Std Dev	min	max	90 th	95 th
						perct.	percet.
Benzene	0.107	0.069	0.123	0.028	1.901	0.204	0.302
1,3 Butadiene	0.038	0.035	0.016	0.004	0.160	0.058	0.067
toluene	0.007	0.006	0.004	1.9x10 ⁻⁵	0.030	0.012	0.015
1,4 di cl benzene	0.0002	0.0002	0.0001	2.5x10 ⁻⁸	0.001	0.0003	0.000
Ethylbenzene	0.006	0.004	0.005	0.001	0.082	0.011	0.016
hexane	0.005	0.000	0.016	4.1 x10 ⁻⁹	0.142	0.012	0.030
naphthalene	0.066	0.055	0.050	1.5 x10 ⁻⁵	0.458	0.132	0.159
Styrene	0.001	0.000	0.001	2 x10 ⁻⁸	0.032	0.002	0.002
o Xylene	0.025	0.017	0.025	4.6 x10 ⁻⁴	0.402	0.051	0.069
Isopropylbenzene	0.001	0.001	0.000	7.6 x10 ⁻⁸	0.002	0.001	0.001
chlorobenzene	0.008	0.004	0.015	4.8 x10 ⁻⁵	0.435	0.019	0.029
TetraChloroEthylene	0.009	0.007	0.015	4.4 x10 ⁻⁶	0.800	0.019	0.026
Bromoform	0.024	0.016	0.050	7.1 x10 ⁻⁶	4.138	0.053	0.071

Table 4.53 Descriptive statistics for probabilistic noncarcinogenic risk assessment at summer season

Season	Mean	Median	Std	min	max	90 th	95 th
			Dev			perct.	perct.
winter	0.92	0.68	1.02	0.22	6.62	1.23	1.49
summer	0.29	0.24	0.08	0.2	0.8	1.08	0.58
average	0.61	0.46	0.55	0.21	3.71	1.16	1.04

Table 4.54 Statistical parameters of cumulative noncancer risk

Figure 4.45 also depicts the contribution of each compound to cumulative cancer risk. Like in cancer risk. the biggest contribution belongs to benzene with 44% in winter and 36% in summer in cumulative noncancer risk. 1.3 butadiene makes the biggest contribution after benzene. Although the concentration of 1.3 butadiene was measured low. its reference concentration is also rather low. Therefore. its contribution to noncancer risk is high.

4.3.5.4 Spatial Distribution of Noncarcinogenic Risk

Although individual noncancer hazard ratio did not exceed the threshold value. the cumulative noncancer risk value exceeded 15 sampling points in winter and 1 sampling point in summer. The spatial distribution map represented in Figure 4.46 and Figure 4.47 show the local distribution of cumulative noncancer risk intensity in summer and winter. The areas with relatively high risk. which exceed the noncancer hazard ratio. were industrial areas or main/most congested roads of Bursa.



Figure 4.45 Cumulative noncancer risk for summer and winter



Figure 4.46 Spatial distribution of cumulative noncancer hazard ratio for winter season



Figure 4.47 Spatial distribution of cumulative noncancer hazard ratio for summerseason

4.3.6 Uncertainty Analysis

There are uncertainties associated with many aspects of this analysis as explained in the section 2.5. To estimate the potential effects of uncertainty regarding the distribution of exposure which is obtained from Monte Carlo simulation. bootstrapping technique was applied to estimate the uncertainty in average emissions and regarding other statistics of the distribution. To obtain reliable results. 200 sets of different input data were generated with 199 sets of resampled data and one 'base' data without any replacement (Efron. 2005). Each dataset with 199 samples was analyzed with Monte Carlo model. resulting in 199 sets of bootstrapping solutions as well as one set of 'base' solutions. The statistics were calculated repeatedly 1000 times for each subsample in order to construct a distribution for each statistics previously presented in Table 4.55 and Table 4.56. Since the estimated individual noncancer risk did not exceed the threshold value. the results for the distribution of noncancer statistics is not presented.

Table 4.55 presents the bootstrapping results of mean. median. min and max value for exposure. The 90% and 95% confidence intervals and the maximum value for the median and mean carcinogenic risk estimates are presented in Table 4.55. The results from base data and the mean and median value from bootstrapping were very close. Hence, the uncertainty due to the distribution fitting was at a low level. Base data set agreed well with those from the bootstrapping data set. Especially good agreement was found for the compounds which have high concentration levels.

Compound		Mean	Median	Std Dev	min	max
	Mean	3.503	2.653	3.170	0.337	41.145
	Median	3.503	2.653	3.170	0.337	41.145
Benzene	Std Dev	0.014	0.010	0.070	0.010	3.084
	90 th pect.	3.503	2.653	3.170	0.337	41.145
	95 th pect	3.503	2.653	3.170	0.337	41.145
	Mean	0.153	0.106	0.162	0.009	2.042
	Median	0.153	0.106	0.162	0.009	2.042
1.3 Butadiene	Std Dev	7.24x10 ⁻⁴	4.51 x10 ⁻⁴	32.34 x10 ⁻⁴	3.23 x10 ⁻⁴	7.24 x10 ⁻⁴
	90 th pect.	0.153	0.106	0.162	0.009	2.042
	95 th pect	0.153	0.106	0.162	0.009	2.042
	Mean	11.991	8.215	14.280	0.794	209.832
	Median	11.991	8.215	14.280	0.794	209.832
toluene	Std Dev	0.064	0.036	0.336	0.025	12.398
	90 th pect.	11.991	8.215	14.280	0.794	209.832
	95 th pect	11.991	8.215	14.280	0.794	209.832

Table 4.55 Uncertainty in statistics of simulated exposure

Compound		Mean	Median	Std Dev	min	max
	Mean	0.151	0.060	0.341	0.001	5.921
	Median	0.151	0.060	0.341	0.001	5.921
1.4 DiCl benzene	Std Dev	0.001	0.000	0.013	0.000	0.485
	90 th pect.	0.151	0.060	0.341	0.001	5.921
	95 th pect	0.151	0.060	0.341	0.001	5.921
	Mean	1.788	1.295	1.817	0.017	22.617
	Median	1.788	1.295	1.817	0.017	22.617
Ethylbenzene	Std Dev	0.007	0.005	0.034	0.002	1.445
	90 th pect.	1.788	1.295	1.817	0.017	22.617
	95 th pect	1.820	1.310	1.990	0.030	28.850
	Mean	0.43	0.25	0.60	0.00	7.71
	Median	0.43	0.25	0.60	0.00	7.71
Hexane	Std Dev	0.00	0.00	0.01	0.00	0.52
	90 th pect.	0.43	0.25	0.60	0.00	7.71
	95 th pect	0.43	0.25	0.60	0.00	7.71

Table 4.54. Uncertainity in statistics of simulated exposure (Continued)

Compound		Mean	Median	Std Dev	min	max
	Mean	0.202	0.077	0.460	0.001	7.548
	Median	0.202	0.077	0.460	0.001	7.548
Naphthalene	Std Dev	0.002	0.001	0.017	0.000	0.592
	90 th pect.	0.202	0.077	0.460	0.001	7.548
	95 th pect	0.202	0.077	0.460	0.001	7.548
	Mean	9.888	7.582	9.248	0.045	111.92
	Median	9.888	7.582	9.248	0.045	111.92
Styrene	Std Dev	0.037	0.029	0.163	0.006	7.153
	90 th pect.	9.888	7.582	9.248	0.045	111.92
	95 th pect	10.210	7.620	9.310	0.060	114.20
	Mean	2.068	0.641	4.757	0.004	69.782
	Median	2.068	0.641	4.757	0.004	69.782
o-Xylene	Std Dev	0.021	0.006	0.111	0.000	4.006
	90 th pect.	2.068	0.641	4.757	0.004	69.782
	95 th pect	2.068	0.641	4.757	0.004	69.782

Table 4.54. Uncertainity in statistics of simulated exposure (*Continued*)

Compound		Mean	Median	Std Dev	min	max
	Mean	0.27	0.14	0.43	0.00	6.15
	Median	0.27	0.14	0.43	0.00	6.15
Isopropyl benzene	Std Dev	0.00	0.00	0.01	0.00	0.38
	90 th pect.	0.27	0.14	0.43	0.00	6.15
	95 th pect	0.27	0.14	0.43	0.00	6.15
	Mean	0.298	0.175	0.437	0.008	6.752
	Median	0.298	0.175	0.437	0.008	6.752
Chlorobenzene	Std Dev	0.002	0.001	0.017	0.000	0.663
	90 th pect.	0.298	0.175	0.437	0.008	6.752
	95 th pect	0.298	0.175	0.437	0.008	6.752
	Mean	0.103	0.075	0.102	0.001	1.234
	Median	0.103	0.075	0.102	0.001	1.234
TetraChloroEthylene	Std Dev	0.000	0.000	0.002	0.000	0.077
	90 th pect.	0.103	0.075	0.102	0.001	1.234
	95 th pect	0.103	0.103	0.102	0.001	1.234

Table 4.54. Uncertainity in statistics of simulated exposure (Continued)

Compound		Mean	Median	Std Dev	min	max
Bromoform	Mean	0.64	0.45	0.77	0.00	11.23
	Median	0.64	0.45	0.77	0.00	11.23
	Std Dev	0.00	0.00	0.02	0.00	0.74
	90 th pect.	0.64	0.45	0.77	0.00	11.23
	95 th pect	0.64	0.45	0.77	0.00	11.23

Table 4.54. Uncertainity in statistics of simulated exposure (Continued)

Table 4.56 Bootstrapping results or the estimation intervals of median and mean cancer risks for summer and winter (x10⁻⁶)

		winter			summer		
Compound		90 th	95 th	100 th	90 th	95 th	100 th
		perct.	perct.	perct.	perct.	perct.	perct.
Benzene	Mean	130	140	270	49	49	54
Denzene	Median	96	97	99	26	28	29
Bromoform	Mean	3.3	3.3	3.7	4.0	4.1	4.7
	Median	2.6	2.6	2.8	2.6	2.7	2.7
1 3 Butadiene	Mean	12.1	12.3	12.5	23	2.3	2.4
	Median	10.2	10.3	10.5	2.1	2.2	2.2

4.3.7 Carcinogenic Risk at Subgroups

The inhalation volumes of participants were calculated for four subgroups. which were adult men. adult women. early children and children as explained in detail in Section 4-6-2. Cancer risk for subgroups was estimated deterministically by combining early children and children groups. It was not found which distribution best fitted the children body weight data. Hence. Monte Carlo simulation could not be achieved to estimate health risk of children. Table 4.57 and Table 4.58 represent the mean. median. min and max risks estimated for children, adult men and adult women.

Children are affected more seriously by the toxic air compounds when compared to the adults under the same environmental conditions according to

Table 4.57. The mean cancer risk of children was 250 and it was 96 times higher than the benchmark cancer level for winter and summer. The cancer risk values caused by benzene concentration were 120 x10⁻⁶ and 45 x10⁻⁶ for male adults in winter and summer seasons. The mean cancer risk of children was two times higher than males and three times higher than females. According to these results. children are of particular concern for being more sensitive to HAPs exposure. Children are more susceptible to toxic air due to their low body weight even with inhalation volume lower than adults even if they are exposed to similar concentrations. Children are also physiologically different from adults as their metabolic and immune systems can be immature and their organ systems develop rapidly and are more sensitive to VOC exposures (Guzelian et al., 1992). Additionally, there is a longer remaining potential lifespan during which subsequent cell transformations leading to carcinogenesis can occur. Because of these factors. early-life exposure to carcinogenic HAPs can increase a child's lifetime risk of cancer. A recent toxicological review of benzene identified children as a population that may be at increased risk compared to adults (USEPA. 1998 and Woodruff et al.. 2000).

Compound	group	Mean	Median	Std Dev	min	max	90 th %	95 th %
Benzene	child	250	214	126	92	597	396	462
	female	80	73	31	39	231	117	133
	male	120	111	38	59	269	169	180
Bromoform	child	10	8	5	4	24	16	18
	female	3	3	1	2	9	5	5
	male	5	4	2	2	11	7	7

Table 4.57 Statistical parameters for deterministically estimated lifetime cancer risks for subgroups in winter season (x10⁻⁶)

Compound	group	Mean	Median	Std Dev	min	max	90 th	95 th
							Perct.	Perct.
Benzene	child	96	54	47	34	223	148	169
	female	30	27	12	14	86	43	49
Broform	male	45	27	14	22	100	63	67
	child	7	5	3	3	16	11	12
	female	2	2	1	1	6	3	4
	male	3	2	1	2	7	5	5

Table 4.58 Statistical parameters for deterministically estimated lifetime cancer risks for subgroups in summer season (x10⁻⁶)

4.3.8 The Source of Uncertainty

Some uncertainty may be caused during the assessment of health effects. which might cause under or overestimation of cancer risk or noncancer risk hazard ratio. The major limitation is that health risk was assessed with outdoor concentration. Indoor exposure sources might also have important contributions (Payne-Sturges et al., 2004; Sax et al., 2006). The health risk might be underestimated due to the lack of data measured in indoor air concentration. The cancer risk values exceeded the limit value even when only ambient air concentration is taken into account. For this reason, it should be comprehensively measured in indoor and microenvironments where people are exposed to pollution in order to estimate the cancer risk.

Another example of uncertainty was the exposure route. Health risk caused by VOC may have also been underestimated since only inhalation route were taken into consideration. Ingestion route. especially drinking water. may be a major route of exposure to certain VOCs. such as bromoform and halogenated VOC.

Finally. the estimated risk values could be underestimated by the limited set of species considered and the incomplete data of toxicity. Some of the compounds could be measured lower value than limit of detection and some of the compounds could not be measured by our analytical system. Finally. the 15 species considered in our study were among the 33 most important urban HAPs based on emissions and toxicities in a 1995 ranking analysis (USEPA. 1999).

CHAPTER 5

SUMMARY OF RESULTS

The weekly sampling periods were conducted in four different seasons from 2005 to 2007 in Bursa. Passive sampling was performed in four campaigns between 2005 and 2007 determine spatial distribution of VOC, NO_2 , SO_2 and O_3 across the city. The passive sampling points were located around roads, in residential areas, in locations that are not under the direct influence of traffic, in two organized industrial zones of the city and at background locations that are outside the city.

The passive sampling study indicated that the lack of uptake rates of VOCs is a limitation in passive measurements of these compounds. This conclusion reached laid a road for the second part of the study, where uptake rates of 34 VOCs were measured and dependence of meteorology is investigates with a one-year-long study in Ankara. Results were also used to convert masses of VOCs collected on passive samplers into atmospheric concentrations at Bursa.

A sampling and analytical method to measure VOCs in Bursa and Ankara was developed and evaluated. The results of sampling and analytical methods give high efficiency and reliability. The sorbent tubes used for both active and passive sampling were analyzed with GC-FID following the unity thermal desorption.

The uptake rate for passive sampling is the most important parameter to calculate ambient concentration from measured mass. In Ankara campaign, uptake rate equation was determined by regression analysis taking meteorological factors into account for 25 compounds. The use of the uptake rate equation depending on meteorological parameter eliminated the uncertainty caused by variations in meteorology.

The generated data set was investigated in terms of seasonal and spatial variation. Toluene was the most abundant compound among the measured VOCs in all seasons and at all sites, accounting for $4.22 \ \mu g/m^3$. M&p Xylene and benzene were the second and third most abundant compounds and their median concentrations were 10.79 and 2.96 $\mu g/m^3$, respectively. The concentrations of VOCs showed clear seasonal variations. BTX compounds (plus 1,2,4-tri-M-benzene) totally accounts for 68% and 73% of the total VOC mass in winter and summer respectively. Increased contribution of BTX compounds in summer is due to increase in toluene and m&p-xylene contributions are due to increased evaporative emissions in summer season. It should also be noted that the contributions of VOCs which are not affected by evaporative emissions, such as benzene, ethylbenzene and o-xylene decreased in winter or remained the same in both seasons.

The cancer and the noncancer hazard risk in Bursa were investigated using VOC. NO_2 . SO_2 and O_3 data collected in this study for summer and winter season in 2007. The questionnaire was filled out by selected people to obtain time-activity pattern and body weight, and finally to calculate the inhalation volume for each participant instead of using standard values recommended by USEPA (2009). The mean inhalation volumes were 30. 15. 17 and 22 m³ for male, female, early child and child, respectively. If the inhalation volume was assumed to be 20 m³ for Bursa population, exposure and risk would have been overestimated for male and early child and underestimated for male and children. The median and mean body weights were found to be 80.3 and 80 for adult man, 65 for adult female, 51.5 and 52.5 for child and 18.1 and 16.5 for early child respectively. USEPA suggested that average body weight value be 70 kg for adults.

13 VOCs which have reference concentration (RfC) or reference dose value (RfD) were evaluated in terms of health aspects with deterministic and probabilistic approach. Three of these VOCs had cancer slope factor. Lifetime cancer risk could be estimated for benzene, 1,3 butadiene and bromoforom. All the statistical parameters used to represent cancer risks for three compounds exceeded the stated level. Benzene had the highest adverse health effect among three compounds according to USEPA (2009) calculation with the mean cancer risk $3x10^{-4}$. Furthermore, the lifetime noncancer hazard

ratio was estimated for all 13 VOCs to be determined as a potential human health concern. None of the VOCs exceeded the threshold value, which was 1. The spatial distribution of individual lifetime cancer risk and sectoral evaluation indicate that vehicle emissions and industrial activities are significant sources of health risk associated with VOC exposure.

The health risks posed by the ambient VOCs were also evaluated with different approaches, namely probabilistic and deterministic approaches. The uncertainty associated with the distributions obtained from Monte Carlo simulation was estimated by bootstrapping resampling technique. It was found that the health risk data obtained from these techniques were quite similar.

Despite the potential underestimation due to the limited set of species considered and the absence of monitoring personal exposure, the estimated lifetime cancer risks still exceeded the acceptable level. Our risk apportionment indicates that additional studies should be conducted to further assess VOCs' potential health effects in Bursa.

VOCs are important precursors of the atmospheric ozone formation species. This study also investigated the airborne concentrations of about 30 VOCs at over 50 points across the city. Maximum increment reactivity (MIR) was used to evaluate the ozone formation potential as ng across the city. M&p xylene, toluene, 1,2,4-Tri-M-benzene, ethylbenzene, o-xylene, 1,3,5-Tri-M-Benzene, styrene and Cyclohexane+Cyclohexene accounted for 91–93% of the 30 VOCs in Bursa for two sampling campaigns. The ozone contribution potential was higher due to high potential emission of m&p xylene and toluene in road site and industrial areas.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSION

The main purpose of this study was to investigate spatial distributions of about 30 VOCs and other conventional air pollutants (NO_2 , SO_2 and O_3) and their associated health effects in Bursa atmosphere. To achieve of the aim, organic and inorganic air pollutants were measured with weekly sampling campaigns from 2005 to 2007 in four different seasons. A second part of the study was to determine uptake rates equation for about 25 VOCs. The field study was conducted in Ankara from January 2008 to June 2008 to evaluate the uptake rates of passive sampling under different meteorological conditions.

The interpretation of these observations during the interpretation of data set can be summarized in the following points:

Both the spatial variation and factor analysis results showed that industrial solvent evaporation and motor vehicles are the most abundant VOC sources contributing to ambient levels in Bursa. Residential sites are mainly affected by vehicular and industrial emissions. However, smaller difference between VOC concentrations measured in residential and industrial or traffic impacted stations, than the corresponding differences measured in summer indicates that VOC emissions from space heating do affect VOC levels in residential areas. However, we were not able to isolate a separate heating factor in FA exercise.

In the study conducted to identify uptake rates, it was seen that uptake rate values decreased as temperature increase while the value of its uptake rate increased as humidity and wind speed increased as well. At the end of the multiple linear regressions performed according to this, uptake rate equations based on meteorology were calculated.

The health risk of VOC is evaluated. The estimated cancer values exceeded the threshold level suggested by EPA or WHO. Despite the potential underestimation due to the limited set of species considered and the absence of monitoring personal exposure, the estimated lifetime cancer risks still exceeded the acceptable level. Our risk apportionment indicates that additional studies should be conducted to further assess VOCs' potential health effects in Bursa.

6.2 RECOMMENDATION FOR FUTURE WORK

Following suggestions are provided for future research:

- This study provides health risk assessment based on ambient air measurements results. The levels of VOC in households, offices and especially schools and kindergarten should be determined to complete the assessment of health risk study. Furthermore, personal sampling should also be performed in order to determine how much people are exposed to toxic compounds.
- The methods should be improved to measure he lighter VOC which carbon number less than 5. This can allow characterization of natural LPG leaks and fossil fuel emissions
- This study, which was conducted for Bursa, should be regularly implemented in other cities and even in remote areas in Turkey to determine the ambient air quality.
- Spatial distribution maps we produced for Bursa should also be produced for other cities of Turkey.

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APPENDIX A

Description Of Sampling Points

Table A.1 Brief description of passive sampling points and their coordinates

Point	Point	Sector	Distrcit	Description
No	Name	5000	Distrett	Description
	Acomlor			Located in inner city and congested
1	Polis	road	Osmangazi	street of , S.P. is placed in the
•	Folis Karakalu	Tudu	Osmangazi	crossroad of most congested street
	Kalakulu			of the city
	Adalet			
2	Meslek		Osmanasi	Leasted in dense residential area
2	Edindirme	urban	Osmangazi	Located in dence residential area
	Okulu			
	Afet			Located in inner city and congested
3	Yönetim	road	Osmangazi	street of , S.P. is placed in the
	Merkezi			most congested street of the city
	Abmot			Located in suburban residential
4	Annet	urban	Osmangazi	area of Bursa, S.P. is stuated on
	Uyar 100			school soccer field
	Ali Osman			Located near the Bursa-İstanbul
5	Sönmez	road	Osmangazi	main road
	Lisesi			main road
6	Başaran	urban	Osmangazi	Located in dense residential area
0	Camii	uiban	Usinanyazi	Ebcated in dence residential area
	Beşevler			
7	Polis	urban	Nilüfer	Located in dence residential area
	Karakolu			
				Bursa Organized Industrial Distrcit
8-20	BOSB	industry	Nilüfer	264 companies in the area (metal,
				textile, automotive)

Table A.1. Brief description of passive sampling points and their coordinates (Continued)

Point	Point	Sector	Distrcit	Description		
No	Name	360101	Distrett	Description		
21	Cumalıkızık	back	Yıldırım	Located in rural area south east of		
	Cokirgo	ground		Dui 3a		
22	Çekirge	urban	Ocmondozi	Located in dense residential area		
22	POIIS	uibaii	Osmanyazı			
	Karakolu					
23	Çeltik Köyü	urban	Osmangazi	Located in sub urban area		
	Demirci	back		Located in rural area south west of		
24	İÖO	around	Nilüfer	Bursa, S.P. is stuated on school		
		9.00.10		soccer field		
	Demirtas	back		Located in rural area north east of		
25	Barai	around	Yıldırım	Bursa, sampling point is near the		
	Daraji	ground		Demirtaş dam		
				Demirtaş Organized Industrial		
26-38	DOSB	industry	Osmangazi	Distrcit, 323 companies in the area		
				(textile, automotive, food, metal)		
30	Emek Polis	urban	Nilüfor	Located in dence residential area		
57	Karakolu	uiban	Midici			
40	Ertuğrul	road	Nilüfor	Located near the Bursa-İzmir main		
40	Camii	Todd	Michel	road		
1 1	Et_Ba	road	Vildirim	Located near the Bursa-Ankara		
41		Todd	mainin	main road		
				Gürsu Organized Industrial Distrcit,		
42-47	GUSAB	industry	Yıldırım	73 companies in the area (textile,		
				food, metal, cold storage)		
48	Havkal	urban	Osmandazi	Located in dence residential area		
-0	псукст	uiban	Osmangazi	and most conjested road (town)		
49	Hifsisiha	urban	Osmangazi	Located in dence residential area		
47	THISISITIC	arban	USITIATIGAZI	and near the public hospital (town)		
				Located near the Bursa-İstanbul		
50	Hobby	road	Osmandazi	main road and crosssection of past		
50	Bahçesi	Todu	USITIATIYAZI	freeway and Bursa-İstanbul main		
				road		

Table A.1. Brief description of passive sampling points and their coordinates (Continued)

Point	Point	Sector	Distrcit	Description		
No	Name	360101	Distrett	Description		
	İhsaniye					
51	Polis	urban	Nilüfer	Located in dence residential area		
	Karakolu					
52	Karayolları	road	Yıldırım	Located near the Bursa-Ankara		
	14. G.M			main road		
				Kestel Organized Industrial		
53-58	KOSAB	industry	Yıldırım	Distrcit, 77 companies in the area		
				(textile, food, metal, plastic)		
59	Küçük	industry	Nilüfer	Located in repair shops		
	Sanayi	5				
	Mehmet					
60	Akif Ersoy	urban	Yıldırım	Located in dence residential area		
	Camii					
	Mevlana					
61	Hacılar	urban	Yıldırım	Located in dence residential area		
	Camii					
62	Mihraplı	urban	Nilüfer	Located in dence residential area		
_	Camii					
63	Mudanya	road	Nilüfer	Located on near the Bursa-		
	Yolu			Mudanya main road		
	Mürrüvet					
64	Baş	urban	Osmangazi	Located in dence residential area		
	Anaokulu					
	Nilüfer	backgrou		Located in rural area south west of		
65	Köyü	nd	Nilüfer	Bursa, point is located in the		
	5			rural's cemetery		
				Nilüfer Organized Industrial		
66-70	NOSB	industry	Nilüfer	Distrcit, 199 companies in the area		
				(textile, metal, chemical)		
71	PTT Kablo	road	Nilüfer	Located near the Bursa-İzmir main		
	Deposu			road		
	Samanlı					
72	Merkez	urban	Osmangazi	Located in dence residential area		
	Camii					

Table A.1. Brief description of passive sampling points and their coordinates (Continued)

Point	Point	Sector	Distrait	Description
No	Name	360101	Districit	Description
72	Sivil	urban	Vildirim	Located near the most congested
75	Savunma	urban	mainin	free way
	Soğanlı			
74	Merkez	urban	Osmangazi	Located in sub urban area
	Camii			
75	SSK	road	Osmangazi	Located in dence residential area
70	SOR	roud	Osmangazi	(town) and cross road
	Sevh			Located in inner city and congested
76	Edibali	road	Osmangazi	street of , S.P. is placed in the
70	Camii	roud	USITIATIGUZI	crossroad of most congested street
	Garrin			of the city (town)
77	Şirinevler	urban	Yıldırım	suburban
	Tedaş			
78	Panayır	rood	0	Located near the Bursa-İstanbul
	Ambar	road	Osmangazi	main road
	Tesisi			
70	Tunç Siper	urbon	Nilüfor	Leasted in sub-urban area
19	Lisesi	uibali	Miluter	
80	Vakıfköy	urban	Osmandazi	Located in sub urban area
00	Camii	arbarr	Osmanyazi	
	Vatan Bilim			
81	Sanat	urban	Osmangazi	Located in dence residential area
	Merkezi			
82	Yeşil Camii	urban	Osmangazi	Located in dence residential area
	Yıldırım		Vildining	Leasted in damas residential and
83	Belediyesi	urban	riidirim	Located in dence residential area
	Yunuseli		Oomongozi	Leasted in damas residential area
ō4	Mahallesi	urban Osmangazi illesi		Located in dence residential area
95	Zümrütevle	urban	Vildurum	Located in dense residential area
00	r Camii	ui val i		

APPENDIX B

Field Sheet

Table B.1 The field sheet used in the sampling campaigns

	VOC BURSA ÖLÇÜM ü örnek yerleştirme ve toplama formu									
			B	AŞLANGIÇ Saat dakik	ταρί	BİTİŞ Saat Dakik	KOORDİNAT		YAĞIŞ (XAĞMUP K	
SORUMLU KİŞİ	ÖRNEK ADI	SAHA ADI	H	A	H	A	(N,E)	SICAKLI	AR v.b)	YORUM
Du fa				 Xunun Armalda	 		alina adimir. D			what babay
BUTO	Bu formu okunakli doldurunuz ve topladiginiz ornekle birlikte labaratuva teslim ediniz. Problem oldugunda derhal haber									

APPENDIX C

Physical Properties of VOC

Table C.1 Calibration gas compounds list and their physical properties

Compound Name	Molecula r Formula	CAS No	Mol. Weight	Boiling Point (°C)	Vapor Pressure (Pa at 25°C)
n-Pentane	C_5H_{12}	109660	72.15	36.07	68400
1,3-Butadiene	C_4H_6	106990	54.09	-4.4	NA
2-Methylbutane	C_5H_{12}	78784	72.15	28	79000
3-Methyl-1-butene	C_5H_{12}	563451	70.13	20	NA
2-Methyl-1-butene	C_5H_{12}	563462	70.13		
2-Methyl-2-butene	C_5H_{12}	513359	70.13	38.57	62143
trans-2-Pentene	C_5H_{12}	109682	70.13		NA
Cyclopentene	C_5H_8	142290	68.12		NA
1-Pentene	C_5H_{12}	109671	70.13		NA
cis-2-Pentene	C_5H_{12}	627203	70.13	36.90	66000
2,2-Dimethylbutane	C_6H_{14}	75832	86.18	49.74	42600
2,3-Dimethylbutane	C_6H_{14}	79298	86.18	58.00	32010
2-Methylpentane	C_6H_{14}	107835	86.18	60.27	28200
3-Methylpentane	C_6H_{14}	96140	86.17	83.28	25300
Isoprene	C_5H_8	78795	68.10	34.00	53200
4-Methyl-1-pentene	C_6H_{12}	691372	84.16		
3-Methyl-1-pentene	C_6H_{12}	760203	84.16	54.00	58128
trans-4-Methyl-2-pentene	C_6H_{12}	674760	84.16	58.60	22931
cis-4-Methyl-2-pentene	C_6H_{12}	691383	84.15	57.00	NA
1-Hexene	C_6H_{12}	592416	84.16	63.40	24800
4-Methyl-1-pentene	C_6H_{12}	691372			NA
Hexane	C_6H_{14}	110543	86.17	68.95	20200
trans-2-hexene	C_6H_{12}	4050457	84.16	67.90	35162

Compound Name	Molecular Formula	CAS No	Mol. Weight	Boiling Point (°C)	Vapor Pressure (Pa at 25°C)
cis-2-hexene	C ₆ H ₁₂	7688213	84.16	68.80	NA
2-Ethyl-1-butene	C_6H_{12}	760214			NA
trans-3-Methyl-2-pentene	C_6H_{12}	616126	84.15		NA
cis-3-methyl-2-pentene	C_6H_{12}	922623	84.16	67.70	16000
2,3-dimethylpentane	C_7H_{16}	590352	100.21	79.20	14000
1,2-dichloroethane	CH_2CI_2	107062	98.96	83.50	12000
Methylcyclopentane	C_6H_{12}	96377	84.16	71.80	18300
2,4-dimethylpentane	C_7H_{16}	108087	100.21	80.50	13100
1,1,1-trichloroethane	$C_2H_3CI_3$	71556	133.40	74.00	13332
1-methylcyclopentene	C_6H_{10}	693890	82.15	75.50	NA
Carbontetrachloride	CCI_4	56235	153.82	76.70	12000
Benzene	C_6H_6	71432	78.11	80.10	12700
Cyclohexane	C_6H_{12}	110827	84.16	81.00	95
Cyclohexene	C_6H_{10}	110838	60.16	83.00	160
2-methylhexane	C_7H_{16}	591764	100.21	90.00	8780
2,2,3-trimethylbutane	C_7H_{16}	464062	100.21	80.90	13652
2,3-dimethylpentane	C_7H_{16}	565593	100.21	89.90	9180
3-methylhexane	C_7H_{16}	589344	100.21	92.00	8210
Bromodichloromethane	CHBrCl ₂	75274	163.83		NA
Trichloroethene	C_2HCI_3	79016	131.40	87.00	7800
Dibromomethane	CH_2Br_2	74953	173.85	97.00	6000
1,2-dichloropropane	$C_3H_6CI_2$	78875	112.99	96.80	7066
1-heptene	C_7H_{14}	592767	98.19	93.64	7510
2,2,4-trimethylpentane	C ₈ H ₁₈	504841	114.23	99.24	6560
Heptane	C_7H_{16}	142825	100.21	98.42	6110
cis-3-heptene	C_7H_{14}	7642106	98.19	95.70	12835
trans-2-heptene	C_7H_{14}	1468613 6	98.19	95.70	6450
cis-2-heptene	C ₇ H ₁₄	6443921	98.19	98.00	11632
cis-1,3-dichloropropene	$C_3H_4CI_2$	1006101 5	110.97	104.30	5733
trans-1,3-dichloroprope	$C_3H_4CI_2$	1006102 6	110.97	112.00	4533
Methylcyclohexane	C ₇ H ₁₄	108872	98.19	100.90	6180

Table C 1 Calibration gas compounds list and their physical properties (*Continued*)

Compound Name	Molecular Formula	CAS No	Mol. Weight	Boiling Point (°C)	Vapor Pressure (Pa at 25°C)
2,2-dimethylhexane	C ₈ H ₁₈	590738	114.23	107.00	
2,5-dimethylhexane	C_8H_{18}	592132	114.23	109.12	7580
2,4-dimethylhexane	C_8H_{18}	589435	114.23	109.50	6417
1,1,2-Trichloroethane	$C_2H_3CI_3$	79005	133.40	112.50	
1-methylcyclohexene	C_7H_{12}	591491	96.17	110.24	3393
Bromotrichloromethane	CBrCl ₃	75627	198.27	105.00	5120
2,3,4-trimethylpentane	C_8H_{18}	565753	114.23	113.40	3600
Toluene	C_7H_8	108883	92.13	110.60	3800
2-Methylheptane	C ₈ H ₁₈	592278	114.23	116.00	NA
m-Chlorotoluene	C ₇ H ₇ CI	108418	126.59	161.00	NA
p-Chlorotoluene	C ₇ H ₇ CI	434	126,59	162.00	NA
o-Chlorotoluene	C ₇ H ₇ CI	95498	126,59	158.5	NA
Dibromochloromethane	CHBr ₂ CI	124481	208.28	119.00	1866
4-methylheptane	C ₈ H ₁₈	589537	114.23	NA	NA
3-methylheptane	C ₈ H ₁₈	589811	114.32	115.00	2600
trans-1,3- dimethylcyclohexane	C_8H_{16}	2207036	112.21	124.00	NA
cis-1,3-dimethylcyclohexane	C_8H_{16}	638040	112.21	120.00	NA
trans-1,4-					
dimethylcyclohexane	C_8H_{16}	2207047	112.21	119.40	3020
cis-1,4-dimethylcyclohexane	C_8H_{16}	624293	112.22	124.00	NA
1-octene	C_8H_{16}	111660	112.10	121.30	2320
Octane	C ₈ H ₁₈	111659	114.23	125.70	1800
trans-2-octene	C_8H_{16}	1338942 9	112.22	125.00	4145
trans-1,2- dimethylcyclohexane	C_8H_{16}	6876239	112.22	123.00	NA
cis-1,2-Dimethylcyclohexane	C_8H_{16}	2207014	112.21		NA
2,2,5-trimethylhexane	C_9H_{20}	3522949	128.26	124.00	2210
1,2,4-Trimethylcyclohexane		2234755		NA	NA
Tetrachloroethene, Perchloroethylene	C_2CI_4	127184	165.80	121.00	1900
Chlorobenzene	C ₆ H ₅ CI	108907	112.56	132.00	1573
1,2-Dibromoethane	$C_2H_4Br_2$		187.86	131.4	1470
Ethylbenzene	C ₈ H ₁₀	100414	106.20	136.20	1270

Table C 1 Calibration gas compounds list and their physical properties (*Continued*)

Compound Name	Molecular Formula	CAS No	Mol. Weight	Boiling Point (°C)	Vapor Pressure (Pa at 25°C)
Bromoform	CHBr ₃	75252	252.75	149.50	667
meta-xylene	C ₈ H ₁₀	108383	106.20	139.00	1100
para-xylene	C ₈ H ₁₀	106423	106.20	138.00	1170
Styrene	C ₈ H ₈	100425	104.15	145.00	667
1-Nonene					
ortho-xylene	C_8H_{10}	95476	106.20	144.00	1170
iso-propylbenzene	C ₉ H ₁₂	98828	120.20	154.20	610
3,6-Dimethyloctane	$C_{10}H_{22}$	1586994 0	134.22		
n-propylbenzene	C_9H_{12}	103651	120.20	159.20	450
tert-Butylbenzene	$C_{10}H_{14}$	98066	134.22	169.00	
3-ethyltoluene	C_9H_{12}	620144	120.20	158.00	
4-ethyltoluene	C_9H_{12}	622968	120.20	162.00	
1,3,5-trimethylbenzene	C_9H_{12}	108678	120.20	164.70	325
2-ethyltoluene	C_9H_{12}	611143	120.20	164.00	NA
1-Decene	$C_{10}H_{20}$	124185	142.28	174.00	
1,2,4-trimethylbenzene	C_9H_{12}	95636	120.20	169.40	270
Decane	$C_{10}H_{22}$	124185	142.28	174.00	
Benzyl chloride	C ₇ H ₇ CI	100447	126.59	179.30	
1,3-Dichlorobenzene	$C_6H_4CI_2$	541731	147.00	172.50	
1,4-Dichlorobenzene	$C_6H_4CI_2$	106467	147.00	174.00	
iso-butylbenzene	$C_{10}H_{14}$	538932	134.22	170.00	250
sec-butylbenzene	$C_{10}H_{14}$	135988	134.22	173.00	240
1,2,3-trimethylbenzene	C_9H_{12}	526738	120.20	176.10	200
p-cymene	$C_{10}H_{14}$	99876	134.22	176.50	267
1,2-Dichlorobenzene	$C_6H_4CI_2$	95501	147.00	180.50	399
1,3-diethylbenzene	$C_{10}H_{14}$	141935	134.22	181.10	
1,4-diethylbenzene	$C_{10}H_{14}$	105055	134.22	184.00	134
n-butylbenzene	$C_{10}H_{14}$	104518	134.22	183.00	137
1,2-Diethylbenzene	$C_{10}H_{14}$		134.22	192.78	
1-Undecene	$C_{11}H_{22}$	2876127 5	154.20	162.00	
Undecane	$C_{11}H_{24}$	1120214	156.31	196.00	

Table C 1 Calibration gas compounds list and their physical properties (*Continued*)

Compound Name	Molecular Formula	CAS No	Mol. Weight	Boiling Point (°C)	Vapor Pressure (Pa at 25°C)
1,2,3,5-Tetramethylbenzene	$C_{10}H_{14}$	527537	134.22		
1,2,4,5-Tetramethylbenzene	$C_{10}H_{14}$	95932	134.22	196.50	
1,2,4-trichlorobenzene		120821	181.45	214.40	
Naphthalene	$C_{10}H_8$	91203	128.16	218.00	134
Dodecane	$C_{12}H_{26}$	112403	170.34	216	
Hexylbenzene	$C_{12}H_{18}$	1077163	162.27	226.00	

Table C 1 Calibration gas compounds list and their physical properties (*Continued*)

APPENDIX D

Retention time of VOCs

Table D.1 The retention time of VOC and comparison the standards gas

	Retention	AAQD	DAMO	
	Time (min)	Standards	PAIVIS	паюден
Hexane	13.852	\checkmark	\checkmark	
trans-2-hexene	14.051	\checkmark		
cis-2-hexene	14.157	\checkmark		
2-Ethyl-1-butene	14.157	\checkmark		
trans-3-Methyl-2-pentene	14.367	\checkmark		
cis-3-methyl-2-pentene	14.533	\checkmark		
2,3-dimethylpentane	14.829	\checkmark		
1,2-dichloroethane	14.829	\checkmark		\checkmark
Methylcyclopentane	15.362	\checkmark	\checkmark	
2,4-dimethylpentane	15.362	\checkmark	\checkmark	
1,1,1-trichloroethane	15.772	\checkmark		\checkmark
1-methylcyclopentene	16.448	\checkmark		
Carbontetrachloride	16.448	\checkmark		\checkmark
Benzene	16.601	\checkmark	\checkmark	
Cyclohexane	17.125	\checkmark	\checkmark	
Cyclohexene	17.125		\checkmark	
2-methylhexane	17.278	\checkmark	\checkmark	
2,2,3-trimethylbutane	17.468	\checkmark		
2,3-dimethylpentane	17.468	\checkmark	\checkmark	
3-methylhexane	17.759	\checkmark	\checkmark	
Bromodichloromethane	17.933	\checkmark		
Trichloroethene	17.933	\checkmark		\checkmark
Dibromomethane	18.047	\checkmark		
1,2-dichloropropane	18.047	\checkmark		\checkmark
Table D 1 The retention time of VOC and comparison the standards gas (*Continued*)

-	Retention	4400		
Compound Name	Time	AAQD Standarda	PAMS	Halogen
	(min)	Stanuarus		
1-heptene	18.387	\checkmark		
2,2,4-trimethylpentane	18.541	\checkmark	\checkmark	
trans-3-Heptene	18.837	\checkmark		
Heptane	19.039	\checkmark	\checkmark	
cis-3-heptene	19.039	\checkmark		
trans-2-heptene	19.171	\checkmark		
cis-2-heptene	19.663	\checkmark		
cis-1,3-dichloropropene	20.177	\checkmark		\checkmark
trans-1,3-dichloroprope	20.177	\checkmark		\checkmark
Methylcyclohexane	20.413	\checkmark	\checkmark	
2,2-dimethylhexane	20.663	\checkmark		
2,5-dimethylhexane	20.663	\checkmark		
2,4-dimethylhexane	20.811	\checkmark		
1,1,2-Trichloroethane	20.811	\checkmark		\checkmark
1-methylcyclohexene	21.109	\checkmark		
Bromotrichloromethane	21.514	\checkmark		
2,3,4-trimethylpentane	21.788	\checkmark	\checkmark	
Toluene	22.138	\checkmark	\checkmark	
2-Methylheptane	22.402	\checkmark	\checkmark	
m-Chlorotoluene	22.494	\checkmark		
p-Chlorotoluene	22.494	\checkmark		
o-Chlorotoluene	22.678	\checkmark		
Dibromochloromethane	22.678	\checkmark		
4-methylheptane	22.815	\checkmark		
3-methylheptane	22.815	\checkmark	\checkmark	
trans-1,3-dimethylcyclohexane	23.315	\checkmark		
cis-1,3-dimethylcyclohexane	23.315	\checkmark		
trans-1,4-dimethylcyclohexane	23.400	\checkmark		
cis-1,4-dimethylcyclohexane	23.400	\checkmark		
1-octene	23.509	\checkmark		
Octane	24.078	\checkmark	\checkmark	
trans-2-octene	24.219	\checkmark		
trans-1,2-dimethylcyclohexane	24.377	\checkmark		

Table D 1 The retention time of VOC and comparison the standards gas
(Continued)

	Retention	A A O D		
Compound Name	Time	AAUD Standarda	PAMS	Haloger
	(min)	Stanuarus		
cis-1,2-Dimethylcyclohexane	24.557	\checkmark		
2,2,5-trimethylhexane	24.692	\checkmark		
1,2,4-Trimethylcyclohexane	24.692	\checkmark		
Tetrachloroethene	25.939	\checkmark		\checkmark
Chlorobenzene	26.076	\checkmark		\checkmark
1,2-Dibromoethane	26.196			\checkmark
Ethylbenzene	26.893	\checkmark	\checkmark	
Bromoform	27.034	\checkmark		
meta-xylene	27.303	\checkmark	\checkmark	
para-xylene	27.303	\checkmark	\checkmark	
Styrene	28.166	\checkmark	\checkmark	
1-Nonene	28.323	\checkmark		
ortho-xylene	28.484	\checkmark	\checkmark	
1,4-Dichlorobutane	28.568			
Acetylene tetrachloride	28.568	\checkmark		
Nonane	28.830	\checkmark	\checkmark	
iso-propylbenzene	29.882	\checkmark	\checkmark	
3,6-Dimethyloctane	30.770	\checkmark		
n-propylbenzene	31.194	\checkmark	\checkmark	
tert-Butylbenzene	31.357	\checkmark		
3-ethyltoluene	31.489	\checkmark	\checkmark	
4-ethyltoluene	31.611	\checkmark	\checkmark	
1,3,5-trimethylbenzene	31.805	\checkmark	\checkmark	
2-ethyltoluene	32.372	\checkmark	\checkmark	
1-Decene	32.722	\checkmark		
1,2,4-trimethylbenzene	32.994	\checkmark	\checkmark	
Decane	33.181	\checkmark	\checkmark	
Benzyl chloride	33.431	\checkmark		
1,3-Dichlorobenzene	33.431	\checkmark		\checkmark
1,4-Dichlorobenzene	33.498	\checkmark		\checkmark
iso-butylbenzene	33.681	\checkmark		
sec-butylbenzene	33.797	\checkmark		

Compound Name	Retention Time (min)	AAQD Standards	PAMS	Halogen
1,2,3-trimethylbenzene	34.27	\checkmark	\checkmark	
p-cymene	34.27	\checkmark		
ortho-Dichlorobenzene	34.753	\checkmark		\checkmark
Indan	34.943			
1,3-diethylbenzene	35.197	\checkmark	\checkmark	
1,4-diethylbenzene	35.502	\checkmark		
n-butylbenzene	35.57	\checkmark		
1,2-Diethylbenzene	35.82	\checkmark	\checkmark	
1-Undecene	36.795	\checkmark		
Undecane	37.235	\checkmark	\checkmark	
1,2,3,5-Tetramethylbenzene	38.216	\checkmark		
1,2,4,5-Tetramethylbenzene	38.384	\checkmark		
1,2,4-trichlorobenzene	41.064	\checkmark		\checkmark
Naphthalene	41.501	\checkmark		
Dodecane	43.42	\checkmark	\checkmark	
Hexylbenzene	44.671	\checkmark		

Table D 1 The retention time of VOC and comparison the standards gas (*Continued*)

APPENDIX E

Method Performance Parameters

		Tube	System		_	
MDL (µg/m³)	Calibration R ²	Precison (%)	Precison	Recovery	Detecte d (%)	Source of compounds
0.00484	0.9996	8 98	0.83	99.95	100.00	Gasoline evaporation ^{1,2}
	0.9998	4.26	2.65	96.78	0	Vehicle exhaust ¹ , Gasoline evaporation ²
0.00489	0.8214					
	0.9998	6.71	3.84	92.15	100.00	Evaporative emission ²
	MDL (μg/m³) 0.00484 0.00489	MDL (μg/m³) Calibration R² 0.00484 0.9996 0.9998 0.9998 0.00489 0.8214 0.9998	MDL (μg/m³) Calibration R² Tube Precison (%) 0.00484 0.9996 8.98 0.9998 4.26 0.00489 0.8214 0.9998 6.71	MDL (μg/m³) Calibration R² Tube Precison (%) System 0.00484 0.9996 8.98 0.83 0.9998 4.26 2.65 0.00489 0.8214 0.9998 6.71 3.84	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

Compound Name	MDL (µg∕m³)	Calibration R ²	Tube Precison (%)	System Precison (%)	Recovery	Detecte d (%)	Source of compounds
3+2-Methyl-1-butene		0.9993	6.67	3.95	91.64	97.60	
2-Methyl-2-butene		0.99994	8.94	4.62	87.95	97.31	Gasoline evaporation ¹
trans-2-Pentene		0.9992	8.98	4.51	89.78	75.45	
Cyclopentene		0.9997	8.57	4.92	91.18	99.10	
1-Pentene		0.9997	10.20	3.25	94.87	98.80	
cis-2-Pentene		0.9991	12.34	4.87	95.12	96.41	
2.2-Dimethylbutane		0.9995	12.46	5.74	98.87	99.40	Evaporative emission ^{2,9} ,diesel exhaust ^{7,} vehicular emission ¹⁰
2.3-Dimethylbutane		0.9999	9.03	4.33	100	99.10	Evaporative emission ²
2-Methylpentane		0.9999	4.73	2.54	86.87	99.40	Evaporative emission ²
Isoprene		0.9993	1.18	1.12	91.87	0	Natural emission ⁸

Compound Name	MDL (µg/m³)	Calibration R ²	Tube Precison (%)	System Precison (%)	Recovery	Detecte d (%)	Source of compounds
3-Methylpentane		0.9991	5.09	3.67	90.48	99.40	Gasoline evaporation ¹ , oil refinery ¹ , Evaporative emission ² , vehicular emission ¹⁰
4-Methyl-1-pentene		0.9991	7.97	3.94	96.74	3.20	
3-Methyl-1-pentene		0.9998	8.12	4.65	94.78	1.57	
trans-4-Methyl-2- pentene		0.9999	11.21	5.97	95.67	6.45	
cis-4-Methyl-2-pentene		0.9996	09.13	3.85	95.54	0	
1-Hexene		0.9995	6.14	2.94	98.85	0	
4-Methyl-1-pentene		0.9996	7.97	3.85	100	0	
Hexane	0.00567	0.9988	3.28	0.39	93.85	94.31	Evaporative emission ² , gasoline vehicle exhaust ^{3,7,9}
trans-2-hexene		0.9988	11.18	3.03	96.74	1.12	

Compound Name	MDL (µg∕m³)	Calibration R ²	Tube Precison (%)	System Precison (%)	Recovery	Detecte d (%)	Source of compounds
cis-2-hexene+2-Ethyl-1- butene		0.9936	12.19	2.01	95.56	12.10	
trans-3-Methyl-2- pentene		0.9961	12.16	6.46	83.54	8.15	
cis-3-methyl-2-pentene		0.9998	11.21	3.13	84.87	4.52	
2.3- dimethylpentane+1.2- dichloroethane		0.9986	10.21	7.48	98.65	5.60	
Methylcyclopentane+2.4 -dimethylpentane	0.00850	0.9998	8.89	2.18	85.64	94.01	vehicular emission ¹⁰
1.1.1-trichloroethane	0.00653	0.9999	12.51	0.58	100	11.68	Dry celaning ¹¹
1-methylcyclopentene+ Carbontetrachloride		0.9964	12.45	2.18	99.54	9.12	Dry celaning ¹¹

Compound Name	MDL (µg∕m³)	Calibration R ²	Tube Precison (%)	System Precison (%)	Recovery	Detecte d (%)	Source of compounds
Benzene	0.00952	0.9997	2.24	1.35	96.87	100	Vehicle exhaust ^{1,2} , architectural or furnishing coatings, painting, Oil refinery ¹ , evaporative emission ³
Cyclohexane+ Cyclohexene	0.02760	0.9997	13.10	3.17	100	96.11	Asphalt emission ¹ , industrial emission ²
2-methylhexane	0.00797	0.9998	12.08	4.58	98.54	88.92	industrial emission ² , gasoline vehicle exhaust ^{3,7,10}
2.2.3- trimethylbutane+2.3- dimethylpentane	0.00772	0.9994	5.33	4.34	100	4.12	
3-methylhexane	0.00870	0.9999	4.62	3.42	100	12.11	vehicular emission ¹⁰
Bromodichloromethane+ Trichloroethene		0.9988	28.17	3.56	94.87	8.12	

Compound Name	MDL (µg∕m³)	Calibration R ²	Tube Precison (%)	System Precison (%)	Recovery	Detecte d (%)	Source of compounds
Dibromomethane+1.2- dichloropropane		0.9987		4.43	96.24	14.12	Dry celaning ¹¹
1-heptene		0.9990	19.36	4.63	100	75.45	
2.2.4-trimethylpentane	0.00686	0.9999	7.78	6.35	95.00	97.01	
trans-3-Heptene		0.9998	11.21	5.51	95.65	31.45	
Heptane+ cis-3-heptene	0.00959	0.9997	9.61	5.22	100	98.80	painting ¹ , industrial emission ² , evaporative emission ³
trans-2-heptene		0.9987	11.21	6.59	95.00	19.54	
cis-2-heptene		0.9994	17.48	6.11	96.87	14.58	
c+t1.3-dichloropropene		0.9998	17.69	6.85	94.65	7.45	Dry celaning ¹¹
Methylcyclohexane	0.00744	0.9999	16.82	5.48	100	12.54	industrial emission ²

Compound Name	MDL (µg/m³)	Calibration R ²	Tube Precison (%)	System Precison (%)	Recovery	Detecte d (%)	Source of compounds
2.2-dimethylhexane+ 2.5-dimethylhexane		0.9999	08.45	6.42	94.65	24.85	
2.4- dimethylhexane+1.1.2- Trichloroethane		0.9996	9.78	7.58	96.00	19.78	Dry celaning ¹¹
1-methylcyclohexene		0.9997	9.54	5.48	96.87	0	
Bromotrichloromethane		0.9998	8.75	7.21	93.54	3.12	Dry celaning ¹¹
2.3.4-trimethylpentane		0.9998	8.69	7.39	96.98	0	
Toluene	0.00832	0.9998	5.32	5.85	94.87	100.00	architectural or furnishing ,painting, oil refinery ¹ , coatings ^{1,2,5,6} , motor vehicle ^{2,3,9} , industrial emission ^{2,4} , diesel engine exhasut ⁴ , printing ⁷
2-Methylheptane	0.00651	0.9999	12.19	4.18	100	97.90	
m+p-Chlorotoluene	0.01689	0.9999	11.67	6.84	74.82	95.81	Dry celaning ¹¹

Compound Name	MDL (µg/m³)	Calibration R ²	Tube Precison (%)	System Precison (%)	Recovery	Detecte d (%)	Source of compounds
o-Chlorotoluene+ Dibromochloromethane		0.9904	11.21	9.87	81.54	38.32	Dry celaning ¹¹
4+3-methylheptane		0.9999	13.14	8.85	98.85	90.72	
t+c-1.3- dimethylcyclohexane		0.9999	11.49	9.84	96.54	91.62	
t+c-1.4- dimethylcyclohexane		0.9999		7.65	94.65	46.41	
1-octene		0.9997	24.62	9.85	86.85	97.60	ou a 1 a
Octane	0.00778	0.9999	14.87	10.51	92.54	97.60	Oil refinery', surface coating ⁶
trans-2-octene		0.9998	18,65	8.95	95.00	18.52	
trans-1.2- dimethylcyclohexane		0.9999	26.48	7.95	96.00	85.63	
cis-1.2- Dimethylcyclohexane		0.9996	11.72	7.51	83.50	96.71	

Compound Name	MDL (µg/m³)	Calibration R ²	Tube Precison (%)	System Precison (%)	Recovery	Detecte d (%)	Source of compounds
2.2.5- trimethylhexane+1.2.4- Trimethylcyclohexane	0.00976	0.9993	26.14	8.41	93.25	8.54	
Tetrachloroethene. Perchloroethylene	0.00609	0.9999	13.62	9.84	94.87	84.43	Dry cleaning ^{1,11}
Chlorobenzene	0.00756	0.9999	11.50	11.85	89.51	97.31	Dry celaning ¹¹
Ethylbenzene	0.00972	0.9999	5.50	9.54	96.57	100.00	architectural or furnishing ¹ Coatings ^{1,6} , painting ¹ , Oil refinery ¹ , evaporative emission ^{3,9}
Bromoform	0.04546	0.9999	14.18	8.94	68.54	77.84	
Styrene	0.01817	0.9978	7.44	10.64	97.85	99.10	Painting ¹ , printing ^{6,7}
1-Nonene		0.9985	13.25	9.84	98.02	95.81	

	MDL	Calibration	Tube	System	D	Detecte	0
Compound Name	(µg/m³)	R ²	Precison	Precison	Recovery	d (%)	Source of compounds
			(70)	(%)			
meta+para xylene	0.00876	0.9999	6.55	5.85	96.54	100.00	architectural or furnishing ¹ Coatings ^{1,5,6} , painting ¹ , Oil refinery ¹ , evaporative emission ^{3,9} , diesel engine exhasut ⁴ , surface coating ⁴ , printing ⁶
ortho-xylene	0.00509	0.9999	9.14	7.98	97.68	99.70	architectural or furnishing ¹ Coatings ^{1,5} , painting ^{1,,} Oil refinery ¹ , evaporative emission ^{3,9} , printing ⁶
1.4-Di-Cl- Butane+1.1.2.2-Tetra- Cl-Ethane		0.9995	13.87	8.95	92.14	86.83	Dry celaning ¹¹
Nonane	0,00913	0.9996	10.22	9.02	98.87	68.26	Asphalt emission ¹ , evaporative emission ³ , printing ⁷
iso-propylbenzene	0.00662	0.9994	12.25	10.03	95.21	99.40	

Compound Name	MDL (µg∕m³)	Calibration R ²	Tube Precison (%)	System Precison (%)	Recovery	Detecte d (%)	Source of compounds
3.6-Dimethyloctane		0.9989	15.56	8.72	98.52	0.00	
n-propylbenzene	0.00344	0.9992	14.25	8.62	96.52	95.81	evaporative emission ³
tert-Butylbenzene		0.9997	16.21	9.08	98.85	0	
3-ethyltoluene	0.00873	0.9989	13.12	10.54	97.85	100	
4-ethyltoluene	0.00940	0.9988	14.22	7.64	96.85	99.70	
1.3.5-trimethylbenzene	0.00907	0.9961	10.48	8.94	97.94	99.70	evaporative emission ³ , gasoline vehicle exhaust ³ , surface coating ⁶
2-ethyltoluene	0.01058	0.9987	15.31	6.87	98.89	98.50	
1-Decene		0.9935	16.17	8.92	96.94	03.45	
1.3-Dichlorobenzene +Benzyl chloride		0.9981	14.81	8.64	81.84	67.96	Dry celaning ¹¹
1.4-Dichlorobenzene	0.00947	0.9981	12.10	11.54	80.00	86.83	Dry celaning ¹¹

Compound Name	MDL (µg/m³)	Calibration R ²	Tube Precison (%)	System Precison (%)	Recovery	Detecte d (%)	Source of compounds
1.2.4-trimethylbenzene	0.00440	0.9984	9.50	9.54	86.84	12.15	Oil refinery ¹ , evaporative emission ³ , gasoline vehicle exhaust ^{3,4} , surface coating ^{4,6} , printing ^{6,7}
Decane	0.01011	0.9979	9.60	9.67	91.98	99.70	Asphalt emission ¹ , evaporative emission ³ , diesel engine exhaust ^{3,7} , surface coating ^{4,6} , printing ⁶
iso-butylbenzene		0.99757	15.85	7.95	99.97	97.60	
sec-butylbenzene		0.9979	26.55	9.84	97.97	93.11	
1.2.3-trimethylbenzene+ p-cymene		0.9972	15.29	8.74	81.97	99.40	
1.2-Dichlorobenzene		0.9969	20.23	9.51	81.98	96.41	Dry celaning ¹¹
1.3-diethylbenzene		0.9957	22.16	10.21	98.65	97.90	
1.4-diethylbenzene	0.00764	0.9931	29.36	9.58	100	98.20	

Compound Name	MDL (µg/m³)	Calibration R ²	Tube Precison (%)	System Precison (%)	Recovery	Detecte d (%)	Source of compounds
n-butylbenzene		0.9941	28.56	11.02	95.98	96.41	
1.2-Diethylbenzene		0.9957	16.43	10.35	98.65	95.81	
1-Undecene		0.9877	17.07	9.54	94.65	96.11	
Undecane		0.9934	21.02	11.54	93.64	11.21	Asphalt emission ¹ , diesel engine exhaust ^{3,4,7} evaporative emission ³ ,
1.2.3.5- Tetramethylbenzene		0.9892	17.04	11.09	91.97	93.41	
1.2.4.5- Tetramethylbenzene		0.9892	19.06	9.65	90.65	98.80	
1.2.4-trichlorobenzene		0.9812	28.59	10.65	78.98	91.32	Dry celaning ¹¹
Naphthalene	0.00833	0.9793	28.32	11.97	88.65	97.31	evaporative emission ³
Dodecane		0.9863	29.56	11.52	94.65	84.43	Asphalt emission ¹
Hexylbenzene		0.9509	28.12	11.98	95.00	33.83	

¹Liu et al., 2005; ²Brown at al.,2003; ³ Srivastava, 2005; ⁴ Fujita, 2001; ⁵Lawrimore and Aneja, 1997; ⁶ Watson et al., 2001; ⁷ Chang et al., 2006; ⁸ Guenther et al., 1994; ⁹ Christensen et al., 1999; ¹⁰ Hoshi et al., 2008; ¹¹ Hellen et al., 2006

APPENDIX F

Questionnaire

Table F.1 The sample questionnire used in the thesis

ODTÜ Çevre Mühendisliği Bölümü-Bursa Çevre İl Müdürlüğü Tarafından Yürütülen "Bursa Atmosferinde Bulunan Organik Kirleticilerin Neden Olduğu Sağlık Riskinin Belirlenmesi Çalışması"Tanımlama Anketi

Uygulayan	Kendisi Teknisven	HN			
		Uygulanma Tarihi	gim ay yıl		
Adres					
Mahalle		Cadde/Sokak			
Apt. No.	Daire No.	Semt			
İlce	P	osta Kodu			
Telefon No.					
1. Uygulanan (18 yaşından büy	Ad Soyad)				
2. Burası sürek	li yaşadığınız eviniz mic	lir yoksa yılın yarısınd	an azını geçirdiğiniz yazlık ya da		
ikinci eviniz m	idir? 🗌 Sürekli deva	m			
	🗌 Yazlık (ikir	nci ev) dur,bu hane uygun	değil		
3. Bu adreste k	aç kişi yaşamaktadır?				
4. Şimdi bu ha	nede sürekli (yıl boyu) y	aşayanlar ile ilgili bazı	bilgiler doldurulacaktır.		
Aşağıdaki sol	ruları bu hanede yaşı	ayan herbir kişi içir	n arka sayfalardaki tablolara		
yanıtlayınız.					
a. Ilk a	dı		Tablo 1		
b. Cins	siyeti		Tablo I		
c. Dog	um yili nlakati tahla E balamaan				
e Avli	k gelir tablo E kolomu son	nındaki seçeneklerden seçin nındaki soconoklordon socin	iz Tablo I		
	- Serra unior volona sol	and a sequence well seque			
Gelir bilgileri,	Gelir bilgileri, bilimsel araştırmalarda, benzer özelliklere sahip bireyleri gruplandırmak için				
sıkça kullanılı	r. Bu araștırma sonund	la elde edilecek olan	verilerin analizi sırasında gelir		
grupları da bi	r değişken olarak ele :	alınacaktır. Lütfen ya	nıtlarınızın gizli tutulacağını ve		

sadece bilimsel amaçlarla kullanılacağını unutmayınız.

Tanımlayıcı Anket Tablo 1

Α	В	С	D	E	F
Sakin No	İlk Adı	Cinsiyet	Doğum Yılı	Memleket	Aylık Gelir
a					
b					
с					
d					
e					
f					
g					
h					
i					
j					
k					
1					
m					
Uygun olanı seçiniz		Cinsiyet: Kız (1) Erkek (2) Cevap yok (55) Uygulanamaz (88)		Memleket: Ege (1) Marmara (2) Batı Karadeniz (3) Doğu Karadeniz (4) Doğu Anadolu (5) Güneydoğu Anadolu (6) Akdeniz (7) Yabancı (8) İç Anadolu (9) Cevap yok (55) Bilmiyorum (99)	Ayhk Gelir: Çalışmıyorum (1) 0-300 milyon (2) 300-600 milyon (3) 600 milyon-1 milyar (4) 1-2 milyar (5) 2 milyardan fazla (6) Cevap yok (55) Bilmiyorum (99)

Demografik ve Kişisel Bilgiler

Bu bölümdeki sorular her hanedeki birincil katılımcı tarafından yanıtlanacaktır. Lütfen her
soru için size uygun olan seçenegi yanındaki kutucugu işaretleyerek belirtiniz. Seçenek
sunulmamış olan soruları, kutucukların içine ya da ayrılmış olan boşluğa yazarak
yanıtlayınız.
5. En son mezun olduğunuz okul a. Hiç okula gitmedim b. İlkokul c. Ortaokul d. Lise e. Meslek yüksek okulu f. Üniversite g. Lisansüstü
6. Cinsiyetiniz
a. Kız b. Erkek
7. Doğum tarihiniz 8. Kilonuz giin ay yıl kg
9. Günde ne kadar zamanınızı evde geçiriyorsunuz?
10. Evde bulunduğunuz süre içinde ne kadar su tüketiyorsunuz?
11. İşyerinizde veya okul/kurs gibi düzenli olarak bulunduğunuz yerlerde günde ne kadar zaman geçiriyorsunuz?
12. İşyeri/okul/kurs vb. yerlerde bulunduğunuz süre içinde ne kadar su tüketiyorsunuz?

Demografik ve Kişisel Bilgiler

Bu bölümdeki sorular her hanedeki birincil katılımcı tarafından yanıtlanacaktır. Lütfen her soru için size uygun olan seçeneği yanındaki kutucuğu işaretleyerek belirtiniz. Seçenek sunulmamış olan soruları, kutucukların içine ya da ayrılmış olan boşluğa yazarak yanıtlayınız.
5. En son mezun olduğunuz okul a. Hiç okula gitmedim b. İlkokul c. Ortaokul d. Lise e. Meslek yüksek okulu f. Üniversite g. Lisansüstü
6. Cinsiyetiniz
7. Doğum tarihiniz 8. Kilonuz $\begin{array}{c} g \ddot{u}n & ay & y vl \\ \hline \end{array} / \hline \end{array} / \hline \end{array} $ kg
9. Günde ne kadar zamanınızı evde geçiriyorsunuz?
10. Evde bulunduğunuz süre içinde ne kadar su tüketiyorsunuz?
11. İşyerinizde veya okul/kurs gibi düzenli olarak bulunduğunuz yerlerde günde ne kadar zaman geçiriyorsunuz?
12. İşyeri/okul/kurs vb. yerlerde bulunduğunuz süre içinde ne kadar su tüketiyorsunuz?

		1.GÜN			
Bugünün Tarihi		0 0	0 0 0	0 0	
gün ay yıl		Pzt Sc	ılı Çarş. Perş. Cuma	Ctesi Pazar	
// 2008					
Yer	Sabah	Öğleden Sonra	Akşam	Gece	
Ulaşım/ Trafik	67891011	12 13 14 15 16 17	18 19 20 21 22 23	24 1 2 3 4 5	
Fy (Bina İci)	6 7 8 9 10 11	12 13 14 15 16 17	18 19 20 21 22 23	24 1 2 3 4 5	
	000000	0 0 0 0 0 0	0 0 0 0 0 0	0 0 0 0 0 0 0	
Okul/İş (Bina İçi)	000000	12 13 14 15 16 17 0 0 0 0 0 0 0	18 19 20 21 22 23 0 0 0 0 0 0 0	24 1 2 3 4 5	
Bar/Lokanta/Kahve	6 7 8 9 10 11	12 13 14 15 16 17	18 19 20 21 22 23	24 1 2 3 4 5	
	000000	0 0 0 0 0 0	0 0 0 0 0 0 0	0 0 0 0 0 0 0	
Diğer (Bina İçi)	000000	0 0 0 0 0 0 0	0 0 0 0 0 0 0	0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	
Ev (Bina Disi)	6 7 8 9 10 11	12 13 14 15 16 17	18 19 20 21 22 23	24 1 2 3 4 5	
EV (Dilla Dişi)	000000	0 0 0 0 0 0	0 0 0 0 0 0	0 0 0 0 0 0 0	
Okul/İş (Bina Dışı)					
	6 7 8 9 10 11	12 13 14 15 16 17	18 19 20 21 22 23	24 1 2 3 4 5	
Diger (Bina Dişi)	000000	0 0 0 0 0 0	0 0 0 0 0 0 0	0 0 0 0 0 0 0	
1. Ulaşım amacıyla yolda geçirdiğiniz süre Image: saat/dakika 2. Bina içinde sigara içen birisiyle geçirdiğiniz süre Image: saat/dakika 3. Arac içinde sigara içen birisiyle geçirdiğiniz süre Image: saat/dakika					
4. Kapalı va d	la acık yüzme havuz	unda gecirdiğiniz sü	re	□□ saat/dakik	
5. Temizlik ür	ünleri (deterian, par	latıcı vb) kullandığı	nız süre	□□ saat/dakik	
6. Halı üzerin	6. Hali üzerinde oturduğunuz va da uzandığınız süre				
7. Garaj ya da	7. Garai va da atölve benzeri kapalı bir alanda gecirdiğiniz süre				
8. Havalandır	8. Havalandırma amacıyla kapı veya camları açık tuttuğunuz süre				
9. Toprak kazmak vb. ağır işler ile koşu, bisiklete binme, aerobik, basketbol,					
futbol vb. a	ağır egzersiz yaptığır	nız süre		🔲 saat/dakik	
10.Yürüyüş, bahçede çalışmak, ayakta iş yapmak, golf oynamak vb.					
hafif egzer	hafif egzersiz yaptığınız süre				
11.Elde bulaşık yıkadığınız süre				🔲 saat/dakik	
12. Duşta geçirdiğiniz süre				🔲 saat/dakik	
13.Banyoda (k	küvete su doldurup i	çine girerek) geçird	ğiniz süre	🔲 saat/dakik	
14.Sohbet etmek, televizyon seyretmek, dinlenmek üzere oturarak					
geçirdiğiniz	z süre			🔲 saat/dakik	
15. Dinlenmek	üzere uzanarak geç	irdiğiniz ve uyuduğu	nuz süre	🔲 saat/dakik	

CURRICULUM VITAE

PERSONAL INFORMATION

Surname, Name	: Civan (Yılmaz), Mihriban
Nationality	: Turkish
Date and Place of Birth	: Manisa, 13.03.1977

EDUCATION

2002-2010	Middle East Technical University, Ankara, Turkey
	Ph.D. after BS in Environmnental Engineering
1995-1999	Dokuz Eylül University, İzmir, Turkey
	BS in Environmnental Engineering

WORK EXPERIENCE

	Intern Engineering Student
July 1997-August 1997	Manisa Organized Industrail District
	Teaching Assistant
	Engineering Department Ankara, Turkey
February 2002- present	Middle East Technical University, Environmental

FIELD OF PROFESSION

Atmospheric chemistry, Air Pollution and its Control, Health Risk Assessment