TEMPORAL VARIATIONS AND SOURCES OF ORGANIC POLLUTANTS IN TWO URBAN ATMOPSHERES: ANKARA AND OTTAWA

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ABSTRACT

TEMPORAL VARIATIONS AND SOURCES OF ORGANIC POLLUTANTS IN TWO URBAN ATMOPSHERES: ANKARA AND OTTAWA

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This study aimed at providing a thorough understanding of temporal and spatial variations of VOCs and underlying factors in different microenvironments in two different urban atmospheres, with different degrees of regulatory enforcement. The VOC data were collected in field campaigns conducted in Ankara, Turkey, and Ottawa, Canada over the years 2000-2004. Insight into the sources of VOCs in different urban atmospheres was sought by using three commonly used receptor models namely; Positive Matrix Factorization (PMF), Chemical Mass Balance (CMB) Model and Conventional Factor Analysis (CFA). Motor vehicle related source profiles were developed to use in receptor modeling. Motor vehicles are the most abundant VOC sources with about 60% and 95% contributions to ambient levels in Ankara and Ottawa, respectively. Residential heating (31%) during winter season, biogenic (9%) and architectural coating (12%) emissions during summer season and solvent use (about 12%) emissions are the next abundant VOC sources in Ankara.

In addition, a new method to estimate the contribution of sources from wind sectors in urban atmosphere was developed and implemented in this study. The comparison of the results of these two cities demonstrated the influence of control measures on ambient levels and sources of VOCs observed in different urban atmospheres. VOC levels in Ankara exceed EU levels and they are about factor of two higher than that are measured in Ottawa owing to lack of implementation of emission control regulations for VOCs in Ankara compared to well adopted regulations in Ottawa.

Keywords: Volatile organic compound, temporal variation, spatial variation, receptor modeling, source profile.

ÖZ

ANKARA VE OTTAWA ATMOSFERLERİNDEKİ ORGANİK KİRLETİCİLERİN MEVSİMSEL DEĞİŞİKLİKLERİ VE KAYNAKLARININ BELİRLENMESİ

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Bu çalışmanın amacı, Uçucu Organik Bileşiklerin (UOB) zamansal ve mekansal değişimleri ile bunları belirleyici faktörlerin yasal düzenlemeleri farklı olan iki ayrı şehirdeki farklı mikro-çevrelerde incelenmesidir. UOB veri seti Ankara ve Ottawa'da (Kanada) 2000-2004 yıllarında gerçekleştirilen saha çalışmalarında elde edilmiştir. Şehir havasındaki UOBlerin kaynaklarını belirleyebilmek amacı ile kaynak modellemesi yöntemi kullanılmıştır. Modelleme çalışmalarında, Pozitif Matrix Faktörizasyonu (PMF), Kimyasal Kütle Dengesi (CMB) ve Geleneksel Faktör Analizi (CFA) modelleri kullanılmıştır. Motorlu taşıtlardan kaynaklanan kaynak profilleri geliştirilmiş ve modellemede kullanılmıştır. Motorlu taşıtlar Ankara ve Ottawa şehirlerinde sırası ile %60 ve %95'lik katkı oranlarıyla en baskın UOB kaynağı olarak hesaplanmıştır. Kimyasal çözücü kullanımı (%12), kış sezonunda evsel ısınma (%31), yaz sezonunda ise bitkisel emisyonlar (%9) ve bina yüzey boyaları (%12) Ankara'daki en etkili UOB kaynakları olarak hesaplanmıştır.

Bu çalışmada ayrıca, kirleticilerin katkı paylarının rüzgar yönlerine göre hesaplanmasını sağlayan yeni bir yöntem geliştirilmiş ve uygulanmıştır. Ankara ve Ottawa çalışmalarının sonuçlarının karşılaştırılması, yasal düzenlemelerin etkisini ortaya koymuştur. Ankara’daki UOB seviyeleri AB limitlerini aşmaktadır ve Ottawa sonuçlarından iki kat daha fazladır. Bu durum, Ankara’da UOBler ile ilgili yasal mevzuatın uygulanmasının henüz yetersiz olması buna karşın Ottawa’da yasal düzenlemelerin etkili olarak uygulanmasından kaynaklanmaktadır.

Anahtar Kelimeler: Uçucu organik bileşikler, zamansal değişiklik, mekansal değişiklik, kaynak modellemesi, kaynak profili.

To My Loving Husband and Caring Family…

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LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
AQCR	Air Quality Control Regulation
BTEX	Benzene, toluene, ethylbenzene, xylene
BV	Breakthrough volume
CFA	Conventional Factor Analysis
CFC	Chlorofluorocarbon
CMB	Chemical Mass Balance Model
DNPH	Dinitrophenylhydrazine
EMEP	European Monitoring and Evaluation Program
EPA	Environmental Protection Agency
EV	Explained Variation
FID	Flame Ionization Detector
GC	Gas Chromatography
GHG	Greenhouse Gases
GWP	Global Warming Potential
HAP	Hazardous Air Pollutants
HCFC	Hydro-chlorofluorocarbon
HDV	Heavy Duty Vehicle
HFC	Hydro-fluorocarbon
IAPCR	Industrial Air Pollution Control Regulation
IUPAC	International Union of Pure and Applied Chemistry
LDV	Light Duty Vehicle
LPG	Liquefied Petroleum Gas
LR	Linear Regression
MC	Motor Cycle
MDL	Method Detection Limit

METU	Middle East Technical University
MFC	Mass Flow Controller
MSD	Mass Selective Detector
NAPS	National Air Pollution Surveillance Network
NG	Natural Gas
NMHC	Non-methane Hydrocarbon
NMOC	Non-methane Organic Compound
NMOG	Non-methane Organic Gases
ODP	Ozone Depletion Potential
ODS	Ozone Depleting Substance
PAH	Polycyclic Aromatic Hydrocarbons
PAMS	Photochemical Assessment Monitoring Stations
PCA	Principal Component Analysis
PERC	Perchloroethylene
PM	Particulate Matter
PMF	Positive Matrix Factorization
PSL	Priority Substance List
QA	Quality Assurance
QC	Quality Control
QI	Qualifier Ion
ROG	Reactive Organic Gases
RRF	Relative Response Factor
RSD	Relative Standard Deviation
RSHM	Refik Saydam Hıfzıssıhha Center
RV	Retention Volume
RVP	Reid Vapor Pressure
SCE	Source Contribution Estimate
SIM	Selected Ion Monitoring
SMW	State Meteorological Works
SPTD	Short Path Thermal Desorption
SRM	Standard Reference Material

SSI	State Statistical Institute
SSV	Safe sampling volume
SVOC	Semi volatile organic compounds
TCA	Trichloroethane
TCE	Trichloroethylene
THC	Total Hydrocarbon
TI	Target Ion
TIC	Total Ion Chromatogram
TOG	Total Organic Gases
UNECE	United Nations Economic Commission for Europe
UNFCCC	United Nations Framework Convention on Climate Change
VOC	Volatile Organic Compound
ANOVA	Analysis of Variance
BV	Breakthrough volume
CFA	Conventional Factor Analysis
CMB	Chemical Mass Balance Model
EV	Explained Variation
FID	Flame Ionization Detector
GC	Gas Chromatography
HDV	Heavy Duty Vehicle
LDV	Light Duty Vehicle
LR	Linear Regression
MDL	Method Detection Limit
METU	Middle East Technical University
MFC	Mass Flow Controller
MSD	Mass Selective Detector
ODS	Ozone Depleting Substance
PERC	Perchloroethylene
PMF	Positive Matrix Factorization
QI	Qualifier Ion
RRF	Relative Response Factor

RSD	Relative Standard Deviation
RSHM	Refik Saydam Hıfzıssıhha Center
RVP	Reid Vapor Pressure
SCE	Source Contribution Estimate
SIM	Selected Ion Monitoring
SMW	State Meteorological Works
SPTD	Short Path Thermal Desorption
SSI	State Statistical Institute
SSV	Safe sampling volume
SVOC	Semi volatile organic compounds
TCA	Trichloroethane
TCE	Trichloroethylene
TI	Target Ion
TIC	Total Ion Chromatogram
VOC	Volatile Organic Compound

CHAPTER 1

INTRODUCTION

1.1. Preamble

This thesis examines ambient volatile organic compound (VOC) concentrations in two urban environments to identify their sources, and their temporal and spatial variations. The opportunity to examine VOCs in two different locations like Ankara and Ottawa arose from the collaboration developed over the past 10 years between faculty members at Middle East Technical University (METU) and Carleton University. Each of these locations could have been studied in isolation but the opportunity for collaboration enabled a more detailed comparative approach involving these two locations with similarities as well as dissimilarities. The comparison of the characteristics of these locations can be summarized in a few key points. Ankara and Ottawa are both national capitals with residential, commercial and institutional sectors, and where major industrial point sources of VOCs are absent. Seasonal variations are similar, although the extremes of temperature and relative humidity parameters are noticeably different. In both locations, motor vehicle related VOC emission sources could be expected to be important. While there is already a significant body of ambient monitoring data in Ottawa, this study is the first comprehensive attempt to generate comparable data in Ankara. Ottawa represents a jurisdiction, which has been the subject of regulations concerning VOC emissions for more than 20 years while regulatory action in Ankara awaits comprehensive and quantitative analysis about the levels and sources of ambient VOCs. The possibility to carry out parallel studies in these two locations thus enables meaningful comparisons both for their similarities as well as their dissimilarities.

1.2. Problem Statement

The Earth's atmospheric environment is changing at an unusual rate. Emissions of trace gases due to anthropogenic activities are causing perturbations in the chemical composition of the atmosphere and these are beginning to have major quantifiable effects on the behavior of the Earth - atmosphere - biosphere system. For example, emission of ozone depleting substances are causing changes in stratospheric ozone (O_3) concentrations, and thus, to the amount of UV light reaching to the Earth's surface. Although estimates are highly uncertain, global temperatures are expected to increase between 1.5°C and 3.5°C, by 2100, due to greenhouse gases emitted from anthropogenic activities. Emissions of volatile organic compounds (VOCs) are resulting in changes to atmospheric chemistry, particularly the oxidizing capacity of the troposphere by its role in production of troposheric O_3. These gaseous pollutants not only have indirect effects by changing the steady state in the atmosphere, but also have direct adverse impacts on human health and ecology.

One of the most intractable air quality problems has been the continued exceedance of the air quality standards for O_3 in a large number of metropolitan areas in the Unites States (Godish, 1991) and other megacities of the world. Tropospheric O_3 has adverse impacts on human health and vegetation (Lipmann, 1991; Lefohn and Foley, 1992). The difficulty of attaining the O_3 standard is due in great measure 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 NO_x in the presence of sunlight (Finlayson-Pitts and Pitts, 1993; Atkinson, 2000). Development of O_3 abatement strategies requires a detailed knowledge of the sources of VOCs and NO_x emissions and the effects on ambient O_3 levels, because the only option to control O_3 is the control of primary precursors.

VOCs are of concern in many urban areas not only due to their role in tropospheric O_3 formation but also due to their adverse impacts on human health.

Many VOCs have been identified as toxic substances, and some of them are either known or suspected carcinogens (Axelrad *et al.*, 1999; EPA, 1993a).

VOCs include over 500 different organic species such as alkanes, alkenes, alkynes, aromatics, aldehydes, ketones, acids, and alcohols (Mackay *et al.*, 1992a). Emissions of VOCs not only comprise a broad spectrum of organic species but also are associated with a wide variety of sources. According to CORINAIR 1990 Inventory, emissions of VOCs in 29 European countries were 989, 1220, 1376, 4920, 6756, 507, and 759 thousand tons per year from anthropogenic sources of commercial, institutional and commercial heating; industrial processes; extraction and distribution of fossil fuels; solvent use; road transport; waste treatment and disposal activities; and agricultural activities, respectively (McInnes, 1996). VOC emissions show a significant temporal and spatial variation (Derwent, 1999). Thus, an accurate assessment of sources and source contributions play a critical role in development of VOC management plans in urban environments.

Studies on VOCs aimed at determining sources and atmospheric concentrations of organic gases in urban and rural atmospheres. In this regard, ambient monitoring programs for VOCs have been initiated in North America and Europe. In North America, over 4,300 monitoring sites operate as part of three national air quality networks where VOCs are monitored in addition to the criteria air pollutants (i.e., SO_2, NO_x, particulate matter (PM) and O_3). 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/NO_x program (CCME, 1997). In the 1990 Clean Air Act Amendments, the US Environmental Protection Agency (EPA) mandated to improve monitoring of ozone and its precursors within specified ozone non-attainment areas. The US EPA initiated the Photochemical Assessment Monitoring Stations (PAMS) program in 1993. Chemical parameters measured at PAMS sites include O_3, NO_x, 56 hydrocarbons and three carbonyl species. PAMS network is 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 (Co-operative program for monitoring and evaluation of the long range transmission of air pollutants in Europe) stations in 1992 (Solberg *et al.*, 1995); however, the number of monitoring stations is expected to increase rapidly in the near future.

Studies on ambient levels of VOCs have been conducted in USA, Canada, and EU countries. However, such studies are scarce in Eastern Europe and Middle East countries. As VOC emissions show large temporal and regional variations (Friedrich and Obermeier, 1999), it is crucial to determine levels and sources of VOCs in each country and to develop management plans accordingly.

In Turkey, inorganic air pollutants, particularly SO_2 and PM, have been a major concern in urban air pollution for many years. These pollutants have been monitored in urban atmospheres since early 1980s. In addition, regulatory actions were taken to reduce their emissions. Many scientific studies on atmospheric levels, sources and impacts of inorganic air pollutants were conducted in Turkish cities. However, only very limited knowledge, in terms of both number of measurement locations and number of organic compounds studied, exists on organic air pollutants in Turkey. Atmospheric levels and sources of individual organic air pollutants have not been identified thoroughly in Turkey at the present.

As being a candidate country for the EU, Turkish environmental laws and regulations will be harmonized with the relevant EU directives over the next decade. Although ambient air quality criteria and objectives may be harmonized with EU countries, emission reduction strategies may not necessarily be the same as those implemented in other European countries. This would be mainly due to differences in emission characteristics in countries. Thus, detailed investigation is required on the type and contribution of emission sources in Turkey. VOCs are monitored in EU countries but such studies are currently not conducted in Turkey.

The outcomes of the study that are specific to Turkey are also important to fill the data gap in this part of the world. Recent publications have indicated that existing legislations and cultural differences influence the ambient concentrations of VOCs by influencing type and amount of emissions (Liu *et al.*, 2000; Hsieh and Tsai, 2003; Na *et al.*, 2003). For example, one observation revealed that the toluene/benzene ratio was much higher in the Asia-Pacific countries than the currently stated value of around two for the USA and European countries (Gee and Sollars, 1998). Although detailed investigation is required, the difference is partly due to the emission sources and strengths in the Asia-Pacific countries. This illustrates that the management plans should be prepared as specific to each country, and in addition, detailed investigation on the emission sources and strengths are required for each country to develop effective management plans.

In Ottawa, despite regional air quality monitoring that has included VOCs for many years, studies on traffic related air toxics in different microenvironments are scarce. Motor vehicle emissions are one of the most significant sources of air pollutants for urban air, particularly in micro-environments such as nose-level ambient air along busy downtown streets, underground parking garages, or the cabin air in vehicles moving in dense traffic. The impact of motor vehicle emissions on urban air quality has generally been assessed and regulated by considering carbon monoxide (CO), NO_x, total hydrocarbons (THC), and PM. More recently, interest has turned to individual volatile and semi-volatile organic compounds (VOC and SVOC) and the detailed characterization of particulate matter in terms of particle size and chemical composition (EPA, 1993a).

Individual chemical species can have very different health implications either directly through their toxic properties, or through their different potential to form ground level ozone. The different health effects of various emissions is particularly important in view of the trade-offs that may be involved among different types of emissions associated with alternative or reformulated fuels or transportation technologies. The extremes of Canadian climate also provide some special challenges in the assessment of traffic related emission impacts under different conditions.

1.3. Objectives of the Study

The objective of this study is to investigate levels of VOCs, factors affecting their temporal and spatial variations and source apportionment of VOCs by comparing a strictly regulated (i.e., Ottawa, Canada) and a loosely regulated (i.e., Ankara, Turkey) urban air sheds. The study aims:

- To determine and compare current pollution states in selected microenvironments in Ankara and Ottawa,
- To establish factors affecting temporal variability of VOCs in the two cities,
- To find out factors affecting spatial variability of VOC levels in different microenvironments in the two cities,
- To develop VOC source profiles for different source types in both cities,
- To determine types of sources contributing on observed VOC levels in Ankara and Ottawa,
- To determine quantitative source contributions in two cities,
- To apply and compare different receptor models to speciated VOC datasets,
- To compare the two cities in terms of levels of VOCs, temporal variability, and sources of VOCs, and
- To develop new data analysis methods or tools for the interpretation of large VOC datasets.

1.4. Novelty and Contribution of This Study

This study provides contribution to the international scientific community on the following issues:

- Temporal and spatial variations in VOC concentrations and the underlying factors are determined by using a large dataset and measurements conducted in different ambient and indoor microenvironments in two different countries.
- A new method of sector analysis namely concentration weighted, wind-based trajectory analysis was developed in this study. The method uses pollutant concentration measured at a receptor and frequencies of occurrence of wind sectors to apportion source regions to predefined wind sectors. This new method was applied to VOC data generated in this study. The results proved that the new method was successful to quantify source regions in urban atmosphere.
- Improvement in the application of a new generation receptor model (i.e., Positive Matrix Factorization) was achieved by the pretreatment of data and uncertainty matrices and the incorporation of diagnostic tools such as regression analysis.
- Comparison of different receptor models was achieved by applying different receptor models to the large dataset generated in this study (very limited study is available in the literature on the comparison of different receptor models applied to speciated VOCs and they have been published only in the last few years).
- This study provides evaluation of the analytical method to measure VOCs.
- This study pioneers in studies on atmospheric organic pollutants in Turkey providing;
    - Determination of ambient levels and sources of large number of organic compounds with sufficient spatial and temporal coverage.
    - Speciated VOC fingerprints (source profiles) of gasoline and diesel fuels used in Turkey, speciated VOC fingerprints of motor vehicle emissions (i.e., cold-start exhaust, hot-start exhaust, evaporative) for the fleet profile in Ankara.
    - The first source apportionment study done for speciated VOCs measured in Turkey.

1.5. Scope of the Study

Background information needed in this study is provided in Chapter 2 in detail. This information includes but not limited to atmospheric chemistry, impacts on human health and environment, emission sources, source apportionment methodologies and recent literature review.

Sampling, analytical and instrumental methods developed and implemented in this study are thoroughly discussed in Chapter 3. Sampling sites and emission sources are described in this chapter. Quality assurance and quality control of the generated data are also presented in this chapter.

Temporal and spatial variations in the generated data set are statistically evaluated in Chapter 4. Seasonal, daily and diurnal variations and the underlying factors are investigated. This section also explains a new method developed to estimate contribution of sources from wind sectors in urban atmosphere. Implementation of the method to the generated data is discussed. Comparison of the data generated in this study with data available in literature is also provided.

Chapter 5 focuses on receptor modeling. Sources of VOCs in Ankara and Ottawa atmosphere are identified and source contributions are estimated by receptor modeling. Application of different receptor models and interpretation of the model results are discussed in this chapter. Preliminary source identification tools such as species ratios and correlations are also discussed. This chapter provides source profiles that are generated to be used in receptor modeling and comparison with literature.

Finally, Chapter 6 gives concluding remarks and outlines the recommendations for future studies.

CHAPTER 2

THEORETICAL BACKGROUND

2.1. Definition of VOC Terms

It is estimated that there are some 60,000 chemicals in current commercial production, with approximately 1,000 being added each year. Most of these chemicals are organic and of these, perhaps 500 are of environmental concern because of their presence in detectable quantities in various components of the environment, their toxicity, their tendency to bioaccumulate or their persistence (Mackay *et al.*, 1992a).

The US EPA (1997a) defines VOCs as organic compounds having a vapor pressure greater than 10^{-1} torr at 25 °C and 760 mmHg. These compounds tend to have relatively high Henry's law constants, i.e., 103-105 $Pa.m^3mol^{-1}$ for hydrocarbons and 10-105 $Pa.m^3mol^{-1}$ for halogenated hydrocarbons. When VOCs are discharged into the environment, they are likely to partition or evaporate fairly rapidly into the atmosphere. The major degradation and removal process thus occur in the air phase; thus, the atmospheric photochemistry or photodegradation of this type of volatile chemical is very important (Mackay *et al.*, 1992b).

The class of VOCs includes species with different physical and chemical behaviors. Pure hydrocarbons containing carbon and hydrogen as the only elements (e.g., alkanes, alkenes, alkynes, and aromatics) are important VOC classes. However, volatile organic compounds containing oxygen, chlorine or other halogens besides C and H are also important. These latter classes include, for example, aldehydes, alcohols, ketones, chlorinated alkanes and alkenes, chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs).

As the VOCs are in extreme number and they are versatile, several terms are used in the literature sometimes inconsistently but interchangeably to describe different fractions of atmospheric organic materials. Watson *et al.* (2001) reviews the common definitions used in the literature under nine different headings. These are: i) *Reactive organic gases (ROG)*, which are organic gases with potential to react (i.e., < 30 day half-life) with the hydroxyl radical and other chemicals in the atmosphere, resulting in ozone and secondary organic aerosol; ii) *total organic gases (TOG)*, which are organic gases with and without high hydroxyl reactivity (TOG typically includes ROG plus methane and halocarbons); iii) *PAMS target hydrocarbons*, which are the 55 target hydrocarbons and non-methane organic compounds (NMOC) measured at photochemical assessment monitoring stations (PAMS) in the U.S. where NMOC is operationally defined as the sum of hydrocarbons up to n-undecane; iv) *non-methane hydrocarbons* (NMHC, also termed as light hydrocarbons), which are C2 to C12 hydrocarbons; v) *heavy hydrocarbons*, which are C10 to C20 hydrocarbons sometimes termed as semivolatile compounds (SVOC) because the >C15 compounds are often found as both gases and particles; vi) *carbonyl compounds*, which are aldehydes and ketones, the most common being formaldehyde, acetone, and acetaldehyde; vii) *non-methane organic gases* (NMOG), which are NMHC plus carbonyls; viii) *Semi-volatile organic compounds* (SVOC), which are compounds that partition between gas and condensed phases when released into the environment including compounds such as polycyclic aromatic hydrocarbons (PAHs), methoxyphenols and lactones, pesticides, and other polar and non-polar organic compounds, and ix) *Volatile organic compounds* (VOCs), which are NMHC plus heavy hydrocarbons plus carbonyls plus halocarbons, typically <C20. VOC has been imprecisely used to describe most of the other categories described above.

In this thesis, however, the term “VOC” is used to describe C2 to C12 hydrocarbons (alkanes, alkenes, alkynes and aromatic) and halocarbons.

2.2. History of theVOC Problem

Photochemical air pollution or photochemical smog was first observed in Los Angeles, California in the late 1940s and early 1950s (Haagen-Smit *et al.*, 1993). Over the succeeding decades it has been subsequently observed in all the major industrial and urban centers. The first observations of photochemical air pollution in Europe were made in the Netherlands in 1965 (Houten, 1966) and since then elevated ozone concentrations have been observed in every European country where continuous measurements have been conducted (Sluyter and van Zantvoort, 1996).

Early studies showed that the main photochemical oxidant present in photochemical air pollution was ozone and its formation process involved sunlight, and oxides of nitrogen and hydrocarbons. It has been recognized for the last 40 years that each hydrocarbon makes a different quantitative contribution on photochemical ozone production. Early smog chamber studies were used to develop the concept of reactivity and from these studies various reactivity scales have been compiled (Dimitriades and Joshi, 1977; Carter and Atkinson 1987; Carter and Atkinson 1989; Carter 1994). In addition to the scientific studies, there has always been a policy focus within North America to identify those reactive hydrocarbons that contribute most to ozone formation on the urban scale (Dodge, 1984). A distinction has been made between hydrocarbons that were thought to be of “negligible’ reactivity and those of “low” reactivity. Increasingly, reactivity is being used in the policy process and hydrocarbons of negligible reactivity are not included in regulations (Dimitriades, 1996).

The European countries appreciated the problems of photochemical air pollution much later than the North American countries. Long-range transport and multi-day photochemical episodes on the regional scale have been perceived to be the more relevant policy issues compared to the urban scale photochemical ozone formation in Europe (NCM, 1991). Other than this divergence in policy approach, no major differences in mechanism or phenomenology have emerged from the

North American and European studies of photochemical air pollution (Derwent, 1999). The European member states have agreed to combat the regional ozone problem through international action within the scope of the United Nations Economic Commission for Europe (UN ECE) and its international convention on Long-Range Transboundary Air Pollution (UNECE, 1991). European countries have agreed to cut emissions of man-made hydrocarbons by up to 30% and to freeze their NO_x emissions as the first step toward reducing episodic peak ozone concentrations. This policy action focused attention on controlling those emissions that contribute most to regional-scale ozone formation. Thus, it has been agreed that the most reactive hydrocarbons must be clearly and unambiguously identified and control actions must be focused on reducing their emissions (Derwent, 1999).

Research on VOCs has aimed at determining sources and atmospheric concentrations of organic gases in urban and rural atmospheres as the first step. In this regard, 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., SO_2, NO_x, PM and O_3). 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/NO_x program (CCME, 1997). In the 1990 Clean Air Act Amendments, the US EPA mandated to improve monitoring of ozone and its precursors within specified ozone non-attainment areas. The US EPA 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. The 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.

2.3. Atmospheric Chemistry

Possible atmospheric fates of VOCs are: i) photolysis, if the substance absorbs light in the actinic UV ($\lambda \geq 290$ nm), ii) attack during daylight hours by OH radicals, iii) attack by O_3, especially if the molecule contains C=C double bonds, and iv) attack at night by NO_3 radicals (Finlayson-Pitts and Pitts, 1986).

Some VOCs react significantly with O_3 and/or degrade by thermal decomposition or photolysis, however, removal by reaction with O_3, or due to photolysis, can be estimated to be much less than 1% of the OH removal rate for most VOCs (Lu, 1996; Atkinson, 2000).

Kinetics and mechanisms of the gas phase reactions of the hydroxyl radical ($OH^{\cdot}$) with organic compounds have been reviewed and evaluated by Atkinson (1990, 2000). Rate constants are also recommended for organic compounds for which experimental data do not exist. The reactions are assumed to be of second order with reactant half life and lifetime of $t½ = 0.693/k[OH]$ and $\tau = 1/k[OH]$, respectively. Actual overall lifetimes may be shorter owing to competing loss processes such as photolysis. Since OH concentrations vary with the intensity of solar radiation, lifetimes will vary by location, season and time of day (Finlayson-Pitts and Pitts, 1986).

The main degradation mechanism for VOCs in the troposphere is the photochemical reactions that result in formation of photochemical smog that includes O_3, peroxy acetyl nitrate (PAN) and variety of other oxidized organic compounds. Tropospheric ozone formation is of great concern due to its adverse affects on human health and environment. Photooxidation of the NO_2 by sunlight is the only significant anthropogenic source of O_3 in photochemical smog.

$$NO_2 + h\gamma\ (\lambda<430\text{ nm}) \rightarrow NO + O \qquad (2.1)$$

$$O + O_2 \xrightarrow{M} O_3 \qquad (2.2)$$

The essential role played by VOC is the oxidation of NO, emitted by combustion process to NO_2 (Finlayson-Pitts and Pitts, 1993). The set of reactions taking place between organic compound and NO_x vary depending on the structure of organics under consideration. There is now a good qualitative and in a number of areas quantitative understanding of the tropospheric chemistry of NO_x and VOCs 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 (Atkinson, 2000). Seinfeld and Pandis (1998) illustrated the general reaction mechanism for the photooxidation of an alkane (RH):

$$\begin{array}{lr}
OH + RH \xrightarrow{O_2} H_2O + RO_2^{\cdot} & (2.3) \\
RO_2^{\cdot} + NO \rightarrow RO^{\cdot} + NO_2 & (2.4) \\
RO^{\cdot} \xrightarrow{O_2} R^{'}CHO + HO_2^{\cdot} & (2.5) \\
HO_2^{\cdot} + NO \rightarrow OH^{\cdot} + NO_2 & (2.6) \\
\hline
RH + OH^{\cdot} + 2NO \xrightarrow{O_2} R^{'}CHO + 2NO_2 + OH^{\cdot} & (2.7)
\end{array}$$

$$OH + NO_2 \xrightarrow{M} HNO_3 \tag{2.8}$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{2.9}$$

Chain initiation by OH occurs at Reaction 2.3. The Reaction 2.8 of OH with NO_2 to form nitric acid (HNO_3) is a major chain termination step. Nitric acid that is formed as a co-pollutant of ozone is a key component of acid rain. Oxidation mechanisms for olefins, aldehydes and aromatics are more complex but again have similar chain initiation, carrying and termination steps. At night, in the presence of O_3 and NO_2, NO_3 is formed as shown in Reaction 2.9. Reaction with NO_3 represents an important nighttime sink of certain VOCs (e.g., phenols, terpenes, etc.) (Finlayson-Pitts and Pitts, 1986, 1993).

2.4. Impacts of VOCs on Environment

Volatile organic compounds are of concern for more than fifty years due to their adverse impacts on environment. These direct or indirect effects of VOCs are as follows:

- Tropospheric ozone formation,
- Effects on human health,
- Effects on vegetation,
- Effects on climate change, and
- Stratospheric ozone depletion.

These issues are discussed in detail in the following sections.

2.4.1. Tropospheric Ozone Formation

Increase in the anthropogenic activities resulted in continuing increase in troposheric ozone concentrations observed over the past century (Ciccioli *et al.*, 1999). It has been found by Volz and Kely (1988) and Anfossi *et al.* (1991) that ground level ozone concentrations in remote areas exceed by a factor of two to three those existing in pre-industrial times. This effect is caused by the increased emission of nitrogen oxides (NO_x) and hydrocarbons released by human activities. Noticeably linked with the increase in tropospheric ozone is the formation of oxidized species derived from the transformation of NO_x and hydrocarbons in air (Finlayson-Pitts and Pitts, 1997).

As discussed in Section 2.2 in detail, the complex sequence of chemical reactions, activated when NO_x and hydrocarbon mixtures are exposed to the actinic region of solar radiation ($\lambda > 290$ nm), is capable of generating a large variety of species, such as peroxyacetyl nitrate (PAN), nitric acid, and oxygenated hydrocarbons (Finlayson-Pitts and Pitts, 1986), termed as photochemical oxidants. The fate of all these pollutants is strictly interconnected through an alternate sequence of day and night cycles (Ciccioli and Cecinato, 1992). Under favorable meteorological conditions both cycles are fully activated. Since these processes are not linear, rapid accumulation of ozone and photochemical oxidants can take place in the atmosphere. Within four to five days, the accumulation of pollutants can be so severe that episodes of photochemical smog pollution having adverse effects on human health, vegetation, and materials can be observed (US EPA, 1986; Ciccioli *et al.*, 1999).

Increased tropospheric O_3 levels will lead to increased OH production and decreased tropospheric lifetimes of species such as CH_4 and the HCFCs. Thus, increased tropospheric O_3 has the potential to impact stratospheric chemistry as well, via the indirect control of how much of the trace species survives to reach the stratosphere (Finlayson-Pitts and Pitts, 1986).

It is obvious that the reduction of tropospheric ozone concentrations can only be achieved by reducing its precursors since ozone is a secondary air pollutant.

2.4.2. Effects on Human Health

VOCs can have direct adverse effects on human health. Many 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 to low quantities over extended periods of time. Some health effects from overexposure to VOCs are dizziness, headaches, and nausea. Long-term exposure to certain VOCs, such as benzene, has also been shown to cause cancer. Chronic neurotoxic effects by n-hexane, irritation of mucous membranes by aldehydes and effects on the central nervous system by toluene and xylenes were also reported (Hester and Harrison, 1998).

US EPA lists 185 Hazardous Air Pollutants (HAP) under Clean Air Act many of which are VOCs. The Canadian EPA requires the Misters of the Environment and of Health to establish priority substance list (PSL). First PSL and second PSL of Canadian EPA identify 25 toxic compounds in each list many of which are VOCs.

2.4.3. Effects on Vegetation

The results of experiments dealing with the effects of VOCs on plants clearly show that indirect effects of VOCs are most relevant, e.g., formation of photo oxidants, climate change (AAS, 2004). Some experimental investigations indicate that ethene has direct phytotoxic effects on plants. Ethene is of special interest, because it is produced by many plants as a phytohormone influencing a variety of physiological processes, such as growth, differentiation and senescence. One of its best-known effects is the stimulation of fruit ripening. However, various stresses (e.g., drought, flooding, wounding, pathogens and gaseous air pollutants) enhance the biosynthesis of ethene, which acts to intensify the stress. Typical symptoms are epinasty of leaves, growth inhibition, internode shortening, abnormal bud withering, premature discoloration and yellowing of leaves, senescence and abscission of flowers, chlorosis and necrosis.

2.4.4. Effect on Climate

United Nations Framework Convention on Climate Change (UNFCCC) defines greenhouse gases (GHG) under two groups namely, direct and indirect GHGs. Direct GHGs include CO_2, CH_4, N_2O, HFCs, PFCs, SF_6 and indirect green house precursors include NO_x, CO, VOC and SO_2 (UNFCCC, 2005). Besides the direct influence on the radiative balance of the atmosphere, VOCs may also cause additional climatic effects. For example, VOCs may form aerosols, which may change cloud properties. Furthermore tropospheric ozone formed through VOCs acts as a greenhouse gas. VOCs also affect climate by influencing the amount of stratospheric water vapor (AAS, 2004).

2.4.5. Effect on Stratospheric Ozone Depletion

Ozone depleting substances (ODS) such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydro-fluorocarbons (HFCs), 1,1,1-trichloroethane (TCA) and carbon tetrachloride are also classified as VOCs due to their high volatility. Among these compounds, TCA and CCl_4 were the subject of this research.

TCA (also known as methyl chloroform) has an ozone depleting potential (ODP) of 0.1 and a global warming potential (GWP) of 0.024 relative to CFC-11 with an ODP of 1.0 and carbon dioxide (CO_2) with a GWP of 1.0. The primary use for TCA is metal cleaning in industrial processes. The share of metal cleaning in the total use of TCA was 76%, 55% and 75% in Japan, U.S.A. and Western Europe, respectively in 1988 (JICOP, 1991). Other uses include aerosols, adhesives, chemical intermediates, coatings and inks, textiles, electronics, and miscellaneous uses. Photochemical reactivity of TCA is negligible. It is relatively inert in the troposphere and thus has an atmospheric residence time of about 25 years.

Carbon tetrachloride is regarded as highly toxic. It is a known animal carcinogen and a potential human carcinogen (ATSDR, 1995). It has an ODP of 1.1 and GWP of 0.345. Carbon tetrachloride is used as refrigerant, propellant, pesticide, cleaning fluid, degreasing agent and used in some industrial applications. TCA was introduced to replace the use of toxic carbon tetrachloride. Thus carbon tetrachloride might also be used in the processes or products where TCA is used. It is relatively inert in the troposphere, thus it has an atmospheric lifetime of 30 to 100 years.

Production and consumption of TCA and carbon tetrachloride was regulated in the world by the Montreal Protocol on ODSs. Turkey has ratified the Montreal Protocol as an Article 5 country. Even before acceding to the Vienna Convention and its Montreal Protocol, Turkey had introduced as part of her laws the entire Convention and Protocol in 1990. Turkey became a party to the London and

Copenhagen Amendments in 1995. As of 30 June 1998, Import Communiqué for the phase-out of ODSs was issued by Undersecretary for Foreign Trade. The Communiqué introduced an import quota system to be in force by the year 2000, the basic requirement for the implementation of policy, and states that the import of CFC-11, 12, 113, 114, 115, carbon tetrachloride and 1,1,1-trichloroethane other than those required for servicing the existing equipment shall be banned commencing on 1 January 2000. The Communiqué also introduced some bans on the import of equipment, which contains CFCs. The first ban came into force on 1 July 1998. Licensing has also been introduced by the Decree on Import of Ozone Depleting Substances. (Oğuz, 2001)

The regulation on the Phase-out of ODSs came into force on 25th July 1999 and adopts 1 January 2000 as the target date for phase-out. The Regulation dictates that commencing on 1 January 2000 only the amounts required for servicing the products functioning of which relies on these substances shall be imported, and no allocation is to be made for use in manufacturing of new products either containing or produced with these substances. The complete phase-out of ODSs will be done by the year 2010.

2.5. Emission Sources

VOCs not only comprise a broad spectrum of species, but also are due to a wide variety of sources. VOCs are emitted from anthropogenic and biogenic sources. Anthropogenic source categories can be listed as: i) Combustion processes, ii) production, treatment, storage and distribution of fossil fuels, iii) application of volatile organic solvents and solvent-containing products, iv) industrial production processes, v) biological processes.

Combustion processes comprise, for example, internal combustion (IC) engine vehicles, combustion plants, and furnaces. Examples of solvent-containing products are paints and varnishes, metal degreasing agents, and adhesives.

Biological processes include the digestive processes of ruminants, the handling of animal manure, and the disposal of organic wastes. (USEPA, 2005)

Biogenic sources include forests, grassland, wetlands, waters, and wild animals as well as forest and grassland fires. Large quantities of VOCs are emitted into the troposphere from biogenic and anthropogenic sources (WMO, 1995; Hein *et al.*, 1997; Guenther *et al.*, 2000; Placet *et al.*, 2000; Sawyer *et al.*, 2000). Vegetation is an important source of certain VOCs, such as isoprene, series of monoterpenes, and oxygenated VOCs (Arey *et al.*, 1991; Winner *et al.*, 1992). VOCs are also emitted into the troposphere from a variety of anthropogenic sources, including combustion sources (vehicle and fossil-fueled power plant emissions), fuel storage and transport, solvent usage, emissions from industrial operations, landfills, and hazardous waste facilities (Placet *et al.*, 2000; Sawyer *et al.*, 2000). 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; WMO, 1995).

2.5.1. VOC Emission From Motor Vehicles

Sources of VOC emissions from motor vehicles have been divided into: (a) tailpipe emissions; b) evaporative and refueling emissions; and (c) crankcase emissions. Evaporative emissions consist of fuel vapor emitted from the engine and fuel system. They are divided into four source categories according to the 1990 Protocol on the 1979 Convention on Long-Range Transboundary Air Pollution Concerning The Control of Emissions of Volatile Organic Compounds or Their Transboundary Fluxes (UN ECE, 1991)

- Diurnal emissions, which result from the ``breathing'' of the fuel tank as it is heated and cooled over the course of a day.

The evaporative emissions associated with the daily (diurnal) variation in ambient temperature result from the vapor expansion inside the fuel tank that occurs as the ambient temperature rises during the daylight hours. Without an emission control system, some of the increasing volume of fuel vapor is vented to the atmosphere. At night, when the temperature drops, vapor contracts and fresh air is drawn into the fuel tank through the vent. This lowers the concentration of hydrocarbons in the vapor space above the liquid gasoline, which subsequently leads to additional evaporation (CORINAIR, 1999).

- Hot-soak emissions produced by the heat from the engine after it is shut down.

  Hot soak evaporative emissions are the emissions caused when a hot engine is turned off. Heat from the engine and exhaust system increases the temperature of the fuel in the system that is no longer flowing. Carburetor float bowls are particularly significant source of hot soak emissions (CORINAIR, 1999).
- Running losses from the fuel system while the vehicle is in operation. Running losses are the result of vapor generated in gasoline tanks during vehicle operation. Running losses are most significant during periods of high ambient temperatures. The combined effect of high ambient temperature and exhaust system heat can generate a significant amount of vapor in the fuel tank.
- Resting losses such as from open-bottom canisters (where used) and from some plastic fuel-system materials, which are reportedly subject to permeation losses, in which fuel slowly diffuses through the material.

All these types of evaporative emissions are significantly affected by the volatility of the fuel being used, the absolute ambient temperature and temperature changes, and vehicle design characteristics. For hot soak emissions and running losses the driving pattern is also of importance (CORINAIR, 1999).

2.5.2. Emission Inventories

The emission inventory is a key component of any air pollution control program. It includes types of emission sources, quantities of emissions, the temporal and spatial characteristics of emissions, and the process and emission control devices that are used at sources. Air pollution control agencies use emission inventories to identify potential control measures and the specific sources to which they will be applied. Inventories are also used to evaluate control effectiveness and to predict future ozone reductions through air quality evaluation models, such as Urban Airshed Model (UAM). A gridded emissions inventory is a critical input to the UAM model and has been one of the largest sources of uncertainty in the model output. (USEPA, 2005)

Due to the non-linear nature of ozone formation processes, it is essential to disaggregate annual emission data into values with small time steps. Usually, such atmospheric models require hourly gridded emission data, including additional information such as source heights above the ground surface. Thus, the preparation of detailed databases and inventories of anthropogenic VOC emissions constitutes a rather complex topic of environmental research activities. Large variety of different source categories, source specific parameters controlling the emissions, and source specific profiles describing the composition of VOC emissions are required. All these aspects must be taken into account within emission inventorying procedures.

In the European scale, road transport and use of organic solvents are major sources of anthropogenic VOC emissions, especially in highly industrialized and densely populated regions. Whereas, VOC emissions from combustion processes contain predominantly pure hydrocarbons (alkanes, alkenes, and aromatics), organic solvents and their vapors also consist of oxygenated hydrocarbons such as alcohols, ketones and esters. It can be stated that VOC emissions show large temporal and regional variations. This underlines the necessity of preparing high-resolution emission inventories (Hewitt, 1999).

2.6. Sampling and Analytical Methodologies

2.6.1. Sampling Methods

Determination of VOCs can be conducted either by real-time instruments on site or by collecting samples on site and then analyzing them in a laboratory. Real-time instruments such as FTIR are quite expensive and thus the use of these instruments is economically infeasible. Therefore, it is generally preferred to collect samples on site and subsequently analyze them in the laboratory. Selection of sample collection method depends on the analysis and sample extraction methods that will be employed. Two main methods for collection of VOCs are: (a) whole air sampling, and (b) sorbent trapping.

In whole air sampling, the air sample is collected in a stainless steel canister or in a Tedlar bag via a system of air pumps. Sorbent trapping is based on collection of VOCs on active surfaces of sorbents. The trapped sample is subsequently extracted from sorbent and then analyzed by instrumental methods. Trapping mechanism could be via physical adsorption, absorption or chemical reactions. Removal of sample from sorbent can be achieved either by a solvent extraction or by a thermal desorption. Selection of a suitable sorbent depends on several factors such as the compound of interest, method of extraction and method of analysis (i.e., by a GC or an HPLC).

2.6.2. Analytical Methods

Gas chromatography (GC) is the most common analytical technique for the quantitative determination of organic pollutants in various environmental matrices. The method is based on principle of chromatographic separation of components of a mixture on a GC column, followed by their identification from their mass spectra.

Air samples cannot be introduced directly to GC-MSD but a preconcentration procedure is required. Samples collected onto sorbents tubes are already concentrated and they are injected to GC after desorption from sorbents. The development and implementation of sampling and analytical methodologies for VOCs represent a significant component of this thesis and are ddressed in more detail in Sections 3.1.1 and 3.1.4.

2.7. Receptor Modeling

The two most common modeling approaches for dealing with air pollution are dispersion models and receptor models. Dispersion models are predictive in nature, i.e., they predict the impact of a specific source at a specific receptor location, given source parameters, meteorological conditions and topography (Turner, 1994). Receptor models provide an estimate of the impact of various sources at a given location at a given time based on the chemical characteristics of the various source emissions and the chemical character of the ambient samples collected at any receptor. These methods are called receptor-oriented or receptor models since they are focused on the behavior of the ambient environment at the point of impact as opposed to the source-oriented dispersion models that focus on the transport, dilution, and transformations that begins at the source and continue until the pollutants reach the sampling or receptor site.

Receptor modeling had been primarily used with particles but is now quite established in source apportionment for VOCs. Receptor models offer a powerful advantage to the source attribution process because their results are based on the interpretation of actual measured ambient data, which is especially important when ubiquitous area sources exist. Despite these advantages, there are some limitations in receptor modeling; i) many emitters have similar species composition profiles, ii) species composition profiles change between source and receptor, and iii) receptor models cannot predict the consequences of emissions reductions (Watson *et al.*, 1998).

Receptor models rely on tracers to identify sources and to be scaled up to yield source mass contributions to the receptor concentrations. To obtain reliable results, these chemical tracers must be stable and measurable species. Receptor oriented models have been employed to identify possible sources of pollution, to resolve the elemental composition of the sources and to determine the contribution of each source to the total pollution level (Cooper and Watson, 1980; Hopke, 1985). In air pollution studies, there exist four multivariate statistical approaches that are most commonly used, Principle Component Analysis (PCA), Conventional Factor Analysis (CFA), Chemical Mass Balance (CMB), and Positive Matrix Factorization (PMF). Three of these models have been used to interpret the data collected in this study and are discussed in detail in Section 3.3.

The PMF approach continues to attract significant interest because it does have inherent advantages as listed previously in this section. PMF is more complex and results are somehow more difficult to interpret, compared to conventional factor analysis, but it provides improved resolution of sources and better quantification of impacts of those sources than PCA and CFA (Huang *et al.*, 1999).

2.8. Control of VOC Emissions

There are three general ways to reduce VOC emissions: organizational, product-oriented and process-oriented measures. Organizational measures, such as optimization and reduction of traffic, are critical to reduce emissions from mobile sources. Organizational measures can also improve industrial product transfer and handling. Product-oriented measures include the reduction or substitution of organic solvents (e.g., in paints, glues, cleaning agents, plant-protective agents, consumer products) and the reduction of solvent use in production (e.g., degreasing, dry cleaning). Process-oriented measures involve more substantial changes in production, e.g., the introduction of low-emission processes or secondary gas cleaning. In principle, low emission processes should be given preference but are frequently more costly. Therefore, secondary gas cleaning is often implemented. A number of cleaning methods are in use and well established: adsorption, absorption, condensation, permeation, combustion, catalytic combustion and biological treatment. The efficiencies of these methods, depending on the specific system can be as high as 90%. (Kahn and Ghoshal, 2000)

VOC emissions of small-scale biomass and coal combustors can be reduced using new combustors with improved low emission design, careful maintenance, proper operation, and use of appropriate fuel. However, significant reduction in VOC emissions can be achieved by improved efficiency of combustors and highly effective thermal insulation of buildings.

Applicable methods to reduce VOC emissions of road transport include more stringent emission standards, reduction of gasoline vapor pressure, optimization and reduction of traffic, and use of zero-emission vehicles (electric vehicles). Effects of the use of reformulated gasoline or alternative fuels (e.g., liquid petroleum gas, compressed natural gas, methanol) should be investigated for particular region. (Yu *et al.*, 2000)

Biogenic VOC emissions from waste dumps can be reduced by limiting the organic fraction (waste reduction or combustion) and by collecting and appropriately treating the gases. VOC emissions from wastewater treatment can be achieved by different water treatment technologies and/or collection and appropriate treatment of the gases. (AAS, 2004)

2.9. Literature Review

2.9.1. Literature on Sampling and Analytical Methodologies

In addition to routine monitoring studies, many studies have focused on sources atmospheric levels, and human exposure to VOCs in North America and Western Europe. In the "Atlanta Ozone Precursors Monitoring Study" (Conner *et al.*, 1995), for example, air samples were collected beside a roadway for one week.

Samples were then pumped into stainless steel canisters. Preconcentrated samples were analyzed by a Gas Chromatograph-Flame Ionization Detector (GC-FID) for 85 individual C2-C14 non-methane hydrocarbons (NMHCs). Detailed speciated hydrocarbon (HC) profiles were developed from this program for use in a Chemical Mass Balance (CMB) model, which provides information about source apportionment (Conner *et al.*, 1995). Grosjean *et al.* (1998) reported a comprehensive study conducted in Brazil on ambient concentrations, sources, emission rates and photochemical reactivities of C2-C10 HCs. In this study, ambient concentrations of 66 HCs were measured in an urban area during one year. Samples were collected in stainless steel canisters and analyzed by a GC-FID and a Gas Chromatograph-Mass Selective Detector (GC-MSD). Temporal variations and sources of ambient HCs were also investigated in this study.

In a study conducted in Munich, Germany, 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). Kourtidis *et al.* (1999) reported a study in Athens, Greece where measurements of C5-C12 HCs were conducted for 36 species to investigate evaporative HC emissions associated with mobile sources.

In a study conducted in Izmir, Turkey VOCs were determined at five different locations that are mostly influenced by traffic emissions during summer of 1998 (Müezzinoğlu *et al.*, 2001). Samples were collected during daytime and nighttime at different sampling durations specific to the site so as to obtain adequate sampling volumes. Samples were collected for few days at each site. Active sampling onto activated charcoal tubes was used followed by solvent extraction by carbon disulfide. Elutions were analyzed by GC-FID to determine 9 VOCs including BTEX compounds at the laboratories of University of Stuttgart, Germany. Concentrations of the VOCs measured at roadside stations were much higher than the concentrations reported for similar studies in the literature.

Çetin *et al.* (2003) collected air samples at three sites located around a petrochemical complex and an oil refinery in İzmir, Turkey to measure ambient VOCs concentrations. A total of 26 samples were collected between September 2000 and September 2001. Samples were collected onto Drager™ charcoal tubes. Concentrations were much higher than suburban concentrations but lower than urban roadside concentrations reported by (Müezzinoğlu *et al.*, 2001).

A number of researchers have demonstrated the temporal variability of VOC data (Derwent *et al.*, 1995; Axelrad *et al.*, 1999; Rappengluck and Fabian, 1999; Demerjian, 2000; Liu *et al.*, 2000; Borbon *et al.*, 2002; Mohamed *et al.*, 2002;). According to these studies, VOC concentrations measured in urban environments show both seasonal and diurnal variations. Variation is mostly related with the atmospheric parameters as well emission rates that are changing temporally.

Most of the researchers point out the significant contribution of local emissions sources to atmospheric VOC levels (Fujita *et al.*, 1995; McLaren *et al.*, 1996; Lawrimore *et al.*, 1997; Fraser *et al.*, 1998; Mugica *et al.*, 1998; Thijsse *et al.*, 1999). The results of studies conducted in different countries and regions resulted in high variations indicating the importance of site-specific studies.

2.9.2. Literature on Receptor Modelling

Over the past few years PMF has been successfully applied in many atmospheric studies. Initially, PMF was applied to data sets of major ion compositions of daily precipitation samples collected over a number of sites in Finland (Paatero and Junto, 1994) and samples of bulk precipitation in which they are able to obtain considerable information on the sources of these ions (Anttila *et al.*, 1995). Polissar *et al.* (1996) applied the PMF model to Arctic data from seven National Park Service sites in Alaska as a method to resolve the major source contributions more quantitatively.

Recently, there has been a series of applications of PMF to various source/receptor modeling situations. Polissar *et al.* (1998) re-analyzed an augmented set of Alaskan NPS data and resolved eight sources. Xie *et al.* (1999) made several analyses of data from an 11-year series of particulate matter samples taken at Alert, NWT in Canada. Polissar *et al.* (1999) examined the semi-continuous aerosol data collected by NOAA at their atmospheric observatory at Barrow, Alaska. Lee *et al.* (1999) applied PMF to urban aerosol compositions in Hong Kong where they identified nine sources that provided a good apportionment of the airborne particulate matter.

Paterson *et al.* (1999) applied PMF to air quality and temperature data collected at a series of sites around the southern part of Lake Michigan in 1997 and used three factors to reproduce 75% of the variation in the data. Huang *et al.* (1999) analyzed elemental composition data for particulate matter samples collected at Narragansett, RI, USA using both PMF and conventional factor analysis. They were successful in resolving more components with more physically realistic compositions with PMF. Chueinta *et al.* (2000) applied PMF to investigate sources of atmospheric aerosol at urban and suburban residential areas in Thailand. Song *et al.* (2001) analyzed fine particle composition data obtained at three sampling sites in the northeastern USA by applying a PMF model.

Aerosol chemical composition data for PM2.5 samples collected at Vermont, USA was analyzed utilizing PMF (Polissar *et al.*, 2001b) and three other receptor modeling techniques (Polissar *et al.*, 2001a) to investigate potential sources. PMF was also used to assess source contributions of fine particle composition data (Li *et al.*, 2004), particle and PAH data (Liu *et al.*, 2003) collected at several sites in New York, NY, USA fine particle data collected in Atlanta, GA, USA (Kim *et al.*, 2003; Kim *et al.*, 2004), in San Gorgonio, LA, USA (Zhao and Hopke, 2004), and in Toronto, Canada (Owega *et al.*, 2004). Source contributions to PM10 and arsenic concentrations in Central Chile were also investigated using PMF (Hedberg *et al.*, 2005).

Although there have been many application in the literature on particle data, use of PMF on VOC data was scarce. Anderson *et al.* (2001) applied PMF to personal exposure and outdoor concentration data for residents in Elizabeth and Bayonne, NJ, USA and Los Angeles, Pittsburg and Antioch, CA, USA from the US EPA's Total Exposure Assessment Methodology (TEAM) and California Air Resources Board (CARB) California indoor exposure studies. Multiple linear regression was also applied to quantify source contributions. PMF was successful to resolve the sources of the observed concentrations. In these studies, environmental tobacco smoke (ETS) and automobile exhaust were identified as the main sources of personal exposure.

The CMB model has been applied in many atmospheric researches in different parts of the world such as Brisbane, Australia (Chan *et al.*, 1999); California, USA (Watson *et al.*, 1994; Schauer *et al.*, 1996; Motallebi, 1999); North Carolina, USA (Lawrimore and Aneja, 1997); Michigan, USA (Scheff *et al.*, 1996); Berlin, Germany (Thijsse *et al.*, 1999); Toronto, Canada (McLaren *et al.*, 1996); Mexico city, Mexico (Vega *et al.*, 2000); Cairo, Egypt (Doskey *et al.*, 1999).

Comparison of PCA, UNMIX, PMF and CMB receptor modeling techniques to identify sources of simulated and measured VOC data were performed by Miller *et al.* (2002) and Anderson *et al.* (2002), respectively. PMF was applied to identify sources of VOCs in Houston, TX, USA (Zhao *et al.*, 2004) and in Santiago, Chile (Jorquera and Rappengluck, 2004). Fuel evaporation and gasoline exhaust were the major sources of VOC data measured at both residential and roadside sites in Chile during spring 1996 campaign.

2.10. Active Legislation on VOC and Tropospheric Ozone

Photochemical ozone formation phenomenon has been an extensive and persistent urban air pollution problem for which the US EPA has had to develop and recommend specific emission control policies and associated implementation regulations. The purpose of ozone policy has been not only to impose restrictions and/or reductions of mass of ozone precursor emissions, but also to encourage development of alternative industrial and commercial products with more favorable environmental characteristics. The US EPA policy specifically includes requirements for inventorying and controlling emissions of photochemically reactive VOCs. The initial version of the current policy was issued in 1971 as part of US EPA's guidance to states for preparation of State Implementation Plans (SIP) for ozone attainment (Dimitriades, 1999). A recommended Policy on Control of VOC offering more limited list of exempt organic compounds was issued in 1977. It is in existence since 1977, with only minor changes to date.

The State of California incorporates the concept of reactivity of VOCs into its regulations for vehicle emissions. The aim was to ensure that different vehicle-fuel combinations are treated equally regarding the ozone-formation potential of the exhaust emissions (CARB, 1991, 1992).

In order to control and reduce VOC emissions from variety of sources regulatory actions are well adopted in Canada, the United States of America and Europe. In Canada, measures developed jointly by the federal government, provinces, and territories to reduce VOC emissions from different source categories are in the form of environmental codes, guidelines, standards, and Memoranda of Understanding (MOUs) issued by the Canadian Council of Ministers of the Environment (CCME). These measures stemmed from the 1990 CCME Phase 1 NO_x/VOC Management Plan. There are 13 codes, guidelines, standards, or MOUs for solvent-use sub sectors that have been completed and endorsed by the CCME. Measures for reduction VOC emissions from motor vehicles are widely adopted.

In Europe, emissions of ozone precursors are generated mainly from the transport sector (EEA, 2003). In Western Europe, the VOC reductions resulted mainly from the introduction of catalysts on new cars, and implementation of the solvents directive in industrial processes and other uses of solvents (EEA, 2003). The approach by the European Union (EU) to the limitation of VOC emissions from organic solvents is addressed under the EU Council Directive 1999/13/EC. The 20 activities targeted for control in the directive are consistent with the ones identified in Canada and the U.S. The EU directive, while primarily intended to address problems associated with VOCs as precursors to ground-level ozone, also targets some specific VOC compounds for more stringent control as a consequence of the direct harm they pose to human health or to the environment (EC, 2004). Directive 2000/69/EC sets limit values for benzene and carbon monoxide in ambient air. Benzene is defined as human genotoxic carcinogen having no identifiable threshold below which there is no risk to human health. Annual average ambient concentrations and target values are defined in this directive. Directive 2002/3/EC relating to ozone in ambient air sets the short and long term limit values for tropospheric ozone concentrations. The directive also recommends routine monitoring of 30 VOCs and NO_x that are ozone precursors.

An international protocol on long-range transboundary air pollution concerning the control of emissions of VOCs or their transboundary fluxes (UNECE, 1991) requires its parties to control and reduce their emissions of VOCs in order to reduce their transboundary fluxes and the fluxes of the resulting secondary photochemical oxidant products so as to protect human health and the environment from adverse effects. Parties should follow a time table in order to:

- Apply appropriate national or international emission standards to new stationary sources based on the best available technologies which are economically feasible,
- Apply national or international measures to products that contain solvents and promote the use of products that are low in or do not contain VOCs, including the labeling of products specifying their VOC content,
- Apply appropriate national or international emission standards to new mobile sources based on the best available technologies,
- Foster public participation in emission control programs through public announcements, encouraging the best use of all modes of transportation and promoting traffic management schemes.

In Turkey, Air Quality Control Regulation (AQCR) that came into force in 1986 (Official Gazette No. 19269 dated 02.11.1986) included limit values for air pollutants in ambient air and emission values from industrial facilities that must be complied. This regulation was revised for industrial sources and a new regulation, Industrial Air Pollution Control Regulation (IAPCR) (Official Gazette No. 25606 dated 10.07.2004) was published. The new regulation sets emission limits for organic gases including speciated VOCs and total hydrocarbons as well as carcinogenic VOCs emitted from industrial sources and emission limit values for BTEX compounds and olefins emitted from refineries and petrochemical plants. Regulation on Control of Air Pollution Emitted from Residential and Commercial Heating (Official Gazette No. 25699 dated 01.13.2005) was published to set permissible fuel characteristics and emission limits including hydrocarbons. This regulation promotes use of natural gas for heating purposes. A new Regulation on Quality of Gasoline and Diesel fuels (Official Gazette No. 25489 dated 06.11.2004) states limit values for lead, benzene, aromatic and olefin composition of fuels that are used in motor vehicles. The production of existing fuels will be banned by 2007. Studies on framework directive are still ongoing. All of these regulations state emission limits for speciated VOCs or total hydrocarbons. However, there exist no limit values for ambient concentrations of VOCs in the current regulations. These regulations are published recently as the requirement of the EU adaptation period and the application will take some time. A new Regulation on the Reduction of Motor Vehicle Exhaust Emissions is still under discussion.

A priori knowledge on the levels and sources of VOCs are required in Turkey in order to adapt and implement these regulations. When the scientific background and regulatory actions in Turkey are compared with those in Canada, the U.S. and Europe, it is seen that detailed investigations on the sources and control strategies of VOCs in Turkey should be carried out.

CHAPTER 3

MATERIALS AND METHODS

3.1. Ankara Campaign

A field campaign was conducted in the summer of 2003 and the winter of 2004 for investigation of speciated VOCs in different microenvironments in Ankara. A sampling and analytical method was developed for the quantitative determination of VOCs. The method developed in this study was thoroughly assessed prior to field application in Ankara. During the field campaign, samples were also collected and analyzed to generate profiles of major VOC sources. Following subsections describe the field characteristics and sampling and analytical methodology used in the Ankara campaign in detail.

3.1.1. The Study Site

The sampling in this study was conducted in different parts of Ankara. Ankara is the capital of Turkey and has the second highest population in the country with approximately 3.5 million inhabitants living in the city according to the 2000 census information (SSI, 2004). The city mainly consists of residential, governmental and public buildings and small-scale businesses. The city is known to house government employees and students. As being the capital city, the majority of the inhabitants work at the government offices. The numbers of industrial facilities are in insignificant scale and thus the major air pollution sources are the heating of residential and governmental buildings and the traffic.

An emission inventory of speciated VOCs was not compiled either in Ankara or in Turkey in the past. The only emission inventory for air pollutants in Ankara was prepared in 1995 (Atımtay *et al.*, 1995) but this inventory was limited to several inorganic air pollutants and total hydrocarbons. In the absence of an inventory, the recent statistical data can help to understand general VOC sources in the city.

Motor Vehicles

The total number of motor vehicles owned in Ankara was 894,183 by the end of March 2004 (SSI, 2004a). The passenger car category constituted the largest share with about 79% of the total number of motor vehicles. The passenger car category was followed by pick-up truck, truck, motorcycle, bus, minibus and other categories having shares of 11%, 3%, 2%, 1%, 1% and 3%, respectively. The total number of motor vehicles in Turkey was 7,813,754 for the same period. According to the state statistical information, Ankara owned the second highest number of motor vehicles in Turkey for that period, accounting for approximately 10% of the car vehicle fleet in the country. In the vehicle density statistics, however, Ankara was in the first place with a vehicle density of 1 vehicle per 4.9 people.

The trend of the change in the number of motor vehicles compared to the change in population in Turkey is shown in Figure 3.1 between the years 1974 and 2003. The rate of increase in population did not change significantly between 1974 and 2003; however, the rate of increase in the number of motor vehicles was almost doubled after the year 1990. Similar trend was observed in many of the provinces including Ankara. Thus, the contribution of motor vehicles on urban air quality in Turkey increased significantly in last few decades, although it is not possible to quantify this owing to lack of data.

Various fuel types are used in motor vehicles. Diesel fuel, leaded gasoline, super leaded gasoline, unleaded gasoline and LPG used in 13%, 43%, 30%, 11% and 3% of the total number of cars owned in Ankara (SSI, 1998). The use of leaded gasoline banned in Turkey by January 2005.

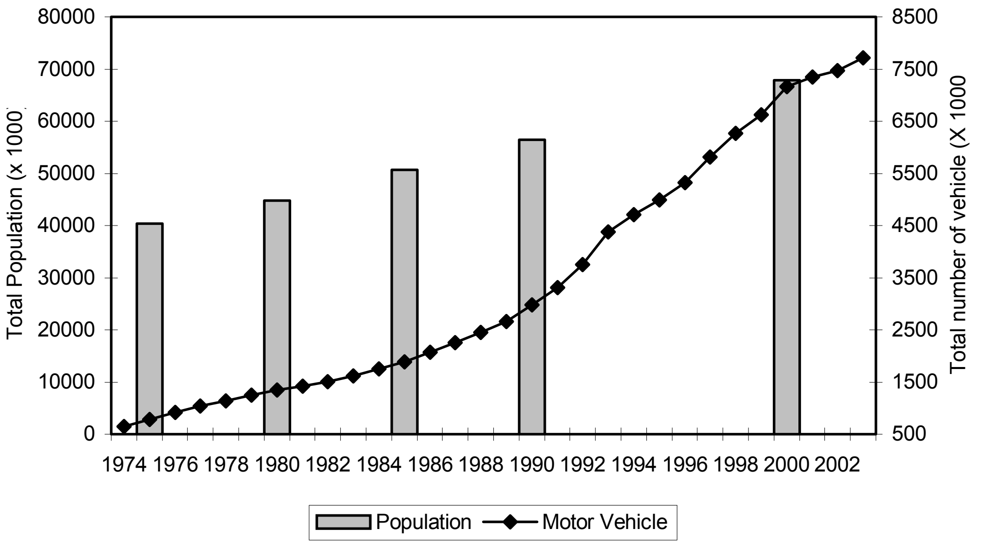


Figure 3.1. Long-term trend in number of motor vehicle and population in Turkey.

Residential Heating

The most recent data for residential heating in Ankara was in 1998 and obtained from the State Statistical Institute. Total number of residences in Ankara was 782,810 in 1998 (SSI, 1998). Stoves are used as the heating system at 57.10% of the residences in Ankara. The residences having heating systems of district heating, central heating, individual and mixed heating accounted for 9.10%, 11.00%, 10.70%, 12.00% and 0.10% of the total number of residences, respectively. Types of fossil fuels used by residences having district, central or individual heating systems were fuel oil (13.50%), coal (28.10%) and natural gas (58.40%). Types of fossil fuels used by residences having stove as the heating system were hard coal (1.74%), coke (0.15%), lignite (2.95%), imported coal (90.41%), wood (0.91%) and others (3.86%). The data pointed out that coal burning was the major source of air pollution associated with domestic heating in Ankara in winter. The data might be changed somewhat in recent years since some of the residences with district, central or individual heating systems using fuel oil or coal as fuel might have switched to natural gas for fuel. However, this change would not affect the main conclusion that the coal is still the main fuel type used in residential heating because the number of residences with district, central and individual heating systems with coal and fuel oil were low. These figures show that although a substantial effort had spent to change the mode of heating in Ankara from solid and liquid fuels to natural gas, fuel oil and coal are still being used in more than 60% of the heating units. This obviously is due to presence of low-income districts and signifies the importance of these districts on the air quality in the city.

Industrial Facilities

There are few industrial facilities in Ankara mainly located at the outskirts of the city. One major organized industrial district namely Middle East Industry and Commerce Center (OSTIM) is located on the northeast part of the city. There are over 3500 small and medium size enterprises working over 100 different sectors at OSTIM. Automobile and spare part sales and services sector is the most common sector with its 477 enterprises working in this sector. Works performed by most of the enterprises mainly include processing metal, plastic and wood parts to manufacture industrial machines or parts, and thus, these activities include intensive melding and painting processes. The major VOC emission sources are the burning of fuel and solvent use at OSTIM. Over 100 enterprises work in chemical and paint supply sector. A cement factory, located in the west of Ankara, is the major industrial facility surrounding the city. Gas stations located in the city also contribute to VOC emissions. Evaporative emissions especially during refueling of storage tanks release significant amount of VOCs into atmosphere.

3.1.2. Sampling Strategy

Sampling was conducted at different microenvironments, which incuded:

- Ambient residential monitoring at Bahçelievler station,
- Ambient background monitoring at Middle East Technical University,

- Ambient roadside monitoring at Atatürk Boulevard,
- Tunnel monitoring at Akay Tunnel,
- Indoor monitoring at SSK underground parking garage,
- Indoor monitoring at Bahçelievler (house) and METU (office), and
- Composite ambient monitoring at Yenimahalle, Keçiören, Cebeci and Gaziosmanpaşa.

Figure 3.2 presents locations of the ambient, roadside and tunnel sampling sites. The first ambient residential sampling station was located at a residential area, at the Bahçelievler district. This area is mainly occupied by residential apartment buildings, schools, hospitals and small retail shops. The sampling station was located about 1 km away from a major intercity highway (Ankara-Konya Road). The station was placed at a backyard of an apartment building, which was about 100 m away from a street where busy traffic was observed at certain times of day.

The second station was set up for background measurements. The background site was located approximately 10 km away from the downtown area and approximately 1.5 km away from the nearest residential area. The Middle East Technical University (METU) campus was selected for the location of the background sampling station. The sampling apparatus was placed in the Metallurgical Engineering building, which is located at far south end of the campus. There were not any major VOC sources in the close proximity of this location. However, nearby-forested area could be a source for biogenic VOCs. In addition, the campus traffic, dormitories and campus housing areas could also have an influence on the results.

The third station was set up on a major street namely the Atatürk Boulevard for the roadside sampling. This part of the city is mainly occupied by commercial buildings, foreign embassies, banks, and various government buildings. The sampling station was about 2 m from the curb and located on a junction across from the U.S. Embassy.

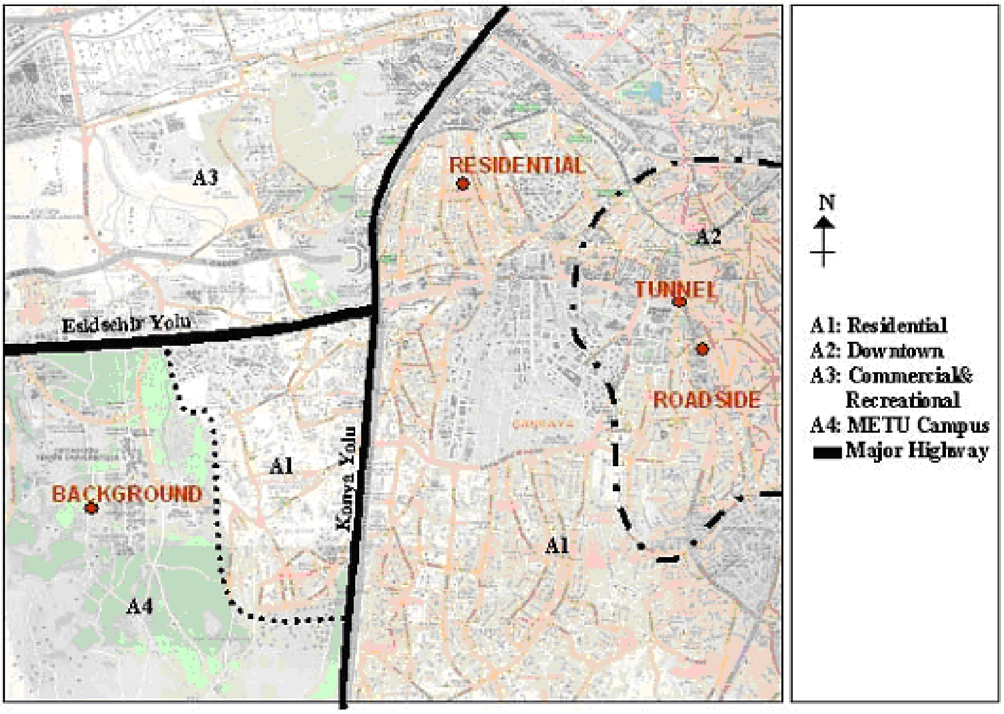


Figure 3.2. Location of the stations used in Ankara campaign.

The fourth station was set up for sampling in a tunnel. The tunnel sampling was performed to produce a running vehicle emission profile for Ankara. The station was located at the Akay underpass that is situated in the downtown area. The Akay tunnel is one of the busiest intersections in Ankara and it contains a set of underpasses that connect several roads with heavy traffic in the downtown area. The traffic in the tunnel is monitored by automated camera system. Thus, the data on vehicle profile and the number of vehicles were retrieved from the videotapes. The traffic flow in the tunnel has frequent stop-and-go conditions particularly during morning and evening rush hours.

3.1.2.1 Ambient Stations

Ambient air samples were collected both in summer and in winter, between July and September 2003, and between January and March 2004, respectively.

Samples were collected three times a day, at consecutive sessions, which lasted four hours. The morning session was performed between 8:00 and 12:00, the noon session was between 12:00 and 16:00 and the afternoon session from 16:00 to 20:00.

Since investigation of temporal variability of VOC concentrations is one of the objectives of this study, evening and night samples were also collected to be able to investigate diurnal variations. The evening session was conducted between 20:00 and 24:00 and the night session was between 24:00 and 8:00 in the morning of the next day. The night session lasted for eight hours. Since VOC concentrations are fairly low at night, no breakthrough was observed in night session, which lasted for eight hours. The morning and evening sampling sessions covered traffic rush hours. The sampling strategy used in summer and winter campaigns is summarized in Table 3.1.

Total number of samples collected at each site in summer and winter campaigns are given in Table 3.2 and Table 3.3, respectively. A total of 157 samples were collected at four sites during the summer sampling campaign. About 70% of the samples were collected during the weekdays and 30% on the weekends. A total of 17 field blanks were also collected at these four sites for the quality control (QC) and quality assurance (QA) purposes. However, analyte compounds were not detected at significant concentrations in blanks.

A total of 254 samples were collected during the winter campaign. As can be seen from Table 3.3, approximately 70% of the data were collected on weekdays at each station. A total of 14 field blanks were also collected at all sites for the QA/QC purposes. Night sessions between 20:00 and 24:00 and between 24:00 and 8:00 in the morning of the next day were only conducted for limited number of days due to logistic limitations.

Number of samples collected in summer campaign was less than winter campaign. A technical problem in working of the instrument for a period during summer, shortage in the number of sampling tube and a technical problem with the sampling pump limiting sampling durations faced during summer campaign resulted in these differences.

Table 3.1. Sampling strategy and site characteristics.

Type of the Site	Residential	Background	Roadside	Tunnel
Name of the Site	Bahçeli	METU	Atatürk Boulevard	Akay Tunnel
Sampling Duration	4 hrs	4 hrs	4 hrs	1 hr
SUMMER-2003				
Sampling Dates	23 Jul-31 Aug	4 -24 Aug	2 - 6 Sep	1 - 6 Sep
Total Sampling Days	31	11	5	6
WINTER-2004				
Sampling Dates	14 Jan-24 Feb	17 Jan-23 Feb	24 Feb- 1 Mar	24 Feb- 1 Mar
Total Sampling Days	33	28	6	6

Table 3.2. Number of samples collected at sampling sites in summer.

Sampling Intervals	**Bahçeli**	**METU**	**Atatürk Boulevard**	**Akay Tunnel**
8:00-12:00	20	9	4	5
12:00-16:00	28	11	5	5
16:00-20:00	26	10	5	6
20:00-24:00	9	0	5	0
24:00-8:00	3	0	5	1
Total	86	30	24	17
Weekday	60 (70%)	22 (73%)	19 (79%)	14 (82%)
Weekend	26 (30%)	8 (27%)	5 (21%)	3 (18%)
Field Blank	11	2	2	2

Table 3.3. Number of samples collected at sampling sites in winter.

Sampling Intervals	**Bahçeli**	**METU**	**Atatürk Boulevard**	**Akay Tunnel**
8:00-12:00	32	27	5	5
12:00-16:00	32	27	6	6
16:00-20:00	31	28	6	6
20:00-24:00	9	8	6	0
24:00-8:00	5	6	6	0
Total	109	96	29	17
Weekday	81 (74%)	68 (71%)	19 (65%)	11 (65%)
Weekend	28 (26%)	28 (29%)	10 (35%)	6 (35%)
Field Blank	7	5	1	1

Samples were collected at a height of 1.5 m in a sampling cabinet, using the apparatus described in Section 3.1.3.7. The same station was used at both Bahçelievler and Atatürk Boulevard sites. At the METU site, the sampling apparatus was placed inside the building and the intake was placed to outside of the building through an opening in a window, which is approximately 10 m from the ground.

3.1.2.2 Tunnel Station

Tunnel samples were collected to generate running vehicle emission profiles. Samples were collected three times a day. The morning samples were collected between 9:00 and 10:00, the noon samples were collected between 13:00 and 14:00, and the afternoon samples were collected between 17:00 and 18:00. The morning and afternoon sessions coincided with the traffic rush hours. Tunnel station was operated parallel to the roadside station. The sample intake was 1 m above the ground and it was approximately 30 cm away from the street curb.

Tunnel station was operated both in summer and winter. Total number of samples collected during summer and winter campaigns are given in Table 3.2 and Table

3.3, respectively. Sample flow rates of 20 ml min^{-1} and 15 mL min^{-1} were used during summer and winter campaigns, respectively. Traffic counts were retrieved from the video camera records of the tunnel.

3.1.2.3 Composite Sample Collection at Ambient Sites

Ambient stations for measurements of VOCs were located only at three sites in Ankara during summer and winter campaigns due to logistical reasons such as the requirements for appropriate shelter, sampling pump and other equipment for continuous sampling. Comprehensive sampling was conducted at these three sites to produce adequate amount of data so that multivariate statistical methods can be used without bias for the interpretation of the data.

In order to investigate VOC levels at different parts of the city, a limited number of samples were collected at different locations in the city. Composite samples were also collected. Locations of the sampling points used in this exercise are shown in Figure 3.3 in Ankara map together with population density map of the city. Sampling locations were selected to represent different parts of Ankara. As can be seen from the Figure 3.3 composite sampling locations are located on heavily populated parts of the city. Residential areas were selected as sampling points to compare findings with that measured at the residential station (i.e., Bahçelievler station). Therefore, sampling started at 8:00 in the morning and finished before 12:00 at noon. Thus, the results are comparable with the results found in 8:00-12:00 session at the Bahçelievler station. Characteristics of the composite sampling locations are depicted in Table 3.4.

Composite samples were collected in duplicate on 3 February 2004 and 23 February 2004. Both sampling days were weekdays. The first date was the 3rd day of a four-day national holiday. Emissions from heating of government buildings, school buses, service buses and minibuses to government offices were absent on that date. Thus, the measured concentrations resulted only from residential heating, passenger cars, buses and minibuses.

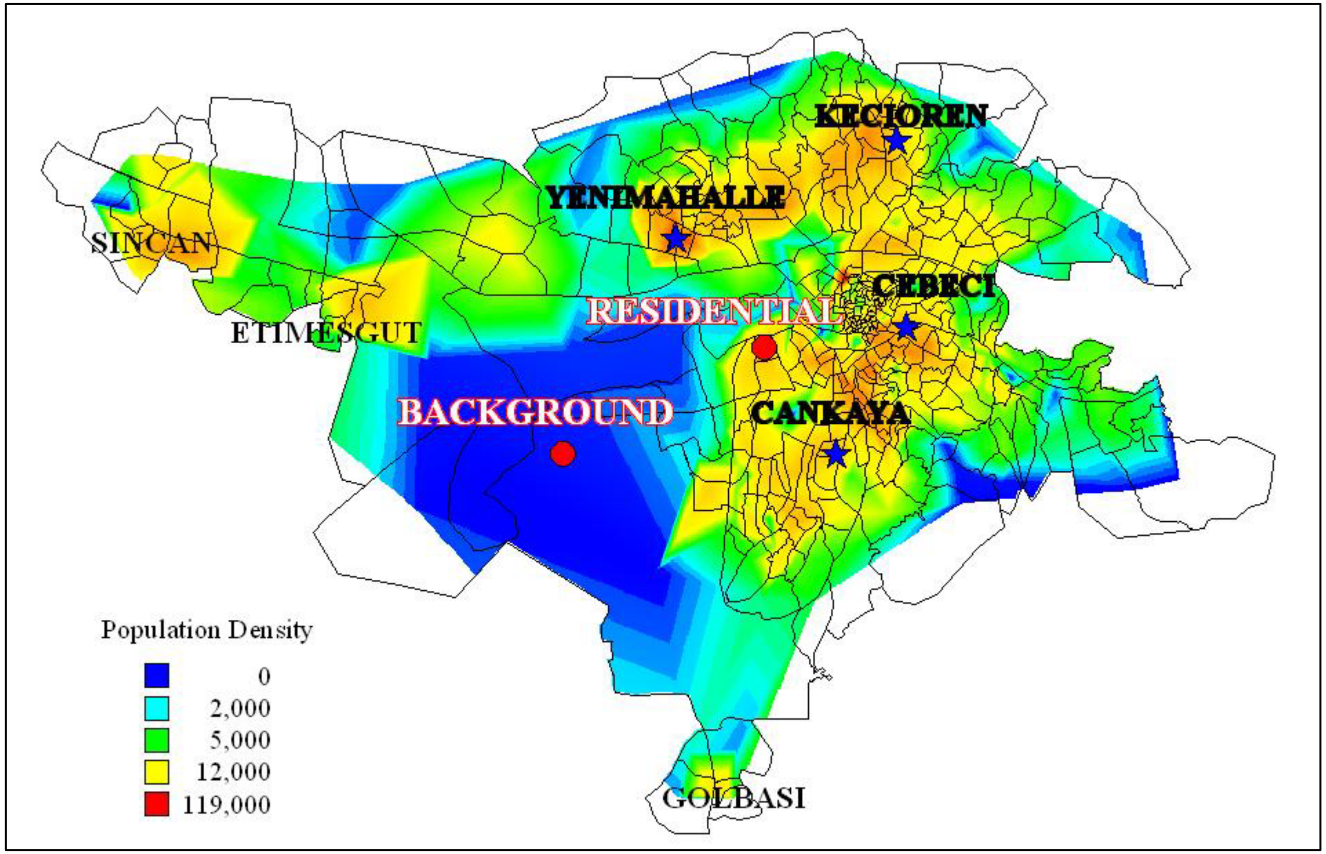


Figure 3.3. Locations of the composite sampling points.

On 23 February 2004 individual samples were collected at each location, in addition to duplicate composite samples. Samples were collected for 15 minutes at each site at 15 mL min^{-1} flow rate. After completion of 15 min sampling at one site, samplers were moved to the second site and air was pulled through the same sampling tube for 15 minutes and sampling system is moved to the third site. This procedure was repeated until all sites are sampled. Hence, VOC concentration measured in the sampling tube is composite concentrations of VOCs at four sites.

Table 3.4. Characteristics of the Ankara composite sampling locations.

Location	**Type**	**Identification**	**Altitude**	**Time**
Yenimahalle	Public park	Residential, small commercial	815 m	9:14
Keçiören	Children playground	Residential	870 m	10:06
Cebeci	Children playground	Residential, small commercial	845 m	10:56
Çankaya	School garden	Residential	905 m	11:47

3.1.2.4 Sample Collection at Underground Garage

A garage sampling was conducted to produce motor vehicle emission profiles such as cold-start tailpipe, hot-start tailpipe, and evaporative for the vehicle fleet in Ankara. The closed underground garage of the SSK business center was used for this purpose. This was a 3-storey underground parking garage located at the bottom of the SSK building situated at Kızılay (downtown).

The SSK business center is occupied by government and commercial offices. Employees working in the center park their cars in the garage in the morning between 8:00-9:30 and leave the garage starting from 17:00 in the evening. The capacity of the garage is 350 vehicles. The ventilation in the garage was poor.

Therefore, the results would be also important as an occupational health issue as there were two people working at each floor and eight people at the entrance level.

Samples were collected both inside and outside (at the entrance) the garage on 4 March 2004, three times in a day. Background samples were collected at these points at 7:00 in the morning, when the garage was literally empty. Samples were collected to produce evaporative emission profile at 10:00 for 30 minutes with 30 mL min^{-1} sampling flow. In the evening when the cold engine is idle tailpipe emissions represent cold-start exhaust emissions. Samples to produce cold-start emission profile were collected at 17:30 for 60 minutes with 20 mL min^{-1} sampling flow. During evening sampling sessions the total number of cars parked in the garage were about 350. A variety of models with different ages, which is quite representative of the passenger car fleet of Ankara were parked in the garage.

3.1.2.5 Sample Collection at Indoor

Air samples were also collected in an office room and a residential house. Office room was in the METU campus. Residential house was located in Bahçelievler district of Ankara. Sampling locations were selected close to the ambient air station locations in order to provide comparison of the results.

Samples were collected on 24th March 2004 only for one day in indoor microenvironments due to restrictions in number of the sampling apparatus and the use of analytical system. Duplicate samples were collected for 1-hr at each location at a sampling flow rate of 30 mL min^{-1}. During sampling, windows and doors were closed at both locations. Indoor samples were collected in order to provide a comparison between VOC levels in outdoor and indoor environments. This comparison is important for exposure assessment. Although number and locations of the indoor samples collected in this study were very limited, the results were critical since this was the first study done in Turkey to determine such a variety of VOCs in indoor environment.

3.1.2.6 Quality Assurance

Two vacuum pumps that were utilized during sampling were SKC Deluxe and SKC Universal air sampling pumps. Flow rate was controlled using mass flow controllers. Rotameters were used to measure the airflow during sampling. The flow rate was controlled and recorded at the beginning, after 30 min and at the end of the sampling. The flow rate, pumping duration, tube number etc., were recorded on field data sheets. Any problem that was encountered during sampling or any source of contamination was recorded on the field data sheet. The ambient temperature and occurrences of precipitation were also recorded on this sheet. Each sample was given a name starting with the date of the sampling day and followed by the session name and the site name (i.e., 082803-8-Bahceli). Table 3.5 shows the format of a field data sheet. The operator filled the field data sheet on site and filled and signed the sample logbook at the laboratory. Sample IDs was also recorded into instrument datasheet at the laboratory prior to analysis.

Powder free surgical gloves were worn during sampling at all times when the field person was in contact with tubes. Sampling tubes closed tightly with their caps in order to prevent contamination. Caps were sealed with Teflon tape from the outer surface and also from the tube connection part to prevent leak or incoming air. Handling procedures that are described in Section 3.1.3.5 were followed. The glass carrying tubes provided dry and hydrocarbon free air during delivery of the sample tubes from or to laboratory. During the summer campaign, samples that were inside the glass carrying tubes were delivered in an icebox. Blue ice packs were placed in the icebox to lower the internal temperature to around +4°C and to protect the sample integrity during delivery. After the samples arrived to the laboratory, they were placed into a refrigerator at -18ºC and left there until the time of analysis. Laboratory and field blanks were analyzed. 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.

Table 3.5. A sample field data sheet.

ANKARA VOC CAMPAIGN FIELD DATA SHEET

Date……………………………………………………………………………………………………

Sample ID……………………………………………………………………………………………

Site ……………………………………………………………………………………………………

Operator ………………………………………………………………………………………………

Tube number	28	32 (Field Blank)
Start	8:00	8:00
Flow rate at start (mL/min)	20	
Flow control time (it should be 30 min after start)	8:30	
Flow rate at control (mL/min)	20	
Stop	12:00	
Flow rate at stop (mL/min)	20	
Total duration (min)	240	

	Start	Stop
Temperature (ºC)	32	28
Precipitation	NA	Light shower

NOTE:

3.1.2.7 *Traffic Data*

Traffic flow in the Akay tunnel is controlled through a video camera system located at different areas of the tunnel. Video camera records are available on the computer. Total number of vehicles passing through the tunnels during sampling sessions both in summer and winter were counted through the video camera records. The vehicle categories were also distinguished from the records. The traffic data recorded at Akay station was used to generate running vehicle exhaust profiles. Vehicles leaving the Akay tunnel traveled along either Atatürk Boulevard or Tunus Street. Thus, the vehicle number recorded at Akay tunnel was also useful to determine the change in traffic pattern at roadside station located on Atatürk Boulevard.

3.1.2.8 Meteorological Data

Surface and aloft meteorological data measured at Ankara Meteorological Station, operated by the State Meteorological Works (SMW), was obtained for the sampling periods. The meteorological station is located on 39° 57` in latitude and 32° 53` in longitude (see Figure 4.26 for the location). Surface meteorological data included hourly measurement of wind speed, wind direction, temperature, precipitation and relative humidity. Upper air data included morning and afternoon mixing height values that were calculated from the radiosonde data. Meteorological data were used to explain dependence of the measured pollutant concentration on meteorological parameters.

3.1.3. Sampling Methodology

In this study, active sampling onto multisorbent adsorption tubes was used for trapping of VOCs in air. Active sampling provided generation of time resolved data for the assessment of diurnal variations and multisorbent sampling media provided collection of a wide range of VOCs in different microenvironments. The characteristics of the sampling system and procedures were described in the following subsections.

3.1.3.1 Equipments

A microprocessor controlled high and low flow vacuum pump, supplied by SKC Universal (SKC Inc., PA, U.S.A.), was used in the field application. The pump has a flow capacity of 5 to 5000 mL min^{-1} and can be set up to sample for up to 7 days onto a single sorbent tube. An SKC tube holder was used during the field application. Portable dual ball rotameter supplied by SKC that provides 5 to 245 mL min^{-1} low flow and 235 to 5000 mL min^{-1} high flow reading was used both in the field and laboratory.

Humonics Veri-Flow 500 electronic flow meter (Supelco, Bellefonte, PA, U.S.A.) having a flow range of 5 to 500 mL min^{-1} with an accuracy of ±2% was used in the method development and validation works. The flow meter is multiple-point calibrated to NIST-certified volumetric standards for nitrogen, helium, hydrogen and air. Two thermal gas mass flow controllers (MFC) supplied by Aalborg (Aalborg Inc., New York, U.S.A.) were used to control flow rates in two different ranges of 0 to 500 mL min^{-1} and 0 to 5000 mL min^{-1}. The MFCs have calibration certificates confirming NIST-traceable standards and operate at inlet pressures between 5 and 60 psi and at gas temperatures between 15°C to 25°C while maintaining ±1.5% full-scale accuracy and linearity.

Oakton Acorn series thermocouple thermometer (Oakton Instruments, IL, U.S.A.) with an accuracy of ±0.25% reading plus 1°C for temperatures less than 99.9°C and ±0.2% of reading plus 0.5°C for temperatures greater than 99.9°C was used.

3.1.3.2 Selection of Sorbents

Three general types of sorbents that are used to adsorb VOCs in gas phase are; carbon molecular sieves, graphitized carbon blacks and porous polymers. A carbon molecular sieve is the carbon skeletal framework remaining after the pyrolysis of a polymeric precursor. These materials are primarily used for collecting very small molecular-sized compounds (e.g., chloromethane, vinyl chloride, and Freon® compounds). The size and shape of the analyte molecule and the size and shape of the pores in the adsorbent particle determine how well the analyte is adsorbed and desorbed. Some commonly used types of carbon molecular sieve sorbents are Carbosieve S-III and Carboxen.

3.1.3.3 Multisorbent Adsorption Tubes

Tenax TA and Carbopack B were used as sorbents in this study. Multisorbent adsorption tubes were custom made. Tenax TA and Carbopack B sorbents having 60/80-mesh size were supplied by Supelco (Bellefonte, PA, U.S.A.). Glass lined stainless steel tubes supplied by SIS (Scientific Instrument Services Inc., NJ, U.S.A.) were in 6 mm outer diameter, 4 mm inner diameter and 10 cm in length. The glass inner surface provided inert medium during sample collection.

Empty stainless steel tubes were cleaned for 2 hrs prior to packing by using Cole Parmer Model 8892 (Cole-Parmer Instrument Company, IL, U.S.A.) ultrasonic shaker and methanol having 95% purity that was supplied by Merck (Merck & Co. Inc., NJ, U.S.A.). The tubes were dried in an oven at 100°C. Cleaned tubes were stored in a sealed jar. A total of 100 mg Tenax TA and 50 mg Carbopack B were accurately weighed using high precision balance supplied by Sartorius (Precision Weighing Balances, MA, U.S.A.) in a clean air room. Sorbents were poured into SIS tubes using a glass funnel. A mechanical vibration was applied to tubes during packing in order to provide a homogenous placement of sorbents within the tubes. Two sorbents were separated from each other by a 3 mm of glass wool placed between them. Sorbents were fixed in the tube by glass wool plugs inserted at both ends of the tube. All the equipments used during packing process were pre-cleaned with methanol. Powder free gloves and dust mask were used at all times during packing process.

A diagram of the custom-made adsorption tube is shown in Figure 3.4. Sampling flow was through the Tenax TA end of the tube that provided adsorption of heavier hydrocarbons onto stronger sorbent before they reach to the weaker sorbent. This resulted in protection of the weaker sorbent from interaction of heavier hydrocarbons that are difficult to desorb from weaker sorbent. Desorption flow was in the opposite direction due to the same considerations. A total of 26 tubes were packed for field campaign. Tubes were re-packed prior to winter campaign.

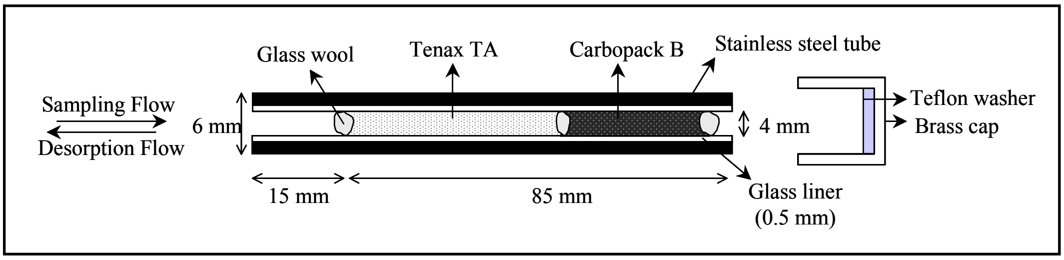


Figure 3.4. Custom made adsorption tube.

3.1.3.4 Conditioning

Concentration of target analytes detected in blank tubes should be minimum for accurate analyses. Contaminants on multisorbent adsorption tubes were desorbed from sorbents by processing the tube under high temperature and high purity gas flow for long durations. This process is called conditioning. Conditioning was performed for; i) newly packed tubes prior to use in any application, ii) tubes prior to use at field if they were not used for long time after conditioning and iii) contaminated sampling tubes.

A conditioning oven with a ten tube conditioning capacity and special connecting parts were designed and custom made in this study. Detailed descriptions of the special parts and conditioning oven are provided in Appendix A. The oven had a heating capacity of up to 400ºC and high purity nitrogen (N_2) gas flow of up to 500 mL min^{-1}. The temperature of the heater blocks was kept constant by a thermostat and the oven temperature was calibrated prior to use in the laboratory. Nitrogen gas flow was controlled by a MFC that was attached to a gas distribution system after a hydrocarbon trap. A scheme and a photograph of the custom made conditioning oven are shown in Figure 3.5.

Conditioning parameters were optimized after several trials at 200ºC, 250ºC, 300ºC and 350ºC conditioning temperatures; 2-hr, 4-hr, 6-hr and 12-hr conditioning durations, and 20 mL min^{-1}, 50 mL min^{-1}, 100 mL min^{-1} and 200 mL min^{-1} N_2 flow rates. Low conditioning temperatures and durations were not effective in cleaning the tubes. Low N_2 flow rate was not effective while very high N_2 flow rates resulted in flushing the sorbents from the tubes. After each trial of different set of conditioning parameters, background chromatograms of the adsorbent tubes were investigated by analyzing the conditioned tube.

The studies demonstrated that 300ºC conditioning temperature, 12-hr conditioning duration and 100 mL min^{-1} N_2 flow were the optimum conditioning parameters for the initial conditioning of multisorbent tubes after packing. When conditioned tubes were stored for long periods of time without using, a 2-hr conditioning duration with the same conditioning parameters resulted in satisfactory background levels (i.e., no target compound was detected).

3.1.3.5 Storage and Handling

Proper storage and handling of sample or clean sorbent tubes are critical for accuracy of results. Conditioned tubes were capped tightly with brass caps having PTFE seals and kept in pre-cleaned glass tubes to prevent possible contamination. Glass tubes were filled with charcoal and anhydrous calcium sulfate at the bottom and fixed with glass wool to provide dry and hydrocarbon free air for storage. Glass tubes were also capped with PTFE caps and placed in freezer at -18ºC for storage. This procedure was applied to both clean and sample tubes for storage prior to use or analysis.

Sample and clean multisorbent tubes were exposed to laboratory air before and after analysis were conducted. Multisorbent tubes were stored in sealed jars filled with charcoal during that time in order to minimize any possible contamination of the sorbents. Photographs of the tools used for safe handling and storage of adsorbent tubes are shown in Figure 3.6.

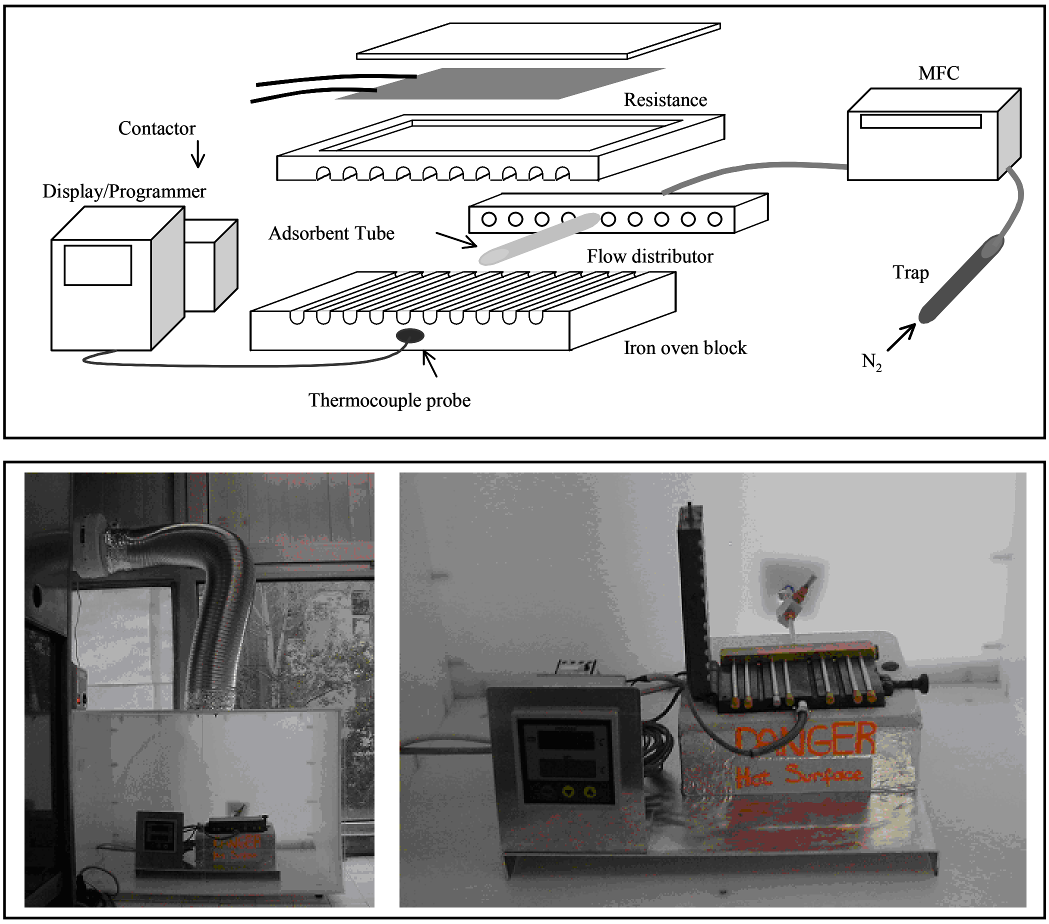


Figure 3.5. Custom made conditioning oven.

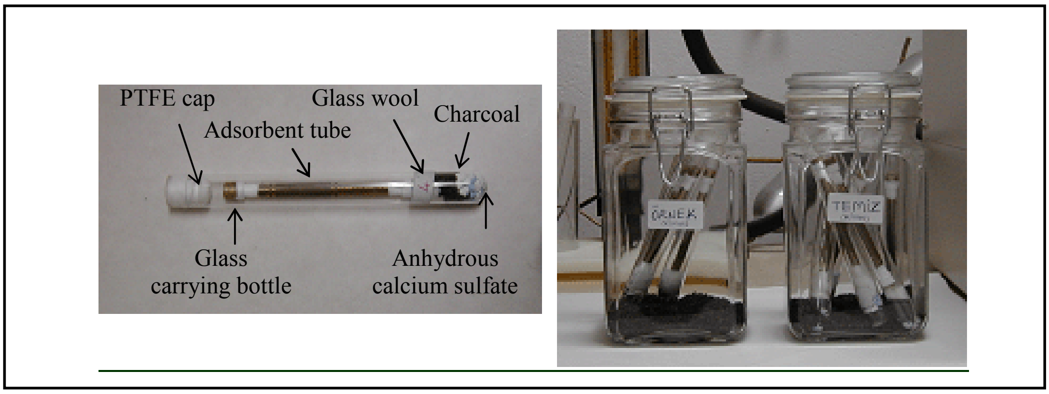


Figure 3.6. Handling of the sorbent tubes.

3.1.3.6 Optimization of the Sampling Parameters

Air samples were collected onto multisorbent adsorption tubes by using a vacuum pump and a tube holder system. Flow rate and sampling durations were the key parameters that must be optimized for a reliable sampling. For an adsorption tube having 6 mm O.D., 50 mL min^{-1} is the theoretical optimum flow rate recommended by the USEPA (1997b). Pump flow rates above 10 mL min^{-1} are generally used in order to minimize errors due to ingress of VOCs via diffusion. Flow rates in excess of 200 mL min^{-1} are not recommended for standard 6 mm OD sample tubes unless for short term (e.g., 10 minutes) monitoring (USEPA, 1997b). Sample volumes recommended by the USEPA (1984) for reliable sampling are 1 and 4 L.

The flow rate used in the sampling was adjusted considering the time weighted average monitoring and safe sampling volume (SSV) requirements. The SSV can be determined in terms of retention volume (RV) or breakthrough volume (BV) either in the field or in the laboratory. Retention volume is defined as the calculated volume of carrier gas per gram of adsorbent resin which causes the analyte molecules to migrate from the front of the adsorbent bed to the back of the adsorbent bed (Heavner *et al.*, 1992). It is usually expressed in liter per gram of adsorbent.

The RV is normally determined by two methods, namely; frontal analysis and elution analysis (Gallant *et al.*, 1978). In frontal analysis, the adsorbent is challenged with a steady state concentration of the adsorbate; therefore, the sample introduction is presented over a long period of time. In elution analysis, the adsorbate is injected onto the adsorbent, followed by passage of a gas through the adsorbent to simulate sampling.

Laboratory test of determining RV by elution analysis includes connection of a sample tube to injection port of a gas chromatography (GC) and flame ionization detector (FID). In this set-up, sample tube acts as a GC column and RV is determined under different temperatures. In such determination SSV is equal to half of RV. In case of field determination, SSV is determined by frontal analysis and it is defined as the two thirds of breakthrough volume (BV). Breakthrough volume is determined in the field using front and back-up tubes. The BV is defined as the sample volume, at which there is 5% breakthrough of analyte onto the back-up tube (USEPA, 1997b).

Breakthrough tests were conducted in the field under actual environmental conditions in order to account for changes in the breakthrough volume under real relative humidity, temperature and concentration values. Field study was conducted at a gas station in order to simulate maximum concentrations of VOCs in ambient air. Breakthrough volume was determined by connecting three sets of two identical multisorbent tubes in series and sampling via SKC Universal (SKC Inc., PA, U.S.A.) microprocessor controlled low flow vacuum pump at a rate of 20 mL min^{-1} for 1-hr, 2-hr, and 3-hr sampling durations. The ambient concentrations were between 0.5 and 55 μg m^{-3} for different analytes. There was no significant breakthrough of analytes except 2-methyl-butane (30% breakthrough) after 3 hr sampling period.

The field tests were also performed at Bahçelievler, the residential site used in this study. The sampling duration of 4-hr and flow rate of 20 mL min^{-1} resulted in no significant breakthrough of the target analytes. Thus, the sampling duration of 4-hr and flow rate of 20 mL min^{-1} were used in the field studies.

3.1.3.7 Sampling Cabinet

Samples were collected at a height of 1.5 m from the ground at ambient air sampling stations. A cabinet made of metal aluminum was designed and custom made to place a pump and a sampling apparatus as shown in Figure 3.7. An air fan was attached to the rear side of the cabinet to lower the temperature inside the cabinet during the summer campaign. A thermometer was attached to the outer side of the cabinet to record ambient temperatures during the summer sampling.

Figure 3.7. Sampling cabinet used in Ankara Campaign.

During the winter campaign inner parts of the cabinet was covered by insulating material to prevent heat loss. A small resistance controlled by a thermostat was used to heat inside the cabinet at a constant temperature of approximately 10ºC. A thermocouple probe was placed at the center of the cabinet and it was connected to the thermostat. It was important to keep the temperature inside the cabinet above 5ºC for sampling pump to operate effectively.

3.1.4. Analytical Methodology

In this study, samples collected onto multisorbent adsorption tubes were analyzed using short-path thermal desorber followed by gas chromatography coupled to mass spectrometry (GC-MS).

3.1.4.1 Target Analytes

The SPTD/GC-MS method was developed for a wide range of VOCs including aromatics, olefins, paraffins, halogenated and biogenic compounds that may be present both in ambient and indoor air. The target analyte selection criteria for this study were based on: i) the prevalence of a compound in indoor and outdoor air, ii) the presumed potential for a compound to induce adverse health effect, iii) the potential for a compound to act as a tracer for specific sources such as petroleum, cleaning solvents, printing, painting, etc. A list of target analytes used in Ankara Campaign together with some of their physico-chemical parameters are presented in Table 3.6.

Table 3.6. Target analytes used in Ankara Campaign.

Common Name	**IUPAC Name**	**CAS No**	**Molecular Weight**	**Boiling Point (°C)**	**Vapor Pressure (Pa at 25 °C)**
Pentane	n-pentane	109660	72.15	36.07	68400
Isoprene	2-Methyl-1,3-butadiene	78795	68.10	34.00	53200
cis-2-pentene	cis-2-pentene	627203	70.13	36.90	66000
2-methyl-2-butene	2-methyl-2-butene	513359	80.14	38.57	62143
2,2-dimethylbutane	2,2-dimethylbutane	75832	86.18	49.74	42600
trans-1,2-dichloroethene	trans-1,2-dichloroethene	156605	96.94	48.00	35863
3-methyl-1-pentene	sec-Butylethene	760203	84.16	54.00	58128
2,3-dimethylbutane	2,3-dimethylbutane	79298	86.18	58.00	32010
trans-4-methyl-2-pentene	trans-4-Methyl-2-pentene	674760	84.16	58.60	22931
2-methylpentane	2-methylpentane	107835	86.18	60.27	28200
cis-4-methyl-2-pentene	cis-4-methyl-2-pentene	691383	84.15	57.00	NA
3-methylpentane	3-methylpentane	96140	86.17	83.28	25300
2-methyl-1-pentene	2-methyl-1-pentene	76203	84.16	60.70	26000
1-hexene	1-hexene	592416	84.16	63.40	24800
cis-1,2-dichloroethene	cis-1,2-dichloroethene	156592	96.94	60.00	26665
Hexane	n-hexane	110543	86.17	68.95	20200
Chloroform	Trichloromethane	67663	119.38	62.00	21331
trans-2-hexene	trans-2-hexene	4050457	84.16	67.90	35162
cis-2-hexene	cis-2-hexene	7688213	84.16	68.80	NA
cis-3-methyl-2-pentene	cis-3-methyl-2-pentene	922623	84.16	67.70	16000
2,2-dimethylpentane	2,2-dimethylpentane	590352	100.21	79.20	14000

Table 3.6. Target analytes used in Ankara Campaign *(Continued)*.

Common Name	**IUPAC Name**	**CAS No**	**Molecular Weight**	**Boiling Point (°C)**	**Vapor Pressure (Pa at 25 °C)**
1,2-dichloroethane	Ethylene dichloride; dichloroethylene	107062	98.96	83.50	12000
Methylcyclopentane	methylcyclopentane	96377	84.16	71.80	18300
2,4-dimethylpentane	2,4-dimethylpentane	108087	100.21	80.50	13100
1,1,1-trichloroethane	Methylchloroform	71556	133.40	74.00	13332
2,2,3-trimethylbutane	2,2,3-trimethylbutane	464062	100.21	80.90	13652
1-methylcyclopentene	1-methylcyclopentene	693890	82.15	75.50	NA
Benzene	benzene	71432	78.11	80.10	12700
Carbontetrachloride	Tetrachloromethane	56235	153.82	76.70	12000
Cyclohexane	cyclohexane	110838	84.16	80.70	12700
2-methylhexane	2-methylhexane	591764	100.21	90.00	8780
2,3-dimethylpentane	2,3-dimethylpentane	565593	100.21	89.90	9180
3-methylhexane	3-methylhexane	589344	100.21	92.00	8210
Dibromomethane	methylene bromide	74953	173.85	97.00	6000
1,2-dichloropropane	Propylene dichloride	78875	112.99	96.80	7066
Trichloroethene	1,1,2-Trichloroethylene	79016	131.40	87.00	7800
1-heptene	1-heptene	592767	98.19	93.64	7510
2,2,4-trimethylpentane	2,2,4-trimethylpentane	504841	114.23	99.24	6560
Heptane	n-heptane	142825	100.21	98.42	6110
cis-3-heptene	cis-3-heptene	7642106	98.19	95.70	12835
trans-2-heptene	trans-2-heptene	14686136	98.19	95.70	6450
cis-2-heptene	cis-2-heptene	6443921	98.19	98.00	11632
cis-1,3-dichloropropene	cis-1,3-dichloropropene	10061015	110.97	104.30	5733
2,2-dimethylhexane	2,2-dimethylhexane	590738	114.23	107.00	NA
Methylcyclohexane	methylcyclohexane	108872	98.19	100.90	6180
2,5-dimethylhexane	2,5-dimethylhexane	592132	114.23	109.12	7580
2,4-dimethylhexane	2,4-dimethylhexane	589435	114.23	109.50	6417
trans-1,3-dichloropropene	trans-1,3-dichloropropene	10061026	110.97	112.00	4533
Bromotrichloromethane	Carbon Bromotrichloride	75627	198.27	105.00	5120
2,3,4-trimethylpentane	2,3,4-trimethylpentane	565753	114.23	113.40	3600
Toluene	methylbenzene	108883	92.13	110.60	3800
1-methylcyclohexene	1-methylcyclohexene	591691	96.17	110.24	3393
Dibromochloromethane	Chlorodibromomethane	124481	208.28	119.00	1866
3-methylheptane	3-methylheptane	589811	114.32	115.00	2600
cis-1,3-dimethylcyclohexane	cis-1,3-dimethylcyclohexane	638040	112.21	120.00	NA
trans-1,4-dimethylcyclohexane	1,4-trans-dimethylcyclohexane	2207047	112.21	119.40	3020
Ethylene dibromide	1,2-dibromoethane	106934	187.87	131.70	1466
2,2,5-trimethylhexane	2,2,5-trimethylhexane	3522949	128.26	124.00	2210
1-octene	1-octene	111660	112.10	121.30	2320
Octane	n-octane	111659	114.23	125.70	1800

Table 3.6. Target analytes used in Ankara Campaign *(Continued)*.

Common Name	**IUPAC Name**	**CAS No**	**Molecular Weight**	**Boiling Point (°C)**	**Vapor Pressure (Pa at 25 °C)**
trans-2-octene	trans-2-octene	13389429	112.22	125.00	4145
trans-1,2-dimethylcyclohexane	trans-1,2-dimethylcyclohexane	6876239	112.22	123.00	NA
Tetrachloroethene, Perchloroethylene	1,1,2,2-Tetrachloroethylene	127184	165.80	121.00	1900
cis-1,4-dimethylcyclohexane	cis-1,4-dimethylcyclohexane	624293	112.22	124.00	NA
trans-1,3-dimethylcyclohexane	trans-1,3-dimethylcyclohexane	2207036	112.21	124.00	NA
Chlorobenzene	Benzene chloride	108907	112.56	132.00	1573
Ethylbenzene	ethylbenzene	100414	106.20	136.20	1270
meta-xylene	1,3-dimethylbenzene	108383	106.20	139.00	1100
para-xylene	1,4-dimethylbenzene	106423	106.20	138.00	1170
Bromoform	Tribromomethane	75252	252.75	149.50	667
Styrene	Ethenylbenzene	100425	104.15	145.00	667
Acetylene tetrachloride	1,1,2,2-tetrachloroethane	79345	167.85	146.30	400
ortho-xylene	1,2-dimethylbenzene	95476	106.20	144.00	1170
Nonane	n-nonane	111842	128.26	150.80	571
iso-propylbenzene	iso-propylbenzene	98828	120.20	154.20	610
n-propylbenzene	n-propylbenzene	103651	120.20	159.20	450
3-ethyltoluene	3-ethyltoluene	620144	120.20	158.00	NA
4-ethyltoluene	4-ethyltoluene	622968	120.20	162.00	NA
1,3,5-trimethylbenzene	1,3,5-trimethylbenzene	108678	120.20	164.70	325
2-ethyltoluene	2-ethyltoluene	611143	120.20	164.00	NA
1,2,4-trimethylbenzene	1,2,4-trimethylbenzene	95636	120.20	169.40	270
benzyl chloride	1-Chloro-2-methyl benzene	100447	126.59	179.30	NA
iso-butylbenzene	iso-butylbenzene	538932	134.22	170.00	250
sec-butylbenzene	sec-butylbenzene	135988	134.22	173.00	240
1,2,3-trimethylbenzene	1,2,3-trimethylbenzene	526738	120.20	176.10	200
p-cymene	4-isopropyltoluene	99876	134.22	176.50	267
ortho-Dichlorobenzene	1,2-dichlorobenzene	95501	147.00	180.50	399
1,4-diethylbenzene	1,4-diethylbenzene	105055	134.22	184.00	134
n-butylbenzene	n-butylbenzene	104518	134.22	183.00	137
1,2,4-trichlorobenzene	1,2,4-trichlorobenzene	120821	181.45	214.40	NA
Naphthalene	Naphthalene	91203	128.16	218.00	134
Hexachlorobutadiene	Hexachloro-1,3-butadiene	87683	260.76	210.00	26
Hexylbenzene	1-Phenylhexane	1077163	162.27	226.00	NA

3.1.4.2 Reagents and Supplies

A gas-phase mixture of VOCs including 148 individual compounds ranging from C2 to C12 was supplied by Environment Technology Center, Environment Canada (Ottawa, Canada). A calibration gas containing 2-20 μg m^{-3} of each compound was prepared in a pressurized 15-L SUMMA polished canister by mixing standards having purity of 98% or higher and seven different stock gas mixtures purchased from Scott Specialty Gases (Plumsteadville, PA, U.S.A.).

The calibration gas was analyzed and quantified against standard reference material SRM 1800 (Non-Methane Hydrocarbon Compounds in Nitrogen) and 1804a (Volatile Organics in Nitrogen) provided by the National Institute of Standards and Technology (NIST) (Gaithersburg, MD, U.S.A.). SRM 1800 contains 15 hydrocarbons, one of which, ethane does not apply to current method of analysis. SRM 1804a contains 19 components, mostly halogenated VOCs. There are 3 components (benzene, toluene, and ortho-xylene) that are common to both SRMs.

The calibration standard was accepted for use when the analyzed concentration values for all 30 components present in the SRMs were within 30% of their respective nominal values. Calibration mixture not only included anthropogenic hydrocarbons but also included halocarbons and biogenic VOCs. Gas tight syringes with 1 μL, 5 mL, 25 mL and 100 mL capacity were supplied by Hamilton (Hamilton Company, Nevada, U.S.A.).

3.1.4.3 Optimization of GC-MS Parameters

System Characteristics

GC-MS analysis of desorbed analytes was performed by a model 5973 MS operated by a 90 L sec^{-1} vapor-diffusion vacuum pump and model 6890 GC system supplied by HP (Agilent Technologies Inc., Palo Alto, CA, U.S.A.).

GC Parameters

Analytical column used in the GC-MS was supplied by J&W (Palo Alto, CA, U.S.A.). It was a DB-1 capillary column that is suitable for hydrocarbon analysis and it was 60 m in length, 0.32 mm in diameter and had 1 μm and 100% dimethlypolysiloxane coating. The column can operate at a temperature range of -60ºC to 325ºC.

The GC was capable of conducting both split and splitless injections of samples. Selection of injection port liner was also important, as it was the initial point for sample introduction into GC. Glass lined stainless steel. Low volume injection port liner supplied by SIS (Scientific Instrument Services Inc., NJ, U.S.A.) was used. The injection port liner used in this study had a 0.75 mm inner diameter at the top half of the liner and 1 mm inner diameter at bottom half of the liner to provide optimum heat transfer. Inner surfaces were glass lined to provide inert surface.

High purity helium (He) gas supplied by BOS (BOS A.Ş., Ankara, Turkey) was used as a carrier gas. Although the purity of the gas was above 99.999%, the gas used in the system was passed through a hydrocarbon and oxygen trap supplied by HP (Agilent Technologies Inc., Palo Alto, CA, U.S.A.). Cryofocusing of the desorbed analytes at the front of the GC column was used to provide better peak resolution. Liquid carbon dioxide (CO_2) was used for both cryotrap and column cooling to sub-ambient temperatures.

GC parameters including oven temperature programming, column flow rate and injection port temperature have influence on peak resolution. Thus, GC parameters were optimized in order to provide a good peak resolution that results in higher sensitivity. GC-MS system was connected to a PC and the system was operated through HP ChemStation software. Data acquisition was also provided through the same software and data were recorded on the PC. Table 3.7 shows the optimum GC-MS parameters used in this study. A typical total ion chromatogram

(TIC) of 13 VOCs are shown in Figure 3.8. The analysis was performed using optimized GC-MS parameters and under selected ion monitoring mode (SIM) of operation. As can be seen in Figure 3.8, a good resolution of the analytes was observed.

Table 3.7. Optimized GC-MS parameters.

Parameter	**Optimum value**
Injector	Splitless, 230ºC
Column flow rate	1.6 mL min^{-1}
Linear velocity	31 cm sec^{-1}
Carrier gas	He
Temperature program	-30ºC hold 3 min, 6ºC min^{-1} to 220ºC, hold 1 min
EI condition	70 eV
Mass range	35-300 AMU
MS quad temperature	150ºC
MS source temperature	230ºC

SCAN Mode of Operation

Identification of the compounds detected in samples is the essential first step in measurement of VOCs. Scan Mode in the GC-MS analysis is qualitative analysis of whole mass spectrum that bases on spectral match. The fit factor in analysis indicates how accurately an ion in the mass spectrum is identified.

In this study, NIST98 mass spectral database that contains over 230,000 mass spectra was used for spectral match. When a problem accounted for identification of an analyte from the spectral match, pure standard of that analyte was analyzed and the resultant mass spectrum was used for spectral match. The mass spectrum and structure of dodecane obtained from NIST98 library are shown in Figure 3.9.

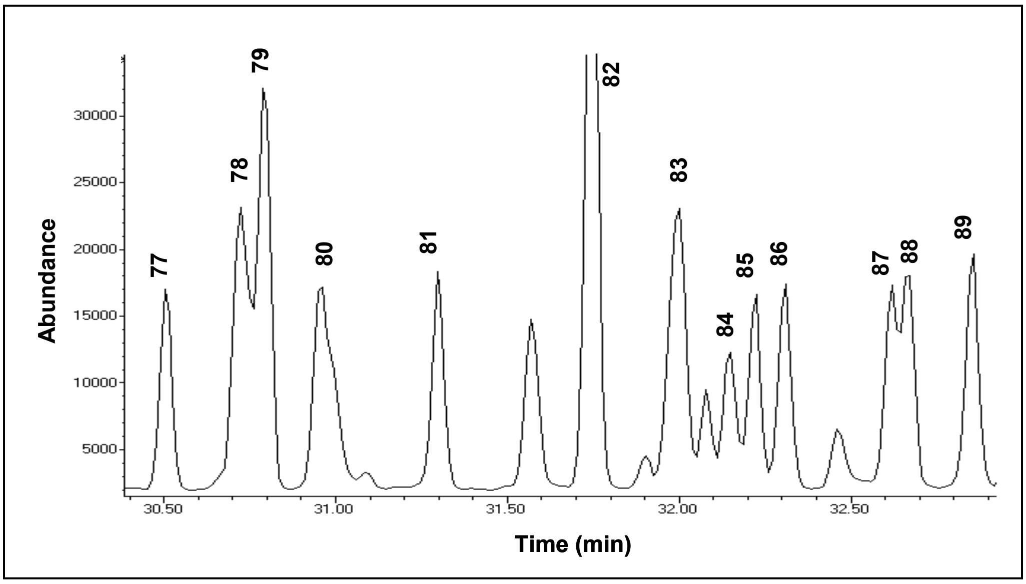


Figure 3.8. TIC of 13 target VOCs under optimized GC-MS conditions.
(See Table 3.7 for the compound names corresponding to numbers on the figure)

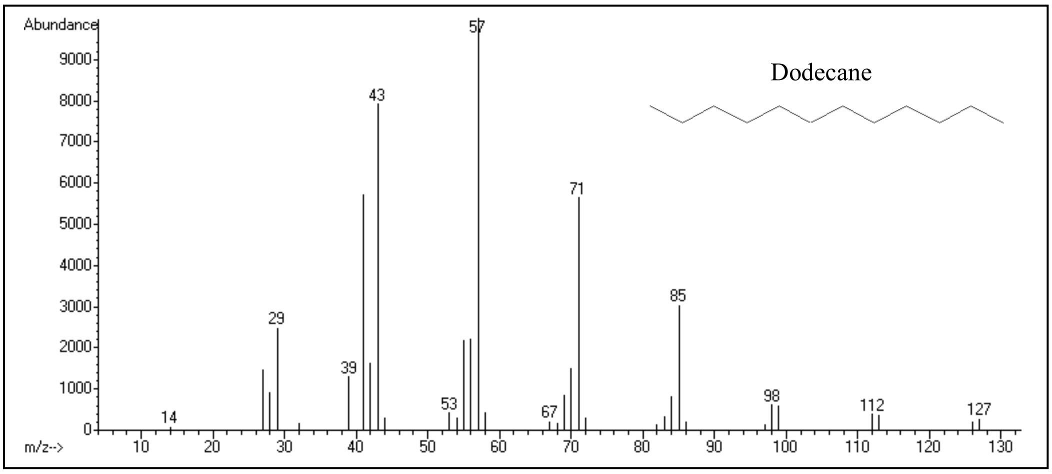


Figure 3.9. Mass spectrum and structure of dodecane.

SCAN mode of MS operation was used for analyte identification. All the ions between 35 and 300 amu was scanned and resulted chromatogram was investigated for analyte identification. When the MS is run under SCAN mode of operation all ions are scanned by the MS repeatedly during the run without making any filtration. This resulted in loss of sensitivity. Baseline levels of the resultant chromatograms are higher than that of SIM mode of operation.

A typical total ion chromatogram of a GC-MS run that was done under SCAN mode for a low-level calibration standard is shown in Figure 3.10. The chromatogram shows the compound between 15.4 min and 17.4 min of the analysis. The SCAN mode of MS operation is not suitable for quantitative analysis of analytes particularly at a very low concentration. The SCAN mode is the only way for qualitative analysis for compound identification. Calibration gas was analyzed under optimum GC conditions and SCAN mode of MS and compounds were identified in the resultant chromatogram. These data were used to generate SIM windows for subsequent operation of MS under SIM mode of analysis for quantification.

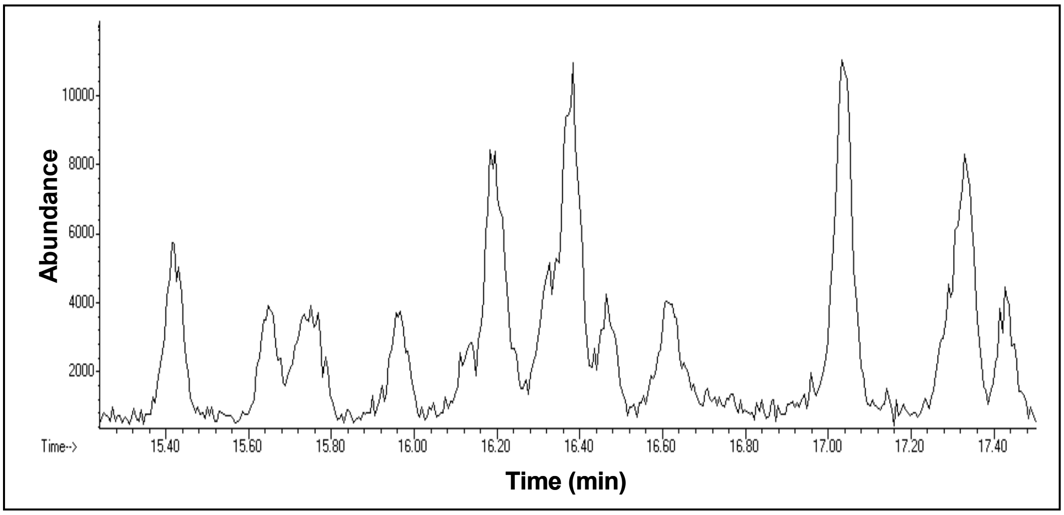


Figure 3.10. A typical TIC for a SCAN mode of MS analysis.

SIM Mode of Operation

Selected Ion Monitoring (SIM) provides detection of very low ion abundances. In this technique, the mass spectrometer is tuned only to a few pre-selected ions;

complete mass spectra are not taken during the GC-MS analysis. Therefore, SIM mode provides higher sensitivity than the SCAN mode of analysis. In this study, samples were analyzed using the SIM mode of GC-MS operation for quantification.

The principal requirements for quantification in the SIM mode are that the ions chosen are specific to the compounds quantified and they should be principal ions in the mass spectra of the target analytes. More than one ion can be monitored for each compound of interest; however, detection limits become increasingly poor as the number of ions increases. Therefore, each target analyte was assigned with one target ion and two qualifier ions.

The ions that provide the most abundant m/z ratio for analyte of interest were selected as target ion (TI). Choosing the ions that give the greatest signal to noise ratio in the sample resulted in the best detection limits for sample analysis. The ions having second and third most abundant m/z ratios were selected as qualifier ions. Use of qualifier ions (QI) increases the accuracy of the analysis by providing better identification of target analytes.

In case of an overlap in the QIs of different analytes, ions having low abundance were also used as QIs. Mass spectrum of each target analytes obtained from NIST98 database was investigated to identify TI and QIs for each target analyte. The SIM parameters including TI, first and second QI and retention time are shown in Table 3.8. SIM parameters of the internal standards used in the quantitative analysis are also provided in the table indicated by symbols.

Total ion chromatogram and extracted ion monitoring chromatogram of 1-bromo-4-fluorobenzene are presented in Figure 3.11. The percent abundances of TI and QIs are monitored as an internal quality control of instrument stability and analytical method. For validity of quantification, the difference between expected and actual percent abundances of TI and QIs should not be more than 20%.

Table 3.8. SIM parameters for target analytes.

No	RT	TI	QI1	QI2	No	RT	TI	QI1	QI2	No	RT	TI	QI1	QI2
*	17.59	130	49	128	33	20.93	174	93	176	65	27.29	91	106	0
1	12.60	43	41	27	34	20.98	63	62	0	66	27.57	91	106	0
2	12.84	67	68	53	35	21.34	130	132	95	67	27.64	173	171	175
3	13.50	55	42	70	36	21.44	56	41	70	68	28.18	104	78	103
4	13.75	55	41	70	37	21.44	57	41	0	69	28.33	83	85	0
5	14.48	57	71	43	38	21.84	43	57	71	70	28.37	91	106	0
6	15.53	61	96	98	39	21.89	69	98	0	71	28.85	57	43	85
7	15.62	41	69	55	40	22.01	55	56	41	***	29.13	174	95	75
8	16.01	43	42	41	41	22.01	56	55	41	72	29.41	105	120	0
9	16.22	69	84	0	42	22.55	75	77	110	73	30.34	91	120	0
10	16.27	43	42	71	43	22.69	57	41	56	74	30.56	105	120	0
11	16.22	69	84	0	44	22.68	83	98	0	75	30.63	105	120	0
12	16.93	57	56	41	45	23.15	57	43	71	76	30.79	105	120	0
13	17.24	56	55	41	46	23.15	57	43	85	77	31.13	105	120	0
14	17.35	61	96	98	47	23.30	75	77	110	78	31.58	105	120	0
15	17.77	57	41	43	48	23.69	117	119	0	79	31.81	91	126	0
16	17.83	83	85	47	49	23.77	43	71	0	80	32.05	91	92	134
17	17.98	55	42	84	50	23.94	91	92	0	81	32.14	105	134	91
18	18.36	55	42	84	51	24.34	81	96	0	82	32.45	105	120	0
19	18.87	69	41	55	52	24.52	129	127	0	83	32.50	134	0	0
20	18.79	57	43	85	53	24.59	43	57	85	84	32.68	146	148	0
21	18.84	62	64	27	54	24.79	97	55	112	85	33.38	119	105	0
22	18.87	56	41	69	55	24.85	97	55	112	86	33.41	91	92	0
23	19.05	43	57	85	56	24.88	107	109	0	87	33.57	105	119	134
24	19.20	97	61	99	57	24.99	57	71	41	88	36.76	180	182	0
25	19.26	57	56	85	58	25.09	55	41	70	89	37.00	128	127	0
26	19.80	67	82	0	59	25.50	43	57	85	90	38.04	225	223	227
27	19.83	78	77	0	60	25.61	55	41	70	91	38.87	91	162	0
28	20.04	117	119	121	61	25.74	97	112	55					
29	20.22	84	41	56	62	25.62	166	164	0					
30	20.56	43	85	57	63	25.74	97	112	55					
31	20.64	56	71	57	**	26.59	117	119	0					
32	20.91	43	70	57	64	26.66	112	77	114					

* Bromochloromethane, ** Chlorobenzene-d5, *** 1-bromo-4-fluorobenzene; internal standards. See Table 4.7 for the compound names corresponding to numbers stated in the table.

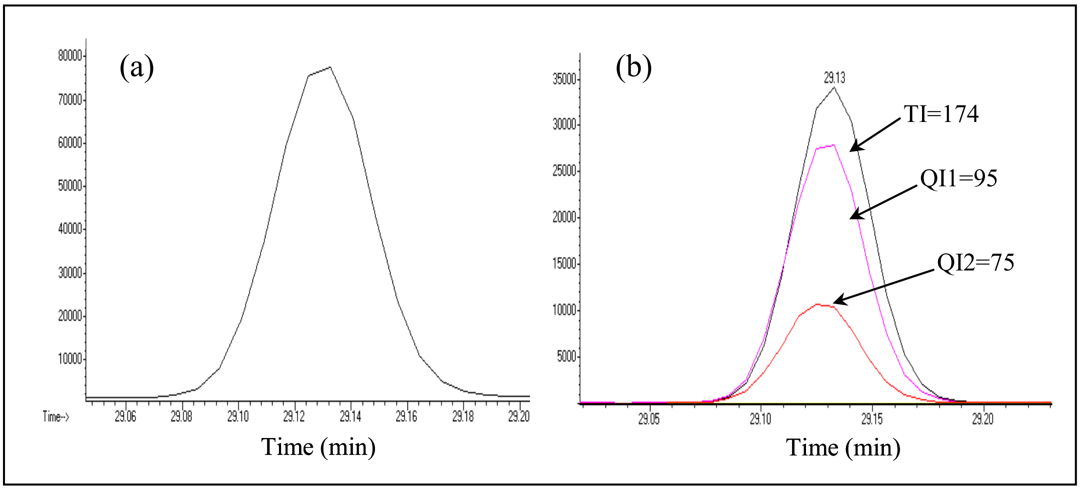


Figure 3.11. TIC (a) and EIM (b) chromatograms for 1-bromo-4-fluorobenzene.

Table 3.9. Acquisition windows for SIM mode VOC analysis.

Window	**RT**	**Ions**
1	6.00	41, 42, 55, 57, 70, 101, 103
2	12.32	61, 63, 55, 53, 43, 42, 27, 41, 67, 68, 70, 96, 108, 110
3	13.47	41, 42, 49, 55, 70, 84, 86
4	14.16	43, 57, 71, 101, 103, 151
5	14.90	41, 43, 55, 61, 67, 68, 69, 96, 98
6	15.90	27, 41, 42, 43, 55, 63, 65, 69, 70, 71, 84
7	16.60	41, 42, 43, 47, 49, 55, 56, 57, 61, 83, 84, 85, 96, 98, 128, 130
8	18.26	27, 41, 42, 43, 55, 56, 57, 62, 64, 69, 84, 85
9	19.12	43, 56, 57, 61, 85, 97, 99
10	19.60	41, 51, 56, 67, 77, 78, 82, 84, 117, 119, 121
11	20.50	43, 56, 57, 63, 71, 85, 114
12	20.90	27, 43, 57, 62, 63, 67, 70, 82, 93, 174, 176
13	21.32	41, 56, 57, 70, 83, 85, 95, 130, 132
14	21.80	41, 43, 55, 56, 57, 69, 71, 98
15	22.36	41, 56, 57, 69, 75, 77, 83, 98, 110
16	23.04	43, 57, 71, 75, 77, 85, 110
17	23.60	43, 61, 71, 83, 91, 92, 97, 117, 119
18	24.33	41, 43, 55, 57, 70, 71, 81, 85, 96, 97, 107, 109, 112, 127, 129
19	25.47	41, 43, 55, 57, 70, 85, 97, 112, 164, 166
20	26.17	55, 77, 90, 91, 106, 112, 114, 117, 119, 171, 173, 175
21	28.08	43, 50 55, 57, 70, 75, 78, 83, 85, 91, 95, 103, 104, 105, 106, 120, 174
22	29.80	43, 55, 56, 57, 71, 91, 105, 120, 134
23	31.90	91, 92, 105, 111, 120, 126, 134, 146, 148
24	33.24	91, 92, 105, 117, 118, 119, 134
25	34.00	43, 57, 71, 127, 128, 180, 182
26	37.50	91, 162, 223, 225, 227

A total of 26 windows were set in the SIM analysis method. The ions monitored within each of the “high resolution” SIM mode windows used in analysis method are listed in Table 3.9. Cutoffs between windows are based on chromatographic considerations. The dwell time for ion in each group was selected to yield approximately 2 scans per second throughout the run. Thus the high number of ions in one window resulted in low dwell times. Windows were set to provide minimum number of ions in each window for maximum sensitivity.

The ChemStation software has a capability to process maximum 30 ions in one window. The maximum number ions in the constructed SIM windows were 17 in the window number 21.

3.1.4.4 Optimization of SPTD Parameters

SIS (Scientific Instrument Services Inc., NJ, U.S.A.) Model TD 4 Short Path Thermal Desorber (SPTD) system was used in this study. The system consists of a Thermal Desorption Unit and an Electronics Control Unit. The Thermal Desorption Unit is placed directly on top of the GC injection port, where it is utilized for the direct desorption of samples into the GC injection port and column. Due to its "short path" of sample flow, this system overcomes shortcomings of previous desorption systems by eliminating transfer lines, which can easily be contaminated by samples, and by providing for the optimum delivery and therefore maximum sensitivity of samples to the GC injector via the shortest path possible, i.e. direct injection into the GC (Batterman, 2001). Analytes of interest were thermally desorbed from the sorbent tubes and directly entered into the GC inlet. Desorbed analytes were cryogenically cooled and trapped at the very front of the analytical column. Cryogenic trap were then quickly heated for rapid introduction of the analytes into column for separation by the GC and identification and quantification by the MS.

The microprocessor controlled electronic system, included in the thermal desorber system, permits either manual operation or automated operation including automatic injection, timed desorption, temperature ramp of heater blocks, control of GC Cryo-Trap Accessory, and remote starting of GC, mass spectrometer and recorder. The maximum desorption temperature permissible with the system was 350ºC and the heater blocks could be ballistically heated or temperature programmed at ramp rates up to 40ºC min^{-1}. Normal desorption times vary from 2 min to 15 min, however, longer desorption times up to 100 min are also possible.

Effect of Desorption Temperature

An appropriate desorption temperature was evaluated to ensure that all analytes were completely desorbed from the multisorbent tubes in order to reach the highest sensitivity and to avoid carryover. Very high desorption temperatures shorten the adsorbent resin life, cause excessive levels of undesired higher boiling compounds to enter the GC injection port and contribute to injection port and septa contamination. Lower desorption temperatures, on the other hand, result in poor recovery of target analytes. Thus, it was important to choose the lowest thermal desorption temperature needed to achieve complete volatilization and purging of analytes from the adsorbent. Adsorbent tubes were injected with gas phase VOC mixture at the sampling end and thermally desorbed and analyzed in the reverse direction to the sample flow.

Dependence of the analyte recovery on the desorption temperature for selected target analytes is shown in Figure 3.12. In the figure, the peak area has been normalized to the maximum value for each individual compound. It was obtained that the peak area responses for all target analytes increased with increasing desorption temperature up to 200ºC. The area responses were still high at 220ºC for some analytes but the variation was higher. The peak area responses decreased with increasing temperature after 220ºC. The decrease may be due to decomposition of analytes. Thus, optimum desorption temperature was chosen 200ºC.

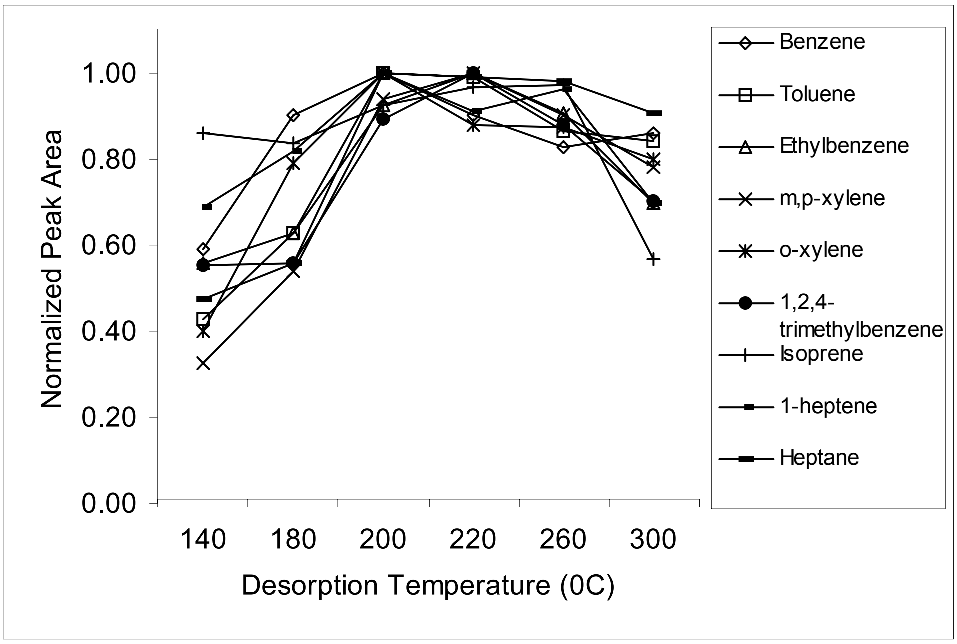


Figure 3.12. Dependence of analyte recovery on desorption temperature.

Effect of Cryotrap Temperature

Dependence of the analyte recovery on cryotrap temperature is shown in Figure 3.13. Cryofocusing of the analytes provide rapid injection and thus narrow bands resulting in good resolution (Camel and Caude, 1995). As can be seen in Figure 3.13, cryotrap temperature has significant influence on analyte recovery providing higher recovery at lower temperatures. Therefore, a cryotrap temperature of -70ºC was chosen as optimum. The results were presented only for selected target analytes but the similar patterns and conclusions were valid for all other target analytes.

Effect of Desorption Time

Dependence of analyte recovery on desorption time is shown in Figure 3.14. Desorption time exhibited relatively small influence on the analyte recovery.

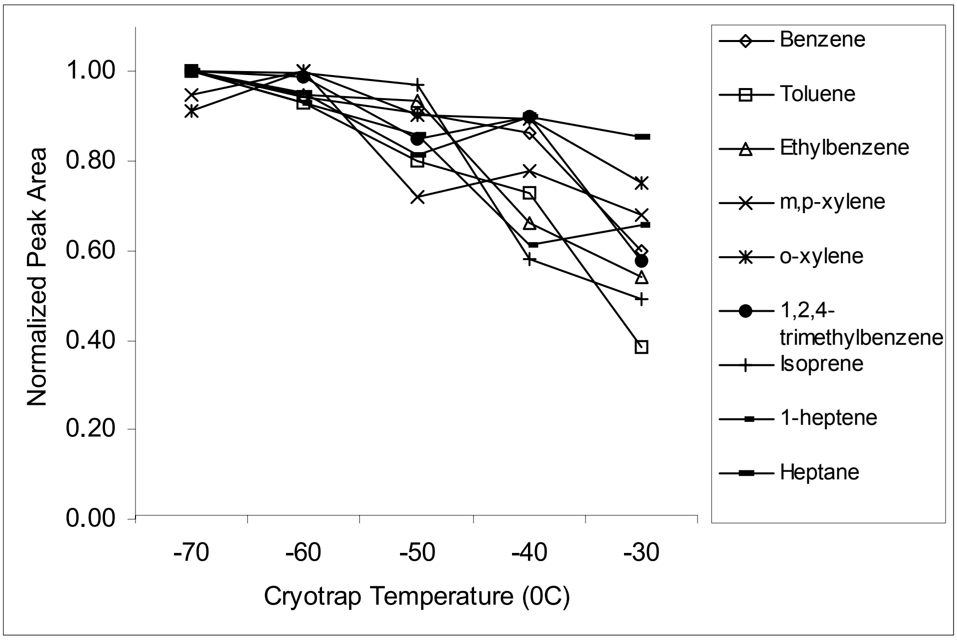


Figure 3.13. Dependence of analyte recovery on cryotrap temperature.

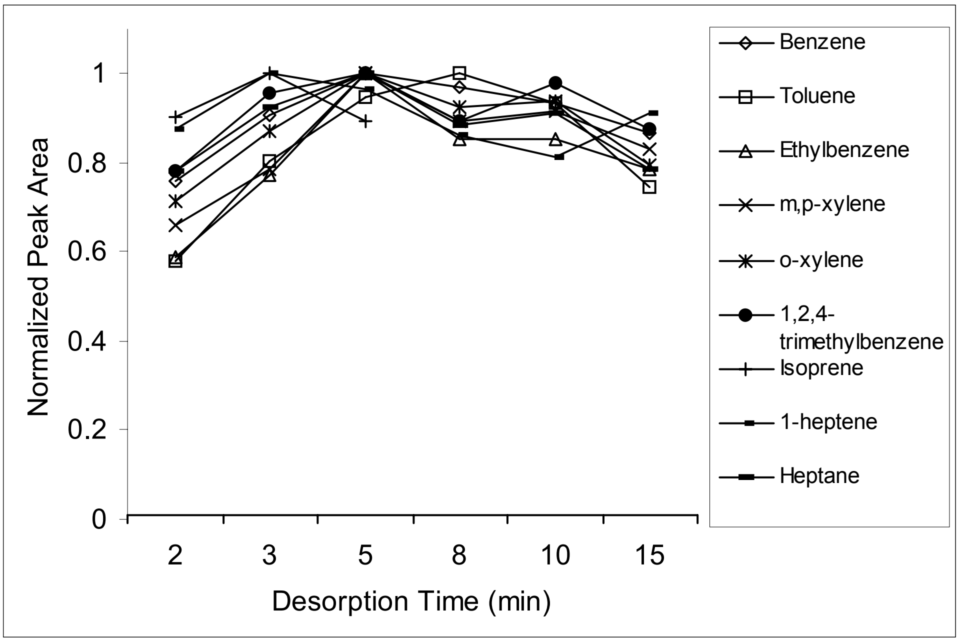


Figure 3.14. Dependence of analyte recovery on desorption time.

Optimum desorption time should be long enough to ensure complete desorption of target analytes from multisorbent tubes. Desorption time of 5 min and higher were found appropriate for this purpose. For isoprene, however, desorption time higher than 5 min resulted in loss of analyte and yielded zero recovery. This may be due to decomposition of isoprene under elevated temperature for extended period of time. Thus, 5 min was selected as the optimum desorption time. Desorption flow rate was set to 20 mL min^{-1} that provided a good recovery of all target analytes. The optimum SPTD parameters that were determined for the multisorbent tube type and target analyte list described in this study were summarized in Table 3.10.

Table 3.10. Optimized SPTD parameters.

Parameter	**Value**	**Parameter**	**Value**
Dry purge flow rate	40 mL min^{-1}	Guard column	None
Dry purge time	1 min	Cryo trap temperature	-70ºC
Injection time	0.30 min	Cryo heat temperature	250ºC
Desorption temperature	200ºC	Cryo heat time	5 min
Desorption flow rate	20 mL min^{-1}	Cryo liquid	Liquid CO_2
Desorption time	5 min		

3.1.4.5 Quantification

There are two major methods of performing calibration: i) external standard method and ii) internal standard method (Patnaik, 1997). In this study, quantification of the samples was performed by the GC-MS analysis under SIM mode of operation and using the internal standard method. Deutoriated isotopes or compounds having similar physicochemical characteristics with the target analytes but inert in nature and absent in the sample might be used as internal standards. The internal standards (ISTD) used in this study were bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d5 and 1-bromo-4-fluorobenzene (BFB). A 10 mL of the gas phase internal standard was added both to sample tubes and calibration standard tubes prior to analysis.

The initial calibration was performed to determine RRF values for target analytes, linearity of response and system sensitivity. The initial calibration included five gradual concentration levels. The acceptance criteria for the initial calibration were that; i) the area response for each internal standard at each calibration level must be within ±30% of the average response over all calibration levels and ii) the correlation coefficient (R^2) 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 chromatogram of the gas phase calibration mixture is presented in Figure 3.15.

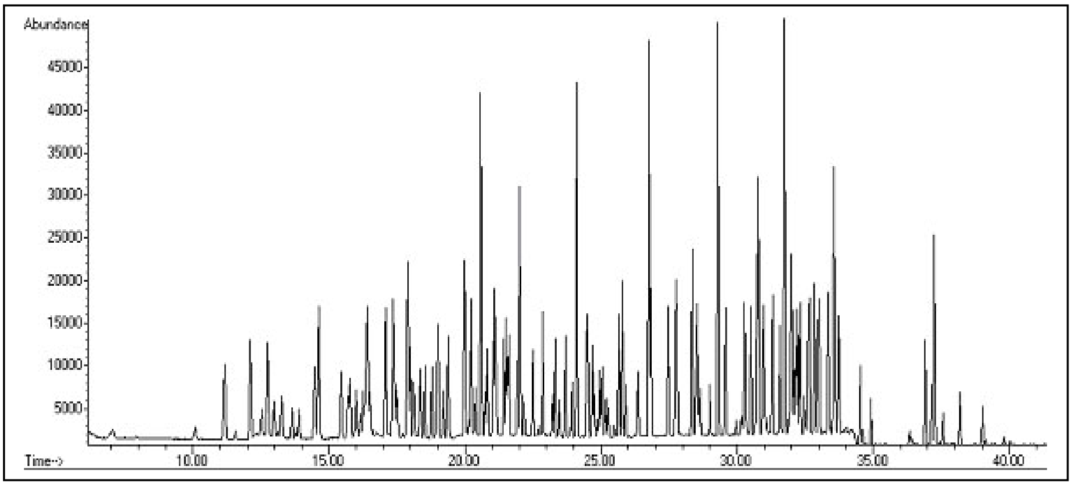


Figure 3.15. Typical calibration standard chromatogram.

Calibration was performed for a mid-level calibration standard in every three days in order to control the acceptance of initial calibration throughout the field campaign. The acceptance criterion was that the percent difference between RRF values of the compounds in daily calibration and RRF values of the compounds in the most recent initial calibration must be within ±30%. The RRF values and concentrations of each target analyte in the sample were calculated according to formulas given previously. The appropriate internal standard was used for each target analyte in the calculation. The calculations were performed automatically by using ChemStation software provided by HP (Agilent Technologies Inc., Palo Alto, CA, U.S.A.).

The ChemStation software also controls the peak identification by controlling the specified target and qualifier ion abundances for each target analyte. As it was described in the previous sections, TI and QIs have specific abundances for each target analyte. The percent abundances of these ions were assigned in the ChemStation software by generating a quantification method that was specific to SIM analysis parameters described in the previous sections. The difference between the percent abundance of target and qualifier ions calculated for initial calibration and the percent abundance of target and qualifier ions calculated for sample should be within ±20%. The ChemStation software performs automatic integration and calculation. However, the integration and calculations were inspected manually for each target analyte in each sample and calibration standard chromatograms. Thus, the calculation was not a completely automated process. A typical sample chromatogram obtained under these conditions is presented in Figure 3.16. The acceptance criteria for the sample analysis was that the retention time observed in the sample chromatogram must be within ±0.1 min of the retention time observed in the most recent valid calibration standard. The criteria stated for RRF values must also be satisfied.

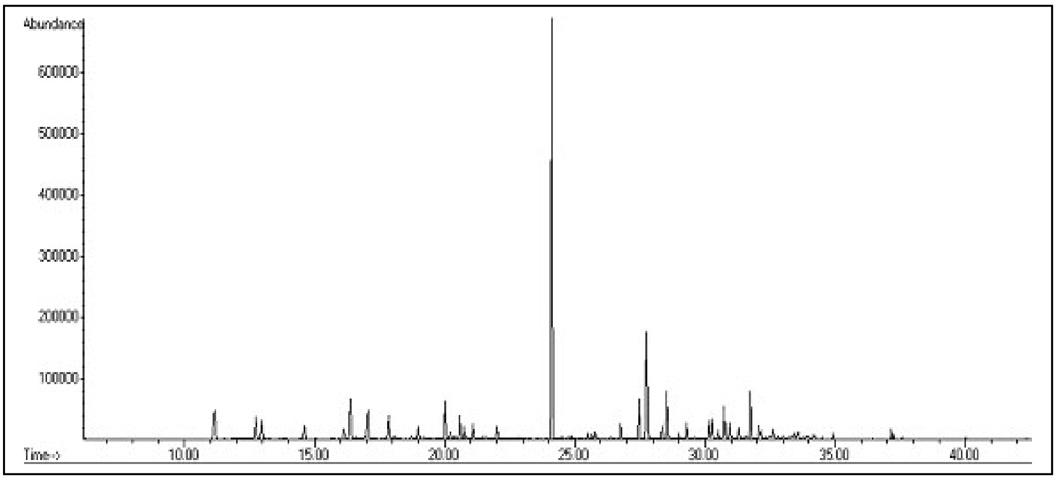


Figure 3.16. Typical sample chromatogram.

Performance of the Analytical Instrument

Before starting any analysis, the instrument was controlled for its performance. Tuning of the instrument was performed by perfluorotributylamine (PFTBA), which already installed in the instrument. Abundances and ratios of m/z 69, 216 and 505 were inspected for any significant change. The tuning should be followed by the calibration. Thus, the tuning was performed before the initial calibration and when a change in the ISTD responses was observed. The USEPA mandated the use of additional tuning substances and set the acceptable performance criteria for environmental analysis of organic pollutants by GC-MS. This substance is 1-bromo-4-flourobenzene (BFB) for volatile organic analysis (Patnaik, 1997). The BFB was used as the internal standard. Thus, BFB was monitored in every analysis.

Another parameter that may influence performance of the instrument is the potential contamination. The injection port, GC oven and AUX were baked at 300ºC for 30 min before starting any analysis. Two runs of laboratory blanks were followed after baking in order to demonstrate that the potential contamination in the system is eliminated. In case of any observed contamination, the source for the contamination was investigated and the cause for the contamination was eliminated.

3.1.4.6 Method Performance Evaluation

Extensive validation was conducted for sampling and analytical methodology. The method detection limit, precision, and recovery (desorption efficiency) values for all target analytes in chromatographic elution order are provided in Table 3.11.

Method Detection Limit

The method detection limit (MDL) is defined for each system by making seven replicate measurements of the compound of interest at a concentration near (within a factor of five) the expected detection limit, computing the standard deviation for the seven replicate concentrations, and multiplying this value by 3.14 (i.e., the Student's t value for 99% confidence for seven replicate) (USEPA, 1997a). The MDL of the analytical method was calculated by the analysis of seven replicates of the gas phase calibration standard at low-level concentration. Standard deviation for the seven replicate concentrations were computed and multiplied by Student's t value for 99% confidence for seven replicate. The computed MDL values ranged from 0.02 μg m^{-3} to 0.26 μg m^{-3} with an average value of 0.17 μg m^{-3} (i.e., 0.04 ppbv).

Precision and Linearity

The precision of the method was determined by performing six replicate measurements of adsorbent tubes that were injected with gas phase VOC mixture containing 0.2-2.64 ng of each analyte per tube. The resulting relative standard deviation (RSD) values ranged from 2.6 to 15.7% with an average value of 7.7%. Most of the target analytes have precision value of less than 10% with the exception of naphthalene (19.2%). The linearity of the method was evaluated with the correlation coefficient (R^2) of the regression line that was drawn for the five-point calibration curve. The method showed a good linear behavior with R^2 values detected for most of the compounds being higher than 0.99.

Blanks

Laboratory and field blanks were evaluated. Clean multisorbent tubes were loaded by gas phase internal standard mixture using standard gas loading apparatus described in Appendix A. These tubes were then analyzed as laboratory blank samples. Results of these analyses yielded information on any contamination in the sorbent tube, in the standard loading system, thermal desorption system or in the GC-MS system. Laboratory blanks were analyzed after each system bake and occasionally to control system against contamination when it was necessary. The GC inlet, GC column and MS auxiliary connection was baked at 300ºC for 30 min if the contamination was observed in the first run of laboratory blank tube.

Laboratory blanks were also analyzed after a calibration gas was analyzed in order to control possible carryover.

Field blanks were subjected to the same field condition as sample tubes. The tubes for field blanks were left at the site as their caps open for 5 min and then the caps were closed. A total of 17 laboratory blanks and 13 field blanks were analyzed under the same conditions of analysis and resulting chromatograms confirmed that no significant impurities were presented which could disturb the gas chromatographic analysis. Results were similar and even lower than the literature values provided for single adsorbent or different combination of multisorbent tubes (ISO, 2002; Batterman, 2000).

Desorption Efficiency

Desorption efficiencies for each VOCs are evaluated as the fraction of the mass recovered from the sorbent compared to that injected into the sorbent tube (Peng and Batterman, 2000; OSHA, 1993). Desorption efficiency is calculated from Eqn. 3.1.

$$\text{Desorption Efficiency}(\%) = \frac{\text{Amount of Analyte Recovered}}{\text{Amount of Analyte Placed on Adsorbent}} \times 100 \quad (3.1)$$

A sorbent tube spiked with gas phase VOC mixture with an average concentration of 7 $\mu g\ m^{-3}$ was analyzed twice and results of the first and the second analysis were used to calculate recoveries. Recoveries for the most analytes ranged between 80 to 100% with an average of 95.7%. However, two compounds (dibromochloromethane and bromoform) showed poor desorption efficiencies of less than 75%. Although all of these compounds are halogenated hydrocarbons, this should not be generalized as poor desorption efficiency values to all halogenated hydrocarbons since there are many other halogenated compounds in target analyte list that showed good recoveries. These two compounds were extracted from target compound list for further analysis due to poor recoveries.

Collection Efficiency

Collection efficiency was evaluated in terms of both retention efficiency and breakthrough under a range of conditions. The retention efficiency and breakthrough volumes for certain sorbents and analytes were provided in the literature (SIS, 1995; ISO, 2000); however, these literature values were given for single sorbent tube designs. The various studies available in the literature for multisorbent tubes are limited to analyte number and sorbent tube combinations (Heavner *et al.*, 1992; USEPA, 1997b; Wu *et al.*, 2003). Thus, laboratory and field studies for the determination of collection efficiencies applicable for target analytes and multisorbent tube combination were conducted in this study.

Determination of retention efficiency at the laboratory was conducted by utilizing elution analysis technique, by combining two adsorption tubes in series (Gallant *et al.*, 1978). A liquid mixture of DWM-550 aromatic hydrocarbons purchased from Ultra Scientific (North Kingstown, RI, U.S.A.) was injected into the sampling end of adsorbent tube with a concentration of 2 mg L^{-1}. A back adsorbent tube was connected to the front tube and high purity He gas at a total volume of 0.3 L was passed through the tubes that were attached to the thermal desorption instrument. Analysis of both the front and the back adsorbent tubes demonstrated that no significant breakthrough was observed for a very high concentration of analytes for short period of elution time that indicated collection efficiency close to 100%.

Studies (Krost *et al.*, 1982; Peng and Batterman, 2000; Foley *et al.*, 2001) showed that breakthrough volume responds to the change in relative humidity and temperature. It was also shown that breakthrough volume depends on VOC concentrations (Foley *et al.*, 2001). Breakthrough tests were conducted in the field under actual environmental conditions in order to account for changes in the breakthrough volume under real relative humidity, temperature and concentration values. Field tests were performed at residential, roadside and tunnel environments under summer and winter conditions for total sample volumes of 3.6 and 4.8 L. For a total of 15 samples collected, breakthrough was observed at most of the samples for 2-methyl-butane, Freon 11, 1-pentene, and 2-methyl-1-butene at values ranging between 15% and 40%. These analytes were excluded from the target analyte list for further evaluations.

Table 3.11. Selected method performance parameters.

No	Compound Name	MDL (ppbv)	Linearity (n=5)	Precision[1] (n=6)	Recovery[2] (%)	Detected[3] (%)
1	Pentane	0.13	0.991	9.34	100.00	98.30
2	Isoprene	0.06	0.996	7.31	100.00	94.60
3	c-2-pentene	0.03	0.994	7.71	95.00	71.34
4	2-methyl-2-butene	0.02	0.997	6.99	100.00	82.89
5	2,2-dimethylbutane	0.11	0.997	9.00	100.00	95.82
6	t-1,2-dichloroethene	0.03	0.991	9.85	95.00	0.16
7	3-methyl-1-pentene	0.04	0.999	6.45	95.00	3.38
8	2,3-dimethylbutane	0.03	0.988	5.88	100.00	98.35
9	t-4-methyl-2-pentene	0.03	0.995	6.47	95.00	56.01
10	2-methylpentane	0.14	0.996	8.16	85.41	99.04
11	c-4-methyl-2-pentene	0.03	0.995	6.50	95.00	50.56
12	3-methylpentane	0.08	0.990	8.22	91.24	98.09
13	1-hexene/2-methyl-1-pentene	0.06	0.998	5.44	100.00	84.13
14	c-1,2-dichloroethene	0.02	0.998	6.19	95.00	7.35
15	Hexane	0.08	1.000	12.00	94.00	98.35
16	Chloroform	0.04	0.996	8.24	84.62	91.43
17	t-2-hexene	0.04	0.994	4.47	95.00	27.55
18	c-2-hexene	0.01	0.998	4.91	95.00	40.41
19	c-3-methyl-2-pentene	0.10	1.000	11.25	83.64	77.39
20	2,2-dimethylpentane	0.03	0.981	4.39	100.00	85.97
21	1,2-dichloroethane	0.04	0.997	6.16	95.00	12.54
22	Methylcyclopentane	0.05	0.997	5.97	84.85	98.49
23	2,4-dimethylpentane	0.03	0.998	4.10	85.71	93.33
24	1,1,1-trichloroethane	0.10	0.998	3.75	100.00	99.60
25	2,2,3-trimethylbutane	0.02	0.991	6.71	95.00	27.31
26	1-methylcyclopentene	0.04	0.997	6.61	100.00	71.12
27	Benzene	0.13	0.996	8.28	93.73	100.00
28	Carbontetrachloride	0.02	0.996	5.01	75.00	100.00
29	Cyclohexane	0.03	0.998	8.24	100.00	94.66
30	2-methylhexane	0.03	0.991	13.61	100.00	96.78

Table 3.11. Selected method performance parameters *(Continued)*.

No	Compound Name	MDL (ppbv)	Linearity (n=5)	Precision[1] (n=6)	Recovery[2] (%)	Detected[3] (%)
31	2,3-dimethylpentane	0.02	0.991	5.82	100.00	96.27
32	3-methylhexane	0.02	0.995	6.39	100.00	94.14
33	Dibromomethane	0.03	0.998	5.97	95.00	7.47
34	1,2-dichloropropane	0.04	0.998	4.07	95.00	9.28
35	Trichloroethene	0.05	0.982	3.94	65.00	71.02
36	1-heptene	0.02	0.995	5.03	100.00	92.20
37	2,2,4-trimethylpentane	0.02	0.983	6.58	95.00	13.44
38	Heptane	0.10	0.998	5.22	100.00	99.04
39	c-3-heptene	0.03	0.997	4.67	95.00	34.07
40	t-2-heptene	0.02	0.996	2.59	95.00	23.04
41	c-2-heptene	0.04	0.995	2.66	95.00	27.49
42	c-1,3-dichloropropene	0.01	0.998	7.40	95.00	0.14
43	2,2-dimethylhexane	0.01	0.997	6.56	95.00	10.73
44	Methylcyclohexane	0.01	0.995	5.92	100.00	99.86
45	2,5-dimethylhexane	0.01	0.992	4.84	95.00	71.63
46	2,4-dimethylhexane	0.02	0.992	4.22	95.00	72.91
47	t-1,3-dichloropropene	0.02	0.995	9.87	95.00	0.16
48	Bromotrichloromethane	0.02	0.999	9.98	95.00	0.14
49	2,3,4-trimethylpentane	0.01	0.998	4.86	95.00	65.18
50	Toluene	0.08	0.995	5.80	92.88	100.00
51	1-methylcyclohexene	0.06	0.996	7.00	95.00	12.38
52	Dibromochloromethane	0.04	0.997	5.66	70.00	2.64
53	3-methylheptane	0.01	0.998	5.10	100.00	93.50
54	c-1,3-dimethylcyclohexane	0.01	0.997	6.98	100.00	85.62
55	t-1,4-dimethylcyclohexane	0.01	0.992	6.34	95.00	82.67
56	1,2-dibromoethane	0.03	0.998	5.39	95.00	25.09
57	2,2,5-trimethylhexane	0.01	0.999	4.25	95.00	5.59
58	1-octene	0.05	0.998	6.17	87.88	80.90
59	Octane	0.06	0.998	10.97	94.00	97.09
60	t-2-octene	0.02	0.995	5.83	95.00	20.98
61	t-1,2-dimethylcyclohexane	0.01	0.998	6.12	94.87	34.65
62	Tetrachloroethene	0.04	0.997	5.80	95.00	99.86
63	c-1,4/t-1,3-dimethylcyclohexane	0.01	0.998	5.81	80.00	44.86
64	Chlorobenzene	0.03	0.996	3.81	90.43	58.99
65	Ethylbenzene	0.06	0.996	7.14	97.15	100.00
66	m,p-xylene	0.12	0.994	12.81	95.00	100.00
67	Bromoform	0.01	0.998	4.66	65.00	61.48
68	Styrene	0.07	0.999	14.41	95.00	94.63
69	1,1,2,2-tetrachloroethane	0.03	0.991	10.94	97.71	10.58

Table 3.11. Selected method performance parameters *(Continued)*.

No	Compound Name	MDL (ppbv)	Linearity (n=5)	Precision[1] (n=6)	Recovery[2] (%)	Detected[3] (%)
70	o-xylene	0.04	0.993	9.30	95.00	100.00
71	Nonane	0.01	0.992	12.57	100.00	97.69
72	iso-propylbenzene	0.03	0.993	7.99	95.00	93.73
73	n-propylbenzene	0.02	0.993	7.39	97.83	98.84
74	3-ethyltoluene	0.03	0.993	10.17	97.30	98.84
75	4-ethyltoluene	0.05	0.994	5.84	96.39	98.84
76	1,3,5-trimethylbenzene	0.03	0.992	8.61	97.87	99.00
77	2-ethyltoluene	0.02	0.994	8.00	98.30	98.46
78	1,2,4-trimethylbenzene	0.06	0.993	8.62	100.00	97.96
79	benzyl chloride	0.05	0.996	6.18	83.07	77.11
80	1,4-dichlorobenzene	0.03	0.999	11.21	100.00	99.45
81	iso-butylbenzene	0.03	0.993	8.52	100.00	93.34
82	sec-butylbenzene	0.03	0.992	7.93	96.08	74.54
83	1,2,3-trimethylbenzene	0.03	0.992	9.02	80.00	89.94
84	p-cymene	0.02	0.992	9.22	95.00	97.99
85	1,2-dichlorobenzene	0.03	0.994	7.80	80.00	5.42
86	1,4-diethylbenzene	0.05	0.994	9.50	100.00	78.04
87	n-butylbenzene	0.02	0.992	10.07	95.00	89.70
88	1,2,4-trichlorobenzene	0.05	0.999	10.37	88.00	12.25
89	Naphthalene	0.01	0.999	19.21	89.36	99.43
90	Hexachlorobutadiene	0.02	0.990	9.03	95.00	0.00
91	Hexylbenzene	0.03	0.999	8.89	95.00	4.85

[1] R.S.D.%; [2] Desorption efficiency; [3] Percent of field samples at which the individual compound was detected for a total of 411 sample.

Storage Stability

Storage stability was evaluated for spiked samples. Six adsorbent tubes were injected with gas phase mid-level VOC mixture containing 1-13 μg m^{-3} of each analyte and then the tubes were sealed. Spiked samples were stored at -18°C. Four samples were analyzed after a storage period of 2 days and two samples were analyzed after 9 days of storage. Recovery rates for stored samples were calculated as the fraction of the concentration measured in the tubes that were analyzed immediately after loading. The average recoveries for the storage of target analytes on multisorbent tubes were 102% and 87% for 2 days and 9 days of storage periods, respectively. There was no significant change in sample amount after 2 days of storage. On the other hand, increase in the amount of target analytes due to sample degradation or decrease in the amount due to sample loss was observed for 9 days of storage period. Samples were analyzed within an average of 2 days after collection to minimize the potential for losses and sample degradation.

3.1.4.7 Analysis of Fuel Samples

Gasoline and diesel fuel samples were analyzed to develop whole and headspace fuel fingerprints specific to Turkey for speciated VOCs. Two different brands of fuels namely British Petroleum (BP) and Petrol Ofisi (PO) were taken from the BP and PO gas stations located in Ankara. One liters of leaded and unleaded gasoline and diesel fuel samples were taken from each gas station. Amber glass bottles of 1-L capacity with Teflon caps were used to carry and store the fuel samples. Samples were labeled including brand name, date and fuel type.

During the preparation of headspace and whole fuel samples, 40-mL amber vials having open top screw caps with two-sided septum (bottom side is made of PTFE and top side is made of silicone) were used. Amber vials and caps were rinsed with methanol in the fume hood and left to dry in the fume hood overnight. Sterilized plastic single-use medical syringes of 10-mL and 2-mL in capacity were used to measure fuel samples into amber vials.

Syringes were also rinsed with methanol and dried in the fume hood overnight. Solvent bottle supplied by Supelco (Bellefonte, PA, U.S.A.) was used during methanol rinsing. Two amber bottles were capped in the fume hood and analyzed as laboratory blank samples. Room temperature was 22±2ºC during all phases of the fuel sample preparations.

Whole Fuel Samples

Whole fuel samples were prepared by spraying small amount of fuel into an empty amber vial that was capped in the fume hood. Fuel bottles were opened in the fume hood and 1 μL of fuel was drawn into a Hamilton 1 μL syringe and injected into a waste flask for 10 times. After proper rinsing of the syringe, 1 μL of fuel sample was injected into 40-mL amber vial through the silicon side of the septum. Sample bottle waited at the room temperature for 5 min then it is submerged into water-bath that is at 60ºC. After 5 min, 1-mL of whole fuel sample was drawn from the bottle through septum by Hamilton 5-mL gas tight syringe. Sample was injected into a thermal desorption tube from its sampling end that was connected to the gas loading apparatus. Sample was purged for 5 min under 50 mL min^{-1} of high purity N_2 flowing through multisorbent tube. High purity N_2 gas passed through a hydrocarbon trap and MFC before entering into thermal desorption tube. Laboratory blanks were also analyzed and no contamination was found at a significant level. The multisorbent tubes loaded with whole fuel samples were then analyzed utilizing the analytical procedure described in the previous sections.

Gasoline and diesel whole fuel samples were prepared by using the same procedure. Diesel samples, however, were prepared after all the gasoline samples were prepared in order to eliminate possible cross contaminations.

Headspace Fuel Samples

Headspace fuel samples were prepared by filling the amber vials partially with fuel samples and waiting for liquid to gas phase equilibrium to reach in closed environment under constant temperature. Amber vials of 40-mL in volume were filled with 10-mL of fuel samples. The same procedure was repeated for all different types and brands of fuels. Sterilized plastic single-use medical syringes of 10-mL in capacity were used to fill fuel samples into amber vials. Different syringes were used for each brand and fuel type. Syringes were discarded after a single use not to cause cross contamination of the fuel samples. Fuels were put into amber vials in fume hood and capped tightly. Vials filled with fuel samples and capped tightly were left in the laboratory, where the room temperature was at 22±2°C, overnight. Before taking headspace samples from the vials, vials were placed into a water bath at 35°C for 1-hr. Then, 0.5 mL of samples was drawn from the headspace of the vials. Hamilton 5-mL gas tight syringe that was cleaned with methanol and dried in the fume hood overnight was used. Samples were drawn from the vials through septum cap. Same gas tight syringe was used for all samples. Syringe was methanol cleaned and dried in fume hood after each use.

Headspace fuel samples were injected into multisorbent tubes via gas injection apparatus. While injecting the sample into apparatus high purity N_2 flow at a constant flow rate of 50 mL min^{-1} was maintained in the system for 5 min. High purity N_2 gas that passed through hydrocarbon trap was then flowed through the mass flow controller (MFC) that operated between 0 to 500 mL min^{-1} airflow to provide a constant flow rate. MFC was calibrated by digital flow meter before use in loading the tubes.

The tubes that were loaded with whole fuel sample were then analyzed utilizing the analytical procedure described in the previous sections. The only difference was the 1:25 split ratio used for headspace fuel samples during the thermal desorption analysis. Headspace fuel samples were highly concentrated and splitless operation of the system resulted in saturated peak shapes. Split ratio of 1:25 resulted in the best quantitative data among other split ratios that were tried.

Diesel headspace samples were prepared by using the same procedure. Diesel samples, however, were prepared after all the gasoline samples were prepared in order to eliminate possible cross contaminations.

3.1.4.8 Handling of Wastes and E&OHS

Thermal desorption technique is environmentally friendly because of the limited amount of solvent use. However, during the preparation of fuel samples excessive amount of solvents especially methanol was used. Waste solvents were stored in high density polyethylene waste bottles that were capped loosely and were delivered to Department of Chemistry for several times during laboratory works for final storage before transported to IZAYDAS by Department of Chemistry. IZAYDAS is a licensed facility for the disposal of hazardous wastes locates in Kocaeli, Turkey.

Since the ultimate aim of the study is to gather data and knowledge to protect environmental and public health, environmental and occupational health and safety (E&OHS) rules were practiced during the laboratory and field works. For example, a half facemask with ABEK cartridge preventing VOC inhalation was used during the preparation of calibration standards. Gloves and safety glasses were worn for all times when solvents and hazardous chemicals were handled. Dust masks were worn during packing of the thermal desorption tubes with Tenax TA and Carbopack B sorbents. Proper ventilation was used at the working areas. A fire extinguisher was placed to an easily accessible location especially during preparation of the fuel samples.

3.1.5. Quality Assurance and Quality Control of the Data

Given the complexity involved in the chromatographic analysis of VOCs, it is justifiable to explore new techniques of quality control or standardization procedure to reduce artifacts or systematic errors in the analysis. It is imperative to be confident about the quality of the data before performing any interpretation of the data set. The anomalies in the data set may arise from; i) problems that may be encountered during sample collection at the field, ii) analytical problems that may occur during instrumental analysis, iii) inaccuracy in integration of the chromatogram, iv) anomalies in meteorological parameters and v) change in source strength. It is important to distinguish whether the anomaly is due to a systematic error or a problem in a single data point. These outliers may result in misleading information on the interpretation. Thus, quality control of the data set must be performed to investigate anomalies.

A multidimensional data validation procedure was applied to the field data set including 411 sampling intervals and 40,278 data points. The data validation procedure, similar to chromatographic techniques, was very complex and time consuming. Independent parameters, including time, compound and meteorology, influence overall concentration pattern of the data. These dimensions were evaluated in the two phase of the data validation procedure. The initial phase of the procedure included generation of; i) times series, ii) scatter plots and iii) fingerprint plots for individual species and for each session. SPLUS 6.0 statistics software was used to handle QC of the large data set.

The compound ratio graphs were also generated for toluene/benzene, m&p-xylene/ethylbenzene, toluene/m&p-xylene and m&p-xylene/benzene ratios. The second phase covered evaluation of the plots to identify anomalies and to find the causes for these anomalies. In case of any anomaly was observed, chromatograms were re-evaluated for misidentification or misquantification. In addition, field and laboratory logbooks were re-evaluated for any possible contamination or problem. Meteorological parameters such as mixing height, temperature and wind speed were evaluated to understand if the anomaly was due to a pollution episode.

Time series plots were drawn for each species. These plots showed variation in the species concentration along with time of campaign. Time series plots were inspected for large "jumps" or "dips" in concentrations, periodicity of peaks, calibration carryover, expected diurnal behavior (e.g., lower concentrations of isoprene during night time), expected relationships among species, and high single-hour concentrations of less abundant species. A sample time series plot generated for the data set of residential station applicable to morning session of winter campaign is shown in Figure 3.17.

Fingerprint plots were drawn for each individual session including all target compounds. These plots provided an overall view of daily changes. Morning, noon, afternoon, evening and night sessions were inspected separately. These plots were inspected for outliers that were indicated by deviation from general pattern. A sample fingerprint generated for the data set of residential station for morning sessions at winter campaign is shown in Figure 3.18.

Scatter plots were drawn to demonstrate correlations between individual species and between individual specie and total VOC. The plots were inspected for benzene vs. toluene, species that elute close together, and isomers. Anomalies such as scattered data points being contrary to the general correlation of the data were inspected. The compound ratios that were most commonly reported for certain sources in the literature were also investigated for significant changes. Large changes in the ratios do not always indicate an anomaly but it can be an indicator to an anomaly in some cases. Thus, the investigation of compound ratios was used as a supplementary tool.

A fingerprint plot drawn for the selected compounds measured at residential station during morning session of summer campaign in Ankara is presented in Figure 3.19. It is clearly seen from the figure that there was a significant increase in the concentrations of compounds and especially in the concentrations of toluene on 28 July 8:00 session.

A scatter plot matrices drawn for benzene, toluene, ethlybenzene, m&p-xylene and total VOC for the same data set is shown in Figure 3.10. A single data point that was clearly separated from the other data points also stands for the results of 28 July 8:00 session. The data validation procedure was successful for the identification of this anomaly. It was found that this anomaly was due to pollution episode.

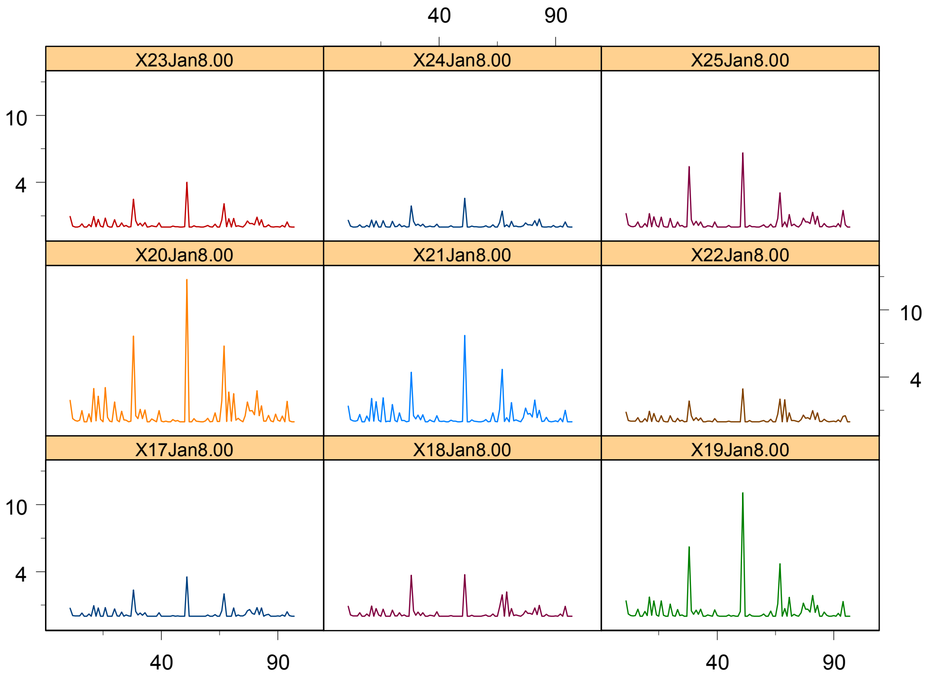


Figure 3.17. Sample time series plot.

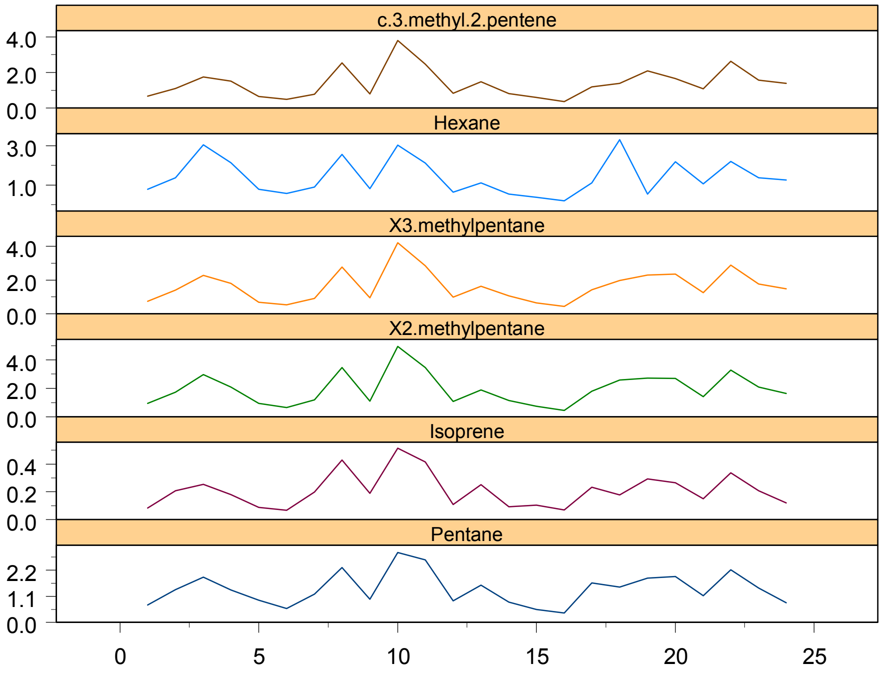


Figure 3.18. Sample fingerprint plot.

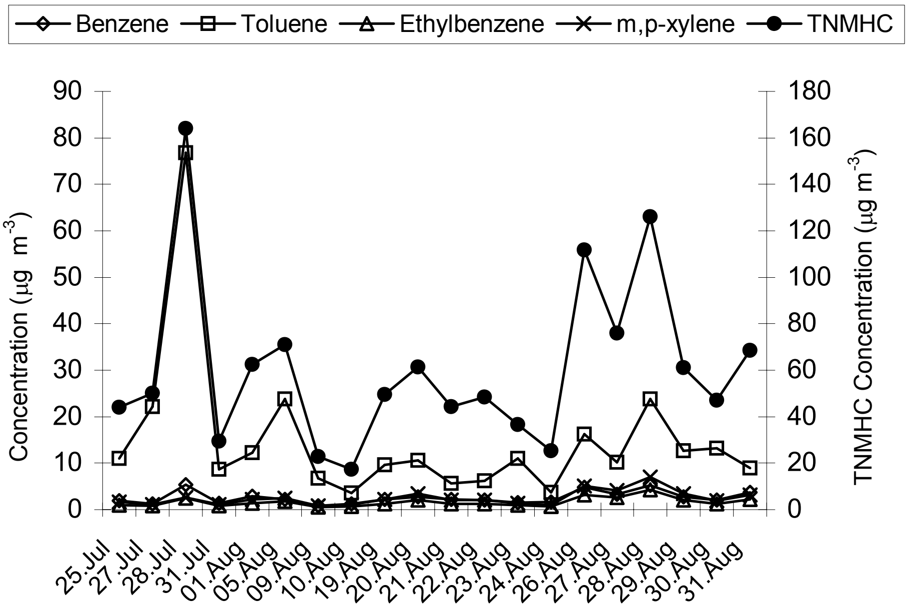


Figure 3.19. Fingerprint plot generated for summer data of residential station.

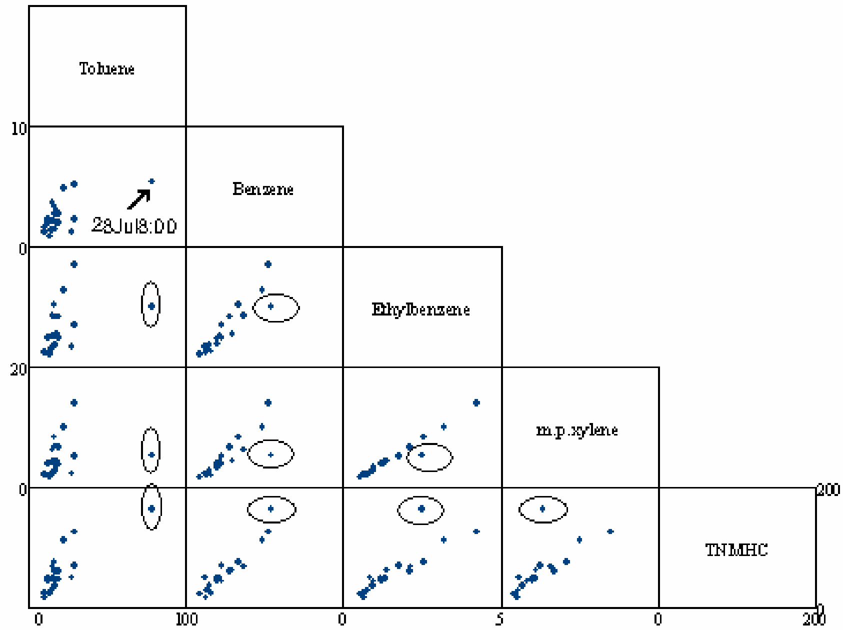


Figure 3.20. Scatter plot generated for summer data of residential station.

3.2. Ottawa Campaign

A field campaign was conducted at Ottawa, Canada in order to investigate levels and sources of air toxics at different microenvironments and at extreme ambient temperatures. The samples were collected inside commuting vehicles and at roadside stations in the winter and summer of the year 2000. The following sections provide detailed information on the study sites and sampling and analytical methodology.

3.2.1. The Study Site

Ottawa is the capital of Canada. It has a population of around 1 million. There is no major industry in or around the city. As being the capital, it is mostly occupied by governmental offices. Thus, the traffic and residential heating are the major sources of air pollution in the city. The national Criteria Air Contaminants (CAC) inventory (1995) identifies a total of 2429 kilotonnes (kt) of VOC emissions in Canada with the most significant sources being transportation (31%) followed by upstream oil and gas (28%), solvent use (19%), industrial sources (10%), residential/commercial fuel/wood combustion (6%) and fuel marketing (4%) (EC, 2004). Thus, the research efforts on the identification and quantification of the sources and levels of exposure to air toxics associated with motor vehicle traffic are significant.

This study aimed at investigation of air toxics originated from motor vehicles in Ottawa. Air samples were collected at two roadside stations and during commuting inside a passenger car and buses. Roadside sampling stations were located on Slater Street, a major one-way artery running west to east through the downtown core and carrying approximately 750 vehicles per hour during the sampling periods. Light duty vehicles constitute 80-90% of the vehicle. The primary roadside sampling station was set-up at pedestrian nose-level, approximately 1.5 m above the sidewalk, 60 cm from the curbside, on the south sidewalk of Slater Street.

A second roadside sampling station was set-up on the rooftop of a three-storey parking structure adjacent to the nose-level sampler during the 2000 study. Also, a permanent National Air Pollution Surveillance (NAPS) network station sampler is located at 88 Slater Street, within two blocks of the nose-level sampling station. The NAPS and rooftop stations provide observations at different heights (4 m and 10 m vs. 1.5 m) and sampling periods (24 h vs. 2 h) relative to the nose-level stations. The rooftop sampler was installed to enable correlation with the data acquired at the NAPS sampling station and nose-level station. Location of ambient stations is shown in Figure 3.21.

Figure 3.21. Location of the sampling stations used in Ottawa campaign.

3.2.2. Sampling Strategy

The air samples were collected at sampling sites in order to determine VOC, SVOC and carbonyl compounds. The sampling strategy and site characteristics of the sampling sites used in Ottawa campaign is depicted in Table 3.12. Nose-level samples were collected over 2-hr periods during the morning rush (7:30-9:30), mid-day (11:30-13:30) and evening rush (15:30-17:30) for 21 days in the winter and 8 days in the summer of 2000. Nose-level 24 hr samples were collected every sixth day for comparison with the NAPS station samples. In-vehicle samples were collected during the morning rush (7:30-10:00) and during the evening rush (3:30-6:00) for 19 days in winter and 14 days in winter campaign.

Table 3.12. Sampling strategy and site characteristics.

Type of the Site	Ambient			In-vehicle	
Name of the Site	Nose-level		Rooftop	Car	Bus
Sampling Duration	2 hrs	24 hrs	24 hrs	>50 min.	>50 min.
Sampling Frequency	3 per day	1 in every six days	1 in every six days	2 per day	2 per day
WINTER-2000					
Sampling Dates	17 January - 6 February		17 January - 6 February	18 January – 17 February	18 January – 22 February
Total Sampling Days	17	4	4	18	19
SUMMER-2000					
Sampling Dates	28 July – 4 August		29 July – 4 August	17 July – 11 August	17 July – 11 August
Total Sampling Days	6	2	7	14	14

Number of samples collected during winter and summer campaigns are given in Table 3.13 and 3.14, respectively. Total number of VOC, SVOC and carbonyl samples collected at all sites were 309 and 167 for winter and summer, respectively. During the winter campaign, 59 VOC samples were collected at roadside stations and 63 samples were collected inside vehicles. A total of 61 SVOC samples were collected at roadside stations.

The number samples collected to determine carbonyl compounds were 53 at roadside stations and 72 for in-vehicle trips. During the summer campaign, the number of samples collected to determine VOC, SVOC and carbonyl compounds at roadside stations were 24, 14 and 17, respectively. The number of samples collected to determine VOC and carbonyl compounds were 56 at in-vehicle.

Table 3.13. Number of samples collected at sampling sites in winter.

Sampling Intervals	Nose-level	Rooftop	In-car	In-bus
Volatile Organic Compounds				
7:30-9:30	16	NA	17	17
11:30-13:30	16	NA	NA	NA
15:30-17:30	17	NA	15	14
24 hrs	4	4	NA	NA
Total	53	4	32	31
Carbonyl Compounds				
7:30-9:30	16	NA	18	18
11:30-13:30	16	NA	NA	NA
15:30-17:30	17	NA	18	18
24 hrs	4	NA	NA	NA
Total	53	NA	36	36
Semi-volatile Organic Compounds				
7:30-9:30	16	NA	NA	NA
11:30-13:30	16	NA	NA	NA
15:30-17:30	17	NA	NA	NA
24 hrs	4	8	NA	NA
Total	53	8	NA	NA

Table 3.14. Number of samples collected at sampling sites in summer.

Sampling Intervals	Nose-level	Rooftop	In-car	In-bus
Volatile Organic Compounds				
7:30-9:30	5	NA	14	14
11:30-13:30	5	NA	NA	NA
15:30-17:30	5	NA	14	14
24 hrs	2	7	NA	NA
Total	17	7	28	28
Carbonyl Compounds				
7:30-9:30	5	NA	14	14
11:30-13:30	5	NA	NA	NA
15:30-17:30	5	NA	14	14
24 hrs	2	NA	NA	NA
Total	17	NA	28	28
Semi-Volatile Organic Compounds				
7:30-9:30	NA	NA	NA	NA
11:30-13:30	NA	NA	NA	NA
15:30-17:30	NA	NA	NA	NA
24 hrs	7	7	NA	NA
Total	7	7	NA	NA

3.2.3. Sampling Methodology

3.2.3.1 Roadside Stations

Roadside and rooftop samples of VOCs were collected in pre-cleaned, proofed and evacuated 6 L Summa canisters equipped with a flow controlling head assembly. The head assemblies consisted of a Veriflo SC423XL flow controller, Matheson 63-3704A-pressure/vacuum gauge, and a Swagelock-Whitey SS-42XS4 stream select valve. The flow controller supplied constant flow with a self-correcting action to compensate for changes in pressure. It controlled flow by maintaining a constant differential pressure across an orifice.

Roadside samples of carbonyl compounds were collected by drawing air at a constant flow rate of 1 L min^{-1} through 2,4-DNPH coated Sep-Pak silica gel cartridges. The cartridges were protected from ozone interference by using Supelco DNPH Ozone Scrubbers. Factors such as traffic density, meteorological conditions, and the number of passengers were recorded during the sampling periods.

Sampling equipments were placed into a cabinet that was constructed at the Emissions Research and Measurement Division of Environment Canada. The sampling cabinet was a 50 cm x 50 cm x 115 cm tall weather-shielded structure. During the winter sampling sessions, the interior of the housing was lined aluminum covered polystyrene insulation and a small electric heater was installed. For the summer sampling the insulation was removed and an electric fan was installed in the rear wall of the housing to prevent overheating within the structure. The sample inlets protruded through the bottom of the housing.

3.2.3.2 In-vehicle Sampling

Samples of VOCs and carbonyl compounds were collected within a light-duty vehicle and a public transit bus. The wintertime in-car samples were collected while the vehicle traveled an approximately 22 km route between Kanata and Carleton University, along roadways with posted speed limits that did not exceed 80 km/hr. The vehicles used were a 1997 Nissan Sentra with approximately 82 000 km accumulated and a 1997 Volkswagon Golf with approximately 48 000 km accumulated at the start of the program. The bus traveled along the OC-Transpo route number 7 between the Glebe area of Ottawa and Carleton University (via St. Laurent Shopping Center). A typical in-car sample was collected over 40 minutes and a typical in-bus sample was collected over 90 minutes.

The summer-time in-car samples were collected while the vehicle traveled an approximately 26 km route, along roadways with posted speed limits that did not exceed 70 km/hr, between Carleton University, Richmond Road at Baseline Road and back to Carleton University. The vehicle used for the summer-time in-car sampling was a 1991 Chrysler Acclaim with approximately 140 000 km accumulated. The bus traveled along OC-Transpo route 7 from Carleton University to downtown Ottawa and back to Carleton University. A typical in-car sample was collected over 50 min and a typical in-bus sample was collected over 55 min.

In-vehicle samples of VOCs were collected in 1 L Summa canisters with same head assembly as used for roadside sampling. Carbonyl compounds were collected on DNPH coated cartridges using a personal sampling pump drawing at 1 L min^{-1}. Samplers used at nose-level station and during in-vehicle sampling in Ottawa campaign is shown in Figure 3.22.

3.2.3.3 Traffic Data

Traffic counts were conducted during the 2-hr sampling sessions at roadside station. Vehicles were classified as heavy-duty vehicle (HDV), light duty vehicle (LDV), coach bus, articulated bus or motorcycle. LDVs included both gasoline and diesel fuelled light duty vehicles. Heavy-duty vehicles were considered to be vehicles larger than and including cube van size. Highway coach buses and school buses were counted as coach buses. Traffic counts were recorded in 15-min intervals throughout the duration of the 2-hr sampling session.

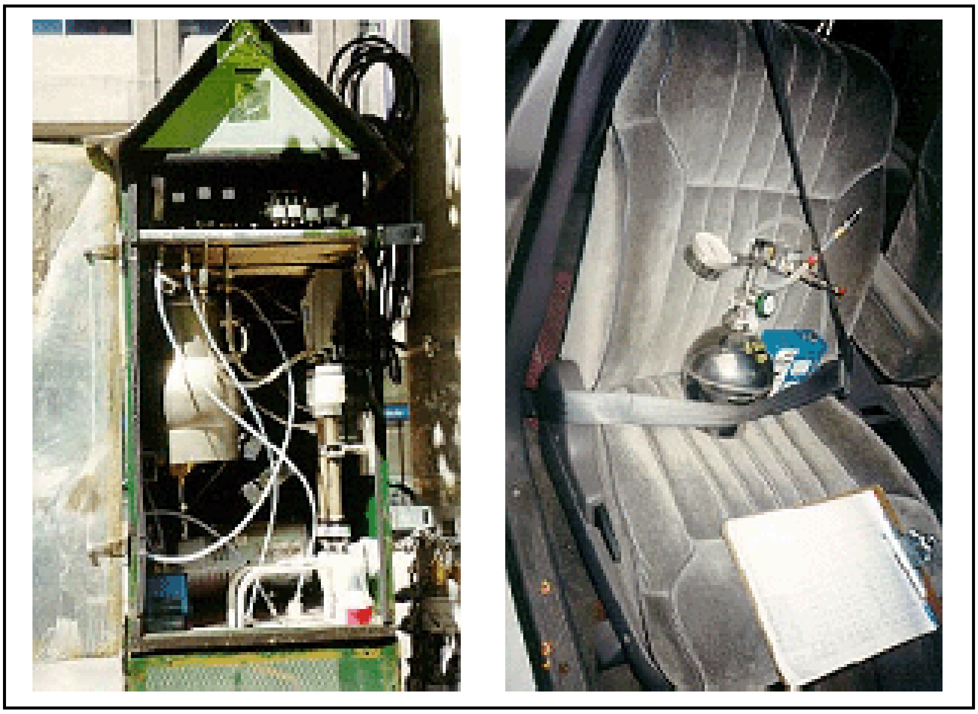


Figure 3.22. Sampler used in Ottawa campaign.

3.2.3.4 *Meteorological Data*

Hourly observations of the temperature, weather condition, wind direction and wind speed made at the Ottawa International Airport were obtained from the Meteorological Service of Canada, Environment Canada. In addition, local temperature and precipitation conditions on Slater Street were recorded before, during and after each sampling session.

3.2.4. Analytical Methodology

Laboratory analyses of all the collected samples for VOC, SVOC and carbonyl compounds were conducted by Emission Research and Measurement Division (ERMD) of Environment Technology Center (ETC), Environment Canada (Ottawa, Canada). The rooftop samples were also analyzed for VOCs and SVOCs by Analysis and Air Quality Division (AAQD) of Environment Technology Center (ETC), Environment Canada (Ottawa, Canada). The analyses were carried out for 165 VOCs, 14 SVOCs and 23 carbonyl compounds at ERMD. Target analytes were slightly different from the target analyte set used in the Ankara campaign. Target analytes included only olefin, paraffin and aromatic VOCs since the study aimed at determining motor vehicle related sources. Thus, halogenated VOC and biogenic compounds were not included in the list of Ottawa campaign.

The samples were analyzed to determine VOCs using a Hewlett Packard 5890 Series II gas chromatograph coupled to a flame ionization detector (GC-FID) together with an Entech M7000 cryogenic concentrator for sample concentration and introduction. The analytical method was calibrated using external standards on a per component basis. The gas-phase hydrocarbon standards used were prepared in-house using a permeation tube gas standard generator (Kin-Tek Laboratories, LaMarque, Texas). The quantitation limits for this set of analytical conditions was approximately 0.2 to 0.5 ng L^{-1}. The rooftop samples were analyzed to determine VOCs by AAQD using a Hewlett Packard 5890 Series II gas chromatograph (GC) coupled to an HP 5970 Mass Selective Detector (MSD) together with a Nutech cryogenic concentrator. Internal standard method was used in these analyses.

The pre-concentrator system does not allow for the determination of methane and sometimes the C_2 hydrocarbons are not well retained on the trap. Methane was determined and the confirmation of the C_2 and C_3 hydrocarbons was accomplished by a simple gas loop injection onto a capillary column in another HP 5890 Series II GC-FID system equipped with a gas-sampling valve. The sample loop was flushed with sample, the pressure inside the loop allowed to equilibrate to ambient conditions and the contents of the loop were injected directly onto the capillary column.

SVOC samples were collected onto glass cartridges packed with Tenax TA at nose-level station. The stainless steel tubes packed with Tenax TA were used to collect SVOC samples at rooftop station. The solvent extraction method was used for determination of SVOCs collected at nose-level. The Tenax TA adsorbent in glass tubes was poured and solvent extracted using high purity pentane supplied by Caledon (Caledon Laboratories Ltd., ON, Canada). An aliquot of this pentane extract was analyzed by a GC-FID. Although a large number of peaks appear in the chromatogram between the normal paraffins from C_{12} to $C_{26,}$ these were not at quantifiable levels and were not identified. Detection limits for the hydrocarbons in the pentane extract were approximately 25 μg L^{-1}. Determination of SVOCs collected at rooftop station were done by thermal desorption. Stainless steel Tenax tubes were thermally desorbed by using thermal desorption unit supplied by Tekmar (Tekmar-Dohrmann, OH, U.S.A.) and analyzed by a GC-MS supplied by HP (Agilent Technologies Inc., Palo Alto, CA, U.S.A.).

Carbonyl compounds selectively react with the 2,4-DNPH forming hydrazones that were retained on the cartridge. The hydrazones were eluted from each cartridge and the solution was made up to volume in a graduated centrifuge tube with HPLC grade Acetonitrile (J.T. Baker). An aliquot of this solution was analyzed by reverse phase HPLC with UV-Visible detection. Quantitation limits for this method are 0.1-0.2 mg L^{-1} of hydrazone in the extract.

3.2.5. Quality Assurance and Quality Control of the Data

Quality assurance and quality control of the data performed prior to data evaluation. Analysis of the field and laboratory blanks and regular calibration checks were performed for the quality control purposes. Samples were labeled properly and field and laboratory logbooks were also used. Detailed investigation on quality assurance of the data was performed at the Carleton University using graphical tools.

Time series plots were generated for each target analytes including all the sampling days. Time series plots were investigated for significant changes in the analyte concentrations. Fingerprint graphs were also useful for data validation and exploratory analysis purposes especially when inspected together with the time series graphs. They were used to identify calibration data, to investigate hours surrounding suspect and invalid data, to obtain overall view of diurnal changes. Significant deviation of the data from the general pattern of the fingerprint plots indicated a pollution episode or an error in the data analysis or quantification. For those data, chromatograms were reevaluated.

3.3. Receptor Modeling

3.3.1. Positive Matrix Factorization

3.3.1.1 Model Description

Positive Matrix Factorization (PMF), which is a least-squares approach for solving the factor analysis problem, is considered as a new type of factor analysis method (Paatero *et al.*, 2002). Unlike more conventional methods of factor analysis such as principal component analysis (PCA), PMF produces non-negative factors, aiding factor interpretation, and utilizes error estimates of the data matrix (Polissar *et al.*, 2001a). The solution is a weighted least squares fit, where known standard deviations for the input data matrix are used for determining the weights of the residuals (Paatero and Junto, 1994).

PMF assumes that an *nxm* data matrix X, with *m* constituents of interest and *n* number of observations, can be factored into the matrices G (*nxp*) and F (*pxm*) with a residual matrix E (*nxm*), as follows:

$$X = G\,F + E \tag{3.2}$$

where, G is a matrix of time variations in source contributions (i.e., factor scores); F is a matrix of source compositions (i.e., source profiles or factor loadings). The number of rows in F, and the number of columns in G are, referred to as the number of factors, p. Each row of F represents a single source of pollutants, and the columns of G contain the source strength at each observation time. The G is a dimensionless matrix whereas the elements of F matrix are in the same concentration unit as data matrix X. E is defined as a residual matrix that is the difference between the measured data matrix X and the modeled data matrix Y as a function of G and F matrices. The component of E (e.i., e_{ij}) is calculated as follows:

$$e_{ij} = x_{ij} - y_{ij} = x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj} \tag{3.3}$$

$(i = 1,\ldots,\mathrm{n}{:}\ j = 1,\ldots,\mathrm{m}{:}\ k = 1,\ldots,\mathrm{p})$

The objective of PMF is to minimize the sum of the squares of the residuals weighted inversely with error estimates of the data points. Furthermore, PMF constraints all of the elements of G and F to be non-negative that means sources cannot have negative species concentrations (i.e., $f_{kj} \geq 0$) and sample cannot have negative source contribution (i.e., $g_{ik} \geq 0$). Thus, the task of PMF analysis can be described as to minimize Q value, which is defined as:

$$Q(E) = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{e_{ij}}{s_{ij}}\right)^2 \tag{3.4}$$

with $f_{kj} \geq 0$; $g_{ik} \geq 0$ and s_{ij} is the error estimate for x_{ij}. The solution of Eqn. 3.4 is obtained by a unique algorithm in PMF in which both matrices, G and F are adjusted in each iteration step. The iteration process continues until convergence is achieved (Paatero and Tapper, 1994).

In summary, PMF has the following advantages:

- It weights data points by their analytical uncertainties and thus it can handle missing or below detection limit (BDL) data.
- It constraints factor loadings and factor scores to non-negative values and thereby minimizes the ambiguity caused by rotating the factors. This feature also results in obtaining physically meaningful results in environmental applications.
- It expresses factor loadings in mass units, which allows factors to be used directly as source signatures.
- It provides uncertainties for factor loadings and factor scores, which makes the outputs easier to use in quantitative procedures such as chemical mass balance (CMB) model. (Huang *et al.*, 1999; Paterson *et al.*, 1999; Chueinta *et al.*, 2000; Qin *et al.*, 2002; Hopke, 2003)

The PMF approach continues to attract significant interest because it does have inherent advantages as listed previously in this section. PMF is more complex and results are somehow more difficult to interpret, compared to conventional factor analysis, but it provides improved resolution of sources and better quantification of impacts of those sources than PCA and CFA (Huang *et al.*, 1999).

3.3.1.2 Input Parameters

2-way PMF, so-called PMF2, program developed by Paatero (1998) was used in this study to investigate sources of VOCs measured in Ankara and Ottawa. There are two types of input to the program, namely; i) data matrix and ii) error estimates of the data matrix. A pretreatment of data is required prior to utilize in the program. Although PMF can handle incomplete data, very high amount of BDL or missing values might result in erroneous results.

In this study, two approaches were used for pretreatment of the data. Firstly, species having 50% or higher missing or BDL values were removed from the input data set. Secondly, a method suggested by Paatero and Hopke (2003) for discarding or down weighting of high-noise variables was utilized. In the suggested method, a variable is called "weak" variable if it contains signal (S) and noise (N) in comparable amounts. Similarly, variables containing much more noise than the signal are termed "bad" variables. The element with the S/N larger than 2 and between 0.2 and 2 can be considered as a normal and a weak element, respectively. However, the element with the $S/N<0.2$ can be considered as "bad" variable. The bad element should be excluded from analysis, unless it is an important marker for one of the sources. Weak and bad variables can be down weighted by adjusting corresponding error estimates. Even a small amount of over weighting is quite harmful and should be avoided. In contrast, a moderate down weighting by a factor of 2 or 3 is recommended by Paatero and Hopke (2003). Regarding bad variables, the recommendation is that such variables be entirely omitted from the model. If this is not desirable then such variables should be strongly down weighted by a increasing their uncertainties by a factor of 5 or 10.

To successfully apply PMF2, error estimates for the data values need to be properly chosen. There is no simple rule for calculating error estimates. Polissar *et al.* (1998) provided a set of guidelines for estimating the input uncertainties. The concentration data and associated error estimates were constructed as follows. For the measured data values, the concentration values were used directly and the error estimates were set to measurement error plus one third of the limit of detection. For the data below the limit of detection, the concentration was set to half of the limit of detection, and 5/6 times the limit of detection was used as the estimated error. For the missing data, the concentration was replaced with the geometric mean value of the measured concentrations for that chemical species, and 4 times the geometric mean value was set as the estimated error. In addition, the estimated uncertainties of species that have scaled residuals larger than ±2 need to be increased to reduce their weight in the solution (Paatero, 1998; Paatero and Hopke, 2003).

Another method of calculating error estimates is the use of error algorithms built in PMF2. There are four different error models in PMF2 that can compute error estimate, s_{ij}, for x_{ij}, based on data point. Error model (EM) -10 is recommended for lognormally distributed data, EM -11 is suggested for Poisson distribution, EM -12 is the default model and is based on the observed value, EM -13 is based on the fitted value and EM -14 is based on the observed and the fitted value. Paatero (1998) recommends EM -14 to be used in environmental applications. EM -14 has the advantage of determining error as a percentage of the measured or fitted value that means large values are given large errors, preventing outliers, common in environmental applications, from overly influencing factor formation. The values of s_{ij} are computed according to Eqn. 3.5 in EM -14.

$$s_{ij} = C_1 + C_2\sqrt{\max(|x_{ij}|,|y_{ij}|} + C_3 \max(|x_{ij}|,|y_{ij}|) \tag{3.5}$$

where, C_1 is method detection limit that is expressed in same units as the data values, x_{ij}; C_2 and C_3 are dimensionless coefficients. C_2 is usually set to zero to omit the square root term (Paatero, 1998). C_3 can take arbitrary decimal values between 0.01 and 0.1. Arrays T, U and V can be used instead of coefficients C1, C2 and C3 in Eqn. 3.5. For each element the computation is based on the larger of the values x_{ij} and y_{ij}.

In this study, methods suggested by Polissar *et al.* (1998) and Paatero (1998) were applied to compute error estimates and the error estimate that provided better model performance parameters was then used in the final runs.

3.3.1.3 Application of the Model

PMF2 was run under robust mode in order to decrease the impact of extreme values or outliers as suggested by Paatero (1998). It must be noted that an "outlier" is not the same as "bad" variable. It is any datum that significantly deviates from the distribution of the other variables. The robust mode was selected to handle outlier values in the data matrix. The robust factorization based in the Huber influence function (Huber, 1981) is a technique of iterative reweighing of the individual data values. The least-squares formulation, thus, becomes:

$$Q = \sum_{i=1}^{m}\sum_{j=1}^{n}\left(\frac{e_{ij}}{h_{ij}s_{ij}}\right)^2 \tag{3.6}$$

where;

$$h_{ij}^2 = \begin{cases} 1 & if \left|e_{ij} / s_{ij}\right| \leq \alpha \\ \dfrac{\left|e_{ij} / s_{ij}\right|}{\alpha} & otherwise \end{cases} \tag{3.7}$$

where, α is the outlier threshold distance. Data values lying more than α standard deviations above or below the fitted value are treated as outliers and receive decreased weight in PMF2. In this study, the value of 4.0 was chosen as outlier distance as suggested by Paatero (1998).

In general, bilinear factor analysis has rotational ambiguity (Paatero *et al.*, 2002). In the PMF2 there are two options namely FPEAK and FKEY to control the rotation problem. By setting a positive/negative value of FPEAK, the routine is forced to add/subtract G factor vectors to/from each other and subtract/add the corresponding F factors from/to each other and thereby yield more physically realistic solutions (Paatero, 1998; Paatero *et al.*, 2002).

There is no theoretical rule for selecting FPEAK to produce a “good” solution. Usually, PMF is run with different FPEAK values to find the range within which the objective function Q does not show significant change. The optimal solution should lie in this range (Paatero *et al.*, 2002; Zhao and Hopke, 2004). A large positive or negative value of FPEAK leads to worsening of the fit (Paatero, 1998). FPEAK values ranging between -1.0 and 1.0 were tried to find the best fit in this study.

Sometimes, the chemical compositions of resolved source do not seem to be realistic based on comparisons with measured source profiles and prior analyses of similar data. Thus, the value can be "pulled down" toward zero to obtain the reasonable profile through the function FKEY (Paatero, 1998; Lee *et al.*, 1999). FKEY can be used for pulling individual factor elements or group of elements to zero (Paatero, 1998). This has been also used by Qin *et al.* (2002) and Lee *et al.* (1999). The influence of FKEY is exponential so that an increase or decrease of two units can result in a significant change. In general, an FKEY value of nine corresponds to a "medium-strong" pull (Paatero, 1998; Zhao *et al.*, 2004). In this study, FKEY function was applied to pull down one or more variables to zero when required as stated in the following sections.

The determination of the number of sources is one of the major problems in PMF as well as in any factor analysis. Zhao *et al.* (2004) suggests three rules to decide about the proper source number that is; i) the resolved source profiles should be explainable, ii) Q value is expected to show a change in slope with the number of sources from rapid to slow at the point of the decided number, and iii) there should be a satisfactory fit between the predicted concentrations and the measured values. Another test of the effectiveness of PMF analysis is the inspection of scaled residuals (e_{ij}/s_{ij}) for each variable (Paatero, 1998; Xie *et al.*, 1999; Polissar *et al.*, 1999; Zhao and Hopke, 2004). These four suggestions were followed in this study in order to decide on proper source number that provides optimum solution.

The results of the PMF analyses are not hierarchical, that is a higher dimension solution does not necessarily contain all the factors of the lower dimensions. Thus, different numbers of factors are tested, and an optimum solution is determined. If the errors are estimated properly, then the theoretical value of Q should be approximately equal to the number of degree of freedom, or approximately equal to the total number of data points (Li *et al.*, 2004).

The quality of the fit to the data was examined by plotting the distributions of the scaled residuals (e_{ij}/s_{ij}) for each variable. In a well-fit model, the residuals e_{ij}, and the error estimates s_{ij} should be about equal and the ratios e_{ij}/s_{ij} should fluctuate between ±2 (Paatero and Juntto, 1994; Chueinta *et al.*, 2000).

Another test of the effectiveness of PMF analysis is the comparison of the predicted data with the measured data (Anderson *et al.*, 2001; Zhao and Hopke, 2004). In this regard, multiple linear regression (MLR) was applied to regress the total VOC mass against the estimated source contributions (Hopke *et al.*, 1980). The regression coefficients should be all positive, if the resolved sources are reasonable. Then the coefficients were used to scale the source profiles and contributions to make them physically more meaningful (Zhao and Hopke, 2004).

PMF2 was run under the considerations discussed so far in the previous paragraphs and solutions were analyzed for global minimum by setting the pseudo-random seed to different values. At the end, the factors were inspected to determine the most interpretable factor patterns. In doing so, source profiles (F factor) and time variations in source contributions (G factor) that were provided by the model were evaluated.

The results from PMF can also be presented in the dimensionless quantity Explained Variance, EV, which shows how important the source is in explaining variance of each element. Explained variance ranges from 0.0 to 1.0 indicating not explaining anything to explaining all of the variance. The EV value of chemical species *j* in the *k*th factor can be obtained by Eqns. 3.8 and 3.9.

$$EV_{kj} = \frac{\sum_{i=1}^{n} \left| g_{ik} f_{kj} \right| / s_{ij}}{\sum_{i=1}^{n} \left(\sum_{h=1}^{p} \left| g_{ih} f_{hj} \right| + \left| e_{ij} \right| / s_{ij} \right)} \qquad \text{for k= 1,\ldots,p} \qquad (3.8)$$

$$EV_{kj} = \frac{\sum_{i=1}^{n} \left| e_{ij} \right| / s_{ij}}{\sum_{i=1}^{n} \left(\sum_{h=1}^{p} \left| g_{ih} f_{hj} \right| + \left| e_{ij} \right| \right) / s_{ij}} \qquad \text{for k= p+1} \qquad (3.9)$$

It is defined so that X is explained by the *p* sources and the residual, the residual is considered as the *p+1*th source, and *p+1* source explains 100% of the mass in X (Paatero, 1998; Hedberg et al, 2005). Profiles of EV are useful for initial qualitative identification of the sources. However, the original factor loadings must be used for determination of the source profiles (Lee *et al.*, 1999).

3.3.2. Conventional Factor Analysis

Conventional factor analysis is a well-established statistical tool for analyzing structure in multivariate data sets. It starts with a large number of correlated variables and seeks to identify a small number of independent factors that can be used to explain the variance in the data (Hopke, 1991). The variables are assumed to be linearly related to some number of underlying factors. The matrix of pair wise correlations among compound concentrations are decomposed into eigenvectors (factors), which are then sorted in descending order. In this study, factors with eigenvalues greater than one are included in interpretations. Varimax rotation (Henry, 1987) was used to redistribute the variance to give a more interpretable structure to the factors.

CFA is based in the correlation structure of the observations and so cannot reliably handle missing data. Compounds that have missing values at more than 10% of the data were excluded from analysis. Unlike PMF, CFA does not have non-negativity constraint and it does not incorporate uncertainty values that are useful for weighing the data.

3.3.3. Chemical Mass Balance Model

3.3.3.1 Model Algorithm

The CMB receptor model uses the chemical and physical characteristics of gases and particles measured at source and receptor to both identify the presence of and to quantify source contributions of pollutants measured at the receptor (Hopke, 1991). These chemical and physical characteristics must be such that: i) they are present in different proportions in different source emissions; ii) these proportions remain relatively constant for each source type; and iii) changes in these proportions between source and receptor are negligible or can be approximated. The CMB is the fundamental receptor model, and the derivation of the principal component analysis (PCA) and multiple linear regression (MLR) receptor models from fundamental physical principles begin with the CMB (Watson, 1984). The CMB was first proposed by Hidy and Friedlander (1972), Kenip *et al.*, (1972), and Winchester and Nifong (1971).

The CMB model consists of a least-squares solution to a set of linear equations that expresses each receptor concentration of a chemical species as a linear sum of products of source profile species and source contributions (see Eqn. 3.10).

$$C_i = \sum_{j=1}^{j} F_{ij} S_j + \varepsilon_i \qquad \text{I=1,...I} \tag{3.10}$$

where; C_i is the concentration of chemical specie i at receptor; S_j: contribution from source j; F_{ij}: fraction of source contribution S_j component of element i; ε_i: uncertainity term.

CMB software applies the effective variance solution developed and tested by Watson *et al.* (1984). The mathematics of the solution is shown in Eqn. (3.11). The CMB model performs iterative solutions to minimize error term. This method gives greater influence in the solution to chemical species that are measured more precisely in both source and receptor samples, and calculates uncertainties for source contributions from both the source and receptor uncertainties.

$$\sum_{i=1}^{I} \varepsilon_i^2 = \sum_{i=1}^{I} (C_i - \sum_{j=1}^{J} F_{ij} S_j)^2 \tag{3.11}$$

The source profile species (i.e., the fractional amount of each species in the VOC emissions from a given source type) and the receptor concentrations, each with uncertainty estimates, serve as input data to the CMB model. The output consists of the contributions of each source type to both total and individual ambient VOC concentrations. The model calculates values for contributions from each source and the uncertainties of those values. Input data uncertainties are used both to weight the relative importance of the input data to the model solution and to estimate uncertainties of the source contributions.

The CMB procedure requires: i) identification of the contributing source types; ii) selection of chemical species to be included; iii) estimation of the fractions of each chemical species contained in each source type; iv) estimation of the uncertainties to both ambient concentrations and source compositions; and v) solution of the chemical mass balance equations. The CMB model assumptions are as follows:

- Compositions of source emissions are constant over the period of ambient and source sampling.
- Chemical species do not react with each other, i.e., they add linearly.
- All sources with a potential for significant contribution to the receptor have been identified and have had their emissions characterized.
- The source compositions are linearly independent of each other.
- The number of source categories is less than or equal to the number of chemical species.
- Measurement uncertainties are random, uncorrelated, and normally distributed.

These assumptions are fairly restrictive and will never be totally complied with in actual practice. Fortunately, the CMB model can tolerate deviations from these assumptions, though these variations increase the stated uncertainties of the source contribution estimates (Watson *et al.*, 1998).

3.3.3.2 Model Performance Parameters

Source contribution estimates (SCE) are the main output of the CMB model. The sum of these concentrations approximates the total mass concentrations. Negative SCE are not physically meaningful, but can occur when a source profile is collinear with another profile or when the source contribution is close to zero. Collinearity is usually identified in the similarity/uncertainty cluster display. When the SCE is less than its standard error, the source contribution is undetectable. Two or three times the standard error may be taken as the upper limit of the SCE in this case. There is about a 66% probability that the true source contribution is within one standard error and about a 95% probability that the true concentration is within two standard errors of the SCE. The reduced chi-square (χ^2), R^2, and percent mass are goodness of fit measures for the least-squares calculation. The χ^2 is the weighted sum of squares of the differences between calculated and measured fitting species concentrations. The weighting is inversely proportional to the squares of the precision in the source profiles and ambient data for each species. Ideally, there would be no difference between calculated and measured species concentrations and χ^2 would be zero. A value of less than one indicates a very good fit to the data, while values between 1 and 2 are acceptable. χ^2 values greater than 4 indicate that one or more of the fitting species concentrations are not well explained by the source contribution estimates. R^2 is determined by the linear regression of the measured versus model-calculated values for the fitting species. R^2 ranges from 0.0 to 1.0. The closer the value is to 1.0, the better the SCEs explain the measured concentrations. When R^2 is less than 0.8, the SCEs do not explain the observations very well with the given source profiles. Percent mass is the percent ratio of the sum of model-calculated SCEs to the measured mass concentration. This ratio should equal to 100%, though values ranging from 80 to 120% are acceptable (Watson *et al.*, 1998).

CHAPTER 4

TEMPORAL AND SPATIAL VARIATIONS

Investigation of temporal and spatial distributions of atmospheric constituents and relative abundances of certain species is a useful prelude to receptor modeling. When coupled with a conceptual understanding of the emission sources, meteorology and chemical transformation mechanisms, the receptor-oriented analysis provides qualitative and even semi-quantitative evidence of relationships between source emissions and receptor concentrations. This section examines the temporal and spatial variations of ambient VOC concentrations measured during Ankara and Ottawa campaigns.

4.1. Ankara Campaign

4.1.1. Supplementary Data

Temporal and spatial variations in VOC concentrations are affected by meteorological parameters and traffic pattern in the city. A thorough understanding of the variability in these parameters is useful in assessing the variability in VOC concentrations. Thus, the following sections describe meteorological parameters and traffic pattern observed in Ankara during summer and winter campaigns in detail.

4.1.1.1 Meteorological Parameters

Meteorological parameters such as temperature, wind speed and direction influence concentration of air pollutants in a region by affecting dispersion and atmospheric chemistry of air pollutants. A thorough understanding of meteorological parameters influencing the study area is useful for data interpretation. Hourly and long term meteorological data recorded at Ankara Meteorology Station, which is located at 39.57 N, 32.53 E (see Figure 4.26) and operated by State Meteorological Works (SMW), were used in this study. Summary of meteorological parameters recorded at Ankara Meteorology Station from 1994 to 2003 are given in Table 4.1. The lowest and the highest average temperatures that were recorded during the 10-year period are -1.0 °C in winter and 29.0 °C in summer. The lowest wind speed was recorded during fall (i.e., 1.7 m sec^{-1}) and the highest during summer (i.e., 2.4 m sec^{-1}). Annual average total precipitation is lower than 500 mm indicating Ankara is located in a dry region.

Table 4.1. Average long-term meteorological parameters recorded at Ankara Meteorological Station.

	Temperature[a] (°C)	**Precipitation[b] (mm)**	**Wind Speed (m sec^{-1})**
Winter	2.43 (-0.97-6.40)	118	1.9
Spring	11.37 (5.77-16.87)	147	2.0
Summer	22.83 (15.87-28.97)	70	2.4
Fall	13.13 (19.40-23.20)	85	1.7
Annual	12.4 (7.10-17.90)	420	2.0

[a] *values in parentheses are ranges.*
[b] *average total precipitation amounts.*

Hourly measurements of meteorological parameters recorded between March 2003 and March 2004 were also obtained from the SMW. The average temperature during the summer campaign is 22.9 °C, which is similar to that observed during long-term measurements (1994-2003). During the winter campaign the average temperature is 1.34 °C at SMW station. This value is slightly higher than the lowest temperature observed during long-term measurements, which is -0.97 °C.

Hourly average wind speed values are 2.51 and 2.81 m sec^{-1} during winter and summer campaigns, respectively. Both of these values are slightly higher than the corresponding average values obtained from long-term measurements at SWM Ankara station. In conclusion, meteorological conditions recorded during the summer campaign are representative of a long-term meteorological data of the region.

Long-term, hourly meteorological data were used to construct wind roses for the study area, which are shown in Figure 4.1. Seasonal wind roses were constructed using the hourly meteorological data recorded in 2003 and 2004. The annual wind rose represents long-term (1994-2003) annual average wind pattern of the region. Northeast (NE) is the prevailing wind direction in all seasons. East-northeast (ENE) is the next most frequent wind direction. During winter and fall seasons, westerly winds are also frequent. Annual wind rose representing long-term data revealed a similar pattern with high frequency of NE and ENE winds and also contribution from west-south west (WSW) direction. Calm conditions (wind speed < 1.0 m s^{-1}) are most frequent during fall (11.8%) and least frequent during spring (3.5%).

Mixing height is another meteorological parameter that influences the ambient concentrations of pollutants. Mixing height is the depth through which pollutants released to the atmosphere are well mixed by dispersive processes. Dispersion of pollutants in the lower atmosphere is greatly aided by the convective and turbulent mixing that takes place. Mixing height determines the vertical extent of dispersion for releases occurring below that height. Releases occurring above mixing height are assumed to have no ground-level impact (with the exception of fumigation episodes). Therefore, deep mixing height, which indicates a larger volume for dispersion of pollutants, results in dilution of emissions and consequently lower concentrations of measured parameters (USEPA, 2004).

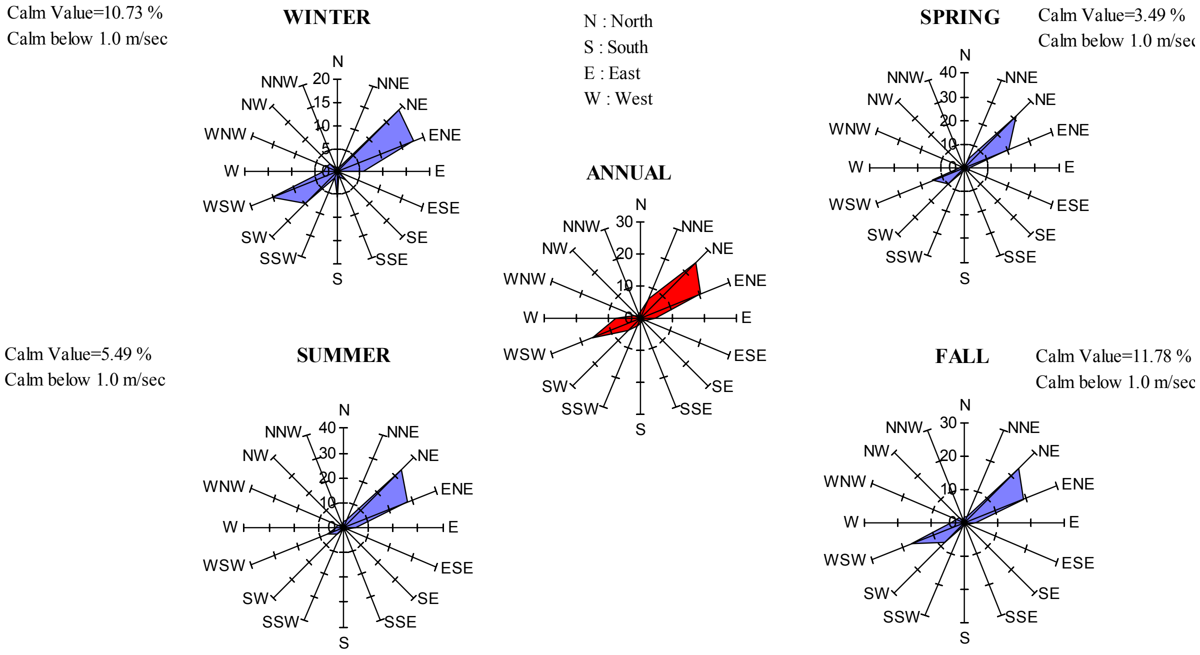


Figure 4.1. Wind roses of the region.

Mixing height values were calculated from radiosonde data measured at Ankara Meteorology Station, which were obtained from SMW. Radiosonde measurements are conducted twice daily on 00 UTC and 12 UTC. The hourly values of mixing height were calculated by using a meteorological pre-processor PCRAMMET developed by the US EPA. Hourly values of stability classes were also calculated with the same pre-processor. PCRAMMET recognizes seven stability classes. The first six categories correspond to Pasquill's (1974) classifications ranging from a very unstable “A” to very stable “F” categories. The seventh category (namely G) indicates a strong, ground-based nocturnal temperature inversion with non-definable wind flow conditions.

Diurnal variation in stability classes and mixing height calculated for winter and summer seasons are given in Figure 4.2 and Figure 4.3, respectively. Mixing height values increase during daytime and decrease during nighttime, with a maximum between 12:00 and 16:00, both in summer and in winter. However, diurnal variation in the mixing height values is more significant in the summer season. This is due to larger differences between the day and nighttime temperatures during summer. The highest mixing heights are observed during summer season.

Unstable atmospheric conditions are observed during noontime both in winter and summer that was influenced by the sunrise. During nighttime, however, stable conditions thus poor mixing are observed in both seasons. Unstable conditions are more frequent during the summer season. Duration of the unstable conditions is also longer during summer season. Higher mixing height values and unstable conditions observed during summer season result in better mixing of atmosphere thus better dispersion and lower concentrations of pollutants than that is observed during winter season, if the emission rate in winter and summer are identical.

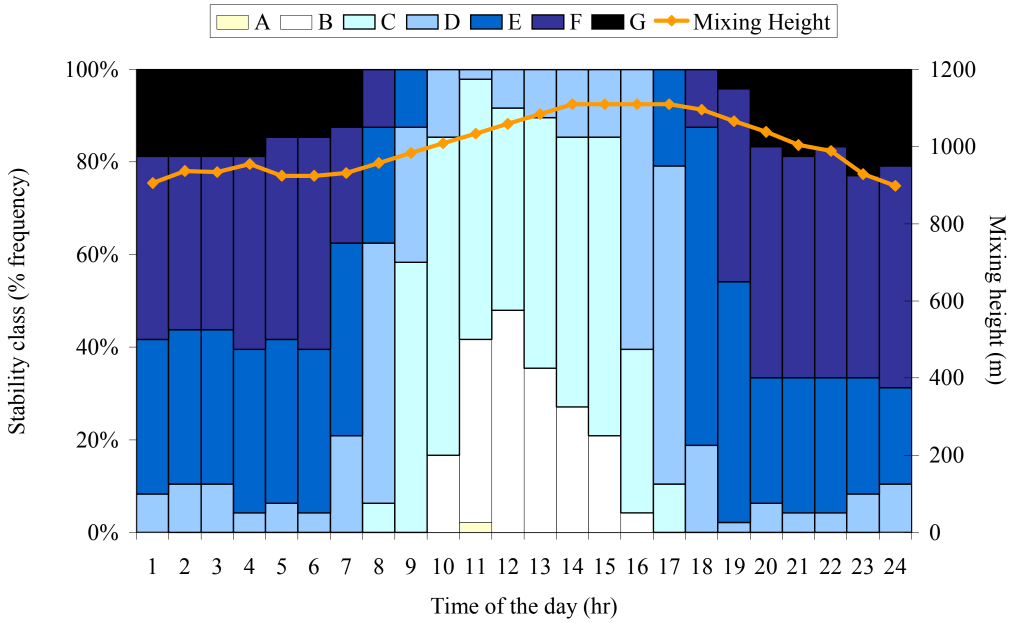


Figure 4.2. Diurnal variation in the stability classes and mixing height in winter.

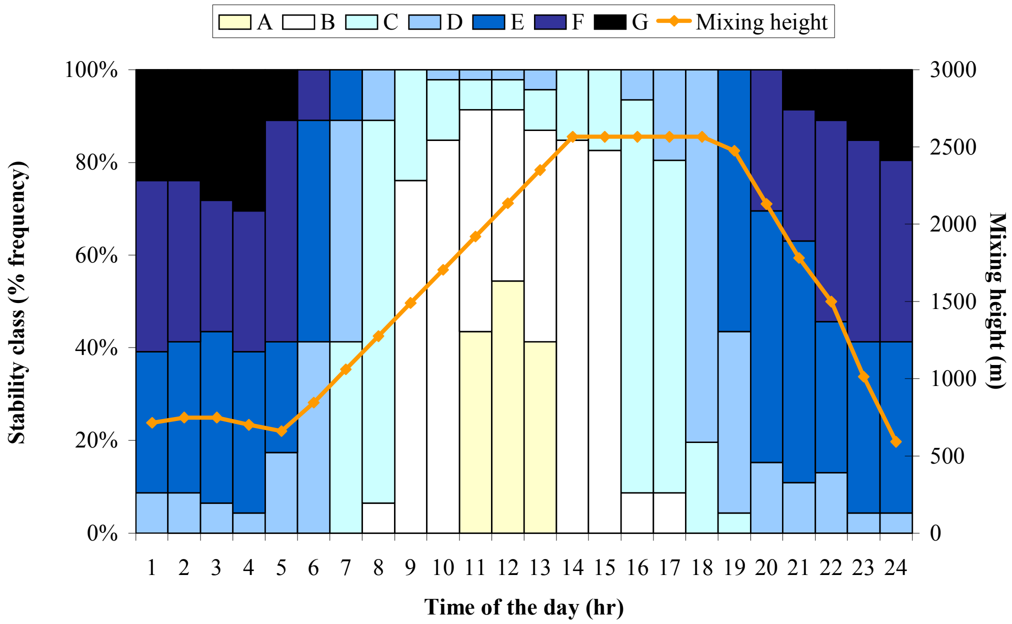


Figure 4.3. Diurnal variation in the stability classes and mixing height in summer.

4.1.1.2 Traffic Count

Motor vehicles are known as major sources of VOCs in many urban atmospheres. Emission pattern of motor vehicle sources can be identified by investigating traffic pattern. Continuous traffic count records are not available in Ankara. There are several records based on short-term campaigns since 1970. The only comprehensive report (EGO, 1992) prepared in 1992 includes traffic count data recorded for one week in summer at several junctions in Ankara. The data had uncertainties and it was outdated. Therefore, the traffic counts recorded at the Akay tunnel during the summer and winter campaigns were used to assess the traffic pattern in the city.

Traffic flow within the Akay tunnel was controlled through a video camera system located at different sections of the tunnel. The traffic records on 2-6 September 2003 and 25-29 February 2004 were used to determine the traffic pattern during this study. Total number of vehicles traveled through the tunnel is shown in Table 4.2. The average number of vehicles recorded in tunnel is 922 vehicle/hour and 561 vehicle/hour during winter and summer, respectively. Lower number of vehicles recorded in the summer is due to lower number of people staying in the city during summer months. People usually take their vacation in summer time in Ankara.

The traffic data recorded in summer do not show significant differences between weekdays and weekends. However, during winter traffic counts recorded in weekdays are approximately 1.5 times higher than that are recorded in weekend days. The average number of vehicles driving through the tunnel is 1025 vehicle/hour during weekdays in winter. The observed variability in weekday to weekend variations in summer and winter is due to variation in number of people working at government offices during summer and winter. The average number of vehicles recorded during winter shows that Saturday/Sunday ratio is 1.6. The reason for such a difference could be that most of the private companies work also on Saturday.

Table 4.2. Total number of vehicles recorded in the tunnel.

Day	Session	Summer	Winter
Tuesday	9:00-10:00	468	N/A
	13:00-14:00	460	N/A
	17:00-18:00	582	N/A
Wednesday	9:00-10:00	543	858
	13:00-14:00	555	377
	17:00-18:00	545	1124
Thursday	9:00-10:00	610	1195
	13:00-14:00	613	847
	17:00-18:00	604	1275
Friday	9:00-10:00	582	1095
	13:00-14:00	417	931
	17:00-18:00	688	1520
Saturday	9:00-10:00	649	915
	13:00-14:00	545	1045
	17:00-18:00	560	863
Sunday	9:00-10:00	N/A	199
	13:00-14:00	N/A	926
	17:00-18:00	N/A	665
Average		561	922
Weekday Average		556	1025
Weekend Average		585	769

The traffic counts shows a well-defined diurnal pattern both in summer and in winter. Average number of vehicles traveling through the tunnel during morning (9:00-10:00), noon (13:00-14:00) and afternoon (17:00-18:00) sessions are given in Figure 4.4. Diurnal traffic patterns observed in summer and winter are similar. The number of vehicles passing through the tunnel reaches to a maximum during afternoon and decrease to a minimum at noon hours. High number of vehicles passing through the tunnel during morning and afternoon are owing to traffic rush hours in the city. The variation in the traffic count data is higher in winter than in summer. This is partly due to high weekday to weekend variation during winter season.

Contributions of vehicle categories to total number of vehicle recorded in the Akay tunnel during winter are depicted in Figure 4.5. Vehicle categories are divided into six groups, including; passenger car (PC), taxi, minibus, bus, truck and motorcycle. Although the number of vehicles recorded in the tunnel are different during morning, noon and afternoon hours, the percent contribution of the vehicle categories were similar at all times.

The PC has the highest contribution to total number of vehicles recorded during morning, noon and afternoon sessions. Approximately 80% of the vehicles recorded in the tunnel are PC. The second highest contributor is taxi with approximately 15% contribution to total number of vehicles. Thus, the PC and taxi totally account for approximately 95% of the vehicles recorded in the tunnel. Although the contribution of buses is quite low (0.5%), their emissions might cause more impact than the PCs since most of the buses operating in the city do not undergo proper inspection and maintenance. The fuel types consumed by the PCs are gasoline, diesel and liquefied petroleum gas (LPG) with 94%, 6% and 1%, shares, respectively (SSI, 1998). Most of the taxis in Ankara are fueled with LPG. Taxis also use diesel and gasoline fuels in smaller amount. Minibus, bus and trucks mostly use diesel fuel.

4.1.2. Descriptive Statistics

Frequency distribution of VOC data shows that data follows a log-normal distribution. Thus, the median, minimum and maximum concentrations of the 20 most abundant species are presented in Table 4.3 for the residential, background and roadside stations. On average, the most abundant 20 species accounted for 77%, 71%, and 75% of the total VOC at the residential, background and roadside sites, respectively. The table includes, medians and ranges of morning, noon, afternoon, evening and night sessions conducted during both summer and winter campaigns.

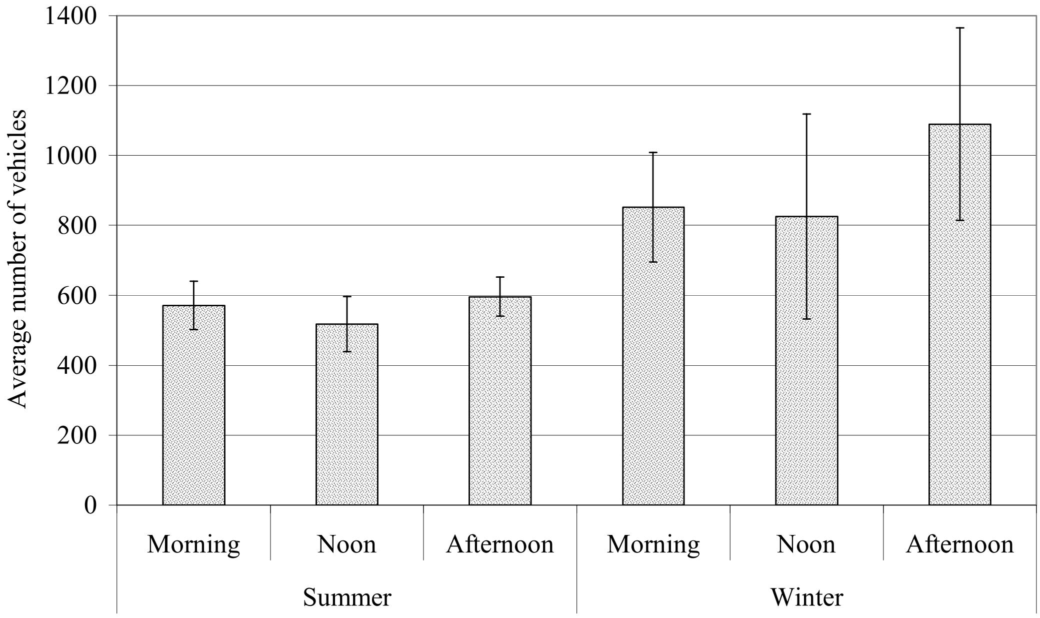


Figure 4.4. Diurnal variations in traffic counts.

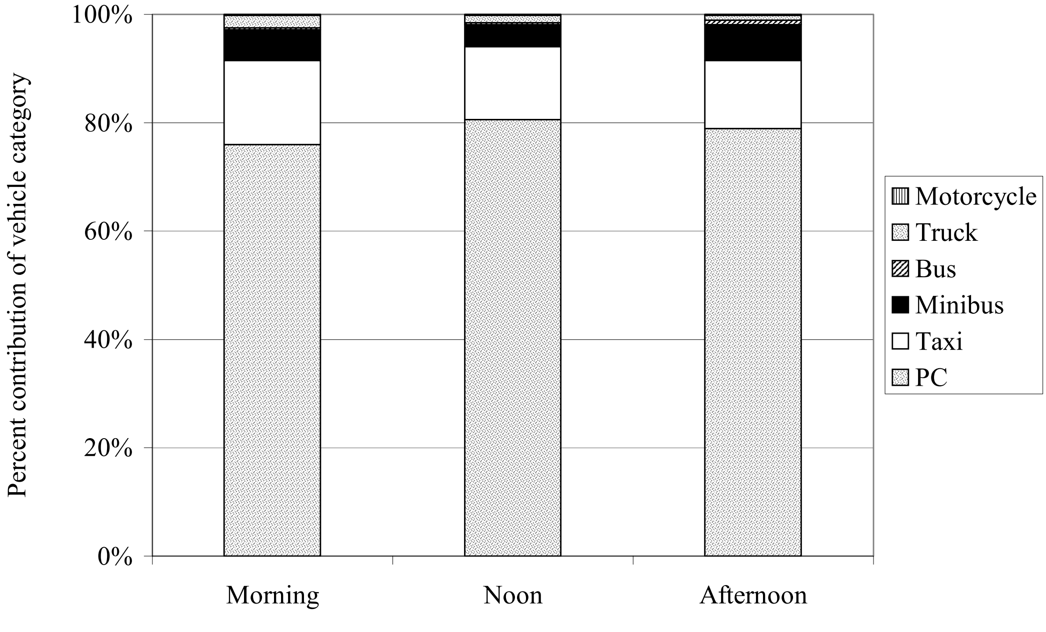


Figure 4.5. Distribution of vehicle categories.

Table 4.3. Statistical summary of the abundant VOC concentrations (μg m^{-3}).

Session	**Residential (N=169)**		**Background (N=118)**		**Roadside (N=50)**	
Compound name	**Median**	**Range**	**Median**	**Range**	**Median**	**Range**
Toluene	8.65	(1.19-52.17)	3.28	(0.21-20.43)	14.45	(2.20-108.82)
m,p-xylene	4.21	(0.55-49.49)	1.49	(0.03-9.33)	12.44	(1.71-69.26)
Benzene	3.06	(0.68-23.50)	1.66	(0.39-11.10)	6.28	(1.29-58.85)
2-methylpentane	2.09	(0.44-27.34)	0.74	(BDL-2.96)	4.10	(0.57-25.68)
3-methylpentane	1.74	(BDL-20.11)	0.64	(BDL-2.93)	3.15	(0.50-18.47)
1,2,4-trimethylbenzene	1.72	(0.02-21.71)	0.45	(BDL-4.22)	5.49	(0.03-35.64)
o-xylene	1.49	(0.22-17.22)	0.53	(0.01-3.58)	4.66	(0.62-27.44)
Pentane	1.43	(0.24-21.19)	0.49	(BDL-2.30)	3.62	(0.65-20.65)
Hexane	1.39	(0.19-11.04)	0.59	(BDL-5.11)	2.37	(0.41-14.92)
Ethylbenzene	1.16	(0.12-14.25)	0.43	(0.05-2.19)	3.27	(0.39-16.12)
3-ethyltoluene	1.02	(BDL-12.96)	0.28	(BDL-2.56)	3.35	(0.01-21.23)
2,2-dimethylbutane	0.86	(0.13-13.64)	0.24	(BDL-1.25)	1.87	(0.27-9.87)
Naphthalene	0.83	(0.03-9.93)	0.23	(BDL-4.25)	1.47	(0.03-25.42)
Carbontetrachloride	0.73	(0.29-1.48)	0.81	(0.42-3.83)	1.28	(0.42-1.82)
c-3-methyl-2-pentene	0.72	(BDL-7.09)	0.29	(BDL-2.49)	1.37	(BDL-15.85)
iso-butylbenzene	0.73	(BDL-5.63)	0.71	(BDL-4.71)	1.58	(BDL-25.77)
Methylcyclopentane	0.65	(0.16-4.95)	0.20	(BDL-1.37)	1.15	(0.24-8.06)
2-methylhexane	0.63	(BDL-7.59)	0.34	(BDL-1.41)	1.56	(BDL-8.07)
3-methylhexane	0.61	(BDL-7.93)	0.26	(BDL-1.10)	1.60	(0.25-8.68)
2,3-dimethylbutane	0.61	(0.14-8.43)	0.19	(BDL-0.91)	1.21	(0.16-7.31)
Total VOC	**44.60**	**(10.89-403.63)**	**19.52**	**(2.59-80.98)**	**101.65**	**(31.35-634.82)**

The median total VOC concentrations, which are the sum of the target analytes for residential, background and roadside stations, are 45, 20 and 102 μg m^{-3}, respectively. The total VOC concentration measured at the roadside station is approximately factor of two higher than that measured at the residential station. Similarly, total VOC concentration measured at the background station is approximately a factor of two smaller than that measured at the residential station. The data indicate decreasing total VOC concentrations with increasing distance from immediate source of traffic.

Toluene is the most abundant specie at all sites with a median concentration ranging from 3 μg m^{-3} at the background site to 15 μg m^{-3} at the roadside station. There are not limit values on atmospheric levels of VOCs in Turkish Air Quality Control Regulation (AQCR). Benzene levels in ambient air are, however, regulated by the EC Directive 2000/69/EC. Annual average benzene concentration is limited to 5 μg m^{-3} by the EC Directive. As can be seen from Table 4.3, the EC limit value is in compliance at the residential and background stations. However, the limit value was exceeded at the roadside station.

Statistical summaries of all target species at each site are provided in Appendix B. Approximately 60 species out of the 91 target species were detected in more than 50% of the samples collected at all sites. The concentrations of the individual species range from near method detection limit (MDL) to over 100 μg m^{-3}. The relatively large ranges of concentrations for many abundant species indicate that seasonal, daily and diurnal variations are significant.

Percentage contributions of 15 most abundant species to total VOC concentrations are given in Figure 4.6. Although the concentrations of the most abundant species vary from one site to another, the fractional abundances are similar, with few exceptions, at all sites. The principal exception is carbon tetrachloride and iso-butylbenzene that had a high abundance at the background station indicating a potential local source.

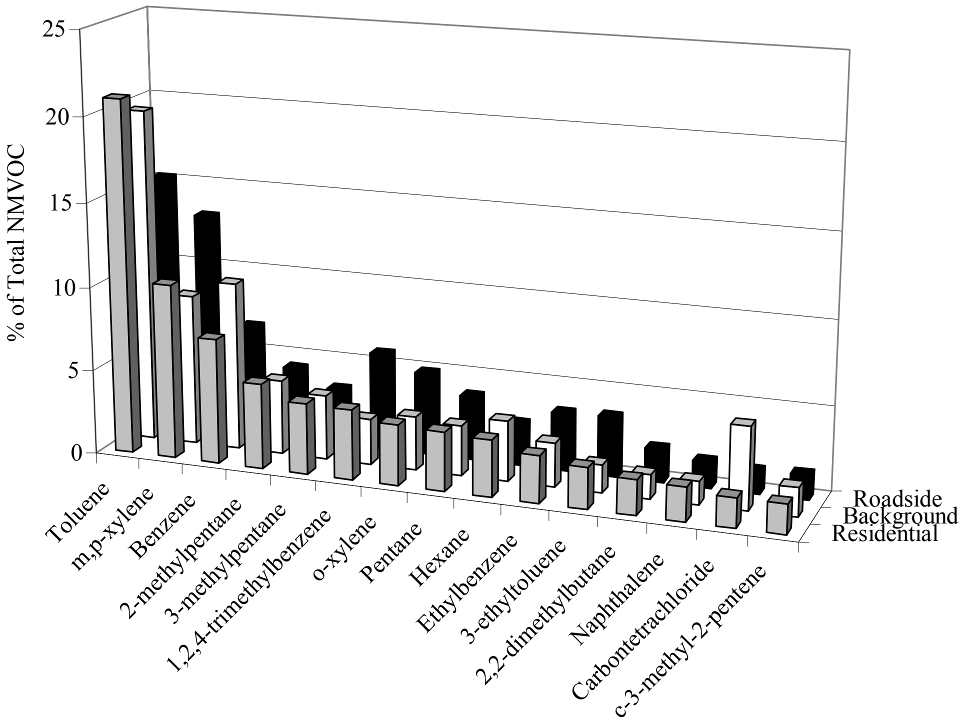


Figure 4.6. Percent abundances of the 15 most abundant species.

The larger abundances of m&p-xylene, 1,2,4-trimethylbenzene, o-xylene, ethylbenzene, 3-ethyltoluene and 1,3,5-trimethylbenzene at the roadside station indicate a greater influence from motor vehicle exhaust emissions at this site as these compounds are known as marker compounds for motor vehicle emissions. The fractional abundances of tetrachloroethene (PERC) are 1%, 1% and 3% at the residential, background and roadside stations, respectively. The higher abundance of PERC at the roadside station can be due to dry cleaning activities at a nearby source (such as hotels and hospitals) as PERC is known to be a good marker specie for VOC emissions from dry cleaning activities (Scheff *et al.*, 1989).

Toluene is the most abundant specie observed at all sites. The fractional abundances of toluene are 21%, 20% and 15% at the residential, background and roadside stations, respectively. Higher fractional abundances of toluene at the residential and the background stations compared to the roadside station indicate toluene sources other than traffic at these sites. The m&p-xylene and benzene are the next most abundant species at all sites. The fractional abundances of m&p-xylene are 10%, 9% and 13% at the residential, background and roadside stations, respectively. Similarly, the fractional abundances of benzene are 8%, 10% and 7% at the residential, background and roadside stations, respectively.

Concentrations of different organic compound groups in the atmosphere can be informative as the compounds in each group are expected to have similar chemical properties (Derwent, 1999). Organic compounds measured in this study are collected under four groups, namely, paraffin, olefin, aromatic and halogenated compounds and median concentration for each group are calculated. Results are given in Table 4.4. At all sites aromatic compounds has the highest concentration, which is followed by paraffins, halogenated compounds and olefins. Concentrations of the olefins are the lowest at all sites due to their high reactivity in the atmosphere. Concentrations of halogenated compounds are similar or higher than that of olefins. Concentrations measured at the roadside station are factors of two-to-five higher than those measured at the residential and background stations.

Percent contributions of each compound group to total VOC concentrations are also presented in Table 4.4. As in individual compounds, concentrations of each group vary from one sampling site to another, but their percent contributions are similar at all sites. Aromatics have the highest contribution to total VOC with an average contribution of 63% at all sites. Paraffins have the second highest contribution, which is approximately 30% at all sites. Thus, the aromatic and paraffins totally accounts for approximately 90% of the total VOC measured at all sites. High contributions of parafinic and aromatic compounds to total VOC concentrations are due to both high contribution of these group of compounds in dominant emission sources and longer atmospheric life times of aromatics and paraffins compared to olefins.

Table 4.4. Concentration (μg m^{-3}) and percent contribution of specie groups.

Group	Residential	Background	Roadside
Paraffin	12.24 (30%)	4.77 (29%)	25.60 (27%)
Olefin	1.62 (4%)	0.58 (3%)	3.15 (3%)
Aromatic	25.69 (62%)	9.96 (60%)	60.79 (64%)
Halogenated	1.82 (4%)	1.31 (8%)	5.46 (6%)

4.1.3. Temporal Variations

4.1.3.1 Seasonal Variation

Roadside Station

Ratio of winter to summer concentrations (W/S) and analysis of variance (ANOVA) of individual compounds measured at each station was investigated in order to understand statistically significant seasonal variations in concentrations of measured VOCs. There is a statistically significant ($p<0.10$) seasonal variation in the total VOC concentration measured at the roadside station. Total VOC concentration measured during winter is higher than that measured during summer campaign (W/S=1.53±2.26). A total 14 compounds including naphthalene, benzene, cyclic hydrocarbons and paraffins have W/S values ranging between from 2.0 to 4.0. A total of 10 compounds including isoprene, tetrachoroethene, aromatics and olefins had W/S values of less than 1.0, indicating that these compounds have higher concentrations during winter season and the rest have W/S ratios ranging from 1.0 to 2.0. Thus, the majority of compounds have higher concentrations in winter, which are statistically significant at 90% confidence level. However, ethylbenzene has a W/S ratio of 0.99 and $p>0.10$ indicating there is not a statistically significant variation in concentrations measured during summer and winter campaigns. Isoprene concentrations are higher in summer campaign than in winter campaign. This behavior is not surprising, because isoprene is a known biogenic compound (W/S=0.70 and $p<0.10$). Tetrachloroethene has a W/S value of less than 1.0. However, $p>0.10$, indicating that low W/S value is probably caused by an outlier in summer data set and there is not a significant seasonal variation in the data. Winter to summer ratios for selected compounds measured at each site are presented in Table 4.5. These compounds are frequently measured at the sites and they are from different compound groups such as olefin, paraffin, aromatic and halogenated.

Higher concentrations measured for most of the compounds at the roadside station during winter campaign are due to increase in the number of motor vehicles during winter as discussed in Section 4.1.1. Meteorological conditions also contribute to the observed general seasonal trend. Stable atmospheric conditions, low mixing height, low wind speed (see Section 4.1.1) and low photochemical reactivity observed during winter season result in poor ventilation in this season. Thus, pollutants remain in the vicinity of emission point with little dilution resulting in higher concentrations of measured parameters during winter.

Residential Station

The total VOC concentrations measured at the residential station do not show a statistically significant seasonal variation (W/S=1.03± 1.39 and $p>0.10$). There are only two compounds, namely benzene and naphthalene, which have W/S ratios greater than unity (approximately 2.0). Higher winter concentrations of these compounds are statistically significant at 90% confidence level ($p<0.10$). A total of 18 compounds have W/S ratios of less than 1.0 and the rest have comparable W/S ratios in summer and winter (W/S ranging between 1.0 and 1.5). Toluene has a W/S ratio of less than 1.0 (i.e., 0.89), but the difference between summer and winter concentrations is not statistically significant ($p>0.10$). Ethlybenzene has also W/S ratio less than 1.0 (i.e., 0.80) and although the difference is small, student-t test suggests a statistically significant seasonal variation ($p<0.10$). Isoprene shows a distinct seasonal variation with higher concentrations measured in summer than in winter (W/S=0.12 and $p<0.10$).

Winter to summer ratios for selected compounds measured at the residential station are shown in Table 4.5. There is no significant seasonal variation in concentrations of most compounds measured at the residential station. Seasonal variations in pollutant concentrations are influenced by both seasonal variations in VOC emissions and meteorological conditions. As discussed in the previous chapter, residential station is located away from major roads and direct emission sources. Concentrations measured at this station are from local sources and pollutants transported from more polluted sections of the city. During winter season, meteorological conditions that resulted in poor mixing lowered probability of pollutant transport relative to that was observed in summer season. Strength of local sources seem to be remained unchanged resulting in insignificant seasonal variation observed at the residential station.

Background Station

Winter to summer ratios for selected compounds measured at the background station are given in Table 4.5. There is a seasonal variation within 90% confidence interval in the concentrations of total VOC measured at the background station. Total VOC concentrations are higher in summer than in winter campaign (W/S=0.71). Seven compounds including naphthalene and cyclic hydrocarbons have W/S ratios ranging between 1.5 and 3.0. Concentrations of these compounds are significantly higher in winter campaign. There are 20 compounds having W/S ratio ranging between 1.0 and 1.5, and the rest of compounds have W/S values less than 1.0. Benzene concentrations are significantly higher in winter campaign (W/S=1.42 and $p<0.10$). Isoprene concentrations measured during summer campaign, on the other hand, are significantly higher than those measured during winter campaign as expected (W/S=0.13 and $p<0.10$).

The majority of compounds measured at the background station have higher concentrations measured during summer campaign than in winter campaign. The background station is located at a sub-urban area. Thus, the major source for the polluted air measured at the background station is pollution transported from polluted sections of the city. During summer season, unstable conditions, higher mixing height values, higher wind speeds are frequently observed as described in Section 4.1.1. These meteorological conditions, which enhanced mixing of lower atmosphere, also favored dispersion and transport of pollutants. Consequently, polluted air masses transported from high emission areas of the city easily reached to the background site and resulted in observed higher concentrations during summer season.

It is also observed that compounds can have different seasonal variations at the same site or the same compound can show different variation at different sampling sites. This is due to differences in emission sources and atmospheric reactivities of individual VOCs. There are few compounds showing the same seasonal pattern at all sampling sites. Benzene and naphthalene concentrations, for example, are higher in winter campaign than in summer campaign at all sites. Naphthalene is known to emit from combustion sources. Increase in residential heating results in increase in naphthalene concentrations measured during winter campaign. The major source of benzene in urban atmosphere is motor vehicles. High benzene concentrations measured during winter campaign may be associated with increase in number of motor vehicles and/or increased cold start emissions during winter season. Isoprene concentrations, on the other hand, are significantly higher in summer campaign at all sites. Isoprene is well recognized as a marker of biogenic emissions and increase in isoprene emissions is frequently reported in literature (Sharma *et al.*, 2000; Watson *et al.*, 2001; Na and Kim, 2001; Borbon *et al.*, 2001) and attributed to photosynthetic processes in leaf of plants that enhanced by increase in light and temperature (Fall, 1999). Isoprene is also emitted from motor vehicles (Borbon *et al.*, 2001; Borbon *et al.*, 2002). This is the reason for relatively high W/S ratio observed for isoprene at the roadside station (i.e., 0.70).

Table 4.5. Winter to summer ratios of selected pollutant concentrations.

Compound	Residential	Background	Roadside
Pentane	0.77	1.09	1.57
	(0.004)[a]	(0.623)	(0.087)
Isoprene	0.12	0.13	0.70
	(0.000)	(0.000)	(0.090)
Hexane	0.92	0.55	1.85
	(0.048)	(0.001)	(0.025)
Benzene	1.93	1.42	2.20
	(0.002)	(0.083)	(0.021)
Carbontetrachloride	1.03	0.41	1.89
	(0.406)	(0.000)	(0.000)
Cyclohexane	0.64	0.90	1.86
	(0.001)	(0.545)	(0.074)
2-methylhexane	0.91	0.57	1.47
	(0.025)	(0.000)	(0.108)
Heptane	1.01	0.62	1.55
	(0.120)	(0.001)	(0.066)
Methylcyclohexane	1.43	0.89	2.18
	(0.609)	(0.439)	(0.024)
Toluene	0.89	0.46	1.45
	(0.162)	(0.000)	(0.200)
Octane	1.22	0.74	1.91
	(0.971)	(0.057)	(0.035)
Tetrachloroethene	0.93	1.00	0.68
	(0.332)	(0.987)	(0.506)
Ethylbenzene	0.80	0.64	0.99
	(0.005)	(0.005)	(0.970)
m,p-xylene	1.00	0.87	1.33
	(0.106)	(0.480)	(0.232)
o-xylene	1.14	0.96	1.53
	(0.381)	(0.857)	(0.091)
Nonane	0.64	0.63	2.06
	(0.000)	(0.002)	(0.093)
1,2,4-trimethylbenzene	1.25	1.07	1.90
	(0.559)	(0.795)	(0.020)
Naphthalene	1.90	1.97	3.58
	(0.100)	(0.078)	(0.016)
1,1,1-trichloroethane	1.11	0.99	1.84
	(0.420)	(0.922)	(0.000)

[a] *Values in parentheses are p values.*

The compound 1,1,1-trichloroethane (TCA) is an ozone depleting substance and it has a long atmospheric lifetime. Furthermore, TCA is a compound for which non-traffic sources, such as solvent use, are dominant. Concentration of TCA measured at the residential and background stations show no significant seasonal variation ($p>0.10$). However, there is a seasonal variation in TCA concentrations measured at the roadside station (W/S=1.84 and $p<0.10$). Potential solvent use at hotels and hospitals in the close proximity of the roadside station could be the source of TCA measured at this station. Higher concentration of TCA measured during the winter campaign might be associated with a temporary change in emission pattern of these sources that occurred during sampling campaign.

Criteria Pollutants

In addition to VOC data generated in this study, inorganic pollutants measured by Ministry of Health were also used to understand temporal variations in VOC concentrations. A total of 11 ambient air-monitoring stations are operated by Ministry of Health, Refik Saydam Hıfzıssıhha Center (RSHM) in Ankara. Routine measurements of SO_2 and PM are performed by automated instruments at 5 stations and by semi-automated measurement technique at rest of the stations. Criteria pollutants, nitrogen oxides (NO, NO_2 and NO_x), ozone (O_3), carbon monoxide (CO), sulfur dioxide (SO_2) and particulate matter (PM) are monitored at only one station, namely the Sıhhıye station that is located at a roadside. The data recorded at this station during the period of summer and winter campaigns were obtained from RSHM and investigated for temporal variations.

Statistical summary of the concentrations of criteria pollutants measured at Sıhhıye station are given in Table 4.6. Carbon monoxide is a primary air pollutant that is directly emitted from a source. It is important because, traffic is the dominating source of observed CO concentrations at a road-site station and in this respect temporal variations in measured CO concentrations can be related to temporal variability in VOC concentrations measured in this study. On the other hand, O_3 is a secondary air pollutant, which is formed in the atmosphere through chemical reactions. Nitrogen monoxide is primary, but NO_2 is a secondary pollutant that forms by photochemical reactions of NO in the atmosphere. Concentration of CO is higher during the winter than in the summer. This is due to the increase in the number of vehicles and an increase in fossil fuel combustion for residential heating during winter in Ankara and also due to decrease in mixing height as discussed in Section 4.1.1. Decreased ambient temperature that affects engine performance can also be a reason for higher CO concentrations observed during winter. Concentrations of O_3 are higher in summer than in winter as expected. Since the O_3 in the troposphere is formed through photochemical reactions between VOCs and NO_x and its concentration in the atmosphere is determined by the variation in solar flux. Concentration of NO_x (i.e., $NO+NO_2$) is 185 µg m^{-3} and 127 µg m^{-3} during summer and winter, respectively. Concentration of NO_2 is higher in summer than in winter. This is due to increased rate of photochemical formation during summer.

Table 4.6. Average concentration of air pollutants recorded at RSHM station.

Pollutants	**Summer 2003**	**Winter 2004**	**Annual**
NO	64 (1-955)[a]	65 (1-691)	54 (1-1,048)
NO_2	121 (30-456)	62 (6-188)	75 (2-717)
O_3	62 (4-205)	24 (13-91)	35 (3-248)
CO	599 (3-9,491)	1,632 (26-14,310)	1,218 (3-14,360)

[a] *values in parenthesis denote ranges; concentrations are in µg m^{-3}.*

The concentration of O_3 was compared with the national and international standards. The Turkish AQCR defines an hourly average value of 240 µg m^{-3} for O_3. The daily average limit value and hourly guideline value given by the World Health Organization (WHO) is 65 µg m^{-3} and 200 µg $m^{-3}$for O_3, respectively. Hourly average limit values given for O_3 by APCR and WHO are complied at most of time. There is not a daily average limit value for O_3 given in Turkish APCR. Daily average limit values given by the WHO were exceeded at 53% of the time during summer season for O_3. Therefore, measures should be taken in order to decrease elevated levels of O_3 observed during summer season in Ankara through controlling its precursors, which are VOCs and NO_x. The data was analyzed to investigate whether VOCs partition on PM and removed from the atmosphere. Correlation coefficients for VOC and PM data are 0.36 and 0.17 for summer and winter, respectively. Correlation coefficients for benzene and PM, and naphthalene and PM are 0.65 and 0.50 for summer and 0.46 and 0.46 for winter, respectively. There is a positive correlation between VOC, benzene and naphthalene and PM except for VOC and PM in winter. This indicates that VOCs do not partition on PM in significant amount rather both of them show similar variation indicating influence of meteorological conditions on both VOCs and PM

4.1.3.2 Daily Variation

Daily variation in total VOC concentrations was assessed for each sampling site. Daily variation in the total VOC concentrations measured at the residential station during summer and winter campaigns are given in Figure 4.7 and Figure 4.8, respectively. There are significant daily variations in the data measured during summer campaign. A pollution episode was observed on 30th and 31st of August 2004. During this episode, concentrations of total VOC are four times higher than average values for the evening and night sessions. Benzene concentrations reached to 24 $\mu g\ m^{-3}$ during this period. During the winter campaign total VOC concentrations were significantly higher on the 15th, 20th and 28th of January.

Daily variations in total VOC concentrations measured at the background station during summer and winter seasons are shown in Figure 4.9 and Figure 4.10, respectively. There are limited data generated during summer campaign, yet they do not show significant daily variations. Daily fluctuations in total VOC concentrations are more pronounced during winter season than summer season. Daily variations in total VOC concentrations measured at the roadside station during summer and winter campaign are presented in Figure 4.11 and Figure 4.12, respectively. Daily fluctuations are more significant during summer than in winter campaign. Concentrations are high on 24th of February that coincided with meteorological conditions of inversion and low wind speed that lower dispersion over the city. Due to close proximity to emissions, roadside concentrations are generally determined by the variations in source strength. However, the occurrence of February 24 episode in the day with low ventilation indicates that meteorological conditions are also important in the formation of extreme concentrations even at the curbside.

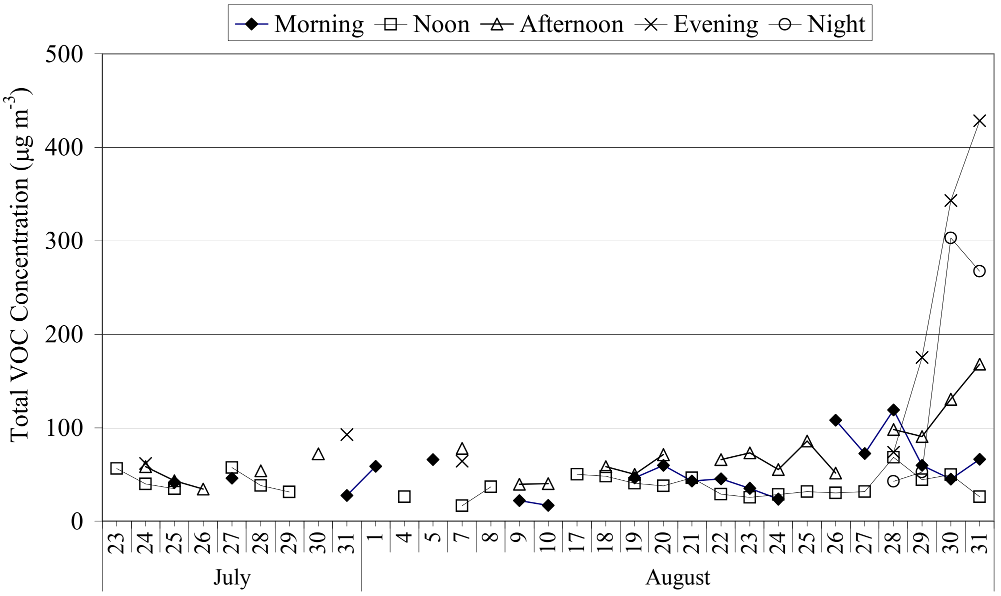


Figure 4.7. Daily variations of total VOC concentrations measured at Residential Station- Summer 2003.

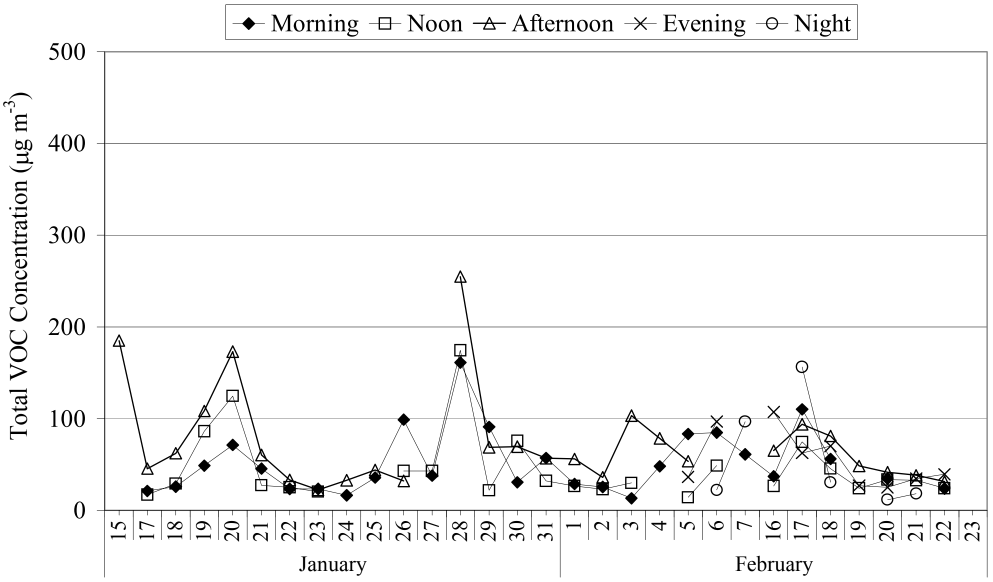


Figure 4.8. Daily variations of total VOC concentrations measured at Residential Station- Winter 2004.

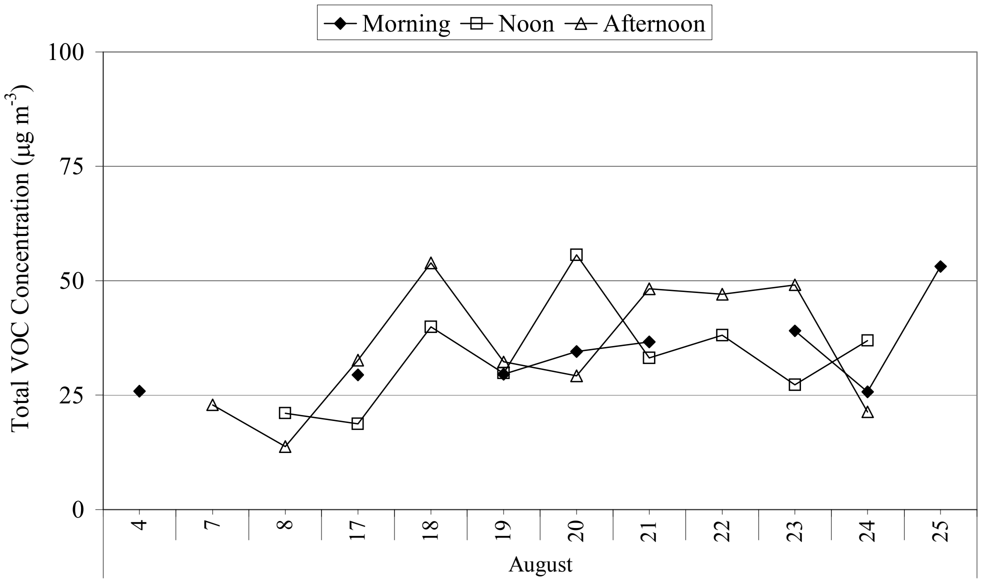


Figure 4.9. Daily variations of total VOC concentrations measured at Background Station- Summer 2003.

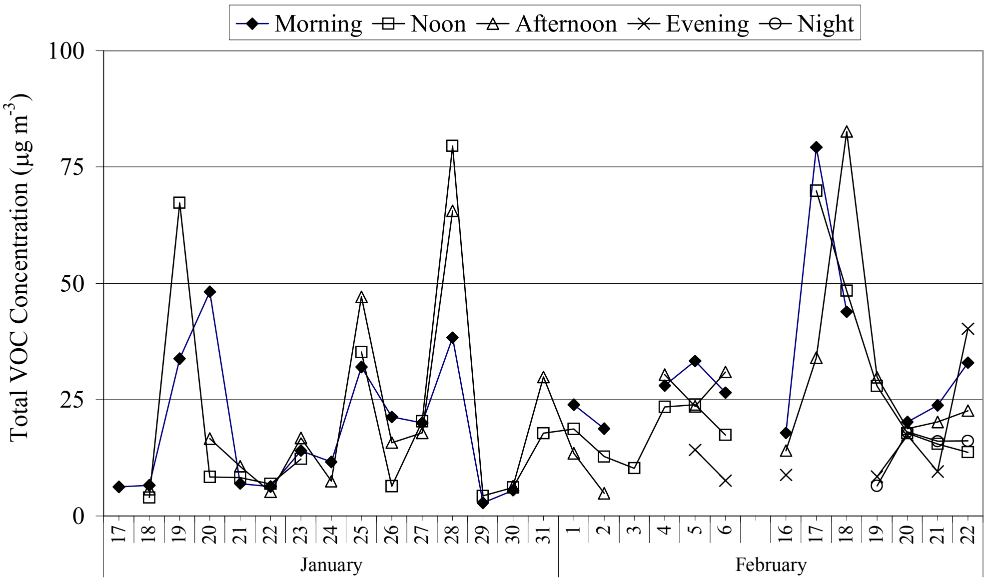


Figure 4.10. Daily variations of total VOC concentrations measured at Background Station- Winter 2004.

Daily variations in inorganic pollutant concentrations measured by RSHM were also evaluated. Figure 4.13 and Figure 4.14 show the daily variations in summer and winter seasons, respectively. Concentrations of all pollutants are significantly high during the 30th and 31st of August. These dates correspond to the pollution episode dates as explained in the previous paragraphs. Similarity in episodes recorded for different parameters, at different locations in the city is a clear indication of the importance of meteorological conditions to generate episodic high concentrations of pollutants over whole city. Daily fluctuations are more pronounced during winter campaign than summer campaign. High concentrations observed on the 15th, 20th and 28th January coincided with the high concentrations measured at the residential station, indicating that the high VOC concentrations measured in these days is not a local, but a city-wide phenomena triggered by the meteorological conditions. High concentrations observed on the 24th of February also coincided with high concentrations observed at the roadside station. The unusual high concentrations of pollutants measured in one of the locations only may be a measurement artifact as well. For example a car may be parked by the station in that particular day

4.1.3.3 Weekend vs. Weekday Variation

Effect of day of week on observed VOC concentration was investigated using ANOVA analysis. Weekday to weekend concentration ratio and *p* values for few selected compounds measured during summer and winter campaigns at each site are shown in Table 4.7. The total VOC and most of the individual VOCs measured at roadside during summer campaign do not show significant weekday to weekend variation at 90% confidence interval. This is due to insignificant change in the number of vehicles recorded during weekday and weekend in summer as discussed in Section 4.1.1. During winter campaign, however, total VOC and most of the VOCs measured at the roadside station are significantly higher during weekday than during weekend at 90% confidence interval. This is due to significant weekday to weekend variation in the number of vehicles recorded during winter campaign as discussed in Section 4.1.1.

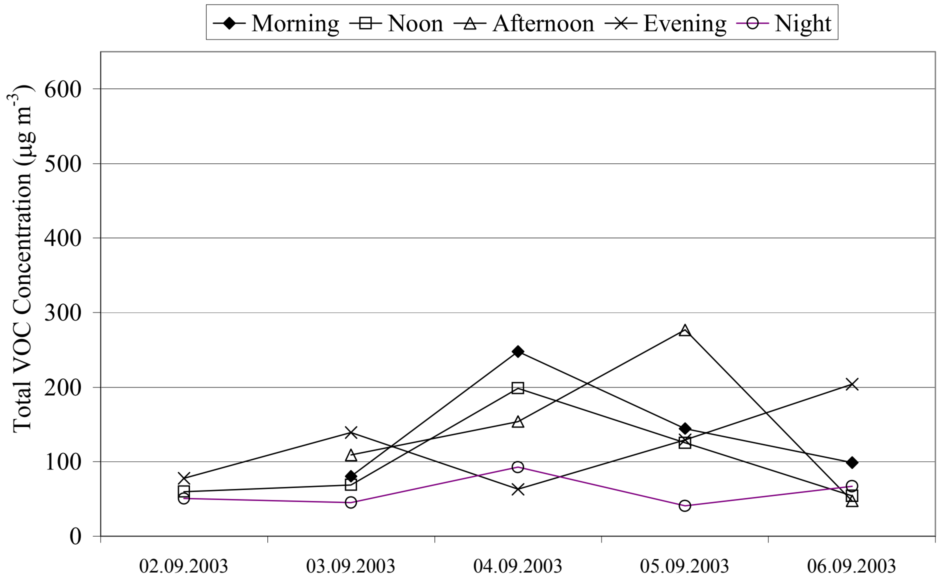


Figure 4.11. Daily variations of total VOC concentrations measured at Roadside Station- Summer 2003.

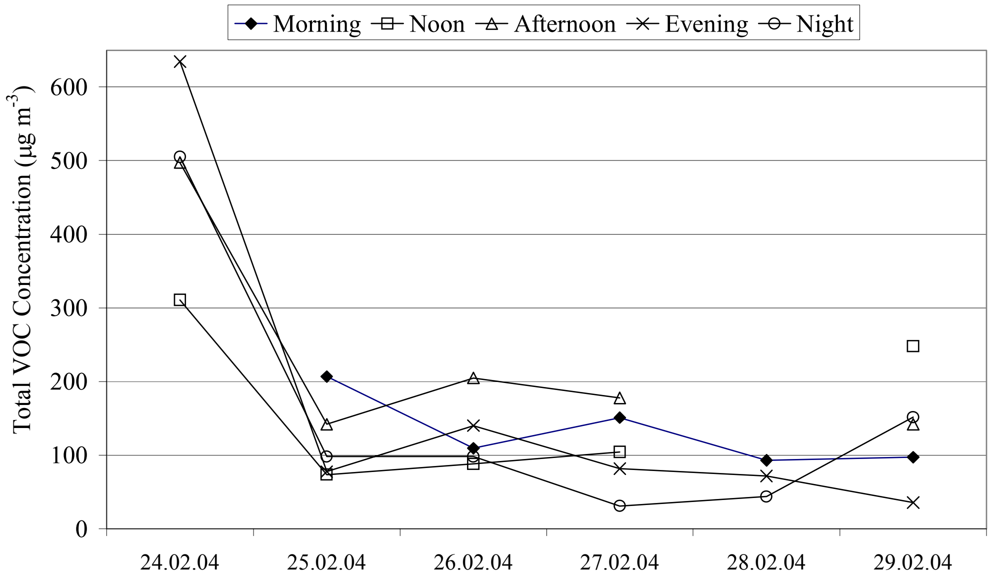


Figure 4.12. Daily variations of total VOC concentrations measured at Roadside Station- Winter 2004.

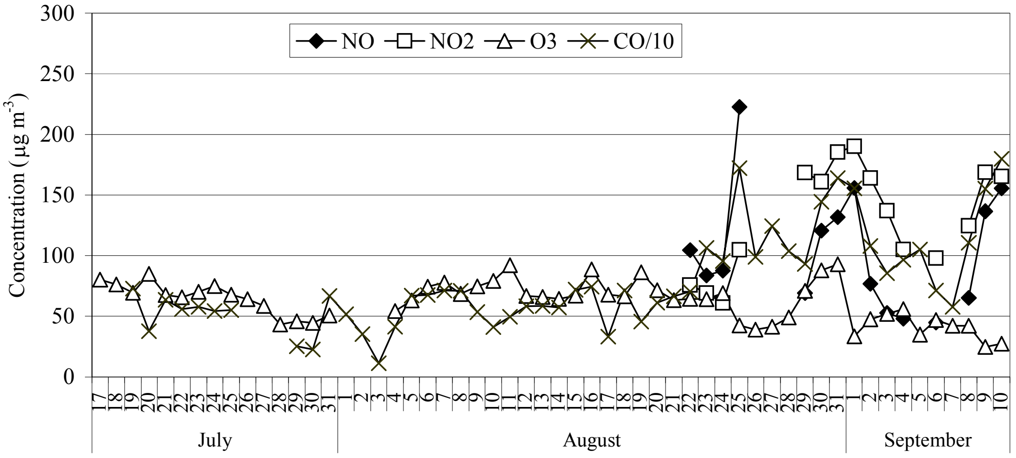


Figure 4.13. Daily variations in concentrations of inorganic pollutants measured at RSHM station- Summer 2003.

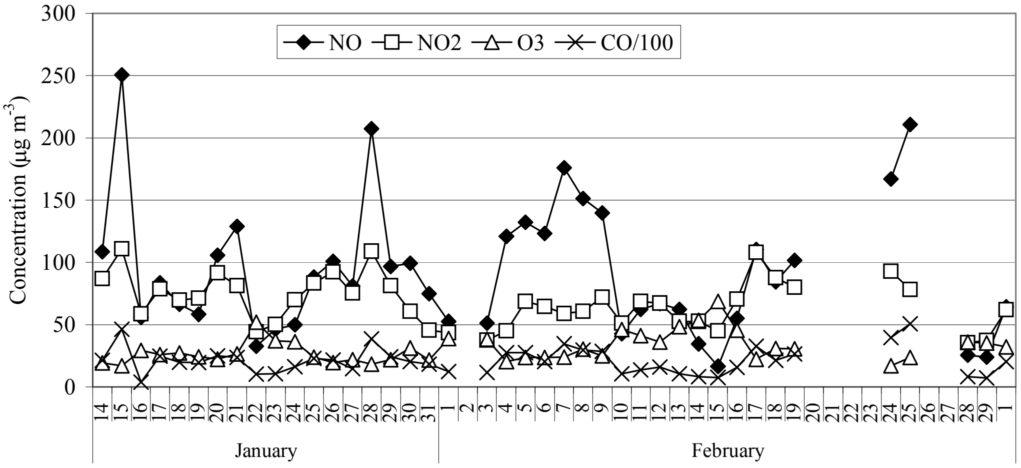


Figure 4.14. Daily variations in concentrations of inorganic pollutants measured at RSHM station- Winter 2004.

A similar weekday to weekend variation is also observed at the residential station during winter campaign, indicating that motor vehicle is a major source affecting VOC concentrations even at locations, which are not very close to major highways. Higher weekday concentrations for most VOCs and total VOC was also observed during summer campaign at the residential station. This variation cannot be explained by the vehicle number that showed no weekday to weekend variation in summer. Therefore, it was clear that there were additional sources.

Total VOC and most of VOCs measured at the background station during summer campaign do not show significant weekday to weekend variation except for toluene. Toluene has higher concentrations in weekday than in weekend. During winter campaign, total VOC and some of the compounds, such as, ethylbenzene, m,p-xylene, naphthalene show a statistically significant weekday to weekend variation, with higher concentrations in weekdays, whereas other compounds such as benzene, pentane, hexane and halogenated compounds do not show significant weekday to weekend variation. The background station is influenced by both motor vehicle related sources and additional sources during both summer and winter campaigns. However, since the site is not under the influence of traffic activity, as much as residential and road side stations, influence of non-traffic sources and reactivity of individual compounds and frequency of transport from the city on measured concentrations of VOC and their temporal variability is expected to be higher. The lack of weekday-weekend difference in measured concentrations during summer campaign is similar to that observed at the residential site. However, lack of difference for some compounds and existence in concentrations of others is probably due to lack of direct relation between traffic emissions which shows a well defined weekday-weekend pattern, and VOC concentrations measured at the METU campus. As pointed out before, reactivity of compounds and frequency of transport from high emission areas in the city, which do not show any weekday-weekend preference are responsible for observed different patterns for different VOC compounds.

Table 4.7. Weekday to weekend ratio of median concentraions for selected compounds.

Compound	**Roadside**		**Residential**		**Background**	
	Summer	**Winter**	**Summer**	**Winter**	**Summer**	**Winter**
Pentane	1.07	2.21	1.59	1.46	0.94	1.32
	(0.850)[a]	(0.071)	(0.015)	(0.044)	(0.835)	(0.140)
Isoprene	1.83	2.86	1.17	1.81	0.91	2.21
	(0.160)	(0.094)	(0.352)	(0.009)	(0.733)	(0.011)
Hexane	1.10	2.08	1.13	1.42	0.93	0.98
	(0.737)	(0.092)	(0.473)	(0.059)	(0.653)	(0.948)
1,1,1-trichloroethane	0.83	1.25	1.18	1.16	1.08	1.07
	(0.097)	(0.003)	(0.073)	(0.034)	(0.672)	(0.317)
Benzene	0.99	2.72	1.42	1.53	0.97	1.12
	(0.969)	(0.064)	(0.038)	(0.026)	(0.859)	(0.588)
Carbontetrachloride	0.87	1.15	1.15	1.14	1.24	1.06
	(0.203)	(0.009)	(0.104)	(0.015)	(0.263)	(0.341)
Toluene	1.45	2.62	1.59	1.80	1.45	1.39
	(0.342)	(0.066)	(0.082)	(0.009)	(0.062)	(0.228)
Tetrachloroethene	14.44	0.20	2.09	1.89	0.96	1.23
	(0.161)	(0.069)	(0.128)	(0.012)	(0.848)	(0.288)
Ethylbenzene	1.20	2.44	1.47	2.01	1.25	1.53
	(0.568)	(0.042)	(0.057)	(0.007)	(0.219)	(0.078)
m,p-xylene	1.33	2.46	1.51	1.83	1.27	1.58
	(0.397)	(0.038)	(0.051)	(0.008)	(0.275)	(0.097)
o-xylene	1.26	2.55	1.53	1.80	1.14	1.62
	(0.474)	(0.033)	(0.044)	(0.009)	(0.563)	(0.089)
1,2,4-trimethylbenzene	1.22	2.71	1.77	1.80	1.15	1.96
	(0.545)	(0.025)	(0.012)	(0.012)	(0.648)	(0.042)
Naphthalene	1.41	3.78	1.56	2.01	0.93	1.85
	(0.183)	(0.083)	(0.035)	(0.007)	(0.803)	(0.101)

[a] *values in paranthesis are p values.*

Weekday-weekend variation in the data recorded at the RSHM station is given in Table 4.8. During summer season, all pollutants, except O_3, do not show statistically significant weekday to weekend variation. This is due to insignificant weekday to weekend variation in the number of vehicles as described in the previous paragraphs and similar to what is observed in all VOC stations. Concentrations of O_3, on the other hand, are significantly higher in weekend than in weekday during the summer season. Similar pattern was also observed at many urban sites in Canada (CCME, 1997). Higher O_3 concentration in weekend is attributed to decreased levels of NO in morning hours during weekend, which results in reduced destruction of O_3 and thus higher noon O_3 peak concentration.

During winter season, NO and NO_2 showed statistically significant weekday to weekend variation whereas O_3 and CO do not. The concentration of CO is higher in weekdays, but the variation was not statistically significant. This is probably due to additional CO source during winter, which is residential heating. Ozone concentrations are higher on weekend as in summer season, but the variation is not significant. This is due to slower rate of photochemical reactions in winter owing to decrease in sunlight.

Table 4.8. Weekday to weekend ratio of median concentrations for pollutants measured at RSHM.

Compound	**RSHM**	
	Summer	**Winter**
NO	1.16	1.45
	(0.603)[a]	(0.084)
NO_2	1.22	1.29
	(0.303)	(0.014)
O_3	0.83	0.83
	(0.021)	(0.125)
CO	1.12	1.33
	(0.475)	(0.115)

[a] *values in paranthesis are p values.*

4.1.3.4 Diurnal Variation

Air pollutants might show diurnal variation due to emission characteristics of sources or change in atmospheric conditions. Diurnal variation in the concentration of total VOC at all stations during summer and winter campaigns are presented in Figure 4.15 and Figure 4.16, respectively. During the summer campaign, peak values were observed at 8:00-12:00 (morning), 16:00-20:00 (afternoon) and 20:00-00:00 (evening) sessions at the roadside station.

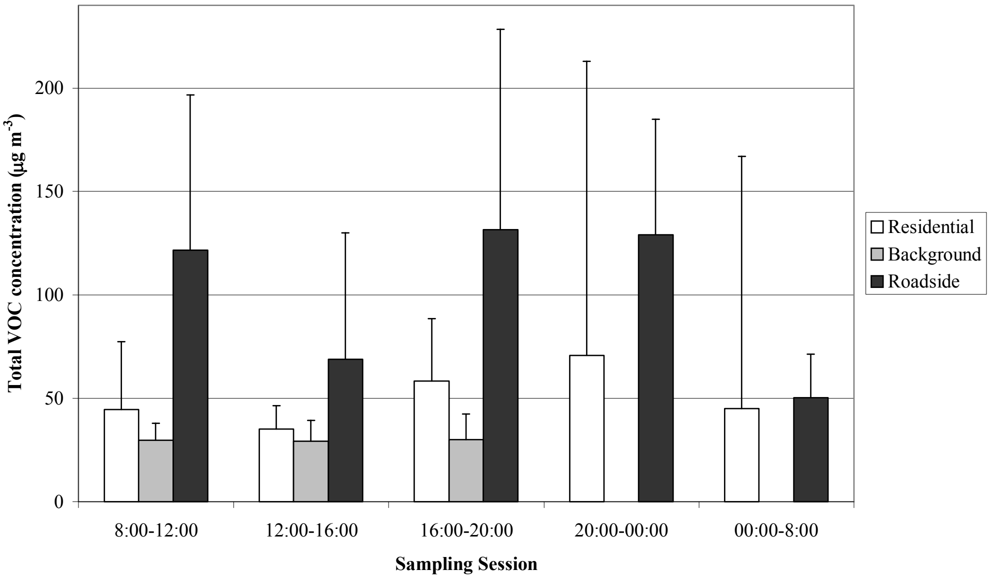


Figure 4.15. Diurnal variation in total VOC concentrations-Summer 2003.

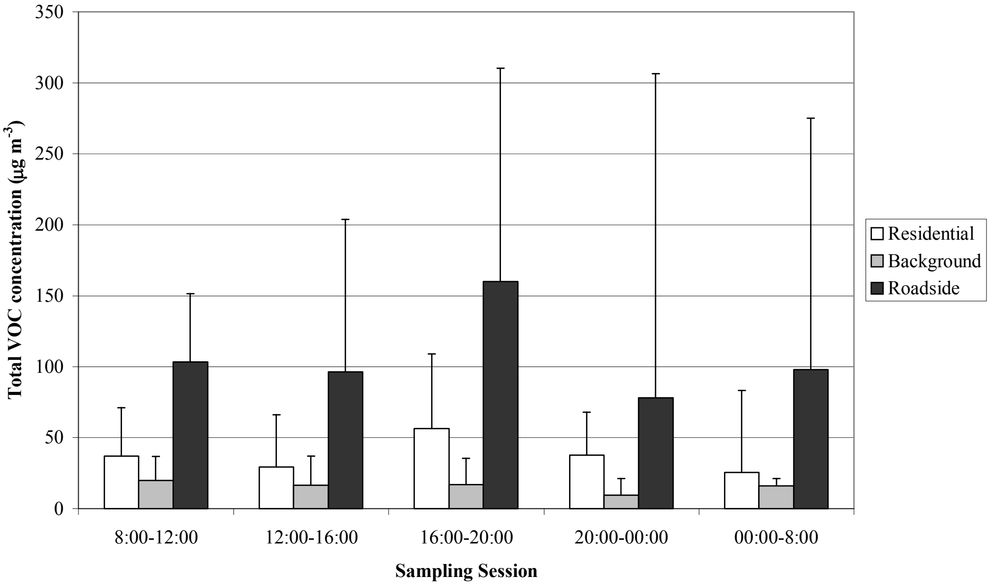


Figure 4.16. Diurnal variation in total VOC concentrations-Winter 2004.

Total VOC concentrations are the lowest at 12:00-16:00 (noon) and 00:00-8:00 (night) sessions. Traffic pattern observed in the city shows morning and afternoon rush hours as discussed in Section 4.1.1. Morning and afternoon peak values in the total VOC concentrations measured at the roadside station show that these peak concentrations are caused by increased emission during traffic rush hours. Traffic counts are not available for evening session, but in Ankara traffic rush continues through the evening during the summer time. Traffic density decreases after 21:00 on weekdays during summer. Therefore, the evening peak is probably also associated with motor vehicle emissions. Low concentrations observed at night session are due to decreased emissions. The decrease in concentrations during noon session is due to both decrease in traffic density and increase in atmospheric instability. Atmospheric conditions such as higher mixing height and unstable conditions are common during noontime and enhance the dispersion of pollutants as discussed in Section 4.1.1. Photochemical reactions are also faster during noontime resulting in decomposition of VOCs in the atmosphere. Strong relation between diurnal emission and concentration patterns indicate that motor vehicles are the major sources at the roadside station during summer campaign.

Diurnal pattern of total VOC concentrations observed at the residential station during summer campaign is very similar to that observed at the roadside station. However, the evening peak was more pronounced at the residential station. Total VOC concentrations measured at the background station showed almost no diurnal variation during summer campaign. This indicates that emission sources other than motor vehicle emissions from nearby sources were effective at the background station. However, it should be noted that smaller number of samples collected at the background site during summer campaign increases the uncertainty in conclusions reached for this station.

Diurnal variations in total VOC concentrations measured at all stations during winter campaign show similar pattern to that observed for summer campaign except for lower evening concentrations measured at winter campaign. Morning and afternoon peak values observed at the residential and roadside stations are due to increase in motor vehicle emissions at these traffic rush hours. Total VOC concentrations measured at the background station show a slight diurnal variation.

Investigation of diurnal variations in VOC concentrations revealed interesting features and dependences of VOC's in Ankara atmosphere. Since diurnal pattern in concentrations of any parameter is clear signal of traffic contribution on its measured concentrations, this signal clearly observed at the roadside and residential stations demonstrated that concentrations of total VOC in these stations are controlled by traffic emissions during most of the measurement period. Small differences in diurnal variations in VOC concentration between summer and winter in these stations, such as longer afternoon peak during summer, is due to changes in living and driving patterns of residents in winter and summer seasons (outdoor activities extending more into night during summer) and shows how even small changes in traffic pattern reflects to VOC concentrations

However, it should be noted that episodes, which are discussed in Section 4.1.3.2, in residential and roadside stations are attributed to meteorology, rather than changes in emissions. These two contradictory conclusions for temporal variations in VOC concentrations in different time scales suggests that, at the roadside and residential stations, concentrations of VOCs are primarily determined by emissions and meteorology can be a determining factor only when extremely low ventilation periods prevail over the city.

Lack of strong diurnal pattern in VOC concentrations at the background station demonstrate that in parts of the city where traffic activity is not as high as those observed at residential and roadside sites, the VOC concentrations are not directly controlled by traffic emissions. In such areas, emissions from non-traffic sources, transport from more polluted parts of the city, reactivity of individual VOCs and meteorology can be more influential in determining observed concentrations of VOCs. The concentrations and temporal variability in concentrations of total VOC measured at the METU site can be typical for VOC levels and variability in other suburban areas as well.

Diurnal pattern in BTEX compounds measured at the residential station during summer and winter campaigns, are given in Figure 4.17 and Figure 4.18, respectively. Diurnal pattern similar to that observed for total VOC is also observed for most of the paraffins, olefins and aromatics measured during summer and winter campaigns. However, there are few exceptions. Isoprene and halogenated compounds show different diurnal pattern from that of total VOC concentrations. Diurnal pattern of isoprene measured at the residential station during both summer and winter campaigns are shown in Figure 4.19. Summer concentrations of isoprene do not show an evening peak. Isoprene concentrations increase through daytime and decrease sharply after sunset. Biogenic emission is the major source of isoprene measured during summer campaign and the emissions are directly related with sunlight (Fall, 1999). During winter campaign, isoprene shows a small diurnal variation, which is very similar to the patterns observed in concentrations of traffic related VOCs. Consequently, emissions from motor vehicles are the main source of isoprene in winter season, probably due to very low isoprene emissions from trees with lower solar flux in winter.

Diurnal pattern in TCA and CCl_4 during summer and winter campaigns is shown in Figure 4.20. These two compounds are also known as ozone depleting substances (ODS). The concentrations of TCA does not show a significant diurnal variation both in summer and winter campaigns, whereas concentration of CCl_4 shows a small diurnal variation in both seasons. It is important to note that concentrations of these two compounds are very low and the variations are not statistically significant.

Inorganic pollutants measured by RSHM at Sıhhıye station were also evaluated for temporal variations. Diurnal variations of the pollutants measured at the RSHM station during summer and winter campaigns are shown in Figure 4.21 and Figure 4.22, respectively.

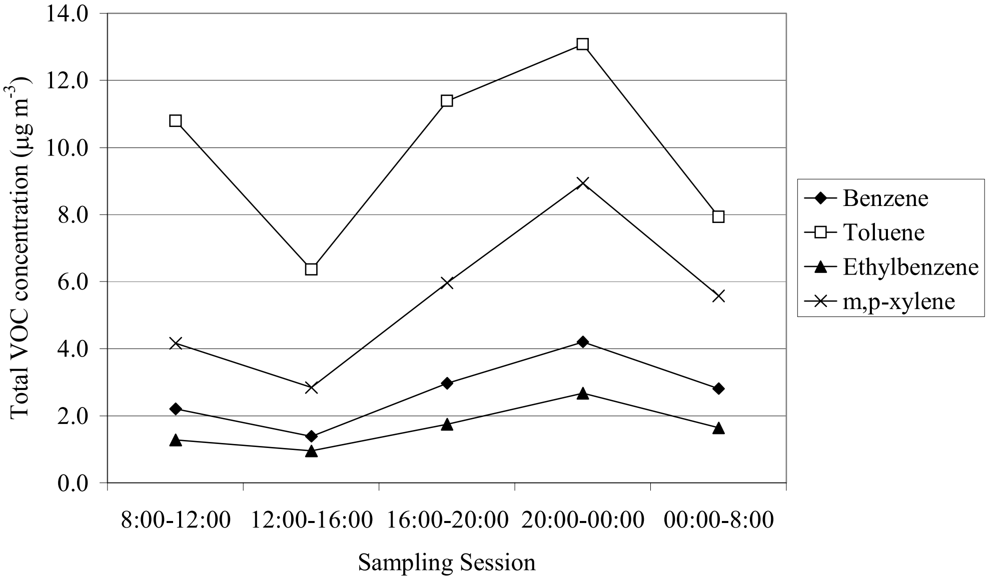


Figure 4.17. Diurnal variation at residential station-summer 2003.

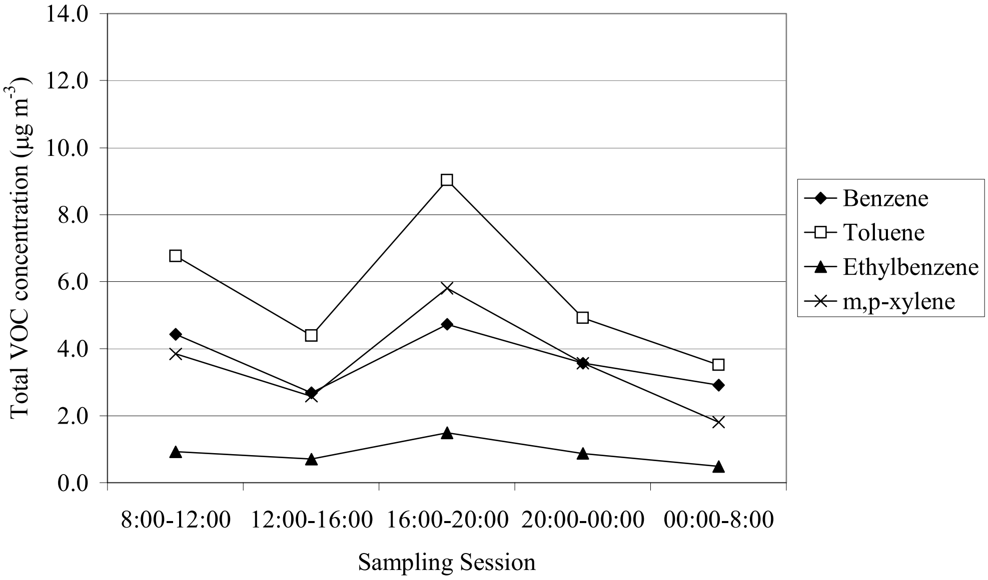


Figure 4.18. Diurnal variation at residential station-winter 2004.

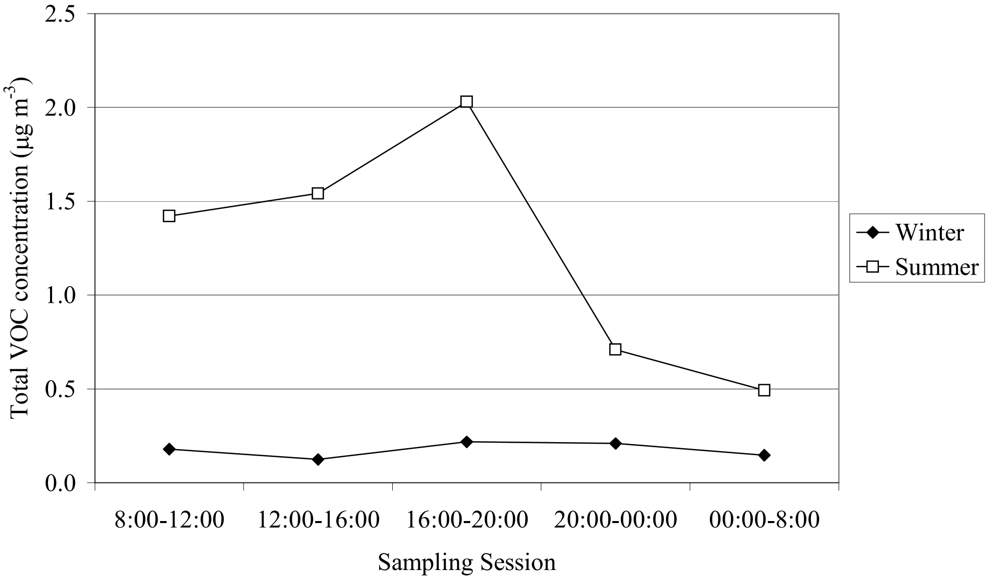


Figure 4.19. Diurnal variation of isoprene at residential station.

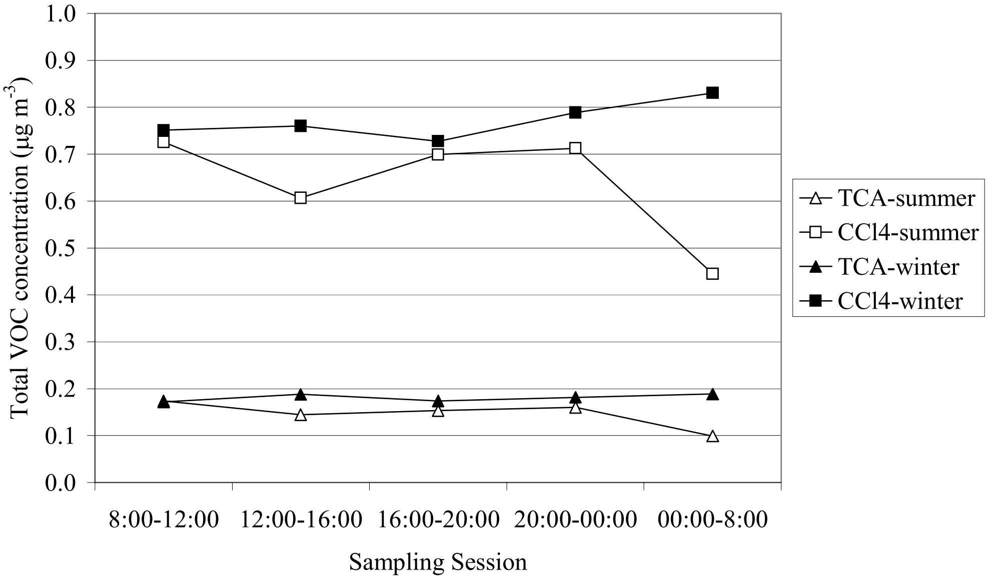


Figure 4.20. Diurnal variation of ODS at residential station.

The NO, NO_2 and CO show a diurnal pattern similar to that observed for traffic count data and patterns observed in most of the VOCs. Since traffic is well known dominating source for CO and NO similarities in the diurnal patterns in their concentrations and those of VOCs further confirm dominating traffic influence on VOC concentrations measured at the residential and roadside stations.

Diurnal variation in O_3 concentration, however, shows a different pattern. Concentrations of O_3 have a noon peak. This is due to formation of O_3 in the atmosphere through photochemical reactions for which the rate increases during noontime with the increased sunlight and frequently reported in literature (Kuntasal and Chang, 1987). The noontime O_3 peak is less pronounced during winter campaign due to decreased rate of photochemical reactions (owing to reduced solar flux).

The NO/NO_2 ratio is 0.53 and 1.05 during summer and winter, respectively. Concentrations of NO_2 are higher than NO during summer season indicating that most of the NO emitted is converted to NO_2. During winter, however, due to decreased rate of photochemical conversion of NO to NO_2 there is not a significant change in concentrations.

4.1.3.5 Ozone Depleting Substances

Some of the compounds, which have potential to deplete stratospheric ozone layer (commonly known as zone depleting substances, or ODSs), such as chlorofluorocarbons (CFCs), hydro-chlorofluorocarbons (HCFCs), hydro-fluorocarbons (HFCs), 1,1,1-trichloroethane and carbon tetrachloride are also classified as VOCs due to their high volatility. Among these compounds, TCA and CCl_4 are measured in this study.

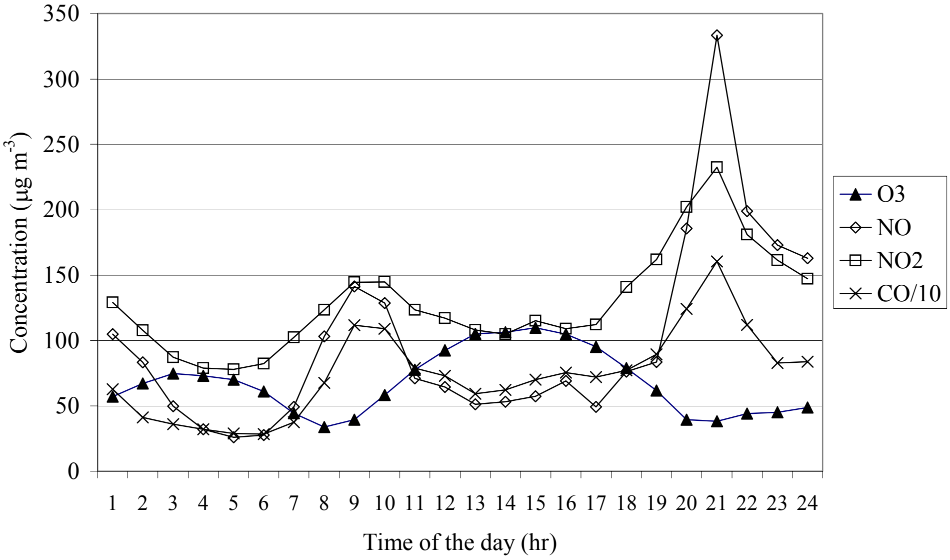


Figure 4.21. Diurnal variations in pollutant concentrations measured at RSHM station-Summer 2003.

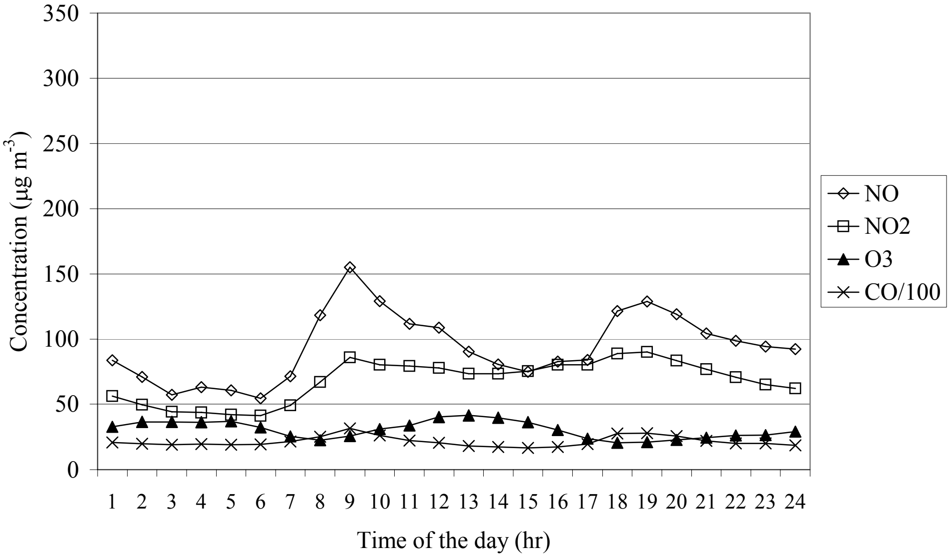


Figure 4.22. Diurnal variations in pollutant concentrations measured at RSHM station-Winter 2004.

Average concentrations of TCA and CCl_4, measured in this study are 0.17 µg m^{-3} and 0.73 µg m^{-3}, respectively. Analysis of temporal variation performed in the previous sections indicated that TCA concentrations measured at the roadside station shows a seasonal variation with higher concentrations during winter. TCA concentrations measured at the residential and roadside stations also shows weekday to weekend variations. Concentrations of CCl_4 measured at the roadside station during winter campaign and at the residential station during both summer and winter campaigns shows weekday to weekend differences. TCA shows almost no diurnal variation but CCl_4 shows a slight diurnal variation. Concentrations of both VOCs are very low (i.e., less than 1 µg m^{-3}) in the atmosphere.

These findings indicated that there might be still some use of TCA and CCl_4 in Ankara. Although the production and import of these substances are banned, the stocks may still be in use. It would be interesting to compare concentrations of these compounds with the levels before the ban came in effect, but unfortunately, there is no information on the concentrations of these compounds in Ankara (and anywhere else in Turkey) atmosphere from the previous years.

4.1.4. Spatial Variations

4.1.4.1 Ambient Stations

Concentration of the VOCs measured at three ambient station operated during Ankara campaign are compared to evaluate spatial variation of VOC concentrations in the city. Ratio of the concentrations of most abundant 20 VCOs and total VOC, measured at residential, roadside and METU stations, are given in Table 4.6. Data generated both summer and winter campaigns are included in the averages given in the table. VOC concentrations of all the compounds measured at the roadside station are about factor of two higher than the concentrations measured at the residential station. Similarly concentrations of most of the compounds measured at the residential station are about 2.5 times higher than that were measured at the background station. The only exceptions are TCA (Re/Ba=1.02), CCl_4 (Re/Ba=0.90) and isobutylbenzene (Re/Ba=1.01) that do not show significant variation in concentration at both stations. It should be noted that although residential and background stations are operated concurrently, measurements at the roadside station were performed one week later in both summer and winter campaigns. However, VOC and total VOC concentrations measured at the roadside station are so high that difference in sampling periods is not expected to change conclusions reached in this section.

Table 4.9. Ratio of median VOC concentrations measured at ambient stations.

Compound name	**Ro/Re**[a]	**Re/Ba**[b]	**Ro/Ba**[c]
Toluene	1.67	2.63	4.40
m,p-xylene	2.96	2.83	8.36
Benzene	2.05	1.84	3.79
2-methylpentane	1.96	2.84	5.58
3-methylpentane	1.81	2.74	4.96
1,2,4-trimethylbenzene	3.20	3.79	12.13
o-xylene	3.14	2.81	8.83
Pentane	2.53	2.89	7.32
Hexane	1.70	2.35	3.99
Ethylbenzene	2.82	2.68	7.56
3-ethyltoluene	3.28	3.70	12.14
2,2-dimethylbutane	2.17	3.64	7.89
Naphthalene	1.76	3.63	6.41
Carbontetrachloride	1.76	0.90	1.57
c-3-methyl-2-pentene	1.90	2.53	4.81
iso-butylbenzene	2.16	1.03	2.23
Methylcyclopentane	1.78	3.19	5.66
2-methylhexane	2.47	1.83	4.54
3-methylhexane	2.61	2.32	6.05
2,3-dimethylbutane	2.00	3.22	6.43
Total VOC	2.28	2.29	5.21

[a]*roadside to residential concentration ratio;* [b]*residential to background concentration ratio;* [c]*roadside to background concentration ratio.*

Comparison of the concentrations measured at the background and roadside stations indicates that concentrations are approximately a factor-of-six higher at the roadside station for most of the VOCs. Concentrations of 2-methyl-2-butene, 2,2-dimethylpentane, 3-ethyltoluene, 4-ethyltoluene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene are more than an order-of-magnitude higher at the roadside station than the corresponding concentrations measured at the background station. These compounds are reactive VOCs and have short atmospheric residence times (around 1-hr). Large differences between the concentrations of reactive species at roadside and background station indicate that these compounds are transported from polluted regions in the city to the METU. Concentration of the CCl_4, which is not as reactive as the compounds listed above, is only a factor of 1.5 higher at the roadside station than at the background station.

The spatial variation analysis indicates that concentrations of most of the VOCs are the highest at the roadside station and the lowest at the background station. Concentration of VOCs decreases with increasing distance from immediate sources. As motor vehicle emissions contribute significantly to most of these compounds this trend is simply a dilution effect and short atmospheric residence times of VOCs. The exception (CCl_4) for which motor vehicle emissions are not significant contributors is noticed by lowest Roadside/Background ratio of 1.57.

4.1.4.2 Composite Sampling

Composite and separate samples were collected in different sections of Ankara in order to investigate spatial variations of VOCs in the city. Number of the sample was limited to winter campaign and two sampling days. Samples were collected at four different locations where the population density was high as discussed in Section 4.1.2.

Samples were collected between 8:00-12:00 and the sampling points were selected away from road with heavy traffic. It should be noted that this exercise was performed to obtain a rough idea about the spatial distribution of VOCs in Ankara and to assess how the concentrations of VOCs at different locations in the city compares with the values measured in this study. Otherwise few samples collected at different parts of the city are not enough to reach reliable conclusions about the spatial distribution of VOCs. Concentrations of VOCs and total VOC measured at different districts are given in Figure 4.23 along with the concentrations measured at the roadside and residential stations in this study.

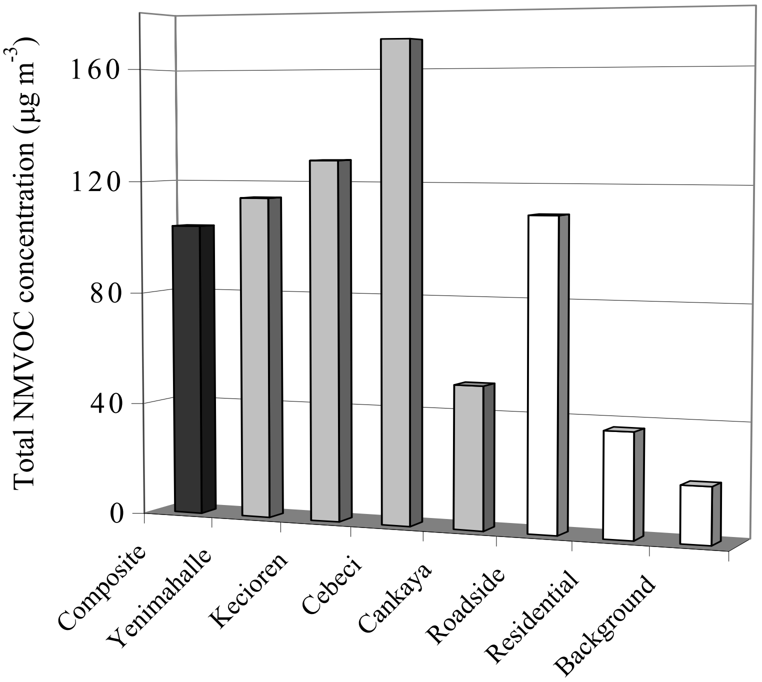


Figure 4.23. Spatial variations in the total VOC concentrations.

The highest total VOC concentrations are measured at Cebeci, which is followed by Keçiören, Yenimahalle and our roadside station at Atatürk Bulvarı. Cebeci has high population and traffic density. Minibuses and buses accounted for majority of the vehicles. Coal combustion for residential heating is common, not only in Cebeci, but also at Yenimahalle and Keçiören, where high VOC concentrations are measured. Concentrations are the lowest at Çankaya site. Çankaya site is also located on a highly populated region and the traffic density is also high. However, the income level at this site is higher resulting in vehicle fleet with better maintenance, equipped with control devices and mostly new cars. Natural gas is used for residential heating at this site. Another parameter that affects spatial variation in pollution concentration is the topography. Topographical map of Ankara is shown in Figure 4.24. Çankaya site is located at a high elevation. Therefore the pollutants are dispersed easily with the wind resulting in lower concentrations measured at this site.

Concentration of total VOC measured during composite sampling is slightly lower than the concentration measured at the roadside station. However, concentration measured at the roadside station is lower than that were measured at Cebeci, Keçiören and Yenimahalle sites. Concentrations measured at the residential and background stations are significantly lower than the concentrations measured at other sites. The residential site is located on a relatively flat topographical area as can be seen in Figure 4.24 that results in better dispersion of pollutants by winds. Ankara has a u-shaped topography on the east. Dispersion is expected to increase at relatively smooth sections in the middle and on the west part of the city and of course at the top of the hills that receive winds.

The 3-D topographical map of the city where the residential station is located is shown in Figure 4.25. The residential station has an access to winds blowing from north. Analysis of spatial variations indicated that there is a significant spatial variation in the concentrations of VOCs measured in Ankara. This variation is enhanced by emission and topographical characteristics of the sites.

The spatial variations of selected VOCs that are among the most abundant compounds and from different compound groups is provided by Table 4.10. Table includes data from the background, residential, and roadside stations for comparisons. These are the morning (8:00-12:00) concentrations. Spatial variations in concentrations of individual VOCs are similar to the spatial distribution of total VOC. Concentrations of benzene (21 $\mu g\ m^{-3}$), naphthalene (7 $\mu g\ m^{-3}$) and toluene (24 $\mu g\ m^{-3}$) are the highest in samples collected at Cebeci. Isoprene concentrations are low at all sites. This compound is not detected at Keçiören and Çankaya sites. During the winter season the major source of isoprene is traffic and the concentrations emitted from traffic are low.

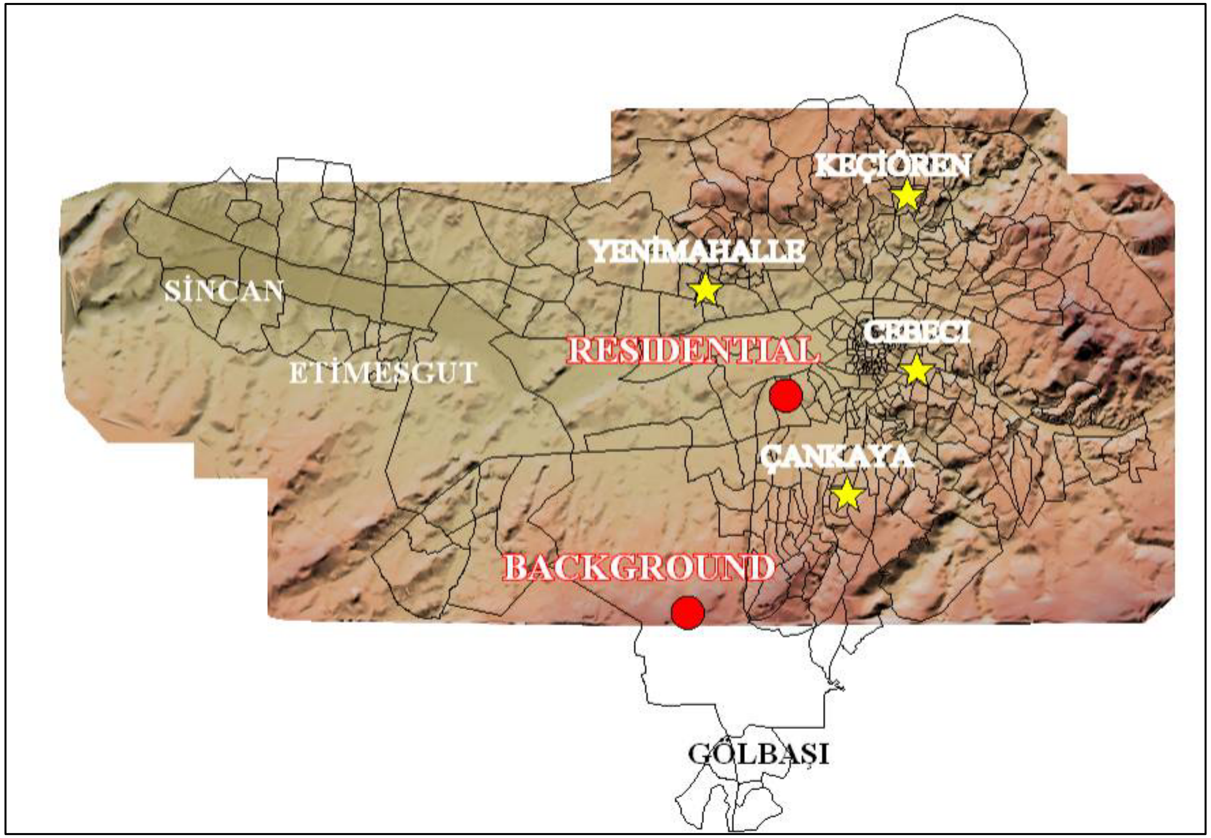


Figure 4.24. Topographical map of Ankara Province.

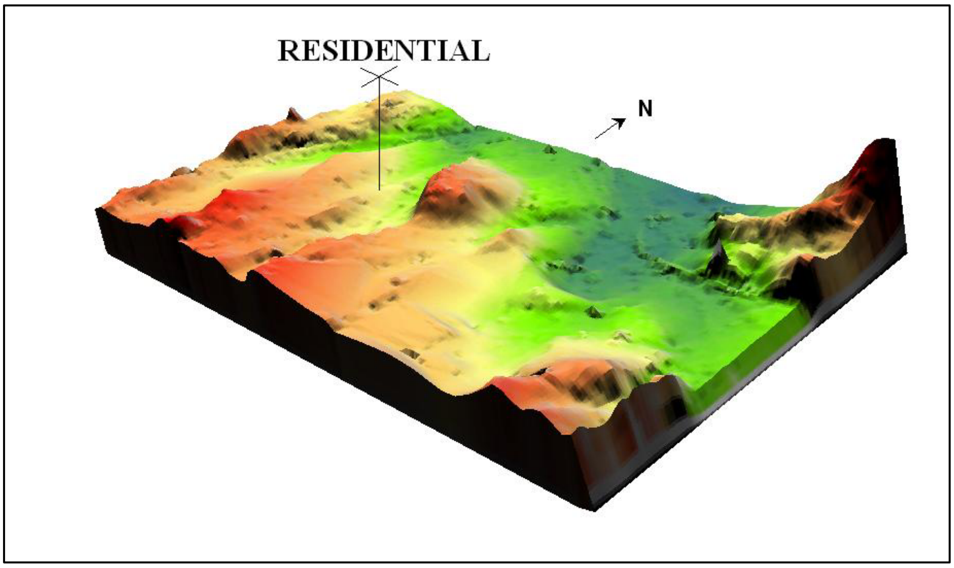


Figure 4.25. 3-D topographical map of the residential station.

Although the measurements discussed in this section do not have a statistical significance, the exercise proved useful to get a general idea about the distribution of VOCs in the city and clearly demonstrated that sampling points used in this study are not among the most heavily polluted parts of the city, which is good, because it shows that results obtained in this study is fairly representative for the city as a whole. However, future studies on health risks of VOCs should target districts such as Cebeci, Yenimahalle, Keçiören and low income districts, where concentrations appear to be significantly higher than those measured in this study.

Another point revealed with this limited study is that distribution of VOC concentrations in Ankara appears to be related with the economic status of districts. This indirectly implies that, although traffic is the mains source of VOCs at sites used in this study, non traffic sources, particularly coal combustion, can be a significant source in low income areas in Ankara.

Table 4.10. Spatial variations in concentrations (µg m^{-3}) of selected VOCs .

Compound name	Composite	Yenimahalle	Keçiören	Cebeci	Çankaya	Roadside	Residential	Background
Isoprene	0.58	1.07	0.00	0.75	0.00	0.57	0.19	0.09
2-methylpentane	3.28	3.72	3.83	4.83	1.76	5.04	1.62	0.73
Hexane	2.84	4.94	4.33	11.96	3.62	3.12	1.11	0.56
Methylcyclopentane	1.24	1.57	1.71	4.29	1.04	1.66	0.62	0.21
Benzene	12.64	11.26	13.79	21.00	7.32	8.13	4.43	2.13
Carbontetrachloride	0.91	1.11	1.08	1.04	0.99	1.60	0.75	0.70
Cyclohexane	0.54	0.61	0.67	1.21	0.41	0.61	0.24	0.13
Toluene	14.73	16.55	19.67	23.96	7.05	16.22	6.77	3.17
Octane	0.77	0.88	1.00	1.13	0.54	0.69	0.21	0.18
Tetrachloroethene	0.47	0.27	0.71	0.38	0.50	1.50	0.31	0.16
Ethylbenzene	2.87	3.10	3.71	4.21	1.36	2.94	0.92	0.43
m,p-xylene	11.50	11.88	14.21	15.63	4.16	13.43	3.84	1.86
Styrene	1.71	3.07	3.50	4.33	2.62	1.12	0.42	0.31
o-xylene	4.48	4.60	5.13	5.75	1.49	5.01	1.49	0.70
Nonane	0.68	0.84	1.00	1.13	0.68	0.52	0.24	0.18
1,2,4-trimethylbenzene	5.17	5.44	6.08	6.25	1.67	6.71	1.72	0.76
Naphthalene	4.93	3.98	5.29	7.38	1.94	2.14	1.15	0.50

4.1.4.3 Indoor and Gas Station Samplings

VOC levels at different microenvironments were also investigated in this study. Although number of samples was limited, data generated for indoor home and gas station was the first complete set of VOCs measured in these microenvironments in Turkey.

Samples were collected at a gas station located in a busy intersection at Beşevler and in two indoor microenvironments. The first sampling location was in a house located in residential part of Ankara and the second sampling location was at an office in the Middle East Technical University campus that is situated at outskirts of Ankara.

Table 4.11 presents concentrations of total VOC and the most abundant VOCs that account for 80%, 81% and 83% of the total VOC concentration measured in the office, the residential home and the gas station, respectively. The measured total VOC concentrations cover a wide range between 522 $\mu g\ m^{-3}$ and 41 $\mu g\ m^{-3}$ at the gas station and the office, respectively. The concentration of individual VOCs also shows a high variation between 0.59 $\mu g\ m^{-3}$ for styrene in the office and 54.91 $\mu g\ m^{-3}$ for 1-hexene/2-methyl-1-pentene at the gas station.

Rank and type of the most abundant species in these three microenvironments are different. VOCs associated with household cleaning chemicals such as chloroform and carbon tetrachloride are detected only in the office whereas 1,4-dichlorobenzene that is another compound associated with cleaning products is detected in both office and residential home. VOCs originate from printing ink solvent such as 1,2,4-trimethylbenzene and styrene are among the most abundant species measured in the office building. Isoprene, a biogenic VOC marker, is also abundant in the office whereas isoprene concentration is small in the air of the residential home and the gas station. The isoprene could infiltrate from outdoor air into the office since the university has significant number of trees on the campus.

Table 4.11. Concentrations of the most abundant VOCs measured at different microenvironments.

Office building– Indoor		**Residential house – Indoor**		**Gas Station - Ambient**	
Compound name	Concentration (μg m^{-3})	Compound name	Concentration (μg m^{-3})	Compound name	Concentration (μg m^{-3})
1,4-dichlorobenzene	9.83	Toluene	13.91	1-hexene/2-methyl-1-pentene	54.91
Pentane	3.90	1-hexene/2-methyl-1-pentene	9.60	2-methylpentane	52.73
Toluene	2.40	Naphthalene	9.01	Toluene	52.28
Chloroform	2.19	Hexane	6.57	m,p-xylene	43.11
Dodecane	2.05	2-methylpentane	5.92	3-methylpentane	37.24
Isoprene	1.98	c-3-methyl-2-pentene	5.08	Benzene	27.52
Undecane	1.48	3-methylpentane	5.04	Pentane	26.05
m,p-xylene	1.34	Pentane	4.60	2,2-dimethylbutane	24.89
2-methylpentane	1.33	m,p-xylene	3.66	Hexane	23.72
Hexane	1.09	1,4-dichlorobenzene	3.25	1,2,4-trimethylbenzene	20.53
Carbontetrachloride	1.05	Methylcyclopentane	2.99	2,3-dimethylbutane	15.61
Benzene	0.96	2-methylhexane	2.13	o-xylene	15.43
1,2,4-trimethylbenzene	0.85	3-methylhexane	2.13	Ethylbenzene	11.47
3-methylpentane	0.80	Dodecane	2.03	3-methylhexane	10.33
Naphthalene	0.80	Benzene	1.96	3-ethyltoluene	9.67
Styrene	0.59	1,2,4-trimethylbenzene	1.59	2-methylhexane	9.41
Total VOC	*40.71*	*Total VOC*	*98.21*	*Total VOC*	*522.10*

Naphthalene is ranked third with a concentration of 9.01 μg m^{-3} in the residential home. This may be due to common use of mothballs in homes in Turkey. Most of the compounds in residential indoor air are associated with motor vehicle emissions indicating contribution of traffic emission to air of residential home. The abundant VOCs measured at gas station originate from gasoline vapor and motor vehicle exhaust.

4.1.5. Summary of Findings

Owing to different atmospheric reactivates individual VOCs degrade at different rates in the atmosphere. In close proximity of an emission source, abundance of individual VOCs is determined by dominating emission source. This polluted air mass is called a "fresh" emission. When the polluted air mass travels away from the emission source VOCs degrade at different rates and result in a change in the abundance of individual VOCs. This air mass is called "aged" emission.

Temporal variations observed at the roadside, residential and background stations indicate that the roadside station is heavily influenced by fresh motor vehicle emissions, whereas residential station is influenced by both fresh and aged emissions that indicate effect of local and distant sources on the pollutant concentrations measured at this location. Motor vehicle emission is a major source affecting VOC concentrations at the residential station but there are additional sources that contribute to VOCs. Two examples of these non-traffic sources are high benzene concentration during winter and high toluene concentration measured during summer campaign. The background station is influenced mostly by aged emissions transported from distant sources, but fresh emissions from local sources have also a minor impact at this site.

Investigation of spatial variations showed that VOC concentrations change significantly at different sites due to change in emission characteristics and topography. Due to atmospheric reactivities of VOCs, concentrations are the highest near the emission sources such as the gas station and the roadside and the lowest at locations away from the emission source such as our background site. VOC concentrations measured at indoor environments are higher than the ambient concentrations.

4.1.6. Concentration Weighted Wind-Based Trajectory Analysis

Back trajectories of air masses are traditionally used to apportion the source regions to the measured concentrations at receptors. This method yields valuable results for the rural air quality studies where long-range transport can be distinguished from the local sources. However, for studies conducted in urban microenvironments, contributions of source regions cannot be assigned by using traditional methods used for back trajectories of air masses. Concentrations measured in urban microenvironments depend strongly on local emissions from both natural and anthropogenic sources. In addition, most of the VOCs are very reactive and a long-range transport is not expected for many of hydrocarbons because of their short lifetimes in the atmosphere.

In this study, a new method was developed to apportion source regions of VOCs measured at urban atmosphere. The method was developed to consider and overcome the difficulties stated in the previous paragraph. The proposed method bases on generation of back trajectories of wind that blows within the city borders. The method uses pollutant concentration measured at a receptor and frequencies of occurrence of wind sectors to apportion source regions to predefined wind sectors.

The formulation to calculate contributions of sources in each sector is similar to that used in calculating the back trajectory of air masses. The formulation to generate wind based back trajectories (simply referred to as “wind trajectories” from here on) is, however, novel to this research. Wind speed and wind direction data are used together with a sector based formula to trace back the wind blowing to the sampling point (i.e., receptor) at a stated time.

For each hour of the sampling session the locations of the sampled air relative to the sampling point in previous hours are determined by using hourly wind speed and direction data. Back-trajectories are constructed until such time as the determined location falls outside the city boundary of interest (+/- 25 km in the East-West direction, +/- 20 km in the North-South direction, Fig. 4.26). The calculation time for these trajectories was less than a few hours in most cases.

Each trajectory location determined as indicated above is attributed to one of the 16 wind-rose sectors relative to the sampling point and the number frequency of trajectory locations in each sector is determined for the entire sampling session by adding up the frequencies determined for each of the 4 hours of sampling. The concentrations $\boldsymbol{C_k}$ of individual VOC species measured during a sampling session are not resolved on an hourly basis and are assumed to be constant over the 4 hour sampling session. By compiling data from all sampling sessions, Eqn. 4.1 and 4.2 can be used to compute a "sector average concentration" (C_j), and the relative contribution of each sector to the total, % C_j.

$$C_j = \frac{\sum_{k=1}^{N} C_k \sum_{i=1}^{4} f_{ij}}{\sum_{i=1}^{4N} f_{ij}} \tag{4.1}$$

$$\%C_j = \frac{C_j}{\sum_{j=1}^{16} C_j} x100 \tag{4.2}$$

where; f_{ij} is the number frequency of trajectory locations falling in the j^{th} sector for the i^{th} hour of sampling for a particular sampling session, and N is the total number of sampling sessions.

The wind trajectory method is applied to the VOC data measured at the residential and background stations in Ankara. The basic assumption for the wind trajectory calculations is that the meteorological data measured at the Ankara Meteorology Station operated by the State Meteorological Works is representative of the average condition at each point in the city. The sector apportionment calculations are performed only for the daytime concentrations measured at the sampling stations because limited number of data was collected at these stations during nighttime.

Population density and major roads in the city are shown in Figure 4.26. The population density is high at all sectors from NW to S (see Figure 3.3 for the population density scale). Yenimahalle that is located in the NW sector is mainly a residential district. Mamak that is located in the E sector and Kızılay/Çankaya that are located in the S sector are both residential and commercial districts. Many of the government buildings, small retail shops, commercial buildings, the parliament building and foreign embassies are located in the Çankaya/Kızılay district that can be considered as the downtown area. There are two main arteries that cross each other at the Çankaya/Kızılay district. The east-west and north-south arteries literally connect the districts located in the east, west, north and south to Kızılay. Thus, the traffic flow from/to this location is very high. The motor vehicle emissions might be the major source of VOCs at this district. The traffic density is also relatively high at the Mamak district. The motor vehicle emissions and emissions from small enterprises could be the source of VOCs at this district. Other than the two main arteries that cross the city center, there are four intercity roads located at the inner circumference of city, namely; Konya road (S-N), Eskişehir road (SW-E), Istanbul road (NW-E) and Samsun road (W-E).

The sector contribution rose plots for benzene concentrations measured at the residential and background stations during the winter campaign in Ankara are shown in Figure 4.26. As can be seen from the figure, although the meteorological parameters are the same at both stations, the contribution rose plots are not similar due to the difference in pollution patterns observed at these stations.

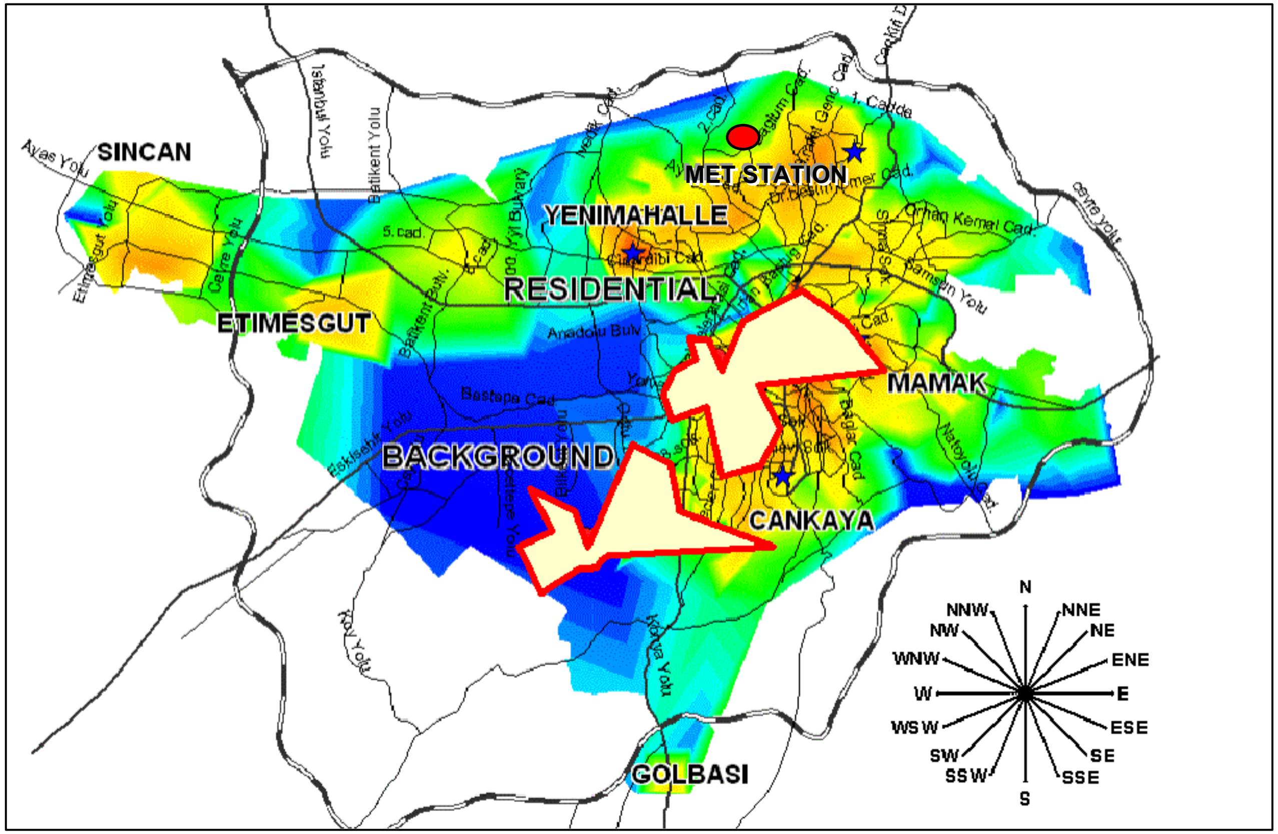


Figure 4.26. Sector contribution rose for benzene-Winter 2004.

The benzene concentration measured at the residential station is mostly influenced by the air masses traveled from NE to E and SE to S sectors. The contribution of sectors E, ENE and NE are 15.0%, 12.0% and 10.0%, respectively. The contribution of sectors S, SSE and SE are 9.5%, 9.0% and 7.5%, respectively. Contributions of sources located at SW (6.5%), WSW (6%) and W (4%) sectors are small compared to the contributions of other sectors. Contribution of sources located in N sector was zero, as there is no wind trajectory passing through this sector. Results indicate that the VOC sources located between E and NE sectors are responsible for 37% of the VOC concentrations measured at the residential station. Similarly, the VOC sources located between S and SE sectors account for 26% of the VOC concentrations measured at this station.

As shown in Figure 4.26, the sector contribution rose for benzene measured at the residential site indicates that E and S sectors and thus districts including Mamak and Çankaya as the main contributors to the benzene concentrations measured at the residential site. Benzene is known as a marker for traffic related emissions. Therefore, the high traffic density at Mamak and Çankaya districts and more frequent wind flow from these sectors has a strong influence on benzene concentrations measured at the residential site. The sector contribution rose also shows that SW sector as a minor contributor to the observed benzene concentrations at Emek. The most likely source in SW sector is the Konya intercity road, which is one of the main arteries in the city.

The sector contribution rose for benzene concentrations measured at the background station during winter campaign in Ankara is also presented in Figure 4.26. The benzene concentration measured at the background station was influenced by the air masses from E, ENE, NE and NNE sectors. The contributions of these sectors on benzene concentrations measured at the background station are 19.0%, 10.0%, 12.0% and 11.5%, respectively. The contribution of remaining sectors, namely, W (7.0%), WSW (6.5%), SW (7.0%) and NW (8.5%) are smaller.

The contribution of sources located in the N sector is zero since there is no wind trajectory passing through this sector. Although sector frequencies of wind trajectories are similar to the frequencies used for the residential station, contributions of southern sectors on benzene concentrations measured at background station are almost negligible This is due to the fact that there is no major benzene (and other VOCs as well) source located to the south of the background station. Thus, benzene concentrations that are low when winds blow from south. This resulted in small contribution of sources located in south sectors.

The sector contribution rose for benzene measured at the background station points eastern and western sectors and thus districts including Çankaya/Kızılay as the major contributor as shown in Figrue 4.26. The Konya road is also located in this direction. The high traffic density at Çankaya/Kızılay district and on the Konya intercity road provides main contributions to benzene concentrations measured at the background station. The Eskişehir intercity road that is located in the NW sector also contributes to benzene concentrations measured at the background station. The area between W and SW sectors is newly developing residential/commercial (Çayyolu and Bilkent) area. As the population data is not available on electronic format populations density is not shown in Figure 4.26, however, this area is a densely populated area. The benzene rose suggests that the emissions in these areas are an important contributor to benzene concentrations measured at the METU, particularly in during winter season.

The sector contribution roses for selected compounds measured at residential station during winter campaign are given in Figure 4.27. The sector contribution roses are generated for all target compounds measured at residential and background stations during the winter and summer campaigns. However, only selected compounds are included in the figure, as roses for approximately 100 VOCs would take too much space. Compounds that correlated with each other also showed similar sector contribution roses, which imply that these compounds may have identical sources. For example, benzene, toluene, ethylbenzene, m,p-xylene, o-xylene, isoprene, naphthalene and 1,2,4-trimethylbenzene have sector contribution roses. These elements are also strongly correlated with each other, as are discussed in Chapter 5. All of these VOCs are known to originate from motor vehicles. Thus, the compounds in this group are identified as related with motor vehicle emissions.

As can be seen from Figure 4.26 and Figure 4.27, isoprene has a very similar sector contribution with benzene, ethylbenzene, toluene. Isoprene is emitted from both biogenic sources and motor vehicles, but the dominating source in nature is bogenic emissions. However, during winter season biogenic emission are negligible and motor vehicle emission becomes the major source of isoprene in Ankara. This is obvious from the Figure 4.27 that isoprene has very similar pattern with other motor vehicle related compounds such as benzene and ethylbenzene.

Napthalene has a slightly different pattern with smaller contribution from ENE and W directions. Although main source of naphthalene is traffic emissions, its concentrations are also high in residential heating emissions (Ollivon, *et al.*, 2002; Mastral *et al.*, 2003; Bi *et al.*, 2003). This might be the reason for slight deviation in the sector contribution rose during winter season, when emissions from space heating becomes prominent. Although pentane is emitted from exhaust, it is also good marker specie for evaporative emissions (Watson *et al.*, 2001). Therefore it has a slightly different sector contribution rose.

TCA is used as solvent as discussed earlier. It has the most peculiar shape indicating almost equal contribution from all parts of the city except N direction. It indicates that TCA is used almost all part of the city. Please note that lack of TCA in N sector is not due to absence of TCA use in N sector, but owing lack of wind flow from that wind sector. Carbontetrachloride, which is also a very good solvent has also a very similar sector contribution rose to that observed for TCA.

Contributions of wind sectors on Toluene/Benzene (T:B) and m,p-xylene/ethylbenzene (mpX:E) ratios were also investigated. As discussed in

Section 5.1.2 in detail studies on vehicle exhaust generally reported a ratio of T:B of 2.0 (Sweet and Vermette, 1992; Scheff and Wadden, 1993). The ratio of mpX:E suggested by Nelson and Quickley (1983) is commonly used to investigate aging in the air masses. The mpX:E ratio of between 3 and 4 indicate fresh emissions.

T:B ratio is about two at almost all part of the city except N direction, indicating that motor vehicle emissions is the major source of VOCs in the city. Since the T:B ratios calculated for all sectors, in the residential site are very similar to the corresponding ratios measured in fresh traffic emissions, then it can be concluded that the traffic emissions are the dominant source not only for benzene and toluene, but also for all VOCs that show similar wind sector dependence with these two compounds. This observation also implies that the concentrations of VOCs, which have wind sector contribution patterns that are different from patterns observed in benzene and toluene, probably affected from non-traffic sources. This conclusion supports, specie-based discussion given in the previous paragraph. The zero contribution observed on the N direction was due to absence of winds blowing from this direction to the residential station.

Ratio of mpX:E can be used to determine age of the air mass, as mentioned prevously (Nelson and Quickley, 1983). The ratio calculated at all stations during winter campaign is approximately 4, indicating relatively fresh emissions intercepted at all stations during winter season. It can also be seen in Figure 4.27 that mpX:E ratio is approximately 4 in all sectors at the residential site in winter, except for north sector. Similarity of mpX:E ratio in all wind sector shows that the site is under influence of fresh emissions from all wind directions, which is expected.

Sector contribution roses for selected compounds measured at residential station during summer campaign are given in Figure 4.28. Summer roses are not completely identical with the winter roses. VOC concentrations transported from SSE and NNW directions are major contributors for most of the compounds.

Benzene, ethylbenzene and toluene have slightly different sector contribution roses from each other in summer although in winter they have identical roses. The analysis showed that ethylbenzene, m,p-xylene, o-xylene and 1,2,4-trimethylbenzene have all very similar sector contribution roses. For the benzene lower contribution in N direction and higher contribution in NNW directions are the reason for a different sector contribution pattern. These slight changes might indicate that benzene has additional sources to motor vehicle exhaust during summer campaign.

The differences are more pronounced for toluene, showing lower contribution in SSE direction and higher contributions on ESE, E and ENE directions. As in the case of benzene, differences observed in sector contributions on toluene concentrations is due to non-traffic toluene sources in summer. These non-traffic sources of both toluene and benzene are discussed in detail in Chapter 5. The NNW was the major source sector contributing to isoprene concentrations (i.e., 14%) measured at residential station during summer campaign. Unlike in winter, when traffic is the main source for isoprene, biogenic emissions becomes the major source of isoprene during summer season, with increased biochemical activity in plants. This is the reason for a different sector contribution rose observed for isoprene.

Naphthalene has a similar pattern to ethylbenzene with high contributions on N and SSE directions. However, naphthalene has higher contribution from WSW direction indicating there might be additional sources for naphthalene in this direction. TCA had the highest contribution from NNW direction being dissimilar to winter campaign. Contribution was almost same on the other sectors. Carbontetrachloride has a similar sector contribution pattern with that of TCA.

The ratio of T:B shown in the Figure 4.28 shows variation in sector contributions. The ratio is approximately 4 in NNW, N, NNE, NE, ENE, E and ESE sectors and it is approximately 2 in all other sectors. As discussed in the previous paragraphs the T:B ratio around two indicates that fresh motor vehicle emissions are the major source. This ratio was observed in most of the sectors, except sectors that lie between NNW and ESE. These differences between sectors suggests that traffic emissions at SE, SSE, S, SSW, SW, WSW, W, WNW and NW sectors are the main contributor to observed benzene and toluene levels in these sectors, but additional sources of toluene in NNW, N, NNE, NE, ENE, E and ESE sectors increases the ratio to 4.

The ratio of mpX:E at all directions was lower than the value of 4 that was observed during winter campaign. The mpX:E ratio observed in the vicinity of emission sources during summer was about 3.5 (see Section 5.1.2). Thus the ratio lower than 3.5 observed at sector contribution rose for residential station indicated that air masses transported from other parts of the city to residential station. This may be explained by reduced traffic around the residential site. Residential site, as its name implies is located in the middle of a residential area, which is far from busy business centers in Ankara. Wind sector contributions and mpX:E ratio demonstrated that in winter fresh emissions from activities of residents living in the area are the main source of VOCs in this station. However, during summer population and activities in that area decrease, roughly, by 30% (assuming, all residents leave the city for one month during June, July and August, which is typical for Ankara). Emissions in distant busy centers in the city do not decrease in the same proportion. Lower mpX:E ratio observed in most wind sectors suggests that these distant sources becomes more significant contributors on observed VOC concentration at the residential site in summer months.

The sector contribution roses for selected compounds measured at background station during winter campaign are shown in Figure 4.29. Benzene, ethylbenzene, toluene and isoprene have similar sector contribution roses. Naphthalene has also a sector contribution rose similar to these compounds except higher contributions on NE and E directions. Pentane has similar contribution rose with benzene except higher contribution on NW direction.

Sector contribution rose for TCA indicated almost equal contribution from all directions except N from where the contribution was zero, due to lack of wind flow from this sector. Carbontetrachloride had a very similar contribution rose to that of TCA. The ratio of the T:B was about 1.5 at all sectors except sectors between ESE and SSW. Lower contributions in these sectors were due to lack of strong emission sources on these regions as stated earlier. The ratio of mpX:E was about 4 at all sectors except ESE.

Concentration weighted wind-based trajectory analysis is a useful tool to identify and quantify source regions affecting a particular pollution measured at a particular location in urban areas. Control measures specific to emission sources on the identified sectors provide an effective way of implying air quality management plans. In this section, similarities and differences between wind sector contribution patterns are discussed and presence or absence of non-traffic sources are evaluated. However, nature of these non-traffic sources is not elaborated, because types of sources affecting sampling stations are discussed in detail in the "receptor modeling" section (Chapter 5) of this thesis.

The interpretation of sector roses for different sites and seasons demonstrates the major differences as TCA has the most peculiar shape in winter indicating almost equal contribution from all parts of the city. It indicates that TCA is used almost all part of the city. Sector rose for naphthalene shows a distinct shape in summer at residential station indicating additional sources of naphthalene. A critical finding is that almost all compounds have different sector contributions in summer and winter.

Major similarities are also understood by detailed interpretation of sector roses. Benzene, ethylbenzene, toluene, isoprene and pentane have similar sector contributions roses in winter at both residential and background stations. Traffic is the major source for these compounds during winter.

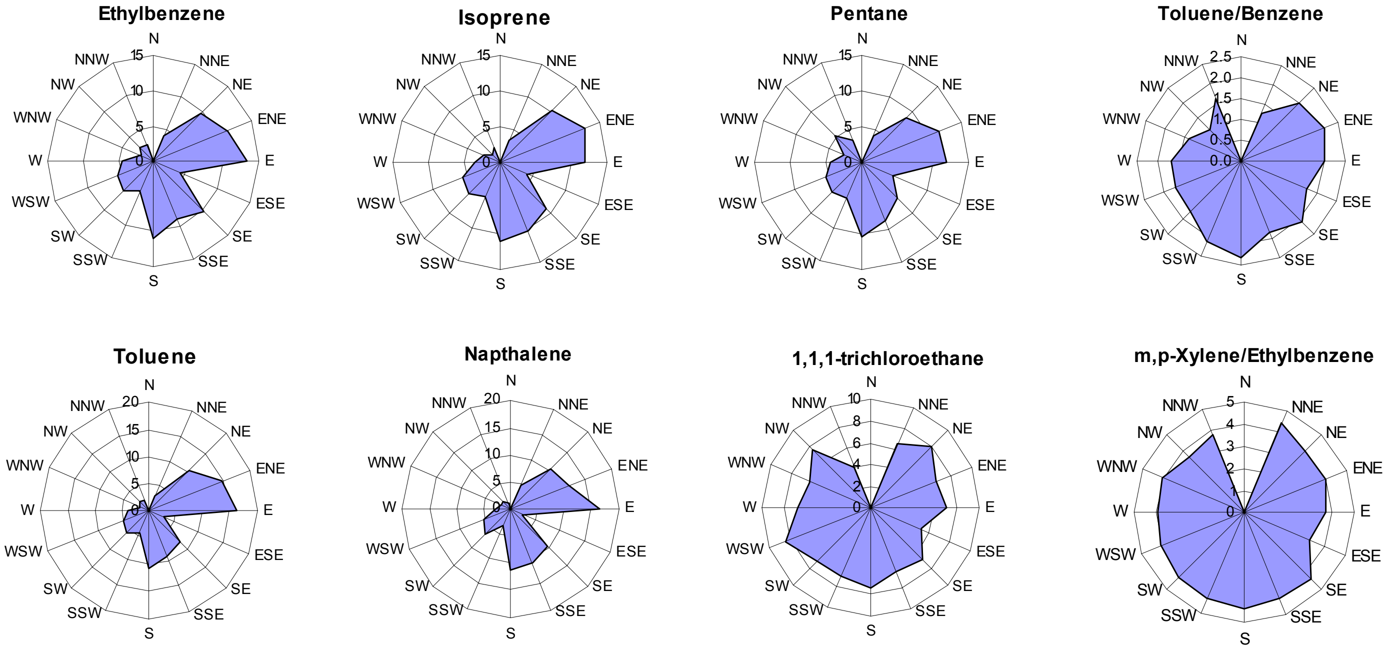
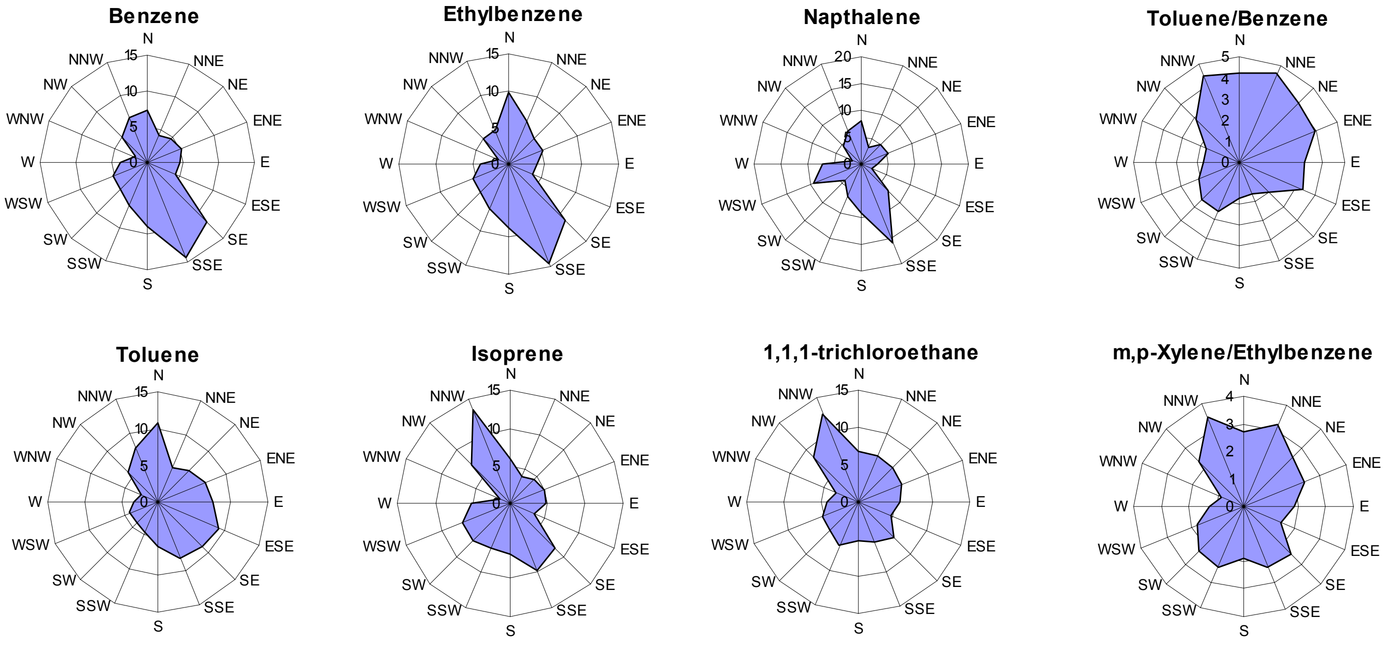


Figure 4.27. Sector contribution roses for selected compounds measured at residential station-winter 2004.



Benzene

Ethylbenzene

Napthalene

Toluene/Benzene

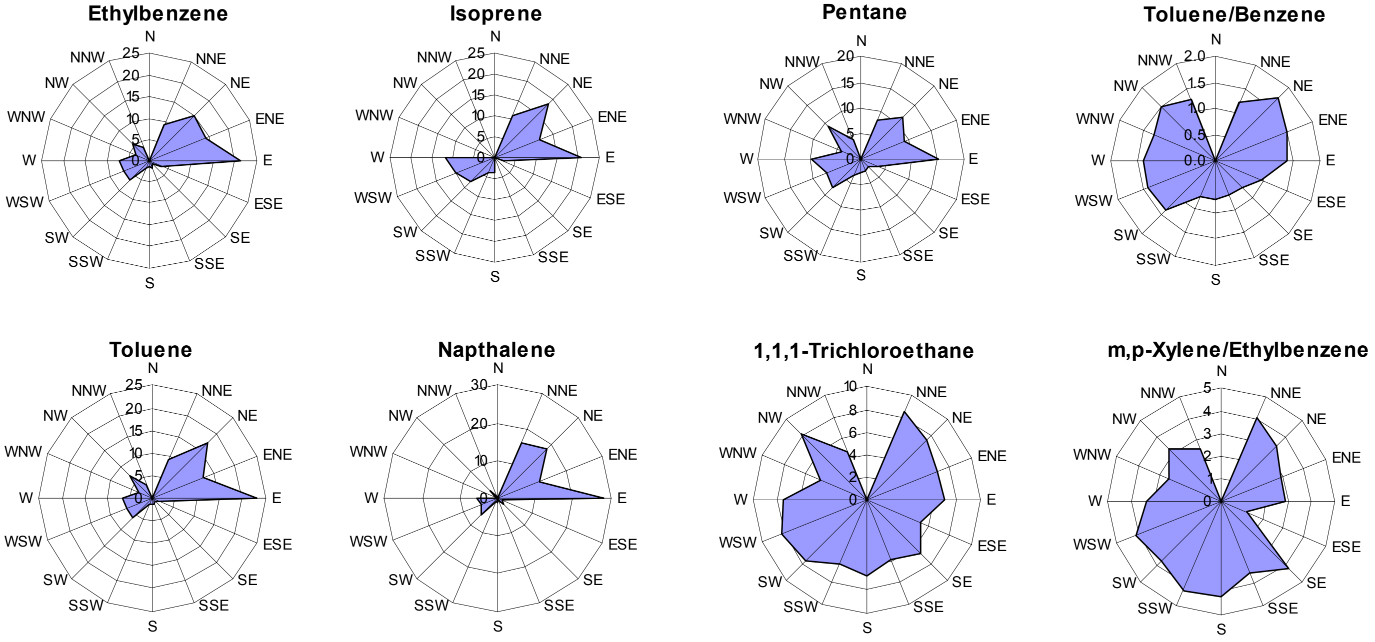
Toluene

Isoprene

1,1,1-trichloroethane

m,p-Xylene/Ethylbenzene

Figure 4.28. Sector contribution roses for selected compounds measured at residential station-summer 2003.



Ethylbenzene

Isoprene

Pentane

Toluene/Benzene

Toluene

Napthalene

1,1,1-Trichloroethane

m,p-Xylene/Ethylbenzene

Figure 4.29. Sector contribution roses for selected compounds measured at background station-winter 2004.

4.2. Ottawa Campaign

4.2.1. Supplementary Data

4.2.1.1 Meteorological Parameters

Hourly meteorological parameters that are reported at the Ottawa Airport were used to assess the meteorology of the study area. Summary of the temperature and relative humidity (RH) data measured at airport are shown in Table 4.12. As can be seen from the table, extreme temperatures are observed at Ottawa especially during the winter season. Temperatures are much lower than winter temperatures recorded in Ankara. The city is quite humid especially during the summer. The RH values reaches 100% during summer months.

Table 4.12. Summary statistics of meteorological parameters.

Season	**RH (%)**	**Temperature (°C)**
Winter	57 (33-85)[a]	-14.0 [-0.5-(-26.8)]
Summer	77 (49-100)	22.0 (13.4-26.9)

[a] *Average values. Values in parenthesis denote ranges.*

4.2.1.2 Traffic Count

Traffic counts were recorded during the Ottawa campaign at the roadside station as discussed in Section 3.2. The average number of vehicles at each category recorded during morning (7:30-9:30), noon (11:30-13:30) and afternoon (15:30-17:30) sessions in summer and winter campaigns are shown in Figure 4.30. Average number of motor vehicles passing along the Slater Street is about 2,000. Light duty vehicle (LDV) has the highest contribution during both summer and winter seasons (i.e., 84%). Coach bus has the second highest contribution at both seasons with an average 11% contribution. Motorcycle (MC) is recorded only during summer campaign. Heavy duty vehicles (HDV) are also recorded.

Traffic count data indicates diurnal and seasonal variations. The number of vehicles is the highest during afternoon session and the lowest during morning session. During the weekday, however, maximum number of vehicles is recorded during morning and afternoon traffic rush hours. Vehicle number is higher during winter campaign than in summer campaign.

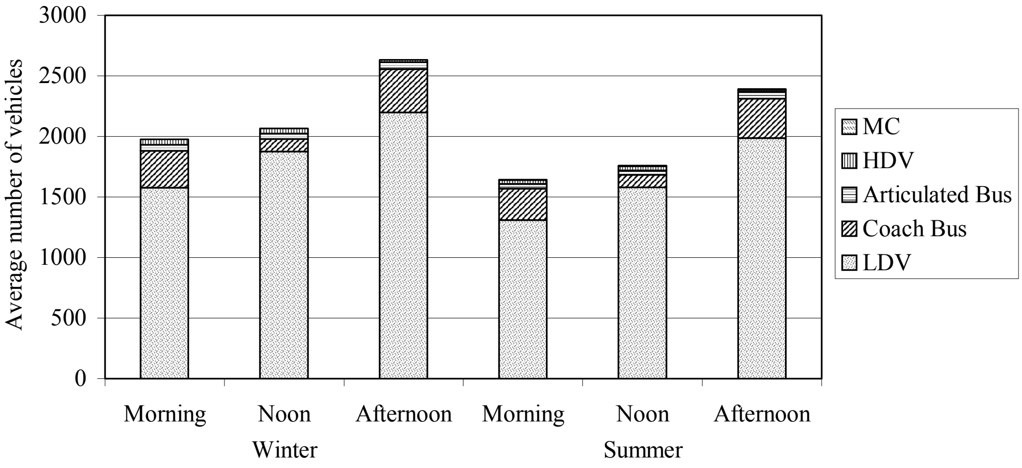


Figure 4.30. 2-hr traffic count data recorded at roadside station.

There are some differences and similarities in the traffic patterns observed in Ankara and Ottawa. First of all, number of vehicles passing through Slater street, both on a daily bases and on session basis, are approximately a factor of two higher than total number of vehicles passing through the Akay tunnel. The composition of traffic in the two cities is also substantially different from each other. In both Ankara and Ottawa LDVs make up most of the traffic (approximately 80%). However, in Ankara taxis make up the second most abundant group. Taxis in Ottawa are included in LDV category as they are not any different from personal cars. In Ankara they are not included in the same category with personal cars, because taxis in Turkey use LPG as fuel, whereas most personal cars are gasoline based. Another very different category in the two cities is minibuses. At Ottawa, minibuses is a minuscule fraction of total fleet, but in Ankara, due to their frequent use in public transport minibuses is the third most abundant group of vehicles. Buses, on the other hand, are the second must abundant category at Ottawa, but they do not make up a significant fraction of the fleet in Turkey. Other vehicle groups, namely trucks and motorcycles makes up a very small fraction of total fleet in both cities. Traffic pattern (variation in traffic density between morning, noon and afternoon sessions) and seasonal variation in traffic counts are similar in both cities.

4.2.2. Descriptive Statistics

A total of 75 samples were collected in Ottawa during summer and winter sampling campaigns. Among 165 target VOCs, 101 of them were detected during analysis. Compounds corresponding to 80-90% of the total VOC concentration and also included in the Priority Substance List (PSL) 1 and 2 of Health Canada and Hazardous Air Pollutants (HAP) list of Clean Air Act were selected for analyses. Compounds in the list have BDL values in less than 10% of all times.

The average concentration of the most abundant 20 compounds measured at the roadside station during both summer and winter campaigns are shown in Figure 4.31. Ethylene is the most abundant compound with about 10% contribution to total VOC measured at the roadside station. 2-methyl-butane, toluene, propane and ethane are the next most abundant compounds. Propane is emitted from both motor vehicles and LPG use. Acetylene is formed only in combustion chamber and it is a marker compound for motor vehicle exhaust emissions.

Box and Whisker plots for the most abundant 54 VOCs, in different sampling sessions in winter are given in Figure 4.32. In the figure, VOCs are listed based on number of C atoms and starting from lower hydrocarbons. Light hydrocarbons, such as ethylene, ethane acetylene, propylene, isobutene, n-butane and 2-

methylbutane dominate the VOCs in all sampling periods. In addition to these light hydrocarbons, some of the heavy hydrocarbons, such as 1,2,4-trimethylbenzene, n-decane, n-undecane and naphthalene and some of the hydrocarbons with intermediate C-number, such as 2-methylpentane, n-hexane, benzene and n-heptane have fair contribution to total VOC mass in Ottawa atmosphere during the winter season.

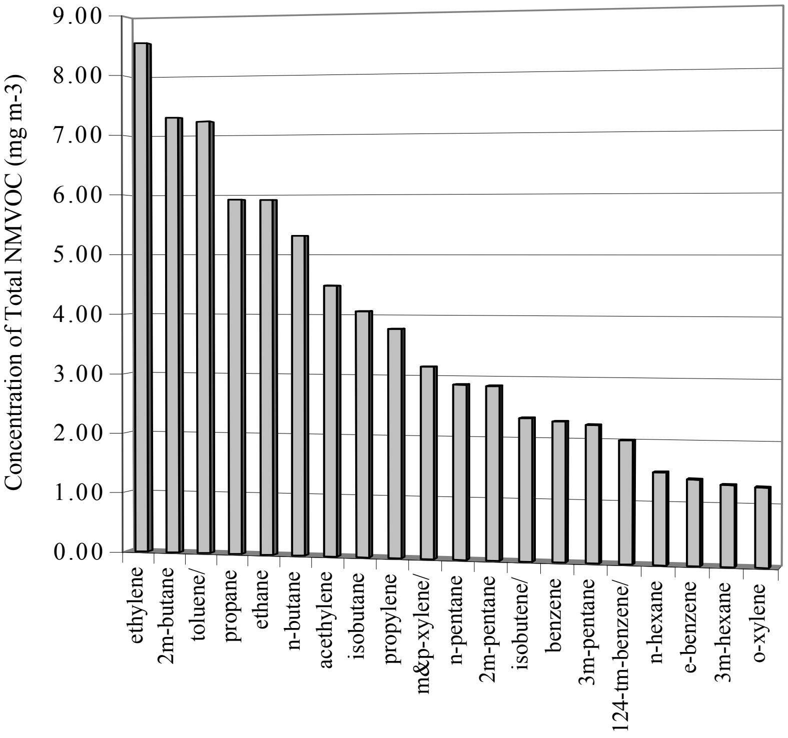


Figure 4.31. Concentration of the most abundant compounds.

The VOC pattern (relative abundances of light and heavy hydrocarbons) at any location is determined by abundances of sources contributing to these groups. The dominant abundance of light hydrocarbons are expected at our sampling point, which is strongly influenced by gasoline powered vehicles, as these light hydrocarbons originate from gasoline powered cars and evaporative emissions (Kourtidis *et al.*, 1999; Watson *et al.*, 2001). The dominance of light hydrocarbons on total VOC is frequently observed in urban areas (Derwent *et al.*, 1995; Rappengluck and Fabian, 1999).

Concentrations of the most abundant 54 VOC's measured in the summer campaign are depicted in Figure 4.33. 3-ip-toluene is the most abundant VOC measured during summer sampling campaign. Toluene is the second most abundant VOC. Its concentration varies between 2.21 and 12.09 μg m^{-3} with a median value of 7.23 μg m^{-3}.

One of the significant differences between the summer and winter data, which can be seen in Figure 4.33, is the high variability in concentrations of all measured VOC's in the summer campaign. This is mostly due to high variation in meteorological conditions within and between days. Temperature varies between 29.9 °C and 10.3 °C between sampling days and it varies between 23.76 °C and 16.76 °C within sampling days. Relative humidity measured during sampling sessions varies between 88% and 46% within day. The weather is rainy for few sampling days. Meteorological parameters affect atmospheric reactions and dispersion of pollutants. Affect of meteorological parameters on observed VOC concentrations are pointed out in other studies in literature (Kendal, 1993; EPA, 1999). Total VOC concentration measured in the summer period is 99.81 μg m^{-3}.

Comparison of relative abundances of VOCs in summer and winter seasons also shows higher relative abundances of light hydrocarbons in the winter season. This may indicate the significance of relative reactivity of light and heavy hydrocarbons in the atmosphere. In extreme cold temperatures during winter campaign (temperature during winter campaign varied between -4.6 and -20.7 ºC) reactivity of all hydrocarbons are significantly suppressed. However, their reactivity is enhanced during warmer summer campaign (maximum temperature varied between 23.6 and 26.9 ºC). This enhancement is more pronounced for light hydrocarbons, which are known to be more reactive than heavier ones (Atkinson, 2000).

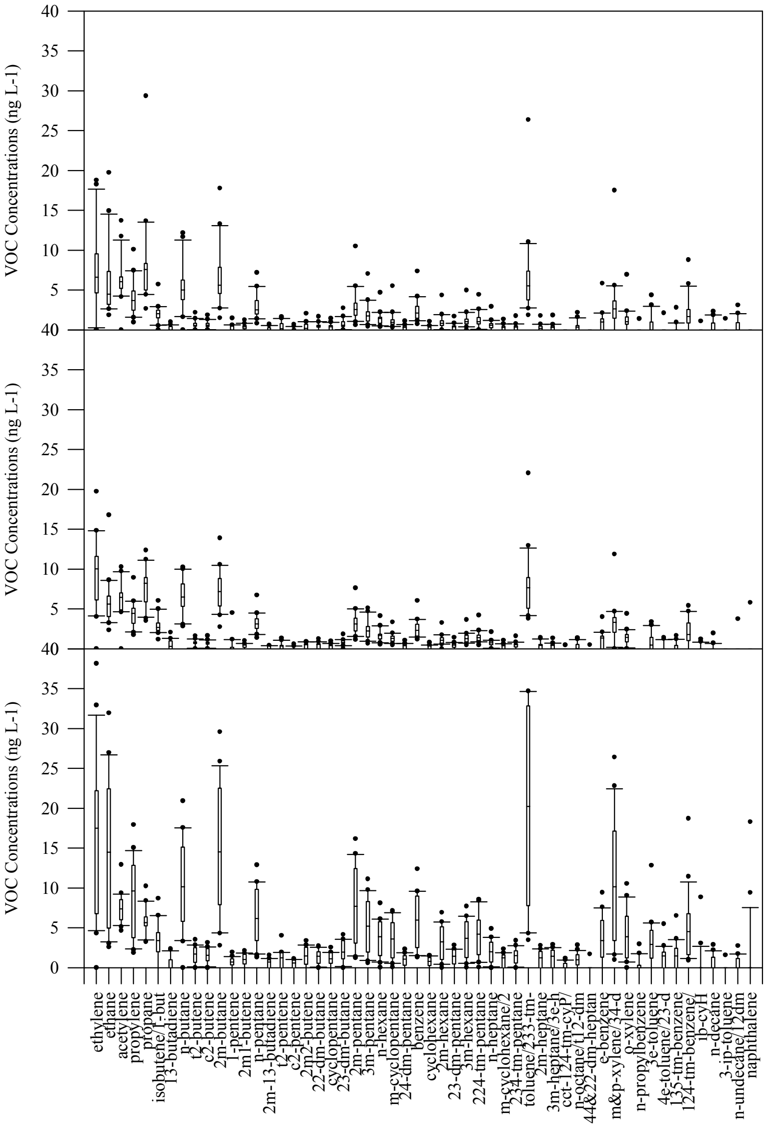


Figure 4.32. Slater Street Nose-Level VOC Data for Winter Sampling Campaign a) morning session b) noon session c) afternoon session.

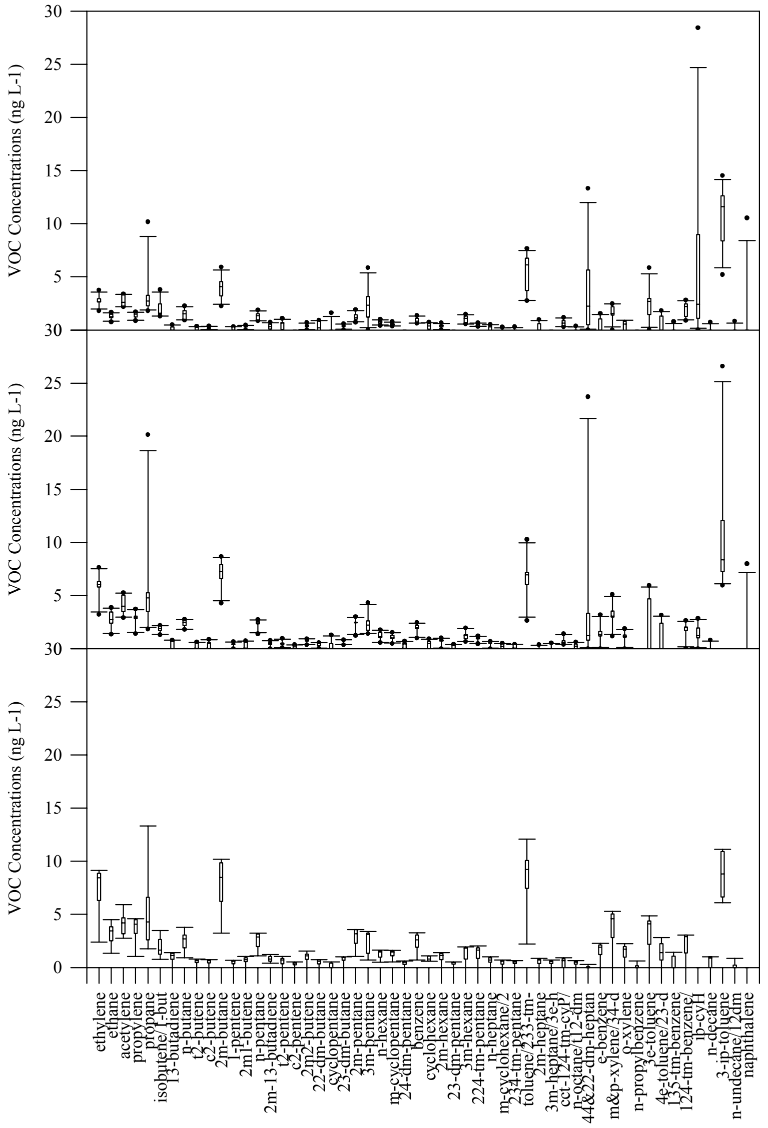


Figure 4.33. Slater Street Nose-Level VOC Data for Summer Sampling Campaign a) morning session b) noon session c) afternoon session.

As the results of Ottawa campaign compared with Ankara results, it is seen that toluene is the third most abundant compound in Ottawa, whereas in Ankara it is the most abundant compound. This is due to differences in sampling protocols of Ottawa and Ankara studies, where C2-C12 VOCs were measured in Ottawa whereas C5-C12 VOCs were measured in Ankara. Another difference is the dominance of heavy hydrocarbons in Ankara more than that observed in Ottawa. Many heavy hydrocarbons such as nonane and naphthalene are more abundant in Ankara than they are in Ottawa. This is due to influence of diesel vehicle emissions in Ankara more than that is observed in Ottawa as explained in detail in Chapter 5. Total VOC concentrations in Ankara (about 101 $\mu g\ m^{-3}$) and in Ottawa (about 99 $\mu g\ m^{-3}$) are seem to be similar but this is due to differences in compound set measured in both cities. Thus, the total absolute VOC concentrations cannot be compared directly.

4.2.3. Temporal Variations

4.2.3.1 Seasonal Variations

Summary statistics of the abundant VOCs measured at the roadside station are shown in Table 4.13. Median concentrations of most of the olefins and paraffins measured during winter campaign are about 1.5 to 2 times higher than summer concentrations. Concentrations of the aromatics, however, are almost same in two seasons. The median total VOC concentrations are also very similar in two seasons although the maximum concentrations measured during winter are about factor of 2.5 higher than that were measured during summer.

For most compounds measured at nose-level station, winter concentrations are higher than or comparable to their concentrations measured in summer campaign. This can be seen in Figure 4.34, where winter to summer concentration ratios of selected 31 VOC’s are plotted. The selection is based on completeness of the data. Hydrocarbons shown in the figure can be tentatively divided into three groups based on their winter to summer concentration ratios. Eleven of the VOCs shown in the figure, including n-butane, isobutane, ethane, acetylene, propane, ethylene, 1-butene, propylene, c2-butene, 1,2,4-trimethylbenzene and t2-butene have significantly higher concentrations in winter.

Table 4.13. Summary statistics of selected VOCs measured at roadside station.

Compounds	**Summer Concentration (μg m^{-3})**		**Winter Concentration (μg m^{-3})**	
Olefins				
Ethylene	6.48	(2.32-9.13)[a]	9.90	(0.20-38.14)
Acethylene	2.76	(0.87-4.49)	5.60	(1.87-31.95)
Propylene	3.05	(0.91-4.58)	4.37	(0.96-17.94)
1-Butene	1.80	(0.76-3.50)	2.79	(0.53-13.07)
Paraffins				
ethane	4.24	(2.47-5.91)	6.38	(0.20-13.71)
Propane	4.75	(0.20-20.12)	6.48	(2.68-29.35)
Isobutane	2.16	(0.94-3.12)	5.19	(0.20-14.60)
n-Butane	2.64	(0.92-3.78)	6.51	(1.62-20.92)
n-Pentane	2.56	(1.11-3.73)	3.15	(0.82-12.88)
3-Methylpentane	2.25	(0.71-4.32)	2.25	(0.44-11.10)
n-Hexane	1.21	(0.51-1.94)	1.61	(0.04-8.12)
Methylcyclopentane	1.26	(0.05-1.83)	1.29	(0.06-7.16)
2,3-Dimethylbutane	0.84	(0.03-1.02)	0.84	(0.20-4.14)
2-Methylpentane	2.63	(1.00-3.57)	3.11	(0.62-16.15)
2-Methylhexane	0.90	(0.20-1.39)	1.06	(0.20-6.93)
3-Methylhexane	1.30	(0.02-1.94)	1.33	(0.03-7.70)
2,2,4-Trimethylpentane	1.01	(0.20-2.04)	1.35	(0.05-8.56)
Aromatics				
Benzene	2.18	(0.72-3.26)	2.61	(0.73-12.40)
Toluene	7.23	(2.21-12.09)	7.22	(1.86-60.01)
Ethylbenzene	1.48	(0.20-3.18)	1.33	(0.20-9.44)
m/p-Xylene	3.24	(0.20-5.27)	3.16	(0.20-26.41)
o-Xylene	1.19	(0.20-2.25)	1.42	(0.20-10.53)
1,2,4-Trimethylbenzene	2.03	(0.20-3.04)	1.85	(0.20-18.72)
Total VOC	99.81	(33.74-195.73)	100.24	(23.19-530.16)

[a] *Median concentrations. Values in parenthesis denote ranges.*

Winter to summer concentration ratios for this group of VOC's vary between 2.8 for n-butane and 1.5 for t2-butane. The second group, including 2-methylhexane, 2,2,4-trimethylpentane, 2-methylpentane, n-heptane, benzene, n-pentane, n-hexane, m-xylen, p-xylene and o-xylene have higher concentrations in winter, but the difference between their winter and summer concentrations are not as large as the differences observed in the first group. Winter to summer concentrations ratios for these compounds vary between 1.4 and 1.2. Remaining 8 VOCs, including methylcyclopentane, 3-methylhexane, ethylbenzene, 2,2-dimethylbutane, 2,4-dimethylpentane, 3-methylpentane, 2-methylbutane, and 2,3-dimethylbutane have comparable concentrations in winter and summer seasons.

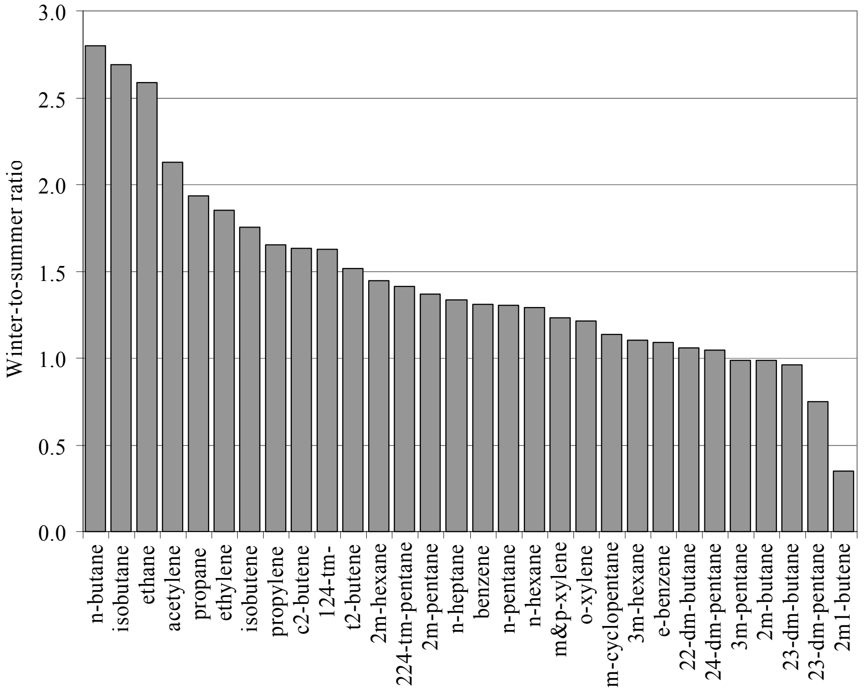


Figure 4.34. Winter to summer concentration ratios of selected VOCs.

There are three parameters that can cause observed seasonal variation in the concentrations of measured VOCs, namely variations in meteorology, emissions and reactivity. Variation in meteorological parameters, particularly variations in mixing height, can result in differences between summer and winter concentrations of VOCs and tends to favor higher concentrations in the winter seasons, as discussed previously. However, variation in meteorology is expected to have the same effect on all measured parameters and cannot explain different winter to summer ratios of different groups of VOCs.

Differences in VOC emissions between summer and winter seasons can also result in observed difference between summer and winter concentrations of measured compounds. Vehicle emission factors, for example, show higher exhaust emissions in winter since it takes longer for catalytic converter to reach its operation temperature. Thus, some VOCs with well-known gasoline exhaust source are in different groups in terms of their winter to summer concentration ratios. Consequently, observed trend in VOC concentrations can partially be explained by different emissions in the summer and winter seasons.

Higher reactivity of VOCs in summer is probably the main reason for observed difference in their concentrations in the two seasons. Higher reactivity of light paraffins and olefins compared to heavy paraffins and aromatic compounds (EPA, 1999) can explain respectively lower summer to winter concentration ratios of light and more reactive compounds in Figure 4.34.

Seasonal variation differs for individual compounds both in Ankara and Ottawa datasets. However, higher winter concentrations for most of the VOCs are observed at roadside stations in both Ankara and Ottawa. Benzene, toluene and 1,2,4-trimethylbenzene concentrations are statistically significantly higher in winter at roadside station in Ankara. However, winter and summer concentrations of these compounds are similar in Ottawa. This could be due to reactivity issue as discussed in the previous paragraphs and partly due to traffic emissions. It should be noted that total number of vehicles recorded during Ottawa campaign do not show significant winter to summer variation whereas they do in Ankara campaign. This is due to differences in living styles in Canada and Turkey. In Turkey most of the people take their annual vacation on summer and travel to costal cities thus vehicle number decrease in cities like Ankara resulting in decrease in traffic emissions.

4.2.3.2 Daily Variations

Daily variation in total VOC data measured at nose-level station during winter and summer campaigns are shown in Figure 4.35 and Figure 4.36, respectively. During the winter campaign total VOC concentrations show a weekday to weekend variation. In the Figure 4.35, January 22, 23, 29, 30 and 5 February are weekend days. Concentrations are lower on these days especially during the afternoon sessions. Concentrations also show variation in weekday. High concentrations are observed on Friday. It is not possible to discuss weekday to weekend and daily variations during summer campaign due to limited number of data measured. However, it is seen from Figure 4.36 that total VOC concentrations measured during morning and afternoon sessions were lower on 30th July that was the only weekend day in the summer data set for 2-hr measurements. The statistical evaluation of the weekday vs. weekend variation in measured VOC data is not done due to insufficient data.

Evaluation of daily variations in Ankara data resulted in identification of pollution episodes occurred in summer owing to long-term observations. Measurements were only conducted for one week in summer in Ottawa. Winter data generated in Ottawa suggest substantial daily variations in VOC concentrations. However, such variations are not observed at roadside station in Ankara during winter. This could be due to limited number of data (only one week) generated in Ankara at roadside station.

4.2.3.3 Diurnal Variations

Concentrations of selected VOCs in morning, mid-day and afternoon sampling periods in two seasons are shown in Figure 4.32 and Figure 4.33 for winter and summer, respectively. Although the concentrations of hydrocarbons measured are comparable in the morning and noon periods, concentrations of all measured hydrocarbons are higher in the afternoon sampling period.

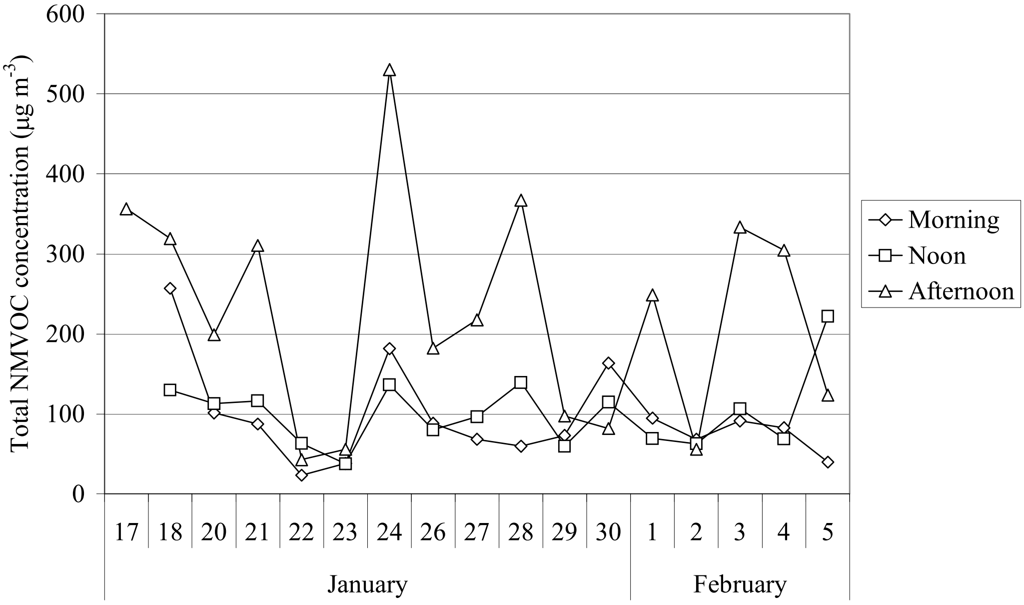


Figure 4.35. Daily variations in the Total VOC concentration-Winter 2000.

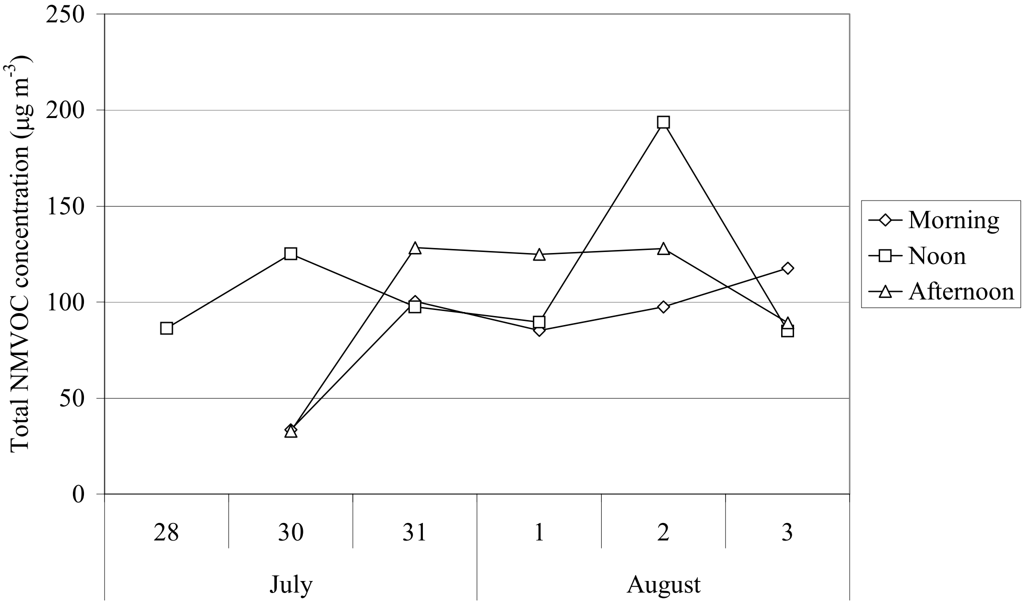


Figure 4.36. Daily variations in the Total VOC concentration-Summer 2000.

The difference between afternoon and noontime concentrations is similar for all measured hydrocarbons. This observed difference in concentrations is attributed to higher number of vehicles in the street during afternoon hours. In this study number of vehicles passing through the street was also recorded for each sampling period. Traffic counts for LDV, coach bus, articulated bus, HDV are shown in Figure 4.30. It is clear from the figure that number of vehicles passing through the street is comparable during morning and noon-time sampling periods and the highest during afternoon sampling period, which coincides with observed diurnal variation in concentrations of VOCs.

The observed diurnal trend in concentrations of VOCs is more pronounced in winter. Although VOC concentrations in summer samples are also highest in the afternoon, the difference in concentrations measured in afternoon and noontime is smaller than the corresponding difference observed in winter. The average afternoon to noon concentration ratio is 2.5 ± 0.9 in winter and 1.3 ± 0.3 in summer. Although the number of vehicles passing through the street at each summer session is slightly lower than corresponding counts in winter, the difference is too small to account for observed large difference in concentrations. Smaller afternoon - noontime difference in the summer season is probably due to differences in meteorological parameters and most likely due to variations of mixing height in summer and winter seasons. The inverse relation between the mixing height and concentrations of pollutants is well established and the mixing height is the largest in summer and in the afternoon (Yatın *et al.*, 2000; Fatogoma and Jacko, 2002). Consequently, the increase in concentrations of VOCs at afternoon session can be compensated with decrease in concentrations due to deeper mixing height at the same sampling session in summer.

Diurnal variations well agreed with traffic pattern in both Ankara and Ottawa data for most of the compounds. This indicates that the motor vehicle related emissions dominate the VOC concentrations measured at roadside stations in both cities.

4.2.3.4 Carbonyl Compounds

A total of 64 samples were collected at nose-level sampling station during winter and summer. Among the 25 target compounds only three were detected at most of the time. The most abundant carbonyl compounds are formaldehyde, acetaldehyde and acetone in the order of decreasing concentrations. The motor vehicle exhaust is the most important source of carbonyl compounds in urban areas. Carbonyl compounds are also key compounds of photochemically generated air pollution (Christensen *et al.*, 2000). Formaldehyde is the most abundant atmospheric aldehyde, followed by acetaldehyde during both summer and winter campaigns. The median concentrations of formaldehyde and acetaldehyde in summer are 0.0051 μg m^{-3} and 0.0027 μg m^{-3}, respectively. In winter, the median concentrations of formaldehyde and acetaldehyde are 0.003 μg m^{-3} and 0.0023, respectively.

Diurnal variation in concentrations of formaldehyde and acetaldehyde are given in Figure 4.37 and Figure 4.38, respectively. Twenty-four hour averages of these compounds are also shown in the figures. Daily average concentrations of formaldehyde and acetaldehyde are smaller than the average values obtained from three short-term sampling performed during the day, indicating that nighttime concentrations of formaldehyde and acetaldehyde are lower than values measured during daytime as expected.

There is a clear diurnal trend in formaldehyde and acetaldehyde concentrations during summer. The highest concentrations are measured in 15:30 samples and lowest concentrations are measured in 7:30 samples. This diurnal pattern is expected, because both formaldehyde and acetaldehyde are secondary compounds produced in the atmosphere by the reactions involving hydrocarbons, NO and HO, their diurnal pattern is determined by the variation of NO and hydrocarbons and solar flux during day time. Higher concentrations of these compounds in the afternoon hours were observed by other researchers (Christensen *et al.*, 2000; Viskari *et al.*, 2000). Diurnal variations are not significant during winter.

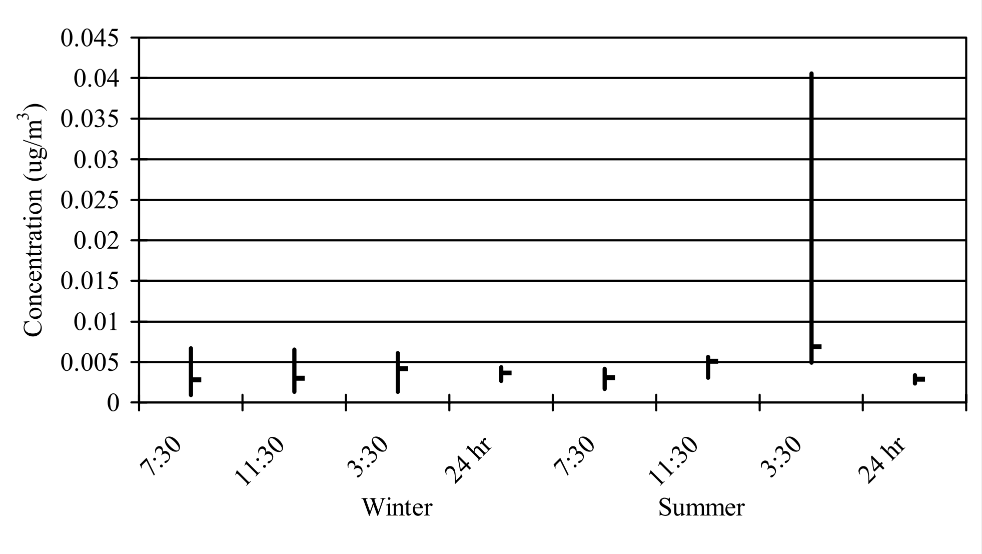


Figure 4.37. Diurnal variations in the formaldehyde concentrations.

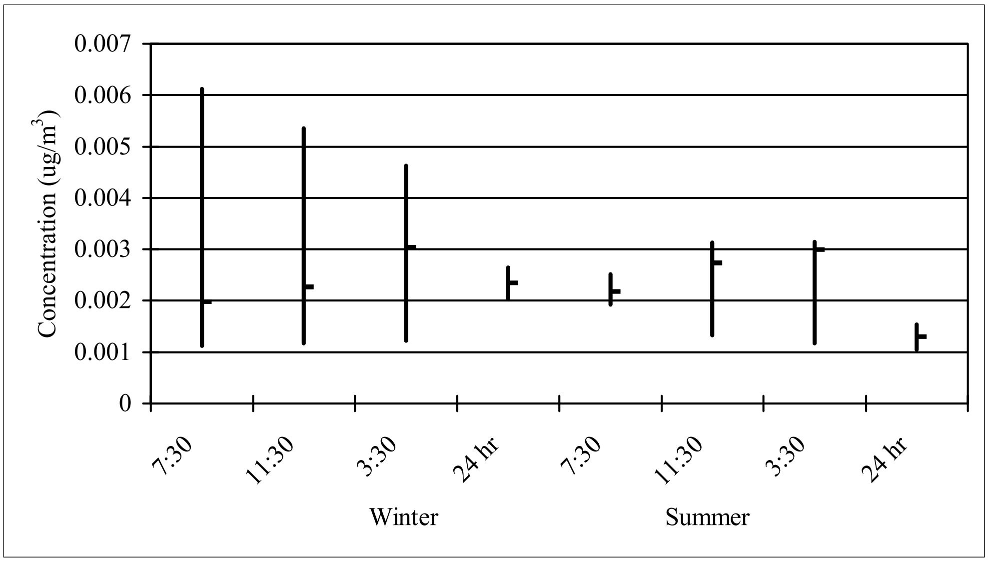


Figure 4.38. Diurnal variations in the acetaldehyde concentrations.

Daily average concentrations of formaldehyde are comparable in winter and summer periods. However, 24-h averages of acetaldehyde concentrations are significantly higher in winter. One would expect higher concentrations of photochemical reaction products in summer due to more extensive photochemical activity in summer season. Observed higher concentration of acetaldehyde in winter and comparable concentrations of formaldehyde in the two seasons is probably owing to higher concentrations of precursor hydrocarbons in winter, as discussed previously, which compensates higher production in summer due to enhanced photochemical activity. Statistical test for summer and winter comparison was not accomplished, as the number of data recorded in summer are few.

4.2.4. Spatial Variations

4.2.4.1 Rooftop vs. Nose-level

Summary statistics of VOCs collected at rooftop sampling station are presented in Table 4.14. Median concentrations of VOCs collected daily for 21 days in winter and 7 days in summer are shown in this table. Concentrations of all measured VOCs, except for 3-methylpentane are lower in the rooftop samples than in the nose-level samples. This is expected due to closer proximity of nose level sampling site to vehicle emissions. The difference varies between factor of 3.0 and 1.3 in winter and between 2.0 and 1.4 in summer samples. This may be due to higher mixing height in summer and approximately 10 m distance between the points where nose-level and rooftop samples were collected.

4.2.4.2 In-car vs. In-bus

Concentrations of the selected VOCs, total VOC, formaldehyde and acetaldehyde measured at in-car and in-bus during winter and summer campaigns are presented in Table 4.15 and Table 4.16, respectively. Toluene, m,p-xyelene and benzene were among the most abundant species observed at in-vehicle samples.

Concentrations show diurnal variation both in summer and winter campaigns. Morning concentrations of most of the VOCs measured in in-car are higher than afternoon concentrations during both summer and winter. Concentrations measured in-bus are higher in afternoon during winter campaign and higher in morning during summer campaign. The 1,3-butadiene is not detected both in-car and in-bus environments during winter campaign.

In-car to in-bus concentration ratios are presented in Figure 4.39 and Figure 4.40 for winter and summer campaigns, respectively. Benzene and toluene concentrations are significantly higher in the in-car samples.

Table 4.14. Summary statistics of selected VOCs measured at rooftop station.

Compounds	**Summer Conc. ($\mu g\ m^{-3}$)**		**Winter Conc. ($\mu g\ m^{-3}$)**	
	Median	**Range**	**Median**	**Range**
Olefins				
Ethylene	2.65	(1.79-3.74)	3.52	(1.93-6.78)
Acethylene	1.24	(0.74-1.65)	2.63	(1.36-4.72)
Propylene	1.49	(0.86-1.69)	1.58	(0.85-2.80)
1-Butene	1.59	(1.28-3.79)	1.12	(0.64-4.78)
Paraffins				
ethane	2.60	(2.18-3.39)	5.26	(4.41-5.90)
Propane	2.72	(1.80-10.17)	3.28	(2.52-4.60)
Isobutane	1.39	(0.87-1.98)	2.44	(1.51-4.11)
n-Butane	1.52	(0.92-2.24)	3.71	(2.21-5.83)
n-Pentane	1.33	(0.85-1.87)	1.84	(0.91-2.49)
3-Methylpentane	2.33	(0.00-5.85)	1.68	(1.03-1.75)
n-Hexane	0.76	(0.41-0.98)	0.88	(0.39-1.20)
Methylcyclopentane	0.52	(0.36-0.77)	0.64	(0.20-1.01)
2,3-Dimethylbutane	0.37	(0.00-0.58)	0.42	(0.20-0.61)
2-Methylpentane	1.16	(0.72-1.90)	1.61	(0.61-2.28)
2-Methylhexane	0.41	(0.00-0.67)	0.33	(0.20-1.09)
3-Methylhexane	1.09	(0.55-1.46)	0.72	(0.20-0.97)
2,2,4-Trimethylpentane	0.52	(0.32-0.65)	0.73	(0.20-1.13)
Aromatics				
Benzene	0.83	(0.62-1.34)	1.29	(0.69-1.76)
Toluene	6.12	(2.75-7.66)	3.08	(1.19-4.66)
Ethylbenzene	0.00	(0.00-1.54)	0.49	(0.20-2.33)
m/p-Xylene	1.56	(0.00-2.46)	1.82	(0.20-3.15)
o-Xylene	0.55	(0.00-0.92)	0.53	(0.20-1.88)
1,2,4-Trimethylbenzene	2.21	(0.88-2.80)	1.38	(0.20-4.11)
Total VOC	75.22	(43.01-110.22)	61.91	(27.01-119.99)

Table 4.15. In-vehicle concentrations of selected compounds-Winter 2000.

Compound	Sampling Period	Summer Conc. (μg m^{-3})		Winter Conc. (μg m^{-3})	
		Median	Range	Median	Range
Benzene	AM	4.29	(2.17-12.13)	2.81	(1.58-7.39)
	PM	4.22	(1.99-8.95)	3.33	(2.17-5.33)
Toluene*	AM	14.74	(4.23-77.73)	7.39	(4.27-25.99)
	PM	10.78	(7.54-30.96)	8.90	(5.60-17.55)
Ethylbenzene	AM	2.83	(BDL-17.94)	2.12	(1.18-7.80)
	PM	1.99	(BDL-6.35)	2.34	(1.46-3.75)
m,p-xylene*	AM	8.28	(2.82-58.12)	6.15	(BDL-18.86)
	PM	6.04	(3.33-16.07)	7.05	(4.22-10.47)
o-xylene	AM	3.01	(BDL-22.42)	2.61	(1.29-8.17)
	PM	2.51	(1.02-5.97)	3.04	(1.61-4.63)
1,3-butadiene	AM	BDL	BDL	BDL	BDL
	PM	BDL	BDL	BDL	BDL
TVOC	AM	221.71	(107.12-650.44)	175.12	(134.15-486.07)
	PM	236.86	(114.87-402.27)	212.41	(146.94-335.29)
formaldehyde	AM	0.0069	(BDL-0.01)	0.009	(BDL-0.02)
	PM	0.0065	(BDL-0.01)	0.0092	(0.01-0.02)
acetaldehyde	AM	0.003	(BDL-0.01)	0.0056	(BDL-0.01)
	PM	0.0016	(BDL-0.01)	0.0058	(BDL-0.01)

* *Peak resolutions by the GC are actually: toluene/2,3,3-tm-pentane, m,p-xylene, 3,4-dm-heptane.*

Table 4.16. In-vehicle concentrations of selected compounds-Summer 2000.

Compound	Sampling Period	Summer Conc. (μg m^{-3})		Winter Conc. (μg m^{-3})	
		Median	Range	Median	Range
Benzene	AM	5.61	(2.36-7.34)	3.66	(2.08-5.49)
	PM	5.32	(2.51-8.42)	3.13	(2.11-5.37)
Toluene*	AM	15.09	(6.76-30.52)	12.14	(5.17-20.90)
	PM	13.48	(6.97-39.15)	10.40	(7.28-18.84)
Ethylbenzene	AM	2.91	(BDL-4.36)	3.38	(2.11-11.04)
	PM	2.54	(1.41-7.58)	3.19	(1.66-4.09)
M,p-xylene*	AM	6.08	(2.34-9.61)	6.72	(3.99-13.84)
	PM	5.53	(2.19-11.99)	5.65	(3.80-10.90)
o-xylene	AM	2.18	(0.79-3.38)	3.00	(1.44-5.31)
	PM	2.17	(0.81-4.15)	2.25	(1.65-4.62)
1,3-butadiene	AM	1.22	(BDL-2.60)	1.22	(BDL-2.07)
	PM	1.27	(BDL-2.55)	1.08	(BDL-2.15)
TVOC	AM	173.75	(86.75-236.55)	235.21	(164.18-432.39)
	PM	172.31	(92.88-351.11)	186.27	(152.17-346.70)
formaldehyde	AM	0.0102	(0.01-0.01)	0.0102	(0.01-0.01)
	PM	0.0108	(0.01-0.01)	0.0108	(0.01-0.01)
acetaldehyde	AM	0.0066	(BDL-0.01)	0.0066	(BDL-0.01)
	PM	0.0058	(BDL-0.01)	0.0058	(BDL-0.01)

* *Peak resolutions by the GC are actually: toluene/2,3,3-tm-pentane, m,p-xylene, 3,4-dm-heptane.*

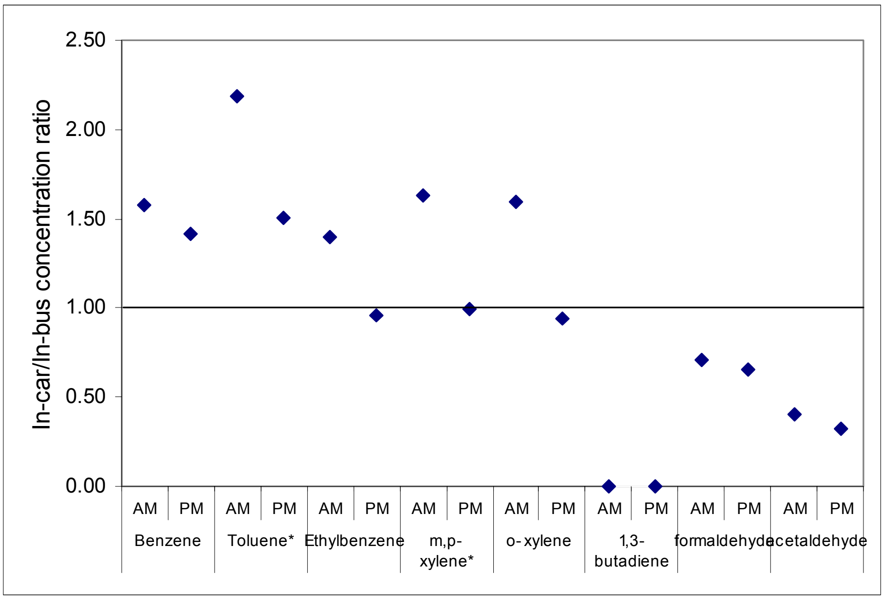


Figure 4.39. In-car to in-bus mean concentration ratio-Winter 2000.

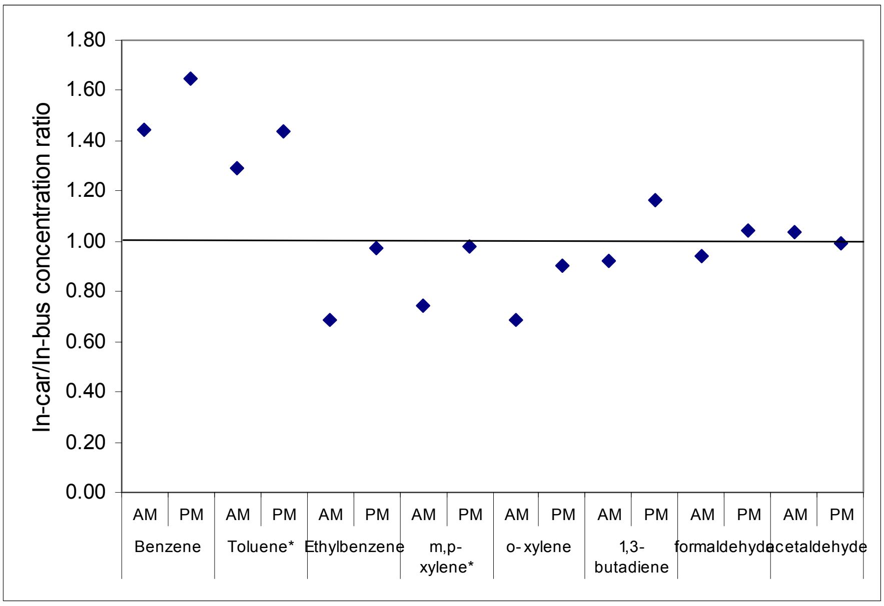


Figure 4.40. In-car to in-bus mean concentration ratio-Summer 2000.

Concentrations of ethylbenzene, m,p-xylene and o-xylene are higher in the in-car samples collected during morning session and do not show variation during afternoon session of winter campaign. Concentrations of these compounds are slightly higher in the in-bus samples collected during summer campaign.

During the winter campaign windows were closed at both car and bus during commuting. Thus, VOC sources inside the vehicles and intrusion from outside air were the major VOC sources measured in vehicles. Materials used to make accessories of passenger cars are significant VOC sources. This might be the reason for higher concentrations measured in car during winter season. During the summer season, however, the car and bus were ventilated and thus the ambient air was the major source during commuting. Therefore, there was not significant difference in concentrations measured in both car and bus. The in-vehicle difference is obvious for benzene and toluene during both summer and winter campaigns. These compounds are emitted from gasoline vehicles and the commuting route of the car that is mostly occupied by passenger cars might be the reason for higher abundance of these compounds measured in car than in bus.

4.2.4.3 Ambient vs. In-vehicle

Concentrations of organic compounds measured at nose-level and in-vehicle environments were compared with ratio analysis. Results for selected compounds are shown in Table 4.17. The concentrations measured in-vehicle are significantly higher than ambient concentrations except BTEX concentrations measured in bus during winter campaign. During winter campaign, BTEX concentrations measured in bus are same or slightly higher than ambient concentrations. The higher BTEX ratio observed for the in-bus samples during summer campaign is due to increase in the in-bus concentrations and decrease in the ambient concentrations during summer campaign.

Table 4.17. Ambient vs. in-vehicle variation in the concentrations of selected compounds.

	Winter		**Summer**	
Compound	**Car/Amb.**	**Bus/Amb.**	**Car/Amb.**	**Bus/Amb.**
Benzene	1.19	0.80	2.47	1.60
Toluene	1.25	0.67	2.02	1.49
Ethylbenzene	1.24	1.04	2.12	2.62
m,p-xylene	1.26	0.95	1.89	2.23
o-xylene	1.37	1.06	1.86	2.38
TVOC	2.29	1.93	1.73	2.11
formaldehyde	1.72	2.34	1.28	1.28
acetaldehyde	0.81	2.02	2.59	2.59

4.2.5. Summary of Findings

Traffic pattern was observed in the concentration of most of the VOCs measured at nose-level station during both summer and winter campaigns. As expected the motor vehicles are the major source in the study area. Propane is among the most abundant compounds indicating LPG use might also be an additional source in the area. Temporal variation is observed in the VOC and carbonyl data collected during Ottawa campaign. Concentrations measured at the roadside station are higher during winter campaign. There is a significant spatial variation in the VOC data. In-vehicle concentrations are higher than that are measured at ambient stations.

There is a clear contrast between the set of sampling locations in the Ankara and Ottawa studies. The sampling stations in Ankara expected to be impacted to varying degrees by the strength of motor vehicle emissions (background, residential, roadside). The sampling in Ottawa (roadside, street canyon (rooftop), and in-vehicle during peak commuting periods) was all done in microenvironments where we might expect the impact of motor vehicle emission strength to dominate the measurements. Although the list of compounds is not the same due to sampling methodology differences between the studies (canister vs.

sorbent tubes) there is an overlapping list of compounds, which could be used to compare results of both cities.

Roadside measurements in Ankara show more similar temporal variation as observed for Ottawa measurements than residential and background measurements. Concentrations for most of the VOCs are higher in winter at both sites. Diurnal variations in VOC concentrations measured in both cities showed traffic pattern indicating influence of motor vehicle emissions on roadside stations. Heavy hydrocarbons are more abundant in Ankara than in Ottawa although number of HDVs recorded at both sites does not have a significant share. This indicates small number of HDVs result in large VOC emissions owing to poor inspection and maintenance of these vehicles in Ankara. Fuel compositions are also different in both cities resulting in increased emissions (especially aromatics as explained in previous chapters) in Ankara.

4.3. Comparison of the Results with the Literature

Comparison of absolute concentrations of VOCs measured at different cities is quite a challenging task as there are many parameters that affect differences. Sampling and analytical protocol including sampling duration, sampler location, sampler height, season and year when data was collected affect ambient concentrations as well as sampling technique and analytical method. Population of city and emission characteristics such as industries and traffic emission are also determining factors.

Concentration varies at residential, background and roadside stations as discussed in the previous sections. Differences are pronounced also at indoor and ambient locations. Therefore, in this section only the results of roadside stations are compared. Sampling duration and sampling frequency also influence the results. Peak concentrations can be observed by frequent and short duration sampling protocol. Nighttime concentrations are significantly lower than daytime concentrations as discussed earlier in this chapter. Thus, comparison of a 24-hr data and daytime data must be done with concern. Rooftop and roadside VOC data measured at Ottawa show that sampler height determines VOC concentrations (i.e., concentrations are lower at higher stations due to enhanced dilution driven by atmospheric mixing). Therefore, sampler height must also be considered for comparison.

VOC concentrations show seasonal variations as discussed in the previous sections. Winter concentrations are higher than summer concentration at both Ankara and Ottawa. Thus sampling season should be known for comparison. Ambient VOC concentrations were much higher in early 1990s in USA and Canada. Levels decreased by recent years by enforcement of regulations to control emissions from solvent use, motor vehicles and industries (USEPA, 1999). Similar decreasing trend was also observed at some of the European countries (EEA, 2003). Therefore, it is important to know data year for comparison.

There is not a unique sampling and analytical procedure to measure VOCs in ambient air. Thus studies in literature show variations in terms of their methodologies. It is not possible to find identical studies for comparison in the literature. Comparison of the data in literature is rational with clear identification of influencing parameters discussed in previous paragraph. Therefore, the studies presented in Table 4.18 are discussed in the following paragraph prior to comparison. Similar studies as mush as they can and recent studies are selected for comparison.

Average concentrations of VOCs measured between 1989-1990 at 25 stations in Toronto, Canada operated by Ontario Ministry of Environment (Kendall, 1993). Sampling interval was 1-hr and data belongs to daytime measurements. Sampling height was 1.5 m. Stations were located at roadside where traffic density changed from low to very high at 25 sites in metropolitan Toronto.

Metropolitan Hong Kong is an industrial city with a 6.8 million population (Chan *et al.*, 2002). Ambient VOC samples were collected at four roadside stations namely; urban industrial, urban commercial, old commercial and residential, and central business on January-February 1998 for 9 days. Samples were collected twice daily between 12:00-14:00 and 16:00-18:00 at a height of 1.5 m. Adsorbent tubes were used to collect samples. Data presented in Table 4.18 is the average of all roadside stations.

Derwent *et al.* (2000) reported VOC data measured at two roadside stations in London, UK. Data was collected at a height of 2 m from ground. On-line GC instrument was used for semi-continuous hourly measurements. Data presented in Table 4.18 is annual averages of the year 1996. VOC concentrations measured at Lille, France for two years between 1999 and 2000 were reported by Borbon *et al.* (2002). Hourly samples were collected by on-line GC instrument at a height of 3 m from ground.

Rappengluck *et al.* (1998) reported VOC data recorded at Athens, Greece for two months between 20 August and 20 September 1994. Samples were collected by on-line GC at 1-hr intervals. VOC data recorded at urban station in Houston, USA operated by Photochemical Assessment Monitoring Station (PAMS) was reported by Sather *et al.* (1997). Samples were collected between May and October 1996. On-line GC was used to collect samples at 3-hr durations for 24-hr a day.

In a study conducted in İzmir, Turkey VOCs were determined at five different locations that are mostly influenced by traffic emissions during summer of 1998 (Müezzinoğlu *et al.*, 2001). Samples were collected on adsorbent tubes packed with activated charcoal, then solvent extracted by carbon disulfide at the laboratories of Dokuz Eylül University, Turkey and analyzed by GC-FID at the laboratories of University of Stuttgart, Germany. Sampling duration is not provided by Müezzinoğlu *et al.* (2001), it is stated that daytime and nighttime measurements were conducted (except for hourly measurements at some sites). The sampling was conducted only for few days at each site during İzmir study.

The VOC concentrations measured in Ankara and Ottawa campaigns were compared with the literature. Table 4.18 presents the results of roadside stations together with the results of roadside stations in the literature. The VOC concentrations measured in Ankara were about 1.5 times higher for paraffins and about 2.5 times higher for aromatics than the concentrations measured in Ottawa. The VOC concentrations measured at nose-level station in Ottawa were the lowest concentrations when compared with the literature. Thus, it can be concluded that the Ottawa atmosphere were relatively clean in terms of VOC pollution.

İzmir, Athens, Toronto and Hong Kong are among the most polluted cities in terms of VOCs. Toronto VOC data is the oldest data in Table 4.18. This might be the reason for high concentration reported in this city. Hong Kong is an industrial city, which might be the reason for high concentrations. Athens data is rather old which might influence high concentrations but it is obvious that it is not the only reason and this city is a polluted one.

The concentrations were the highest at İzmir, Turkey. The benzene, toluene, ethylbenzene and m,p-xylene concentrations measured at İzmir were about two times higher than the concentrations measured at Athens. Ethylbenzene and m,p-xylene concentrations measured in İzmir were about 10 times and o-xylene concentrations were about 25 times higher than that were measure in Ankara, Hong Kong and London. Hexane concentrations measured in İzmir were about four times higher than that were measured in Toronto, Houston and Hong Kong.

The VOC concentrations measured in Ankara atmosphere were in between concentrations measured in London, UK and Lille, France. Benzene concentrations measured in Ankara were higher than that were measured in London and Lille atmospheres. Toluene, m,p-xylene and o-xylene concentrations were also higher in Ankara atmosphere. The concentrations measured in Ankara were about 10 times lower than that were measured in İzmir. The reasons for such a big difference in measured concentrations could be explained by differences in sampling and analysis protocol, emission sources and meteorology. The sampling was conducted only for few days at each site during İzmir study, thus it is difficult to distinguish if these days were the pollution episode days.

Table 4.18. Comparison of the average VOC concentrations (µg m^{-3}) with the literature.

	This Study				**Literature**						
Compound name	**Ankara Roadside**		**Ottawa Nose-level**		**Toronto, Canada**[1]	**Houston, USA**[2]	**Hong Kong, China**[3]	**London, UK**[4]	**Lillie, France**[5]	**Athens, Greece**[6]	**İzmir, Turkey**[7]
	Winter	**Summer**	**Winter**	**Summer**							
Olefins											
Ethylene			9.90	6.48	12.60	8.60					
Acetylene			5.60	2.76	4.50						
Propylene			4.37	3.05	6.80						
Paraffins											
Ethane			6.38	4.24	28.80	18.83					
Propane			6.48	4.75	24.40	18.21					
Isobutane			5.19	2.16	15.80	10.05					
n-Butane			6.51	2.64	33.00	14.09					
n-Pentane	4.18	2.71	3.15	2.56	16.80	12.18					
n-Hexane	2.83	1.55	1.61	1.21	11.20	14.61	15.60				51.10
Methylcyclopentane	1.45	0.78	1.29	1.26	3.30						
2-Methylpentane	3.88	3.54	3.11	2.63	19.00						
3-Methylhexane	1.74	1.29	1.33	1.30	16.10						
Aromatics											
Benzene	7.24	4.59	2.61	2.18	12.80	6.62	26.70	5.97	2.49	37.38	55.91
Toluene	14.73	10.46	7.22	7.23	69.50	15.94	77.20	13.65	8.75	79.91	104.79
Ethylbenzene	2.94	3.23	1.33	1.48	6.10		3.10	3.17	1.13	17.37	37.35
m/p-Xylene	13.06	8.60	3.16	3.24	25.10	10.00	12.10	9.29	3.08	49.08	82.95
o-Xylene	5.01	3.01	1.42	1.19	7.40		4.60	3.47	1.09	23.89	84.69
1,2,4-Trimethylbenzene	6.58	3.55	1.85	2.03	10.60						34.90
Toluene/Benzene	**2.03**	**2.28**	**2.77**	**3.31**	**5.43**	**2.40**	**2.90**	**2.28**	**3.51**	**2.14**	**1.87**

[1]Kendall, 1993; [2]Sather et al., 1997;[3]Chan et al., 2002; [4]Derwent et al., 2000; [5]Borbon et al.,2002; [6]Rappengluckеt al., 1998; [7]Müezzinoğlu et al., 2001.

Toluene to benzene concentration ratios in addition to absolute concentrations are also provided in Table 4.18. As discussed earlier in this chapter and is discussed in detail in Chapter 5, T:B ratio is an indicator for abundance of motor vehicle related sources. T:B ratios change between 2 and 3 with the exceptions of Toronto (i.e., 5.5), Ottawa-summer (i.e., 3.3) and Lille (3.5). High T:B ratios indicate other toluene sources in these cities in addition to motor vehicle emissions.

CHAPTER 5

RECEPTOR MODELING

Identification and quantification of air pollution source characteristics is an important step in the development of urban and regional air quality control strategies. Receptor modeling, using measurements of pollutant concentrations at one or more sampling sites, is often reliable way to provide information regarding source contributions to air pollution (Paterson *et al.*, 1999).

The receptor-modeling techniques used to identify and apportion sources of VOCs measured during Ankara and Ottawa campaigns have previously been presented in Section 3.3. The Positive Matrix Factorization (PMF) technique was used as the primary tool while two other receptor models namely, Chemical Mass Balance Model (CMB) and Conventional Factor Analysis (CFA) were also used for comparison purposes. Application of the models and the associated results and discussions are provided in the following sections. In addition, preliminary source identification tools are discussed and emission profiles that are generated in this study, to be used in the receptor modeling are provided.

5.1. Ankara Campaign

5.1.1. VOC Emission Profiles Generated for Ankara

The development of certain receptor models, such as CMB, for the determination of sources of ambient air pollutants requires that the composition of the pollutant at the point of emission should be known. The composition pattern of species emitted from a source category is referred to as a source profile or an emission profile. An emission profile can be expressed as the weight fraction, which is a ratio of each compound to the total mass of compounds in the source emission. Accurate speciated source profiles are needed for a successful development of emission control strategies. VOC source profiles have been developed for several urban areas of the U.S.A., Canada, Japan and Australia (Wadden *et al.*, 1986; Conner *et al.*, 1995; McLaren *et al.*, 1996; Sagebiel *et al.*, 1996).

In Turkey, VOC emission inventories have not been generated yet. However, it is postulated that potential major emission sources of VOCs in Ankara could be motor vehicles, residential heating and solvent use as explained in Section 3.1. Among these emission sources, emission profiles for motor vehicles including several fuel profiles are generated for Ankara during this study. The source categories for which the emission profiles are generated include running vehicle exhaust, cold-start, hot-soak (evaporative), whole gasoline, headspace gasoline, whole diesel and headspace diesel. Emission profiles generated in this work are presented, discussed and compared with the profiles available in the literature in the following sections.

There are only a very few researches attempted at developing VOC emission profiles for Turkey during the last few years. Önoğlu and Atımtay (2002) studied emission factors for BTEX compounds in exhaust gases of widely used six passenger cars at different road conditions in Turkey. Üner *et al.* (2000) investigated hydrocarbon compositions of exhaust gases emitted from vehicles equipped with catalytic converters. The profiles developed in this study are considered significant in providing new information to the literature on VOC emission profiles, which include a variety of sources and conditions, and a wide range of compounds, for Turkey.

5.1.1.1 Fuel Profiles

<u>*Whole Gasoline*</u>

Whole-gasoline profiles can be used to represent emissions of unburned gasoline during cold-start conditions, rapid accelerations, and running losses from saturated fuel-injection systems (Doskey *et al.*, 1999). It has also been known that emissions of VOCs from vehicles are strongly dependent on the composition of the fuel used (Perry and Gee, 1995; Sagebiel *et al.*, 1996; Na *et al.*, 2002). The liquid or whole gasoline profile was developed for Ankara in this study. Liquid gasoline samples that were purchased from two different companies were analyzed as explained in Section 3.1. During the time of the sampling, both unleaded and leaded gasolines were available in the market. The compositions of two different fuel brands, which are sold in Ankara, are shown in Table 5.1. For the comparison, the source profile generated for the whole gasoline is presented for an identical compound set that was also developed for ambient measurements. Therefore, the composition values in weight percent presented in Table 5.1 are normalized values for the compound set ranging from C5 to C12.

Composition of the whole gasoline profiles for Brand-1 and Brand-2 do not show a significant variation for most of the compounds with a deviation of approximately ± 10%. However, heavier aromatic compounds including n-propylbenzene, 3-ethyltoluene, 4-ethyltoluene, 1,3,5-trimethylbenzene, 2-ethyltoluene and 1,2,4-trimethylbenzene have higher contribution in Brand-1 Unleaded Gasoline than Brand-2 Unleaded Gasoline. On the contrary, these compounds have lower contributions in Brand-1 Leaded Gasoline than Brand-2 Leaded Gasoline. This situation results in slight differences in overall contribution of compound groups. For example, contribution of aromatic compounds to Brand-1 Unleaded and Brand-2 Unleaded Gasoline profile compositions are 44% and 40%, respectively. Similarly, total aromatic content of Brand-2 Leaded Gasoline is higher (i.e., 38%) than that of Brand-1 Leaded Gasoline (i.e., 35%). Benzene content of both brands is almost same (i.e., 3%). Toluene content, however, is slightly different for unleaded gasoline. Toluene content is higher in Brand-2 Unleaded Gasoline than that of Brand-1 Unleaded gasoline.

The unleaded and leaded whole gasoline source profiles as mass fraction averaged for the two brands are shown in Figure 5.1. Market sale volumes for different brands were not available in Ankara, thus the averaging did not take sales volumes in to account. This approach, however, did not cause any significant deviation from actual figures since the two gasoline profiles for two brands were very similar. As can be seen from the figure, the most abundant compounds in whole gasoline profile are m&p-xylene, toluene, 2-methyl-pentane, 1-hexene and benzene. Paraffins have the highest contribution with 45% and 47% for unleaded and leaded gasoline profiles, respectively. Aromatics have the second highest contributions for both profiles with 42% and 36% contributions for unleaded and leaded profiles, respectively. Percent weight contribution of aromatic compounds are higher in unleaded gasoline than in leaded gasoline. This indicates that aromatics replaced lead in the unleaded gasoline to increase octane number (Gwilliam *et al.*, 2004). It should be pointed out that if unleaded gasoline is used in vehicles which are not equipped with catalytic converters, emissions of toxic compounds, such as benzene, toluene etc. would increase significantly, because aromatics are freely added to unleaded gasoline to increase the octane number with the assumption that they will be destroyed in the converter and will not be emitted to atmosphere. In Turkey, by the year 2001 vehicles with catalytic converter accounted for about 30% of the fleet (Önoğlu, 2004). Most of the gasoline in use in Turkey is produced by TÜPRAŞ at four refineries located at İzmir, İzmit, Kırıkkale and Batman. According to year 2003 operation report data, 76% of gasoline produced by TÜPRAŞ was unleaded and 24% was leaded gasoline (TÜPRAŞ, 2003).

It is clear from the discussion that if unleaded gasoline with high aromatic content is used by a fleet mostly lacks of catalytic converter it would cause elevated concentrations of toxic aromatics in the ambient air in Turkey. Therefore, the measures to increase number of vehicles equipped with catalytic converter and to decrease aromatic content of unleaded gasoline should be considered. Also, unleaded gasoline should not be sold to the cars that are not equipped with converters. Leaded gasoline will not be produced in refineries in Turkey, starting with the year 2007, which means leaded gasoline will disappear from the market, but vehicles without catalytic converters will not. The decision on immediate phasing out leaded gasoline should be reconsidered.

Table 5.1. Whole gasoline profiles for two different brands.

Compound name	**Brand-1 (Wt %)**		**Brand-2 (Wt %)**	
	Unleaded	**Leaded**	**Unleaded**	**Leaded**
Pentane	2.82	3.47	2.86	3.03
2,2-dimethylbutane	1.80	2.87	1.67	2.76
2,3-dimethylbutane	1.47	2.03	1.35	1.91
t-4-methyl-2-pentene	0.07	0.09	0.07	0.08
2-methylpentane	4.52	5.87	4.17	5.34
c-4-methyl-2-pentene	0.08	0.10	0.08	0.10
3-methylpentane	3.47	4.87	3.62	4.43
1-hexene/2-methyl-1-pentene	6.65	9.24	6.84	8.44
Hexane	2.55	2.68	2.50	2.53
c-3-methyl-2-pentene	2.59	4.06	2.31	4.02
2,2-dimethylpentane	0.35	0.27	0.31	0.25
Methylcyclopentane	1.29	2.04	1.19	2.02
2,4-dimethylpentane	0.50	0.35	0.45	0.36
Benzene	3.16	2.60	3.19	2.64
Cyclohexane	0.45	0.85	0.41	0.80
2-methylhexane	2.03	1.62	2.06	1.64
2,3-dimethylpentane	0.95	0.72	0.90	0.69
3-methylhexane	2.32	1.95	2.43	1.93
1-heptene	0.12	0.13	0.11	0.12
Heptane	1.88	1.44	1.85	1.47
c-2-heptene	2.85	2.09	2.72	2.14
2,2-dimethylhexane	0.07	0.05	0.07	0.05
Methylcyclohexane	0.36	0.48	0.33	0.47
2,5-dimethylhexane	0.14	0.10	0.13	0.10
2,4-dimethylhexane	0.29	0.21	0.27	0.21
Toluene	6.63	7.37	8.97	7.13
3-methylheptane	0.77	0.55	0.71	0.56
c-1,3-dimethylcyclohexane	0.07	0.09	0.06	0.10
2,2,5-trimethylhexane	0.36	0.26	0.34	0.26
Octane	0.49	0.33	0.44	0.35
Ethylbenzene	2.47	1.89	2.41	2.04
m,p-xylene	8.18	7.56	9.20	7.95
o-xylene	4.14	3.33	3.96	3.59
Nonane	0.09	0.05	0.07	0.06
iso-propylbenzene	0.27	0.18	0.20	0.20
n-propylbenzene	1.04	0.70	0.74	0.85
3-ethyltoluene	2.90	2.18	2.18	2.63
4-ethyltoluene	1.76	1.22	1.24	1.45
1,3,5-trimethylbenzene	2.15	1.50	1.40	1.85
2-ethyltoluene	1.11	0.75	0.70	0.92
1,2,4-trimethylbenzene	4.25	3.26	2.88	4.10
iso-butylbenzene	0.06	0.04	0.03	0.05
sec-butylbenzene	0.06	0.04	0.03	0.05
1,2,3-trimethylbenzene	0.90	0.58	0.44	0.77
1,4-diethylbenzene	0.90	0.60	0.32	0.92
Naphthalene	0.15	0.08	0.04	0.14
Paraffins	**43.94**	**48.80**	**47.44**	**46.23**
Olefins	**11.97**	**16.36**	**12.83**	**15.50**
Aromatics	**44.09**	**34.84**	**39.73**	**38.27**

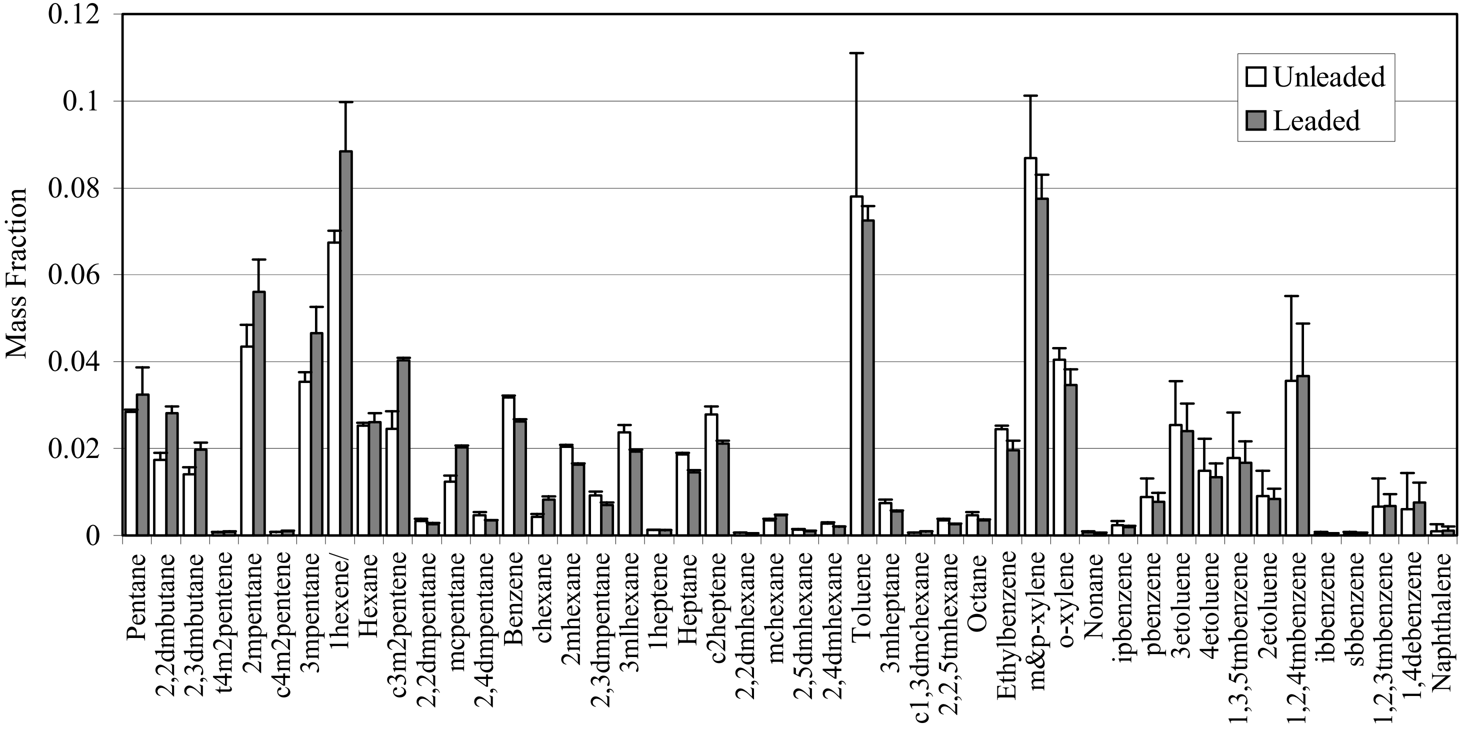


Figure 5.1. Whole gasoline source profiles generated for Ankara.

Whole gasoline profiles developed for Ankara are compared with the profiles available in the literature. Unleaded whole gasoline profile developed for Ankara together with the whole gasoline profiles for Ottawa, Atlanta, Cairo and Seoul are shown in Table 5.2. The data available in the literature are selected so as to enable comparison from different geographical regions. Only the unleaded gasoline profile developed for Ankara was compared with the literature since the data on leaded gasoline profile is scarce in the literature. The whole gasoline profiles for Atlanta and Ottawa are very similar. The Seoul profile has a different composition from rest of the profiles for most of its compounds. Cairo profile has a similar pattern to that of Atlanta and Ottawa except its very high aromatic content including benzene, toluene, ethylbenzene, m&p-xylene and o-xylene.

Ankara profile has a distinct pattern showing similarities to Ottawa, Atlanta and Cairo profiles. Toluene content in the Ankara profile (i.e., 7.8%) is very similar to that of the Atlanta profile (i.e., 8.1%). Benzene content, on the other hand, is about two and three times higher than that of Atlanta and Ottawa profiles, respectively. Benzene content of the Ankara profile (i.e., 3.2%) is same as the Cairo profile. Benzene is a known human carcinogen thus its concentration in gasoline is limited to 1% in the EU and the U.S.A. (Gwilliam *et al.*, 2004). The high benzene content in the Turkish fuel should be decreased by the year 2007 as a requirement of a new regulation on quality of gasoline and diesel fuel that came into force on 11th June 2004 (Official Gazette Number 25489). The use of leaded fuel will be banned by the year 2007 according to the same regulation.

Ethylbenzene, m&p-xylene and o-xylene contents of the Ankara profile is approximately a factor of two higher than that of Atlanta and Ottawa profiles but it is lower than that of the Cairo profile. Contribution of 1,2,4-trimethylbenzene is almost same in all profiles except for the Seoul profile. Percent contributions of total paraffins, olefins and aromatics in all profiles are provided in Table 5.2. The olefin contribution provided in the literature for Cairo is very low indicating that the samples were analyzed for a selected set of olefin compounds. Therefore, olefin content of the Cairo profile was not used for comparison.

Table 5.2. Comparison of the whole gasoline profiles (wt. %).

Compound name	**Ankara, Turkey**[1]	**Ottawa, Canada**[2]	**Atlanta, U.S.A.**[3]	**Cairo, Egypt**[4]	**Seoul, S.Korea**[5]
Pentane	2.84	4.18	2.76	4.91	5.70
2,2-dimethylbutane	1.74	0.37	0.36	0.26	0.80
2,3-dimethylbutane	1.41	0.97	0.88		1.40
2-methylpentane	4.34	3.54	2.88	4.08	6.70
3-methylpentane	3.54	2.22	1.79	2.50	4.50
Hexane	2.53	2.19	1.50	3.98	4.50
Methylcyclopentane	1.24	1.51	1.10	1.30	
2,4-dimethylpentane	0.47	0.65	0.75	0.43	0.90
Benzene	3.18	0.92	1.53	3.20	2.90
Cyclohexane	0.43	0.25	0.25	0.45	0.50
2-methylhexane	2.04	2.23	1.28	2.71	5.00
3-methylhexane	2.38	1.48	1.27	2.71	4.00
Heptane	1.87	0.91	0.85	2.64	2.80
Methylcyclohexane	0.35	0.49	0.57	0.05	1.10
2,4-dimethylhexane	0.28	0.53	0.76	0.60	
Toluene	7.80	6.74	8.11	13.50	12.90
3-methylheptane	0.74	0.70	0.61	1.65	1.30
Ethylbenzene	2.44	1.64	1.80	3.15	1.50
m,p-xylene	8.69	5.56	6.30	12.82	5.20
o-xylene	4.05	2.19	2.60	4.39	2.20
1,3,5-trimethylbenzene	1.78	1.02	1.42	1.91	1.30
1,2,4-trimethylbenzene	3.57	3.26	4.18	3.47	4.80
Naphthalene	0.09	0.29			
Paraffins	**45.69**	**49.88**		**38.20**	**55.60**
Olefins	**12.40**	**10.34**		**1.80**	**8.60**
Aromatics	**41.91**	**32.57**		**47.83**	**30.80**
Total BTEX	**25.85**	**17.06**		**37.06**	**24.70**

[1] *This study;* [2] *CPPI, 1994;* [3] *Conner et al., 1995;* [4] *Doskey et al., 1995;* [5] *Na et al., 2002.*

The contribution of paraffins, olefins and aromatics are not available in the literature for the Atlanta profile. Therefore, data provided by Gwillian *et al.* (2004) was used for the U.S.A. Gwillian *et al.* (2004) provided that aromatic and olefin contents of industry average baseline gasoline profile are 32% and 9.2%, respectively. Comparing the contribution of aromatics for the profiles provided in Table 5.2 yield that Ankara (i.e., 42%) and Cairo (i.e., 48%) profiles have significantly higher aromatic content than the rest. Gasoline specifications in the

EU set a maximum content of aromatics to 35%. Thus, the aromatic content of the Ankara gasoline should be decreased. Ankara gasoline has the highest olefin content (i.e., 12.4%). Maximum olefin content of gasoline is set to 18% in the EU. Thus olefin content of the Ankara gasoline is lower than the EU limit value. Paraffin content of the Ankara gasoline (i.e., 46%) is lower than that of Ottawa (50%) and Seoul (55%) gasoline. This is due to high percent contribution of aromatics in Ankara gasoline. These findings can be summarized as follows:

- Different brands investigated in this study have very similar whole gasoline compositions in Ankara. It is probably because these gas stations received gasoline from the closest thus the same refinery.
- Aromatic content of the Ankara gasoline is high. High contribution of aromatics is distinguished especially for unleaded gasoline indicating aromatics are used as octane enhancers. Fuel oxygenates as additive or reformulated gasoline can be considered to decrease high aromatic content of the unleaded gasoline.
- Use of high aromatic content in the unleaded gasoline in Ankara without introducing catalytic converter to a significant share of the vehicles in use might result in significant increase in the toxic aromatic emissions.
- Benzene content of Ankara gasoline is high (i.e., 3%). According to the new regulation on gasoline and diesel fuels came into force in Turkey in 2004, benzene content will be decreased to 1% as in the EU and the U.S.A.

Headspace Gasoline

Fugitive emissions from gasoline service stations and bulk terminals and hot-soak emission profiles are similar and can be developed from an analysis of the headspace vapor of liquid gasoline (Doskey *et al.*, 1992; Scheff *et al.*, 1996). Gasoline vapor or headspace gasoline profiles are developed in this study in order to resolve evaporative sources in the receptor modeling. Headspace gasoline samples are prepared and analyzed as described in Section 3.1. However, due to analytical problems the data produced by the analysis could not be used in this study. Thus, it is not reported in this section.

Gasoline vapor composition can also be calculated from the liquid gasoline composition and vapor pressure data using Raoult's Law. Mole fraction of components in vapor phase is calculated according to Raoult's Law as given in Eqn. 5.1.

$$y_i = x_i \frac{P_i}{P} \tag{5.1}$$

where y_i is mole fraction of component i in the vapor; x_i is mole fraction of component i in the liquid; P_i is vapor pressure of pure component $i;$ P is total pressure. The vapor pressures of pure components were calculated for a specific temperature by using the Antonie equation, which relates vapor pressure and temperature as shown in Eqn. 5.2.

$$\log P = A - \frac{B}{T + C} \tag{5.2}$$

where, A, B, and C are constants determined by experiment for each individual species (Reid *et al.*, 1998). Gasoline vapor compositions at 20 °C were calculated. Calculated source profiles for unleaded and leaded gasoline vapor are presented in Figure 5.2. Light hydrocarbons are the most abundant species both in unleaded and leaded headspace gasoline profiles as expected due to their very high vapor pressures. Heavy hydrocarbons and aromatics are almost absent in headspace profiles due to low vapor pressures. Most of the abundant light hydrocarbons are paraffins. Contribution of paraffins is higher for leaded gasoline than for unleaded gasoline. On the contrary, contribution of aromatic compounds is higher for unleaded gasoline than for leaded gasoline. It is due to higher aromatic and lower paraffin contents of unleaded whole gasoline profile than that of leaded whole gasoline profile generated for Ankara as explained in the previous section.

Headspace profiles generated in this study is compared with the profiles available in the literature. Headspace profile compositions for the unleaded gasoline in Ankara and the profiles developed in Ottawa, Atlanta, Chicago and Cairo are presented in Table 5.3. Only the unleaded gasoline profile was compared with the literature since the profiles for leaded headspace profile is scarce in the literature. The Ottawa headspace profile was calculated in this study according to Raoult's Law as described earlier for the Ankara profile. Ottawa, Atlanta and Chicago headspace profiles presented in Table 5.3 have very similar compositions. The headspace profile generated for Ankara has a similar pattern but different compositions as for Ottawa, Atlanta and Chicago profiles. Contributions of most of the compounds provided in Table 5.3 are much higher in the Ankara profile than Canada and the U.S.A. profiles. The Ankara profile had a similar composition with the Cairo profile. Contributions of most of the compounds are similar in both profiles. There are few compounds with higher contributions in the Ankara profile namely; 2,2-dimethylbutane, 2-methylpentane, 3-methylpentane, methylcyclopentane, 2-methylhexane and 3-methylhexane.

Benzene contribution was about 4% in Ankara and 3% in Cairo profiles where it was about 0.3% in Ottawa and 0.8% in Atlanta profiles. It was party due to higher benzene content in Ankara and Cairo whole gasoline profiles as explained in the previous section. Ethylbenzene, m&p-xylene and o-xylene contributions in headspace gasoline profiles were less than 1% due to their low vapor pressures.

Diesel Fuel

Liquid diesel fuel profiles can be used to represent emissions of unburned diesel fuel during cold-start conditions, rapid accelerations, and running losses from saturated fuel-injection systems. The liquid and vapor diesel fuel profiles are generated for Ankara in this study. Liquid diesel samples purchased from two different companies were analyzed as explained in Section 3.1. The average compositions of two brands for liquid and vapor compositions are shown in Table 5.4.

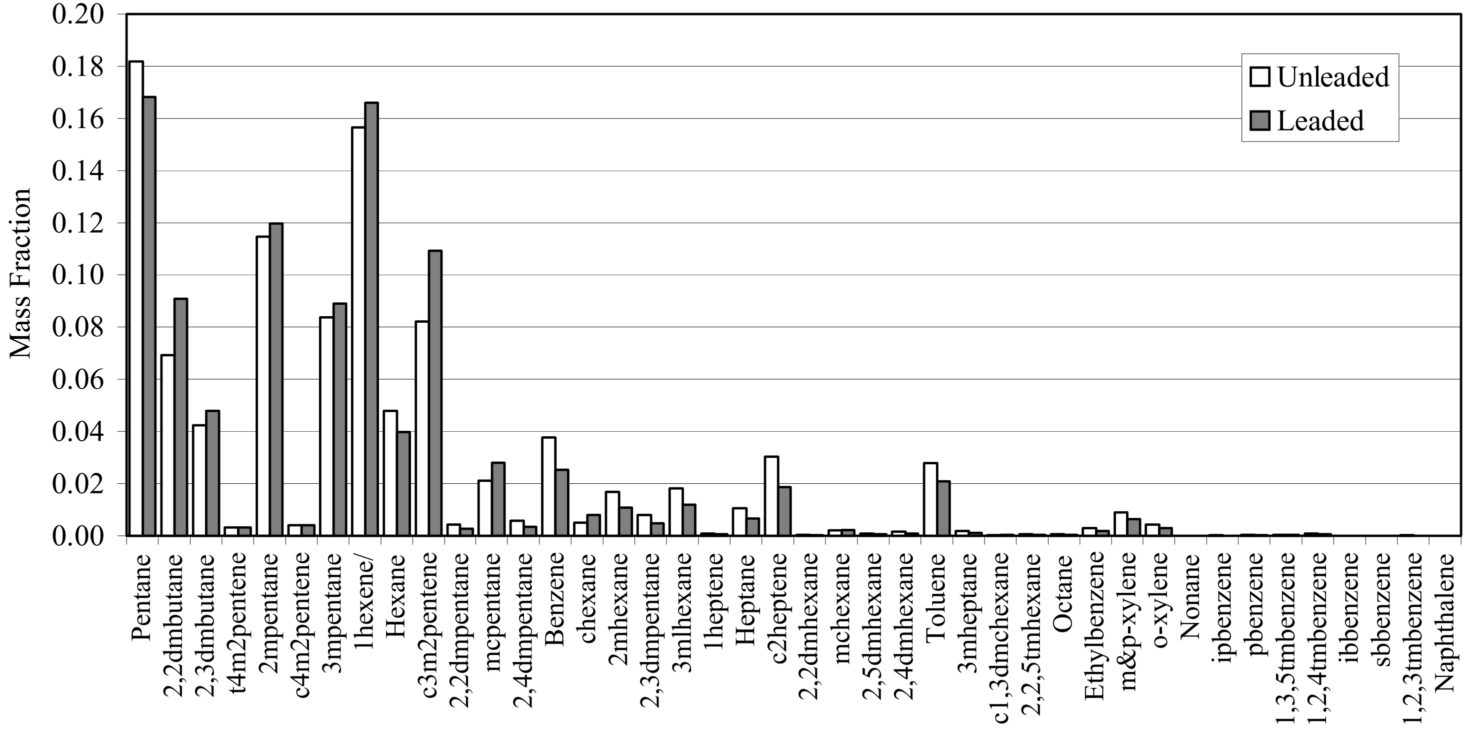


Figure 5.2. Headspace gasoline source profiles generated for Ankara.

Table 5.3. Comparison of the Headspace Gasoline Profiles (wt. %)

Compound name	**Ankara, Turkey**[1]	**Ottawa, Canada**[1]	**Atlanta, U.S.A.**[2]	**Chicago, U.S.A.**[3]	**Cairo, Egypt**[4]
Pentane	18.19	6.58	7.40	9.70	18.24
2,2-dimethylbutane	6.92	0.37	0.68		0.71
2,3-dimethylbutane	4.23	0.72	1.49	2.34	
2-methylpentane	11.47	2.30	3.53	2.27	8.21
3-methylpentane	8.39	1.29	1.93	1.37	3.96
Hexane	4.78	1.02	1.20	2.21	5.05
Methylcyclopentane	2.13	0.64	0.81	0.72	1.51
2,4-dimethylpentane	0.58	0.20	0.52	0.70	
Benzene	3.78	0.27	0.86	0.73	3.03
Cyclohexane	0.52	0.07	0.12		0.43
2-methylhexane	1.68	0.45	0.46		0.75
2,3-dimethylpentane	0.80		0.46	1.10	0.54
3-methylhexane	1.83	0.28	0.44	0.48	0.75
Heptane	1.07	0.13	0.21	0.22	1.09
Methylcyclohexane	0.20	0.07	0.12		
2,5-dimethylhexane	0.10		0.08	0.17	
2,4-dimethylhexane	0.17	0.08	0.15	0.15	0.24
Toluene	2.77	0.59	1.26	1.85	3.74
3-methylheptane	0.18	0.04	0.01		0.31
2,2,5-trimethylhexane	0.07		0.06		
Octane	0.08		0.03	0.04	0.13
Ethylbenzene	0.29	0.05	0.11	0.12	0.18
m,p-xylene	0.89	0.15	0.32	0.33	0.69
o-xylene	0.44	0.06	0.12	0.11	0.17
Nonane	0.00		0.01		
iso-propylbenzene	0.01		0.05		
n-propylbenzene	0.04		0.02	0.01	
1,3,5-trimethylbenzene	0.05	0.01	0.04	0.01	
1,2,4-trimethylbenzene	0.09	0.02	0.11	0.04	
1,2,3-trimethylbenzene	0.01		0.02	0.01	

[1] *This study;* [2] *Conner et al., 1995;* [3] *Doskey et al., 1992.* [4] *Doskey et al., 1995*

Diesel fuel is known to include heavy hydrocarbons and polyaromatic hydrocarbons as organic content. Light hydrocarbons are depleted in diesel fuel. This provides a mean to differentiate between emissions from gasoline and diesel fueled vehicles. It was reported that diesel fuels typically include C9-C26 hydrocarbons with most of the mass lying between C12 and C18 (Hammerie *et al.*, 1995). The source profile generated in this study is presented for an identical compound set to that of ambient measurements to be used in receptor modeling.

Table 5.4. Diesel fuel profiles generated for Ankara (wt. %).

Compound Name	Liquid	Vapor
Pentane	1.27	8.87
2,2-dimethylbutane	0.37	2.91
2,3-dimethylbutane	0.33	1.84
2-methylpentane	1.82	7.75
3-methylpentane	1.28	5.46
Hexane	1.81	6.87
c-3-methyl-2-pentene	1.45	7.59
Methylcyclopentane	0.78	4.03
2,4-dimethylpentane	0.11	0.29
2,2,3-trimethylbutane	0.09	0.24
Benzene	1.87	3.37
Cyclohexane	0.39	1.97
2-methylhexane	1.09	1.99
2,3-dimethylpentane	0.28	0.78
3-methylhexane	1.17	2.13
1-heptene	0.15	0.66
Heptane	2.45	4.42
Methylcyclohexane	1.20	3.78
2,5-dimethylhexane	0.12	0.19
2,4-dimethylhexane	0.26	0.40
2,3,4-trimethylpentane	0.17	0.07
Toluene	9.76	5.31
3-methylheptane	1.53	1.52
c-1,3-dimethylcyclohexane	1.10	1.26
t-1,4-dimethylcyclohexane	0.58	0.64
Octane	3.80	2.71
t-2-octene	0.16	0.13
t-1,2-dimethylcyclohexane	0.34	0.36
c-1,4/t-1,3-dimethylcyclohexane	0.35	0.38
Ethylbenzene	2.17	0.79
m,p-xylene	10.48	2.68
o-xylene	4.03	1.01
1-nonene	2.34	0.78
Nonane	7.98	1.92
iso-propylbenzene	0.52	0.14
3,6-dimethyloctane	0.77	0.14
n-propylbenzene	1.45	0.26
3-ethyltoluene	3.28	0.48
4-ethyltoluene	1.91	0.29
1,3,5-trimethylbenzene	2.15	0.27
2-ethyltoluene	1.83	0.24
1,2,4-trimethylbenzene	6.11	0.71
iso-butylbenzene	0.22	0.02
sec-butylbenzene	1.14	0.12
1,2,3-trimethylbenzene	2.57	0.23
p-cymene	0.71	0.06
1,4-diethylbenzene	2.67	0.16
n-butylbenzene	0.92	0.06
1,2-diethylbenzene	0.43	0.03
Undecane	5.70	0.36

Therefore, the contribution values in weight percent presented in the Table 5.4 are for the compound set ranging from C5 to C11. Heavy hydrocarbons and aromatics including nonane, undecane, toluene, m&p-xylene and 1,2,4-trimethylbenzene are the most dominant compounds in the liquid diesel fuel profile, whereas light hydrocarbons are almost negligible. On the other hand, headspace diesel profile is composed of mostly light hydrocarbons. Pentane, 2-methylpentane, heaxane are among the most dominant species in headspace profile. Heavy hydrocarbons and aromatics are not dominant in the headspace profile due to their very low vapor pressure. Liquid and diesel fuel profiles generated for Ankara are not compared with the literature since the diesel fuel profiles in the literature are provided for heavy hydrocarbons in which only few compounds were identical to our dataset.

5.1.1.2 Motor Vehicle Emission Profiles

Motor vehicles emit VOCs at different stages of its operation. Vehicles can be a source of VOCs during a start (cold-start emissions), driving (roadway emissions), immediately after the vehicle is stopped (hot-soak emission), and during resting phases (evaporative emissions). In this study, cold-start and hot-soak emissions were measured for an integrated sample of vehicles of various ages inside of a parking garage, which contained mainly light duty vehicles, in Ankara. Roadway emissions were sampled with a tunnel study. Evaporative emissions are simulated by headspace gasoline composition.

Running Vehicle Exhaust

There are three widely used methods to determine vehicle exhaust emission profiles, namely; a dynamometer test on individual vehicles, which is performed in Ottawa part of this study, a tail-pipe exhaust sampling of an individual vehicle traveling on a road and measurements in a roadway tunnel, which is performed in Ankara part of the study. In the former approach, operating conditions and fuel composition can be controlled. However, it is disadvantageous in terms of cost and time and does not represent a composite of the large number and different types of on-road vehicles (Na *et al.*, 2004). The tail-pipe measurements provide information on individual vehicles during real driving conditions, but again such sampling can be performed in a limited number of vehicles and representativeness is always an unresolved question. The tunnel method, which was used in the Ankara part of this study, has been widely used to determine the VOC speciation of cumulative vehicle emissions in the past decade (Pierson *et al.*, 1990; Gertler *et al.*, 1996; Mugica *et al.*, 1998). Compositions of VOC species in a tunnel air are believed to be representative of a large number of vehicles and fuel types used broadly in urban areas (Lonneman *et al.*, 1986). However, tunnel studies can not provide information on emissions from individual vehicles vehicles.

Most tunnel studies conducted so far have focused on high-speed driving conditions in highway tunnels (Gertler *et al.*, 1996; Fraser *et al.*, 1998). This driving pattern may not be realistic enough to represent traffic-related pollution in urban areas, because vehicle speeds, and emissions, differ during typical urban driving which includes the accelerating, cruising, and decelerating stages (Na *et al.*, 2004). In this study, to obtain actual vehicle exhaust emission profiles for VOC in Ankara, a measurement was carried out at a tunnel under high and low speed driving conditions with both moving and stationary vehicles. The tunnel description and the sampling methodology are discussed in Section 3.1.

In the present study, vehicle emissions were measured both in summer and winter because the composition of vehicle fuel and vehicle exhaust might vary from season to season (Cadle *et al.*, 2000; Gwilliam *et al.*, 2004). The running vehicle exhaust profiles generated in the Akay tunnel during summer and winter seasons are shown in Figure 5.3. The compound set shown in the figure is identical to that used in the ambient measurements. As can be seen from the figure, toluene and m&p-xylene are the most abundant species followed by 1,2,4-trimethylbenzene, benzene, o-xylene and ethylbenzene. Running vehicle exhaust profile includes both light and heavy hydrocarbons but the contribution of heavy hydrocarbons are higher. Aromatics have the highest contribution in exhaust profile with about 70% of total VOC weight.

Summer and winter exhaust profiles have similar patterns. However, contribution of individual compounds and compound groups are different. As can be seen in Figure 5.3, aromatic compounds starting from benzene have higher contribution in the summer profile than in winter profile. On the other hand, light hydrocarbons, which are mostly represented by paraffins, are higher in winter profile.

The seasonality in the running vehicle exhaust profile is partly related with the seasonality in fuel composition. It has been reported that motor vehicle fuel composition is changed seasonally to ensure optimum vehicle start-up and driving conditions. Fuel used in winter should have higher volatility than summer fuels (Stump et al, 1990). Fuel volatility is adjusted in summer and winter reported as change in Reid Vapor Pressure (RVP). RVP is a measure of how quickly fuel evaporates. Incorrect fuel RVP might result in difficult starting in cold weather, vapor lock in hot weather and crankcase oil dilution. Vapor pressure is generally adjusted by changing concentration of volatile fraction in the fuel.

In Turkey there are two different grades of gasoline, namely the summer grade (produced between 1st April and 31st October) and the winter (produced between 1st November and 31st March). RVP values in Turkish unleaded gasoline are 35-70 kPa and 60-95 kPa in summer and winter grades, respectively (TÜPRAŞ, 2003). During summer season, volatility of the gasoline is low as indicated with lower RVP values. Volatility of the gasoline is decreased by increasing aromatic content and decreasing olefin and paraffin content of the fuel, as aromatics have lower vapor pressure than paraffins and olefins.

Since vehicle exhaust gases include both combusted and uncombusted fuel, there are similarities and differences between running vehicle exhaust and whole gasoline profiles. For example, benzene contribution is higher in the exhaust profile (i.e., about 6%) than in the whole gasoline profile (i.e., about 3%). Higher benzene fraction in exhaust, relative to whole gasoline, is attributed to formation of benzene through dealkylation of higher molecular weight aromatics (McLaren *et al.*, 1996; Fraser *et al.*, 1998).

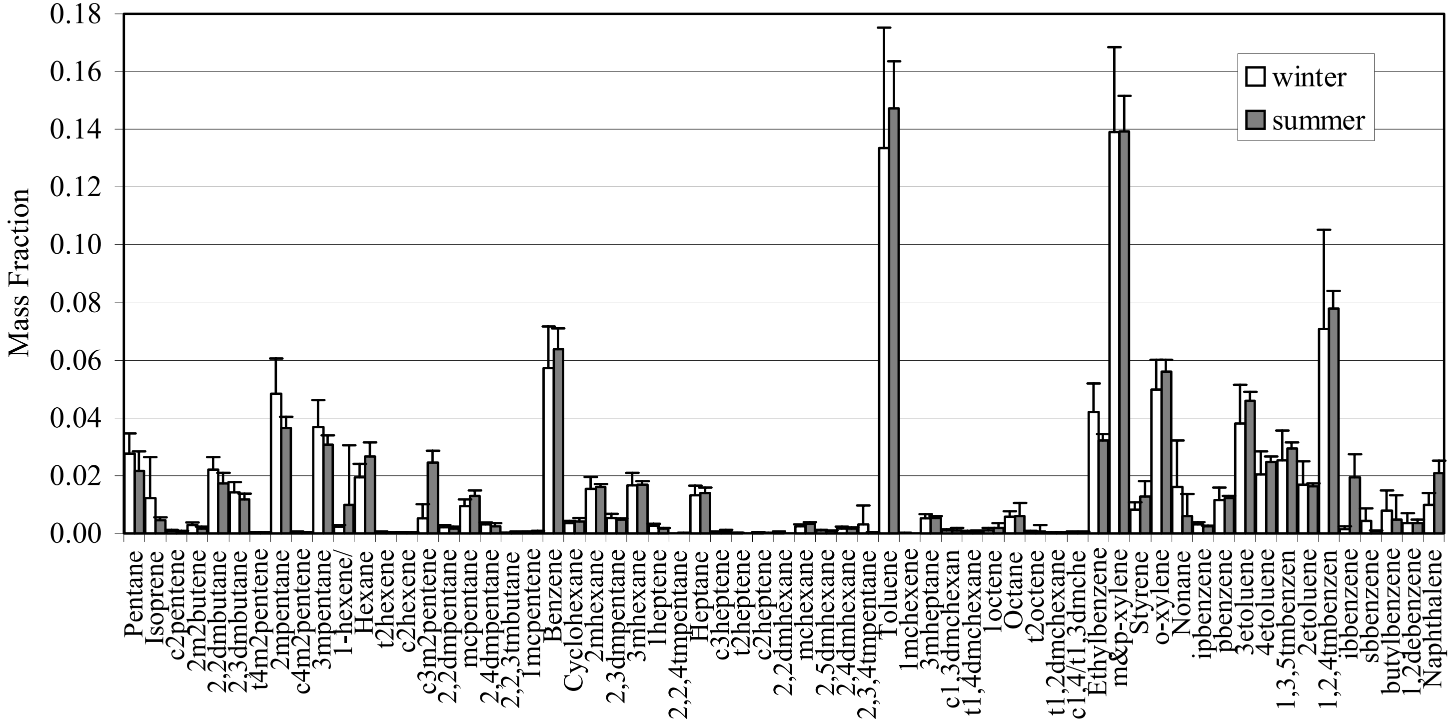


Figure 5.3. Running vehicle exhaust source profiles in Ankara.

The levels of benzene in vehicle exhaust have attracted a considerable attention because benzene is classified as known carcinogen by the US EPA (Calabrese and Kenyon, 1991). Since the exhaust gases include both combusted and uncombusted VOCs, it is necessary to control benzene-producing VOCs as well as benzene content in vehicle fuel in order to reduce benzene in vehicle emissions (Na *et al.*, 2002). The running vehicle exhaust profile generated for Ankara was compared with the profiles available in literature. The weight percent composition of the Ankara profile together with tunnel, dynamometer and roadway profiles obtained from literature is presented in Table 5.5.

Tunnel-1 and Tunnel-2 data are generated for Tuscora Mountain Tunnel, Pennsylvania (U.S.A.) and Fort McHenry Tunnel, Maryland (U.S.A.), respectively (Sagebiel *et al.*, 1996). The dynamometer source profile represents the chemical composition of exhaust emissions from a non-catalyst, gasoline fueled, light duty vehicle (LDV). The profile was derived from tests on older non-catalyst vehicles performed by two independent laboratories (Harley *et al.*, 1992). The roadway profile was generated by Doskey *et al.* (1992) for Chicago. The exhaust profile data for Ankara is presented in the Table 5.5 as the average profile for summer and winter seasons.

Table 5.5 have similar pattern with the average running vehicle exhaust profile generated for Ankara except for the roadway profile. The contribution of individual species, however, varies from one profile to other. Tunnel-1 and Tunnel-2 profiles have a very similar pattern and contribution profile. The dynamometer profile is also similar to tunnel profiles except deviations in few compounds. For the compound set presented in Table 5.5 the highest weight percent contributions of individual compounds is observed at Ankara profile. For example, contribution of toluene to the Ankara profile (i.e., 14%) is about two times higher than corresponding contributions found in tunnel profiles and three times higher than those in dynamometer and roadway profiles. Similarly, m&p-xylene contribution is the highest at the Ankara profile (i.e., 14%) then the rest of profiles and o-xylene contribution in the Ankara profile (i.e., 5%) is about two times higher than those in other profiles. Contribution of benzene in the Ankara profile (i.e., 6.0%); however, is very similar to that of the Tunnel-2 profile (i.e., 5.6%).

Table 5.5. Comparison of exhaust profiles (wt. %).

Compound name	**This Study**	**Tunnel-1**[1]	**Tunnel-2**[1]	**Dynamo.**[2]	**Roadway**[3]
Pentane	2.46	2.94	3.35	1.90	3.71
Isoprene	0.84	0.33	0.39		
c-2-pentene	0.08	0.39	0.42		
2,2-dimethylbutane	1.96	0.85	0.90	0.30	
2,3-dimethylbutane	1.30	1.17	0.86	0.60	3.21
2-methylpentane	4.24	3.14	2.93	1.30	
3-methylpentane	3.37	1.76	1.82	1.10	1.69
1-hexene/2-methyl-1-pentene	0.60			1.60	
Hexane	2.29	1.43	1.46	0.80	2.08
Methylcyclopentane	1.12	1.08	1.17	1.20	
2,4-dimethylpentane	0.27				1.12
Benzene	6.06	4.50	5.67	3.60	3.35
Cyclohexane	0.38	0.18	0.33	0.40	
2-methylhexane	1.58				
2,3-dimethylpentane	0.51	0.91	0.74		
3-methylhexane	1.67	1.49	0.92		
Heptane	1.36	0.74	0.59	0.60	
Methylcyclohexane	0.29	0.44	0.46	0.50	
2,5-dimethylhexane	0.09				
2,4-dimethylhexane	0.17				
2,3,4-trimethylpentane	0.17	1.26	0.79		
Toluene	14.04	8.68	8.78	5.80	5.61
3-methylheptane	0.52	0.49	0.44		
Octane	0.59	0.32	0.26	0.20	
Ethylbenzene	3.71	2.14	1.74	1.20	1.02
m,p-xylene	13.92	7.27	6.50	4.20	3.52
Styrene	1.05	0.96	0.98		
o-xylene	5.30	2.67	2.49	1.60	1.27
Nonane	1.11	0.23	0.06		
iso-propylbenzene	0.28	0.18	0.30		
n-propylbenzene	1.19	0.67	0.51		
1,3,5-trimethylbenzene	2.74	1.23	1.03	0.60	
2-ethyltoluene	1.66				
1,2,4-trimethylbenzene	7.43	4.60	3.27	1.80	

[1] *Sagebiel et al., 1996;* [2] *Harley et al., 1992;* [3] *Doskey et al., 1992.*

There are only few species for which the contribution is not the highest for the Ankara profile. Weight percent contribution of pentane, 2,3-dimethylbutane, and 2,4-dimethylpentane is the highest for the roadway profile. Contribution of 1-hexene/2-methyl-1-pentene is higher in the dynamometer profile.

In conclusion, the Ankara running vehicle exhaust profile has a similar pattern but higher contributions than the profiles available in the literature. The prominent feature of vehicle emissions in Ankara is the higher mass percentages of toluene, m&p-xylene and o-xylene. The Ankara profile has a unique feature influenced by the differences in fleet characteristic (e.g., fleet age, inspection and maintenance, LDV and HDV shares in fleet, exhaust gas control equipments), fuel characteristic and driving conditions.

Cold-Start and Hot-Soak Emission Profiles

The VOCs are also emitted from vehicles during the cold-start and hot-soak phases of the driving cycle. Samples that were collected in an underground garage located at downtown Ankara was analyzed to produce cold and hot-start emission profiles as described in Section 3.1. Samples were collected both inside and outside the garage and the results were corrected for the intrusion of outdoor air into the garage.

Cold-start and hot-soak profiles developed for Ankara are presented together with the profiles available in the literature for comparison in Table 5.6. The Ankara cold start profile was compared with the profiles generated by Doskey *et al.*, (1992) for Chicago. There is a significant variation in both profiles. The mass contributions of m&p-xylene, o-xylene and ethylbenzene are about three times higher than the Chicago profile. Correlation between these profiles is also not good (R^2=0.42). The Ankara hot-soak profile was compared with the profiles for Chicago (Doskey *et al.*, 1992) and Atlanta (Lonneman *et al.*, 1991) developed by garage studies and a profile for the U.S.A. developed by a dynamometer test (Sigsby *et al.*, 1987).

Table 5.6. Hot soak and cold start emission profiles.

	This Study		**Literature**			
Compound Name	**Hot Soak**	**Cold Start**	**Cold Start-1**[1]	**Hot Soak1**[1]	**Hot Soak2**[2]	**Hot Soak3**[3]
Pentane	7.60	3.77	4.27	8.37	3.71	4.26
c-2-pentene	0.14	0.55				
2-methyl-2-butene	0.47	1.79				
2,2-dimethylbutane	3.64	3.47				
2,3-dimethylbutane	2.35	2.90	4.40	4.62	3.02	3.19
t-4-methyl-2-pentene	0.08	0.15				
2-methylpentane	6.87	6.36				
3-methylpentane	5.27	4.98	2.33	2.25	1.74	1.95
1-hexene/2-methyl-1-pentene	9.95	0.63				
Hexane	3.65	3.74	2.71	2.42	1.32	1.13
c-3-methyl-2-pentene	3.40	5.13				
Methylcyclopentane	1.95	2.60				
2,4-dimethylpentane	0.40	0.58	1.53	0.94	0.68	
Benzene	4.73	4.85	3.30	1.48	2.02	
Cyclohexane	0.55	1.05				
2-methylhexane	1.72	2.03				
2,3-dimethylpentane	0.68	0.87				
3-methylhexane	2.05	2.28				
1-heptene	0.11	1.22				
Heptane	1.48	1.43				
Methylcyclohexane	0.29	0.88				
2,4-dimethylhexane	0.17	0.72				
Toluene	10.59	9.83	8.17	3.19	6.62	
3-methylheptane	0.46	1.23				
c-1,3-dimethylcyclohexane	0.05	0.25				
t-1,4-dimethylcyclohexane	0.03	0.15				
Octane	0.29	0.58				
Ethylbenzene	2.09	2.63	1.34	0.41	1.20	
m,p-xylene	9.29	9.05	3.93	1.44	4.07	2.50
o-xylene	3.69	4.10	1.50	0.50	1.58	1.30
Nonane	0.06	0.30				
iso-propylbenzene	0.17	0.31				
n-propylbenzene	0.72	1.00				
3-ethyltoluene	2.53	3.03				
4-ethyltoluene	1.45	1.70				
1,3,5-trimethylbenzene	1.71	1.90				
2-ethyltoluene	0.87	1.19				
1,2,4-trimethylbenzene	4.36	4.91				
iso-butylbenzene	0.04	0.06				
sec-butylbenzene	0.05	0.07				
1,2,3-trimethylbenzene	0.79	1.05				
1,4-diethylbenzene	1.00	0.04				
n-butylbenzene	0.13	0.01				
Naphthalene	0.45	0.48				

[1] *Doskey et al., 1992;* [2] *Lonneman et al., 1991;* [3] *Sigsby et al., 1987.*

Atlanta and dynamometer profiles are similar to each other except m&p-xylene, which have about factor of two higher mass contributions in the Atlanta profile. Comparison of the profiles yielded that there is a significant variation in the mass contributions of species in each profile. This variation is the most significant for mass contributions of benzene, toluene, ethylbenzene, m&p-xylene and o-xylene. The results indicated that the cold-start and hot-soak profiles generated for Ankara is significantly different than the profiles available in the literature.

Cold start and hot-soak profiles were also compared with the other motor vehicle related source profiles generated for Ankara in this study. It is stated by Singer *et al.*, (1999) that excess emissions during cold-start operations contribute a significant fraction of VOCs. Cold start emissions occur when both the engine and catalytic convertor are cold. The typically rich air/fuel ratio and the ineffective catalyst under these conditions give rise to a mixture of unburned gasoline and untreated combustion gases (Singer *et al.*, 1999).

Comparison of the cold start profile with the other motor vehicle profiles generated for Ankara verifies this fact. Ankara cold start profile results the best correlation with the unleaded whole gasoline (R^2=0.75, intercept=1.00) and running vehicle exhaust (R^2=0.79, intercept=1.13) profiles as can be seen in Figure 5.4. Comparison with the whole gasoline data shows a better precision except for 1-hexene/2-metyl-1-pentene.

Hot-soak emissions are evaporative emissions caused when a hot engine is turned off. Heat from the engine and the exhaust system increase the temperature of the fuel in the system that fuel does not flow any longer. Carburetor float bowls are particularly significant source of hot soak emissions. Therefore, the hot-soak emissions are expected to be similar to that of headspace emissions. During the hot-soak sampling in the garage, few vehicles were continued to enter the garage thus this profile was named as evaporative and exhaust emission profile rather than only hot-soak profile.

The correlation plot of the Ankara hot-soak profile with the other profiles generated in Ankara is shown in Figure 5.5. The comparison of the correlations yields that this profile has the best correlation with the headspace unleaded gasoline profile (R^2=0.70, intercept=1.03). Comparison with the exhaust profile results in relatively poor correlation (R^2=0.58, intercept=0.89), indicating the profile is mostly associated with evaporative emissions rather than exhaust emissions.

In addition to production of hot-soak and cold-start emission profiles, the garage study is also important to demonstrate very high concentrations of toxic organics existed in the garage air. Underground parking garage have very poor ventilation system and VOC concentrations measured in the garage were about 70 times higher than that were measured in ambient air during the evening rush hour. For example, the highest benzene, which is a known human carcinogen, concentration was 350 $\mu g\ m^{-3}$ during the evening rush hour, as an average of one hour sampling. People work in the garage for 8-hr per day and they are exposed to very high levels of motor vehicle emissions. Therefore these people face with significant health risks resulting from motor vehicle emissions.

In summary, the fuel and motor vehicle related emission profiles that were developed for Ankara during the Ankara campaign are significantly different from the profiles available in the literature. The main reasons for this are due to fuel formulations, which change from country to country depending upon the refinery technology, the fleet characteristics including fleet age and control technologies, driving conditions and meteorological conditions. Therefore, it is necessary to develop source profiles, which are specific to the area of concern, to be used in receptor modeling studies.

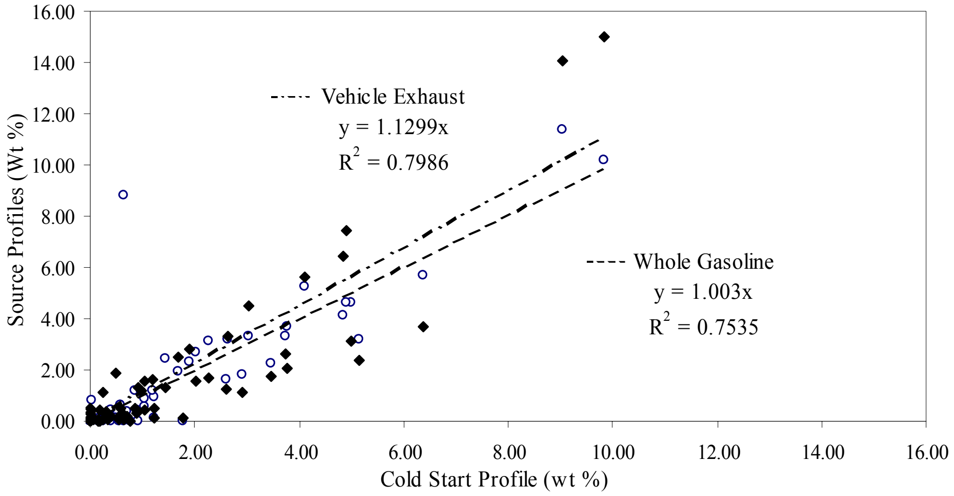


Figure 5.4. Correlation of Ankara profiles with the cold start profile.

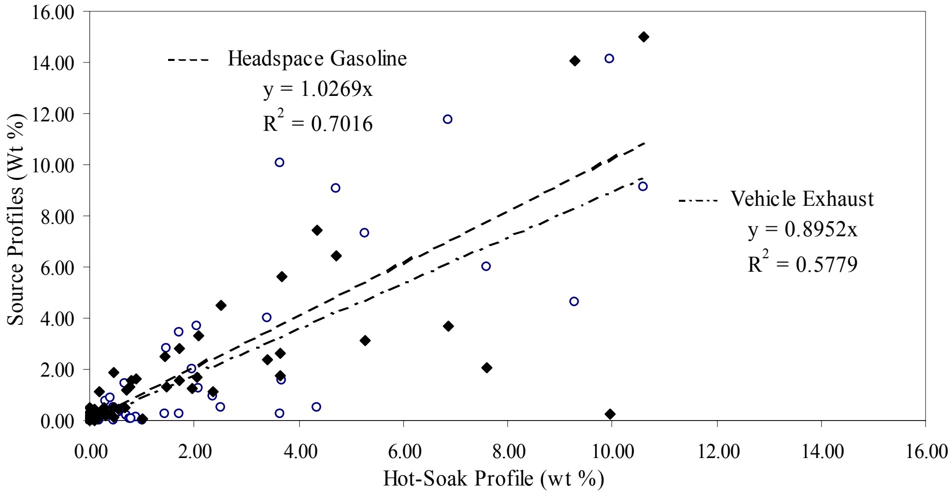


Figure 5.5. Correlation of Ankara profiles with the hot-soak profile.

5.1.2. Preliminary Source Identification

5.1.2.1 Species Ratios

Concentration ratios of species are informative about the major sources influencing VOC emissions at the place of measurement and the reactivity of the air mass that the sample is collected from. There are two specie ratio commonly used in the literature, namely toluene:benzene (T:B) and m&p-xylene:ethylbenzene (mpX:E). These ratios are evaluated for the VOC data collected in Ankara during summer and winter campaigns. These evaluations should be considered as preliminary assessments for the source identification. It is beneficial to analyze these ratios before starting receptor modeling to have a preliminary view on possible sources.

Studies on vehicle exhaust generally reported a ratio of T:B of 2.0 (Sweet and Vermette, 1992; Scheff and Wadden, 1993). T:B ratios in the ambient air and tunnel samples collected in Ankara are presented in Table 5.7. During both summer and winter periods, the T:B ratios observed at roadside and tunnel stations are about 2.0 as indicated for the vehicle exhaust sources in the literature. The ratio of T:B is similar for residential and background stations in both seasons. During the winter campaign, the T:B ratio observed at residential and background stations are close to 2.0 indicating vehicles are the major source for VOCs at these sites.

During the summer campaign, the T:B ratio observed at residential and background stations are about 4.5 indicating another source of VOCs at these sites in addition to the motor vehicles. The background site was located in a sub-urban area and the VOC concentrations measured at this site was about two times lower than that was measured at the residential site. Since the traffic activity, particularly during summer when there is no classes in the university, is very low, observed concentrations of VOCs can at least be partly accounted for transport from more polluted areas in the city, resulting in lower concentrations, but similar T:B ratios with the residential station. The ratio of T:B for the other urban areas and tunnel studies are presented in Table 5.8.

Table 5.7. T:B ratios observed at each station in Ankara.

Station	Winter	Summer
Residential	1.78	4.51
Background	1.61	4.53
Roadside	2.04	2.28
Tunnel	2.34	2.21

Table 5.8. T:B ratios available in the literature.

Urban areas			
EU			
Birmingham (UK)	2.0	Rome (Italy)	2.4
Lille (France)	2.1	Thessaloniki (Greece)	2.5
Munich (Germany)	1.9		
Asia			
Yokohama (Japan)	3.2	Hong Kong (China)	5.0
Seoul (S.Korea)	8.2	Manila (Philippines)	10.0
Bangkok (Thailand)	10.0		
Latin America			
Santiago (Chile)	2.5	Sao Paulo (Brazil)	2.0
Quito (Ecuador)	3.3	Caracas (Venezuela)	2.5
Tunnels			
Cassiar (Canada)	1.8	Tuscora (U.S.A.)	1.5
Sepulveda (U.S.A.)	2.1	Fort McHenry(U.S.A.)	1.9

Sources: Birmingham, Lille, Munich, Rome, Yokohama, Seoul: Ne et al. (2003); Thessaloniki: Kourtidis et al. (2002); Bangkok, Manila, Santiago, Quito, Sao Paulo, Caracas: Ho et al., 2004; Hong Kong: Lee et al. (2002); Cassiar, Sepulveda: Main et al. (1999); Tuscora, Fort McHenry: Sagebiel et al. (1996).

Tunnel studies results in a T:B ratio of about 2.0. At the urban sites in the EU countries, T:B ratio is about 2.0 indicating that the vehicle exhaust is the major source of VOCs. A similar behavior is also observed in the Latin American countries except Ecuador. Ho *et al.* (2002) indicated that stations showed significant variations in the T:B data. In the Asian countries very high T:B ratios are observed. Gee and Sollars (1998) suggested that there are large additional sources of toluene in these Asian cities or that there are major difference in the fuel or vehicle used. Lee *et al.* (2002) suggested that the reason is use of unleaded fuels with a high aromatic content (45%) in Asian cities.

Some of the VOC species are commonly used as indicators of the age of the air mass. The ratio of these target species in the emissions is assumed to be relatively constant throughout the day and the relative abundance of the more reactive species should decrease with the time during the daylight periods due to photochemical reactions. The relative abundance of the less reactive species gradually increases. The ratio of mpX:E suggested by Nelson and Quickley (1983) is commonly used to investigate aging in the air masses. The atmospheric lifetimes of m&p-xylene and ethylbenzene are about 3-hr and 8-hr, respectively. As the air masses travel to a distance m&p-xylene react more rapidly in the atmosphere and at the downwind point the ratio decreases. The ratio of mpX:E observed at different sites in Ankara are presented in Table 5.9.

During the winter sampling the ratio of mpX:E at the roadside and tunnel stations were about 4.3. The ratio close to 4.0 was also observed at the residential site. There was just a slight decrease in the mpX:E ratio at the background site. During the summer sampling, a similar situation was observed except the decrease in the ratio for the background station was pronounced. During the summer, elevated temperature accelerates the atmospheric reactions. Thus, the polluted air mass traveled from more polluted part of the city might explain the decrease in the mpX:E ratio.

Table 5.9. mpX:E ratios observed at each station in Ankara.

Station	**Winter**	**Summer**
Residential	4.09	3.20
Background	3.60	2.45
Roadside	4.44	3.67
Tunnel	4.27	3.46

5.1.2.2 Species Correlations

Investigation of correlation between species provides useful information on the possible emission sources of species. The Pearson correlation coefficients and correlations plots were investigated for the VOC data collected at the residential, background and roadside stations located in Ankara. Pearson correlation coefficients (ρ_{xy}) were calculated using Eqn. 5.3.

$$\rho_{xy} = \frac{\mathrm{cov}(X,Y)}{\sigma_x \sigma_y} \tag{5.3}$$

$$\mathrm{cov}(X,Y) = E(X-\mu_x)(Y-\mu_y) \tag{5.4}$$

where; cov(X,Y) is the covariance between the random variables X and Y; μ_x, μ_y and σ_x, σ_y are the means and standard deviations, respectively, of the random variables X and Y; *E* denotes the statistical expected value or expectation operator. The value ρ_{xy} is always between 1.0 and -1.0.

The correlation plot and the correlation coefficients between selected species measured at the residential station during winter and summer campaigns are shown in Figure 5.6 and Figure 5.7, respectively. Correlation between all individual species was inspected but the results were presented only for the selected compounds for convenience. Benzene, toluene, ethylbenzene, xylenes are known markers for automobile emissions and are named shortly as BTEX. Among these species, toluene might have other sources such as solvent use in addition to vehicle exhaust. Results for the 1,1,1-tetrachloroethane (TCA), carbontetrachloride (CCl_4) and isoprene are also presented in Figure 5.6 and Figure 5.7.

For the winter campaign, good correlations (i.e., $\rho > 0.9$) between BTEX and isoprene species measured at residential station are obtained. As mentioned earlier BTEX compounds are associated with motor vehicle related sources. Isoprene is a well-known marker for biogenic emissions. During the winter season, however, biogenic emissions are low. Isoprene is also known to emit from motor vehicle related sources (Borbon *et al.*, 2001; Borbon *et al.*, 2002). From the correlation analysis it is found that motor vehicle emissions are major source for isoprene emissions, during winter. Correlations between BTEX compounds and TCA and CCl_4 are very poor (i.e., $\rho<0.2$). However, there is a good correlation (i.e., $\rho=0.75$) between TCA and CCl_4. This result indicates that TCA and CCl_4 are emitted from a source other than motor vehicles. Most of the halogenated compounds including TCA and CCl_4 are known to emit from sources, in which solvents are used (Nazaroff and Weschler, 2004).

Correlation analyses for the summer VOC data collected at the residential station shows similar results to that observed for winter data except for isoprene. Figure 5.7 shows that the correlation between isoprene and all other compounds are poor (i.e., $\rho<0.5$) during summer campaign. Biogenic emissions increase during summer period. Thus isoprene concentrations measured at the residential station is found to be dominated by biogenic emissions during summer. There is a good correlation between TCA and CCL_4 indicating that they originate again from the same source, which is solvent use. Correlations between BTEX compounds are also good.

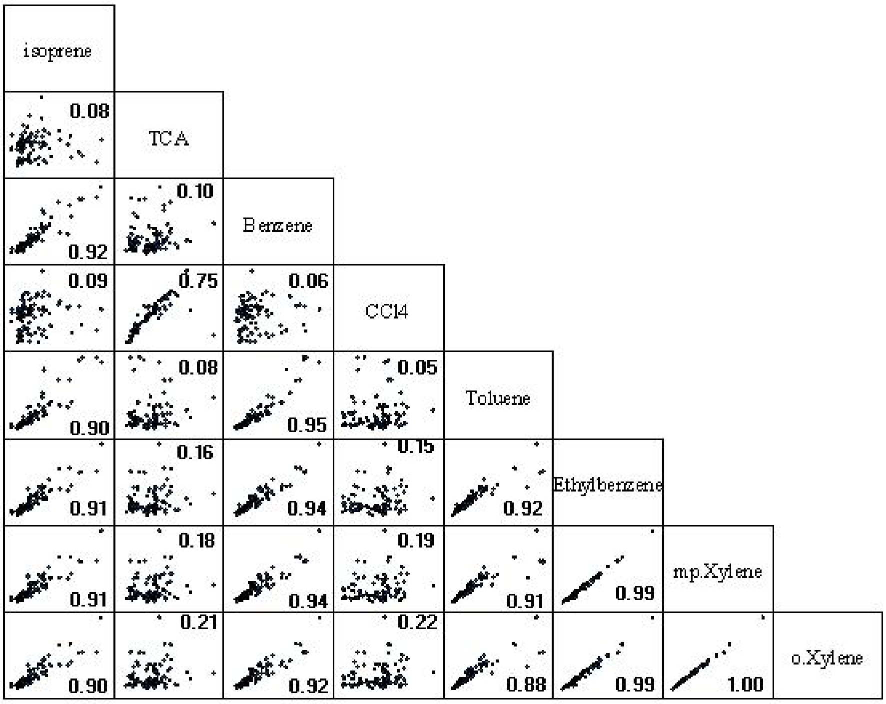


Figure 5.6. Correlation plot and coefficients at residential station (winter).

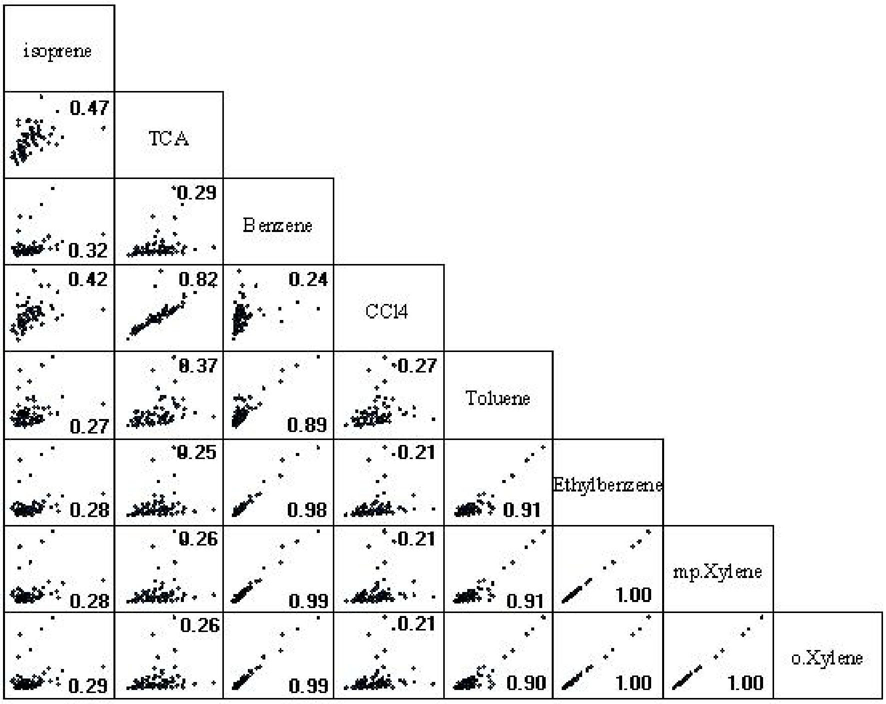


Figure 5.7. Correlation plot and coefficients at residential station (summer).

Similar results are observed from correlation analysis for the roadside station. There are some differences in results of the background station. The correlation coefficients calculated for the data collected at the background station during summer and winter campaigns are shown in Table 5.10. The correlations and thus the sources of BTEX, isoprene, TCA and CCL_4 compounds measured during winter campaign are very similar to that explained for the residential station for winter campaign. However, correlation coefficients observed at the background station are lower than that of the residential station. This could be due to aging of polluted air mass traveled from the residential station. The ratio of mpX:E discussed in previous section has also suggested similar transport as the source of VOCs measured at the background station during summer campaign.

Table 5.10. Correlation coefficients of selected compounds in background station.

Winter (N=85)								
	Isp	TCA	Bnz	CCL_4	Tln	Ebz	mpX	oX
Isp	1.00							
TCA	0.25	1.00						
Bnz	**0.76**	0.32	1.00					
CCL_4	0.27	**0.79**	0.26	1.00				
Tln	**0.88**	0.28	**0.89**	0.25	1.00			
Ebz	**0.80**	0.24	**0.82**	0.19	**0.90**	1.00		
mpX	**0.87**	0.29	**0.86**	0.28	**0.95**	**0.93**	1.00	
oX	**0.86**	0.30	**0.86**	0.29	**0.94**	**0.93**	**1.00**	1.00
Summer (N=27)								
	Isp	TCA	Bnz	CCL_4	Tln	Ebz	mpX	oX
Isp	1.00							
TCA	**0.77**	1.00						
Bnz	0.34	0.50	1.00					
CCL_4	**0.66**	**0.64**	0.22	1.00				
Tln	-0.04	0.13	*0.20*	0.19	1.00			
Ebz	0.11	0.17	**0.63**	0.26	*0.55*	1.00		
mpX	0.25	0.27	**0.57**	0.43	*0.36*	**0.86**	1.00	
oX	0.22	0.23	**0.56**	0.36	*0.26*	**0.80**	**0.98**	1.00

Isp:isoprene; TCA: 1,1,1-tricholorethane; Bnz: benzene; CCL4: carbontetrachloride; Tln: toluene; Ebz: ethylbenzene; mpX: m&p-xylene; oX: o-xylene

During the summer campaign correlations for toluene, benzene and isoprene deviate slightly from that explained for the residential station for the summer campaign. There is a very poor correlation (i.e., ρ=0.2) between toluene and benzene measured during summer campaign at the background station. Correlations between benzene and ethylbenzene and xylenes also decrease during summer period (i.e., ρ is about 0.6). The correlations between toluene and ethylbenzene and xylenes are poor. The most probable reason for different correlations in the background station observed during the summer campaign is the different reactivity of different species. As it is explained in previous section, mpX:E ratio indicate that air mass measured at the background station during the summer campaign is an aged air mass traveled from polluted parts of the city. Thus concentration of individual species changed at receptor (i.e., background station) depending on their reactivity in the atmosphere and transport time.

Isoprene has low correlations with the BTEX compounds at the background site during summer. However, there are good correlations between TCA, CCL_4 and isoprene. This good correlation is not because these compounds are originated from a similar source but because diurnal emission pattern of these compounds is similar. Emissions of these compounds are mostly influenced by diurnal temperature variations. Emissions increase with increasing temperatures during daytime and decrease with decreasing temperatures during night times. Emission patterns of BTEX, on the other hand, depend on traffic pattern, which is different from temperature variations.

Both ratio and correlation analyses provide a preliminary information about the probable sources of VOCs in the study area. However, they do not provide conclusive evidence about the source types and their contributions. It is useful to perform these analyses before starting receptor modeling to have a broad idea about sources. Accurate source identification and quantification is done by receptor modeling as explained in following sections.

5.1.3. Positive Matrix Factorization

2-way Positive Matrix Factorization (PMF), so-called PMF2, program developed by Paatero (1998) was used in this study to investigate sources of VOCs measured in Ankara and Ottawa. PMF, which is a least-squares approach for solving the factor analysis problem, is considered as a new type of factor analysis method (Paatero *et al.*, 2002). Unlike more conventional methods of factor analysis such as principal component analysis (PCA), PMF produces non-negative factors, aiding factor interpretation, and utilizes error estimates of the data matrix (Polissar *et al.*, 2001a). Model algorithms and literature review are discussed in Chapter 2 in detail.

5.1.3.1 Residential Station Winter Campaign

Input Parameters

Ambient concentrations of 91 VOCs were measured at the residential site in Ankara during winter campaign. Input data was pretreated for the missing and BDL values prior to use in the model. Firstly, VOC data were inspected for missing values and found that missing values for 59 compounds were observed at 30% or lower of the measured data points. Then, the compounds with 30% to 50% missing values were reviewed. Only one compound, chlorobenzene, had missing value greater than 30 % but less than 50%, rest of the compounds had missing values greater than 50%. Chlorobenzene was also included in data set.

Secondly, S/N ratio was inspected to identify “bad” variables. According to S/N values, 9 compounds were identified as “bad” variables and thus they were excluded from the data set. The remaining 51 compounds were processed to replace missing and BDL values with the proper input values as described in Section 2.7.1. The input data matrix was constructed with the pretreated 51 compounds and a total of 94 data points.

Error estimates for the input data values were computed using the error model (EM) -14 built in PMF2. Three different C3 values, 0.10, 0.05 and 0.01, were used during calculations. PMF2 was run under fixed number of factors and initial conditions to investigate effectiveness of the C3 values on the model performance. Number of factors was set at 3 during error estimation runs. The Q value was inspected to decide on the optimum C3 value that provided the best model fit. Theoretical Q value for the input data set was 4794. The modeled Q values for 0.10, 0.05 and 0.01 C3 values were 1616, 2629 and 4495, respectively.

Error estimates are also calculated using the method given by Polissar *et al.* (1998), which is provided in Section 2.7.1. Uncertainty matrix was constructed and used in the PMF2 run. Model was run under the same initial conditions and number of factors as that was used during EM -14 runs in order to provide comparison. The calculated Q value was 4613 for the new uncertainty matrix, which was close to the theoretical Q value. The model fit was better when using the uncertainty matrix calculated by Polissar *et al.* (1998) guidelines than that was calculated by PMF2 algorithms. Therefore, the uncertainty matrix calculated by Polissar *et al.* (1998) guidelines was selected as an input to the model.

Application of the Model

Determination of the number of factors (i.e., sources) is the critical step in PMF2. Four rules discussed in Section 2.7.1 were utilized in order to select the optimum number of sources that provided the optimum solution. PMF2 runs using number of factors 3, 4, 5 and 6 yielded calculated Q values of 4613, 3512, 3098 and 2738, respectively. Model runs with 6 factors yielded the lowest calculated Q value that is approximately 2 times lower than the theoretical Q value. Three factors solution had the closest calculated Q value to the theoretical Q value, but the resulting factors were not explainable. Therefore, 6 and 3 factors solutions were not considered as the optimum solution. Further analyses were performed to decide on the number of factors 4 or 5 as the optimum number of factors.

Effect of transformation on the model performance in terms of factor profiles, scaled residuals and calculated Q value was investigated. FPEAK tool was applied using values ranging between -1.0 and 1.0 to test different rotations. PMF2 runs with 5 factors and FPEAK values of -0.5, -0.1, 0.0, 0.1, 0.5, 0.6 and 0.7 yielded calculated Q values of 3172, 3128, 3098, 3125, 3158, 3339, and 3367, respectively. Model did not achieve convergence for the runs with FPEAK values of –1.0 and 1.0. Increase in the FPEAK values resulted in increase in the calculated Q values. However, different FPEAK values did not yield significant changes in source profiles or scaled residuals. Therefore in this study, considering the physical meaning of the resolved sources and the distribution of the scaled residuals, the FPEAK value was finally set equal to zero. FKEY tool is not used for this data set.

Scaled residuals were re-inspected for individual compounds at each output file that was resulted in utilizing the model with input settings of FPEAK=0.0 and number of factors of 4 and 5. For the compounds having scaled residuals beyond ±2 limit value (see previous section for details), input data matrix was re-inspected and the uncertainty values were increased by a factor of 50 for the outlier data points. Final decision on the number of factors was based on identification of source profiles. This was done by comparing source profiles generated by the model with those provided in the literature and with those developed in this study. Comparison of the predicted and measured data through LR was also used to decide on the number of factors. In this study, number of factors 4 was selected as the optimum number of factors that provided the best solution and the optimum model performance parameters.

Results of the Model

PMF2 analysis, with the application of the robust mode resulted in four factors (i.e., sources) that explain variation in the VOC data generated at residential site during winter campaign. Factors identified by PMF2 are interpreted qualitatively by evaluating source profiles (i.e., factor loadings), time variations in source contributions (i.e., factor scores) and explained variations (EV) that were generated by the model. The source profiles are used as the final criteria for source identification. EV profiles are used for reference only. Source profiles are also compared with the profiles available in the literature and the profiles developed in this study for a quantitative interpretation of the sources. Each factor is interpreted separately in the following paragraphs.

Factor 1

The source profile, EV and source contribution plots generated for Factor 1 are shown in Figure 5.8. Accompanying the factor, individual error estimates are also computed for all of the factor elements. Error estimates are also shown in Figure 5.8 together with factor profiles. Source contributions are averaged over each sampling sessions, namely morning (8:00-12:00), noon (12:00-16:00), afternoon (16:00-20:00), evening (20:00-00:00) and night (00:00-8:00). Benzene, toluene, m,p-xylene, 1,2,4-trimethylbenzene and light hydrocarbons are dominant species in the source profile for Factor 1. BTEX compounds are well-known markers of motor vehicle exhaust emissions (Watson *et al.*, 2001). Light hydrocarbons dominating in the source profile are common to light duty vehicle (LDV) exhaust emissions. EV plot shows that factor 1 explains approximately 30% - 60% of the variance of light hydrocarbons. On the other hand, the source is not effective to explain variances of heavy hydrocarbons. Source contributions shown in Figure 5.8 indicate a diurnal variation with a high contribution during evening rush hour and low contributions during noon, evening and night sessions. Source contributions have high standard deviation that might have increased due to inclusion of both weekend and weekday data to the model. Diurnal variation in the source contributions observed for this factor is an indication of a traffic pattern (see Section 4.1.2). This factor is interpreted as LDV motor vehicle exhaust. The further comparison of profile with the profiles generated in this study is conducted to ensure that it is exhaust profile.

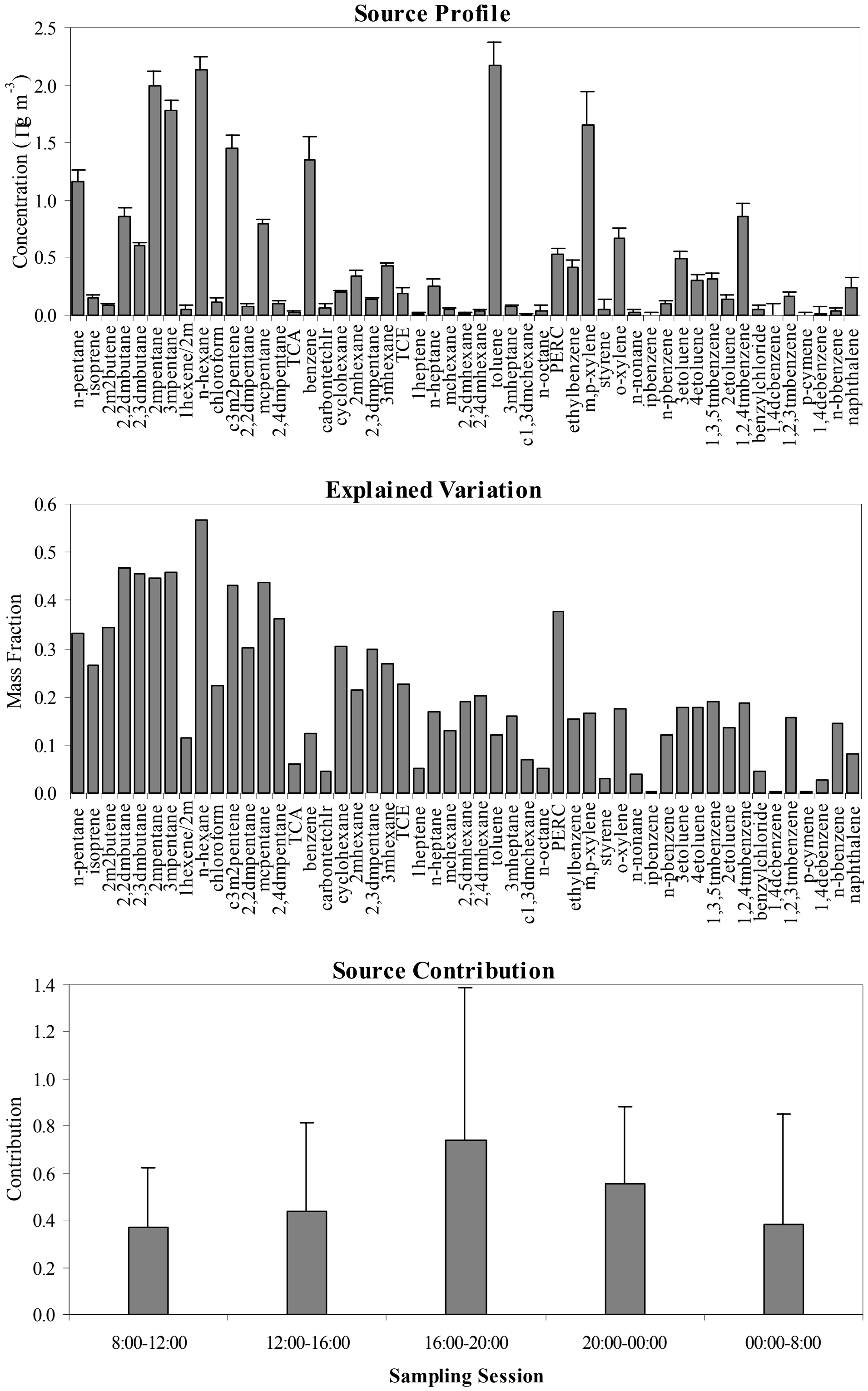


Figure 5.8 PMF2 results for Factor1-residential site, winter 2004.

Comparison of the source profile for Factor 1 with the several source profiles generated in this study is shown in Figure 5.9. Figure 5.9(a) shows unleaded gasoline, leaded gasoline, diesel, running vehicle exhaust and cold start profiles generated in Ankara study together with Factor 1 source profile computed by PMF2. Gasoline, exhaust and cold start profiles result in a better fit with Factor 1 profile than the diesel profile. Correlation analysis between these source profiles and profile for Factor 1 yields that the cold start profile has the highest correlation (R^2=0.77) with the Factor 1 profile, as shown in Figure 5.9 (b). For these reasons, Factor 1 was identified as the ***cold start LDV exhaust source***.

Factor 2

Results of the PMF2 run are plotted for Factor 2 in Figure 5.10. Source profile plot generated for Factor 2 indicates that benzene, carbon tetrachloride, toluene and 1,4-dichlorobenzene are the dominating species in this factor. Factor 2 does not have a distinct source profile pattern. EV plot shown in Figure 5.10 indicates that this source explains approximately 70% - 80% of the variances of 1,1,1-trichloroethane (TCA) and CCl_4 and 40% - 50% of the variances of the chloroform, 1,4-dichlorobenzene and 1,4-diethylbenzene in the data set.

TCA has been widely used as a solvent in industrial activities such as paint and ink manufacturing, aerosol manufacturing, adhesive manufacturing and pulp and paper production. TCA is also used as a solvent in cleaning and surface coating operations. Volatilization losses from its use in cold cleaning of metals, vapor degreasing and as a solvent and aerosol are the major sources of TCA emissions. For the general population, the most likely sources of exposure to TCA are home consumer products, household cleaners and polishes, building products, and contaminated food and water (Nazaroff and Weschler, 2004). Its wide use as a solvent in industry and for consumer products has resulted in large amounts being released to the environment.

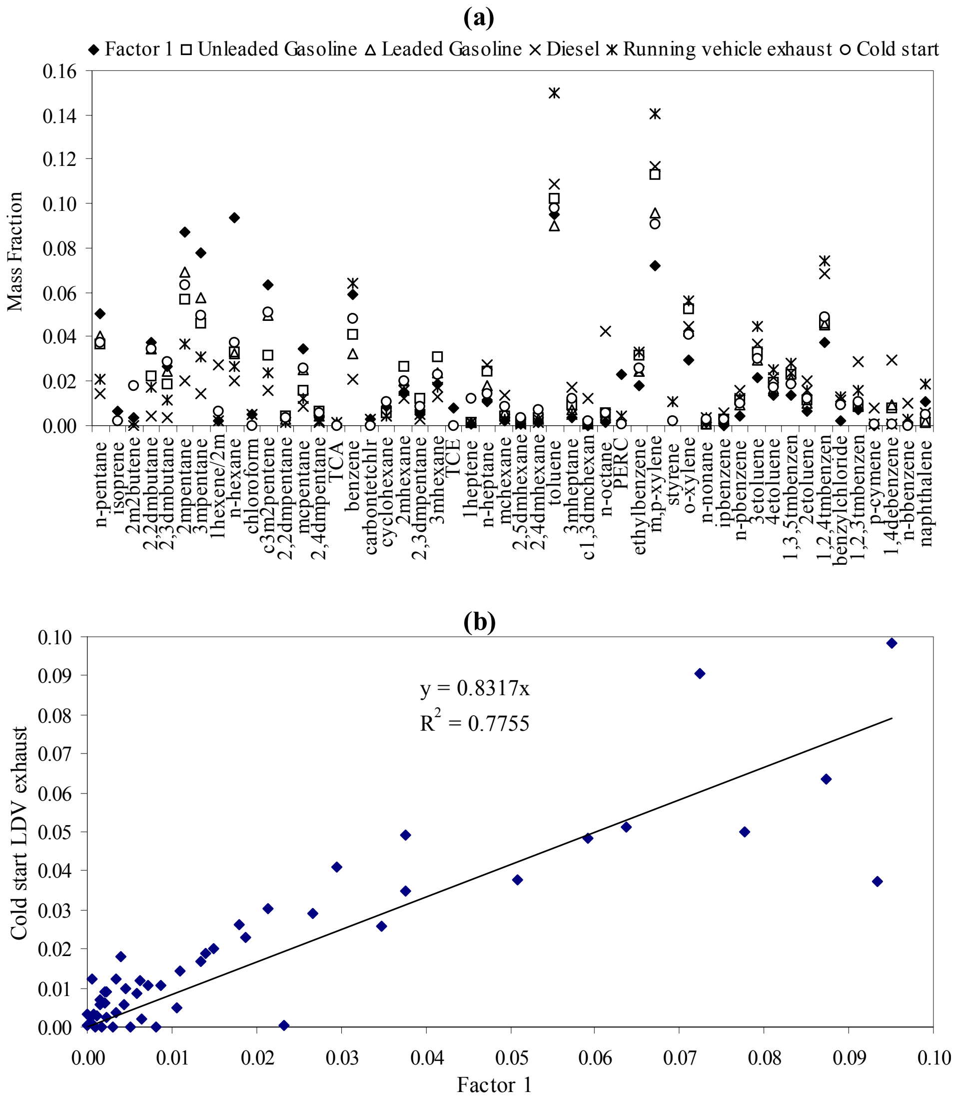


Figure 5.9. Comparison of the source profiles, (a) selected normalized source profiles generated during Ankara campaign and profile for Factor 1; (b) correlation between cold start and Factor 1 profiles.

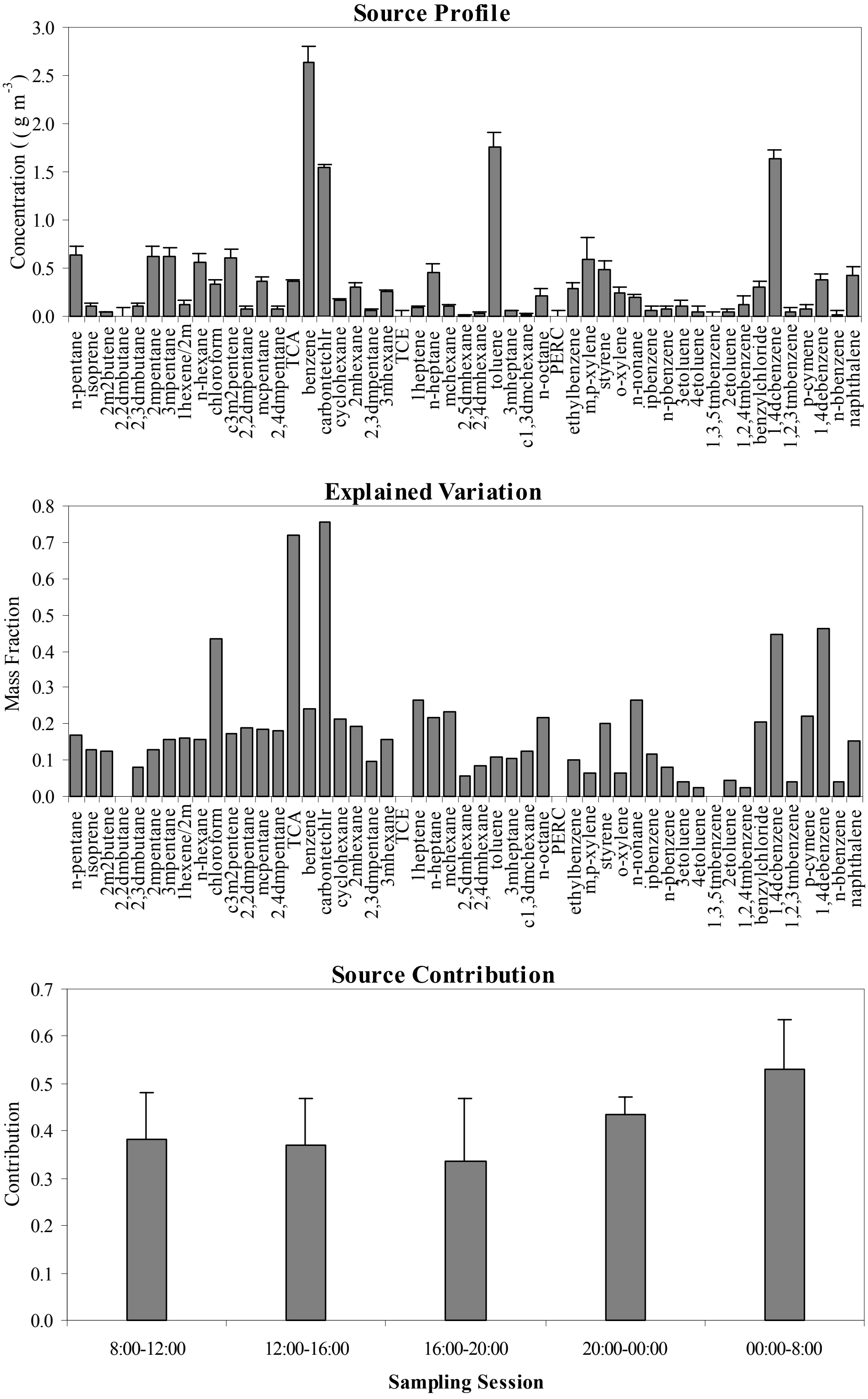


Figure 5.10. PMF2 results for Factor2-residential site, winter 2004.

Carbon tetrachloride is regarded as a highly toxic compound. It is a known animal carcinogen and a potential human carcinogen. It is also an excellent solvent for many applications. Because CCl_4 is chemically stable, it has a long atmospheric lifetime. It was used in the production of refrigeration fluid and propellants for aerosol cans, as a pesticide, as a cleaning fluid, as degreasing agent and in fire extinguishers (ATSDR, 1995). TCA, CCl_4, and chloroform are commonly used in household cleaning products and polishes (Sack *et al.*, 1992).

Source contributions for Factor 2 do not result in a diurnal variation as can be seen in Figure 5.10. Standard deviations are also low. This might be due to atmospheric residence times of the compounds that are explained by this factor are quite high (in the order of years) yielding an almost constant background concentration levels in the city.

Factor 2 is identified as the ***solvent source***. The possible sources of the solvent in Ankara are believed to be household cleaning products and utilization of solvent in small enterprises that are distributed within the city. Composition of Factor 2 (profile) were not compared with the solvent profiles available in the literature, because solvent profiles show different patterns for individual use such as surface coating, dry cleaning, etc. In addition, even the similar use may result in slightly different profile in different countries due to local legislations on solvent use. For example, the State of California in the U.S.A. requires special solvent and coating formulations to comply with air quality emissions requirements, so the profiles generated for California are likely to be very specific to this particular area (Watson *et al.*, 2001).

Factor 3

Results of the PMF2 run for Factor 3 are presented in Figure 5.11 for source profile, EV and source contributions.

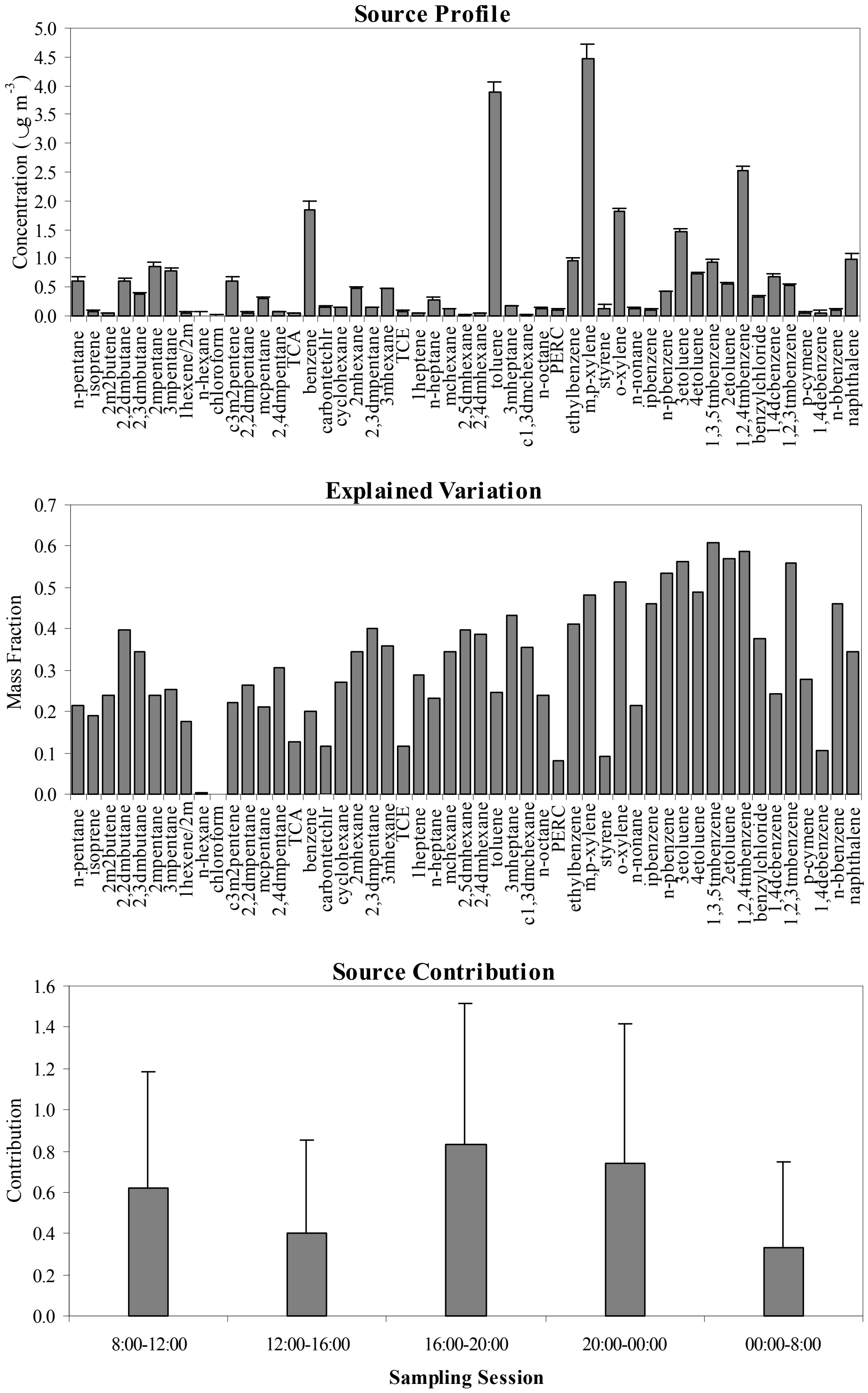


Figure 5.11. PMF2 results for Factor 3-residential site, winter 2004.

As can be seen from the source profile plot, m&p-xylene, toluene, benzene and 1,2,4-trimethylbenzene are the most abundant species in this source. BTEX compounds are known as marker for motor vehicle exhaust as indicated in previous paragraphs. Source profile plot shown in Figure 5.11 also indicates that concentrations of heavy hydrocarbons are slightly higher than that of light hydrocarbons. Explained variances show that this source explains approximately 30% of the variances of light and 40% - 60% of the variances of heavy hydrocarbons.

Source contributions show a well-defined diurnal pattern for Factor 3. Source contributions are higher during morning and evening rush hours than the contributions during noon, evening and night sessions. Diurnal variation in source contribution observed for Factor 3 is similar to the traffic pattern observed in Ankara (see Section 4.1.2). Source contributions present high standard deviations that may indicate that contribution are log-normally distributed. Factor 3 is interpreted as motor vehicle exhaust mostly associated with diesel vehicles including heavy-duty vehicle (HDV) and LDVs. The profile is also compared with the profiles developed in this study and the profiles available in the literature.

Selected source profiles generated during Ankara campaign together with modeled source profile for Factor 3 are shown in Figure 5.12. Figure 5.12(a) shows the normalized source profiles for unleaded gasoline, leaded gasoline, diesel, running vehicle exhaust and cold start profiles generated in Ankara campaign and source profile for Factor 3. Source profiles that are in concentration units are normalized to total mass for the species that are input to the PMF2 model. Factor 3 profile is very similar to the running vehicle exhaust profile. Figure 5.12(b) shows correlation between normalized source profiles of running vehicle exhaust and Factor 3. The correlation is very high (R^2=0.96). Thus, it is clear that Factor 3 is a running vehicle exhaust source. Factor 3 is also compared with the source profiles available in the literature.

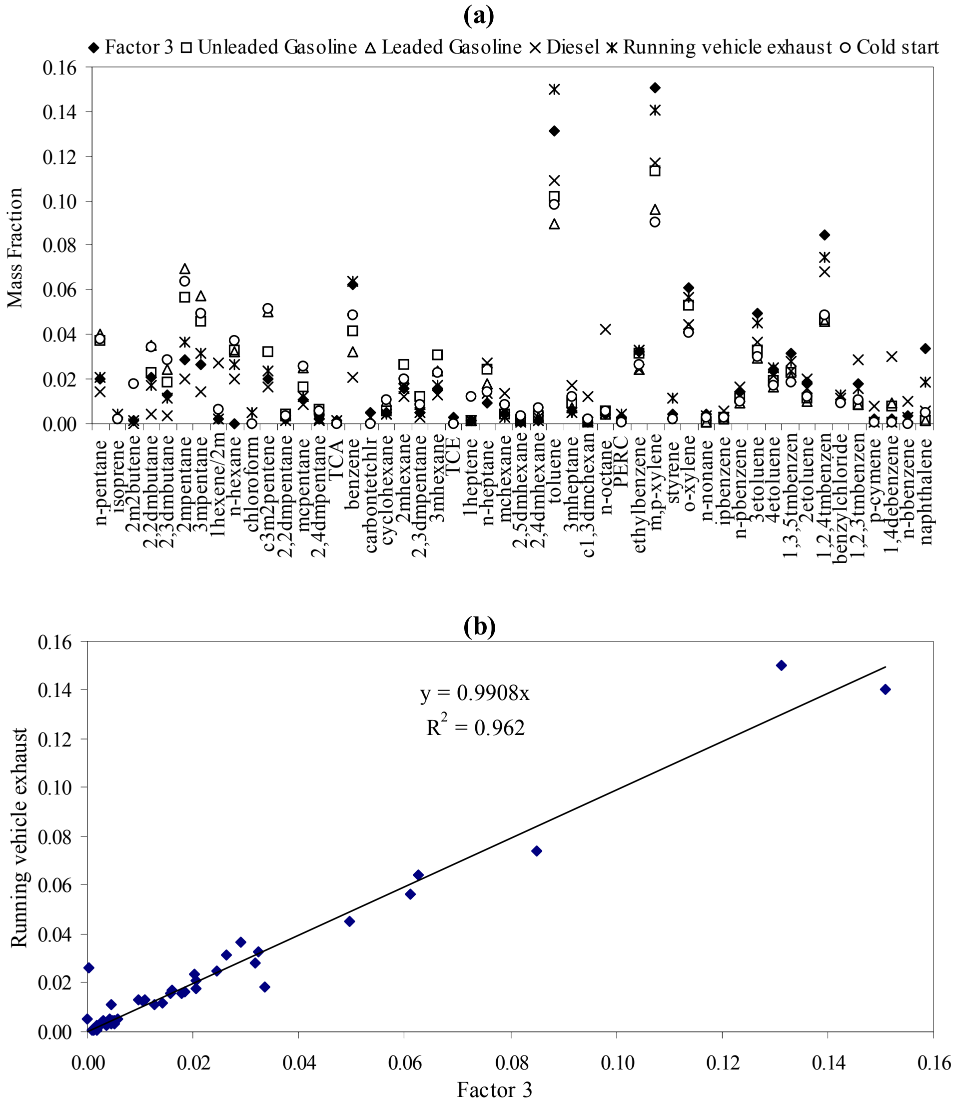


Figure 5.12. Comparison of the source profiles, (a) selected normalized source profiles generated during Ankara campaign and profile for Factor 3; (b) correlation between running vehicle exhaust and Factor 3 profiles.

Source profiles were taken from SPECIATE version 3.1 database developed by the US EPA. There are about 10,000 source profiles for speciated VOCs in the SPECIATE database. Profiles are inspected and the ones that correspond to probable VOC sources in Ankara and Ottawa such as vehicle exhaust, surface coating, printing, dry cleaning, etc. are retrieved from the database. Additionally, source profiles available in the literature are also used for comparison. The selected source profiles obtained from SPECIATE database and literature together with source profile for Factor 3 are presented in Figure 5.13.

Tunnel-1 profile is light duty gasoline vehicle exhaust profile generated at Tuscora Tunnel, Pennsylvania, U.S.A. (Conner *et al.*, 1995). This profile is taken from the SPECIATE database profile number 2521. Dynamo.-1 profile represents the chemical composition of exhaust emissions from non-catalyst gasoline LDV. The profile was derived from tests on older non-catalyst vehicles performed by two independent laboratories (Harley *et al.*, 1992). The profile was taken from the SPECIATE database profile number 6001.

Tunnel-2 profile was obtained from literature. This profile represents the vehicle exhaust profile generated in Lincoln Tunnel in the U.S.A. (Lonneman *et al.*, 1986). Dynamo.-2 vehicle exhaust profile was generated by Sigsby *et al.* (1987) through dynamometer tests on 46 in–use passenger cars. Roadway profile was obtained from the literature (Conner *et al.*, 1995). Running vehicle exhaust profiles were generated in Atlanta, GA in the U.S.A. during 1990 Atlanta Ozone Precursor Monitoring Study where motor vehicle emissions were sampled beside a roadway in a tunnel-like underpass during periods of heavy traffic.

Source profiles obtained from the literature do not have exactly the same set of VOCs as in the source profile for Factor 3. The common species show similar pattern with the profile for Factor 3 but ratios of species are not similar. Some of the literature profiles providea better fit to Factor 3 profile than others.

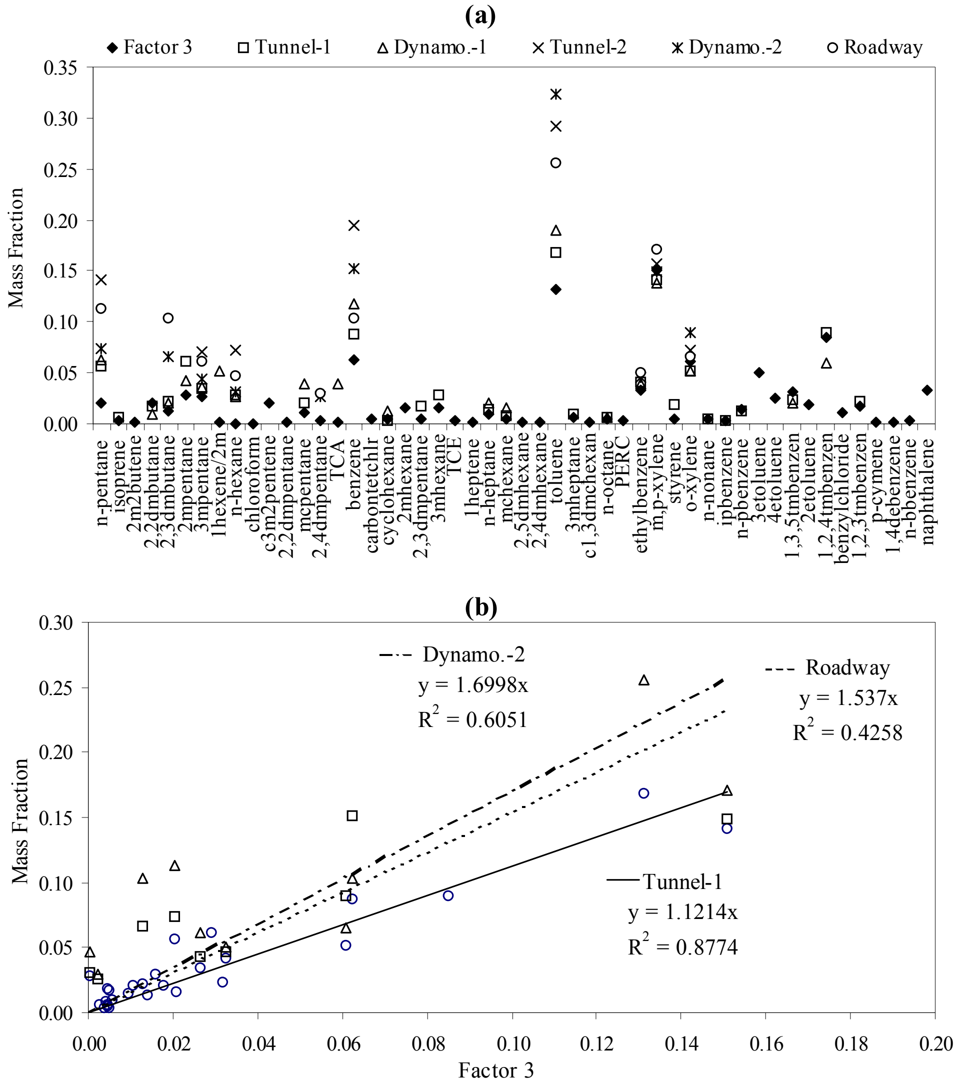


Figure 5.13. Comparison of the source profiles, (a) selected normalized source profiles available in the literature and profile for Factor 3; (b) correlation between selected literature and Factor 3 source profiles.

Figure 5.13(b) shows correlation between normalized source profile for Factor 3 and Tunnel-1, Dynamo.-2, and Roadway profiles. Species show a wide scattering. Except for the Tunnel-1 profile, correlations are poor. The Tunnel-1 profile shows a good correlation (R^2=0.87) with Factor 3 profile.

Evaluation conducted for different source profiles indicate that most of the profiles show a wide scattering and a limited number of profiles provide a better fit to the modeled profile for Factor 3. There are vast amounts of possibilities to find the profile that provide the best fit to our modeled profile. One should also consider that exhaust emission profiles might differ in various countries due to differences in fleet characteristics (e.g., fleet age, models, types, inspection and maintenance, etc.), driving cycles and fuel characteristic. Therefore, the best practice is to compare the PMF2 results with the local source profiles whenever possible.

Factor 3 is identified as ***running vehicle exhaust*** source. Since the factor profile explains most of the variation in heavier hydrocarbons, the factor is a running vehicle exhaust source mostly associated with diesel exhaust.

Factor 4

Results of the PMF2 run for Factor 4 are presented in Figrue 5.14. Figure provides source profile and source contribution plots together with their uncertainties and the EV plot. Toluene, benzene and m,p-xylene are the most abundant compounds in the source profile. Concentrations of rest of the compounds are almost negligible. Lack of many hydrocarbons, which is usually associated with motor vehicle emissions, indicates that Factor 4 is not a motor vehicle related source. The EV plot does not show a distinct pattern. Factor 4 explains 20% - 40% of the variances of toluene, benzene, trichloroethene (TCE) and 1-hexene/2-methyl-1-pentene. Variances of other VOCs explained by Factor 4 are smaller.

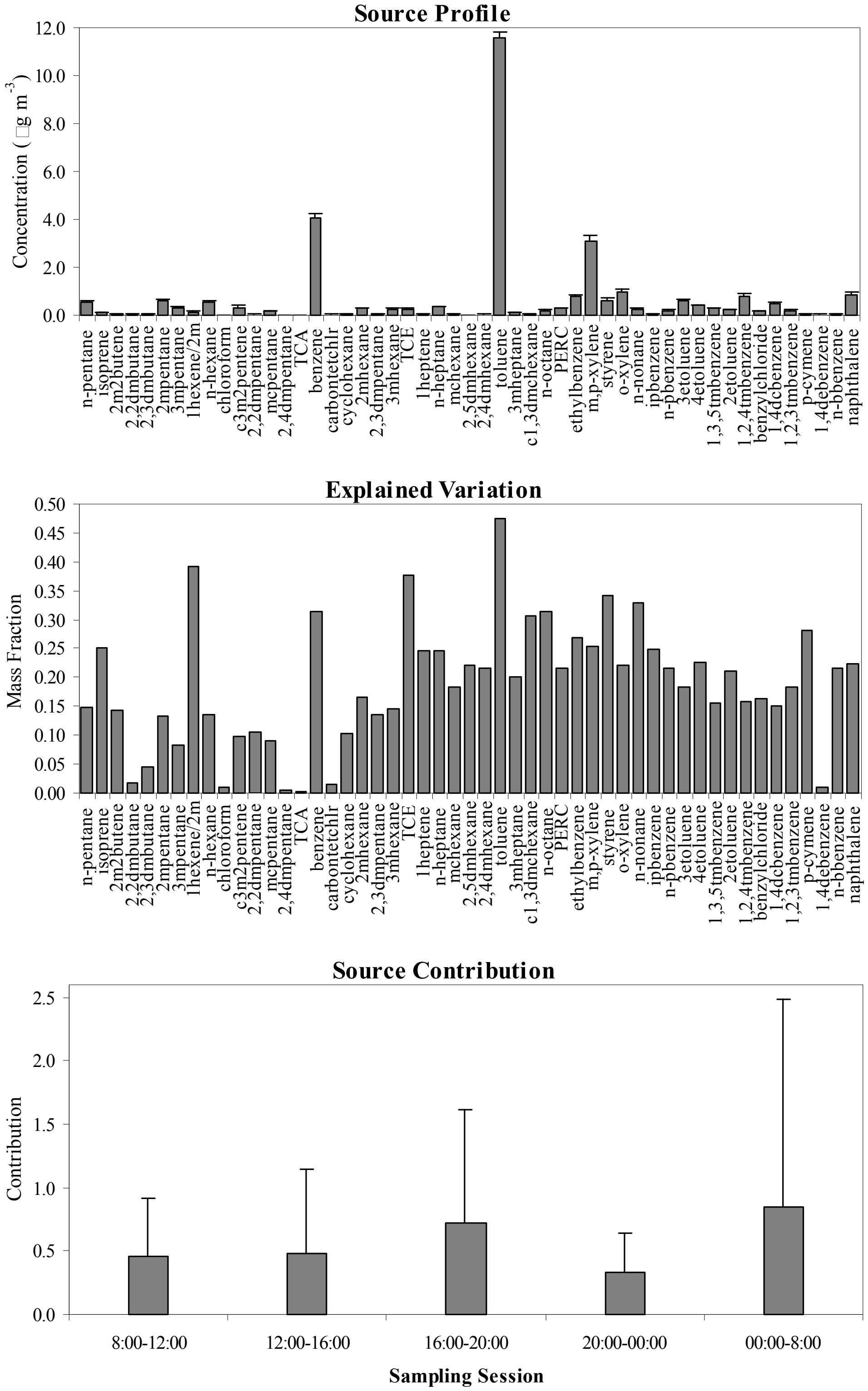


Figure 5.14. PMF2 results for Factor 4-residential site, winter 2004.

Source contributions show a diurnal pattern with the highest contributions during night session, which is fairly similar to diurnal variation in SO_2 concentrations measured in regular air quality monitoring stations. The standard deviations for source contributions are high indicating a significant day-to-day change in source contributions, which is typical for log-normally distributed contributions. Simply looking at profiles and explained variances do not allow relating Factor 4 to any known source. But comparison of Factor 4 profile with various profiles reported in the literature helped for identification.

Numerous profiles for different source types are compared with Factor 4 profile for conclusive identification of this factor. The profile generated by Kubica *et al.* (2004) for coal combustion in small residential appliances in Poland provides the best fit to the modeled source profile for Factor 4. All species except pentane have a very good fit with Factor 4 profile, and Factor 4 is identified as ***a coal combustion source for residential heating.***

The source profiles for Factor 4 and coal combustion profile generated by Kubica *et al.* (2004) excluding pentane is shown in Figure 5.15. Correlation between these two profiles are also investigated and found that the correlation is excellent with R^2=0.92 and intercept of 1.24. Toluene to benzene ratios (T/B) is also similar in both profiles. T/B value is 2.75 and 2.84 for coal combustion and Factor 4 profiles, respectively. It is reported that Poland has the highest coal combustion use for residential heating among the EU countries (Kubica *et al.*, 2004). Similarly, about 60% of the residences still use coal in residential heating in Ankara (SSI, 1998). PMF2 is successful to resolve this important source from the Ankara data.

Source Contribution Estimates

Linear regression (LR) was used to regress the modeled total VOC concentrations against the measured total VOC concentrations. LR helped ascertain the optimal number of factors as well.

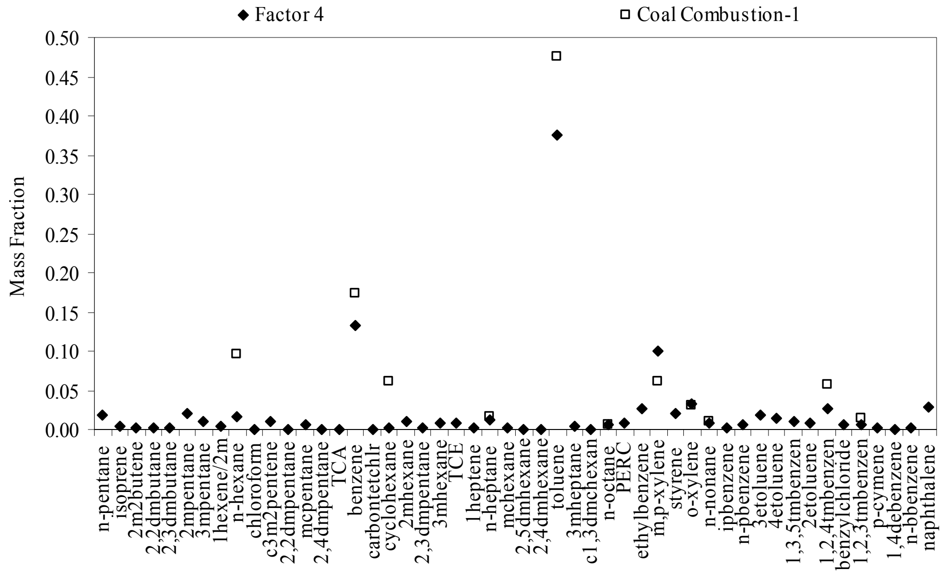


Figure 5.15. Coal combustion and Factor 4 profiles.

LR was conducted by multiplying the factor scores by the factor loadings computed by PMF2. Summing these modeled concentrations over all factors gave a total modeled concentration that was used to compare the model-predicted total VOC concentration to the measured total VOC concentration for each observation. An unrealistic number of factors for the PMF2 model very often result in negative values for the coefficients of LR (Polissar *et al.*, 2001). Thus the number of factors was selected, in part, to avoid negative regression coefficients. PMF2 solution with 4 factors satisfied this criterion.

Linear regression between the model-predicted and measured total VOC concentrations is shown in Figure 5.16. R-square values and ratios of the modeled to measured concentrations are examined to determine how well the regression model fit the measured data for total VOCs. LR resulted in R^2 value of 0.99 with intercept of 0.98.

These results indicate that the resolved sources by PMF2 effectively reproduce the measured values and accounted for most of the variation in the total VOC concentration. Ratio of the modeled to measured total VOC concentrations is 0.97 indicating model results are very close to measured data.

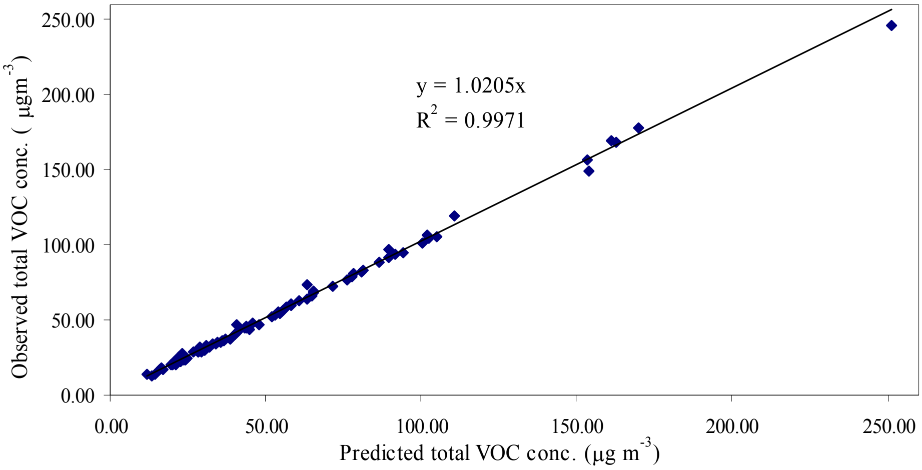


Figure 5.16. Observed versus predicted VOC concentrations.

In addition, the percent contribution of each factor to total VOCs was determined by dividing the modeled concentration for each factor by the total modeled concentration. The average source contribution estimates (SCE) of each factor to the measured total VOC concentration are shown in Table 5.11.

Running vehicle exhaust contributes the most accounting for 34% of the total VOC concentration measured at the residential site during winter campaign. Residential heating scored the second highest contribution with a SCE value of 31%. Cold start LDV exhaust and solvent use results the SCE values of 22% and 13%, respectively. On the average, motor vehicle related sources contribute to 56% of the total VOC concentration. Thus, motor vehicles and residential heating are the major sources of VOCs measured at the residential site in Ankara during winter campaign.

Table 5.11. Source contribution estimates for residential station during winter campaign.

Factor No	Source	% SCE
1	Cold start LDV exhaust	21.84
2	Solvent use	12.48
3	Running vehicle exhaust (diesel emission dominating)	34.14
4	Residential heating	31.54

Model Performance Parameters

One of the advantages of PMF2 is to provide performance evaluation tools such as goodness of fit value (i.e., Q) and scaled residuals. Q value is inspected to decide on the optimum number of factors. Minimum Q value that is the closest to the theoretical Q value indicates a better fit of the model to measured data. PMF2 solution with 4 factors resulted in a calculated Q value of 3512 that was about 25% lower than the theoretical Q value. This indicates a good fit that can also be seen from the result of the LR analysis. Scaled residual errors were also inspected. Most of the scaled residuals are between -2.0 and 2.0 with a random distribution of positive and negative values. The frequency distributions of scaled residual errors only for selected compounds are shown in Figure 5.17.

5.1.3.2 Residential Station Summer Campaign

Input Parameters

Ambient air samples collected at the residential station in Ankara during summer campaign were analyzed for a total of 91 VOCs. PMF2 was utilized to resolve sources emitting VOCs in Ankara during summer season. The ambient data was pretreated for missing and BDL values.

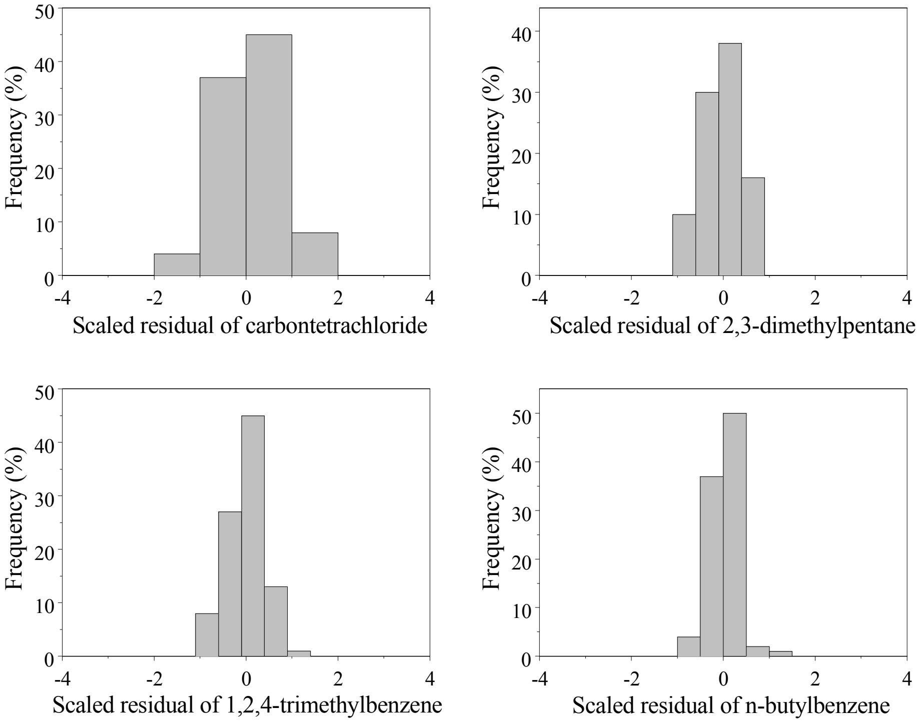


Figure 5.17. Frequency distribution plot for scaled residual errors.

The total numbers of compounds in the data set with less than 30% and 50% missing values were 53 and 58, respectively. Compounds with less than 50% missing data were included in the input dataset. The S/N ratio was also inspected. According to S/N values 7 compounds were identified as “bad” variables. The bad variables were excluded from the data set. Four compounds, namely c-2-pentene, 2,4-dimethylhexane, 2,5-dimethylhexane and 2,3,4-trimethylpentane, resulted in S/N values close to 0.2.

Preliminary model runs indicated that distribution of scaled residual errors for these compounds were beyond the limits of ±2.0. Different initial parameters in PMF2 run did not resulted in improvement of their scaled residuals. Thus, these four compounds were also excluded from the input data set since none of them is important marker specie for any of the sources found. The remaining 47 compounds were processed to replace missing and BDL values as described in Section 2.7.1. In the end, the input data matrix was constructed with the pretreated 47 compounds and 74 data points for each compound.

Both EM-14 algorithm built in PMF2 and the guidelines provided by Polissar *et al.* (1998) were utilized in order to estimate errors for each input data points belonging to winter campaign. Comparison of the results of the two methods yielded that error estimates calculated using the method proposed by Polissar *et al.* (1998) were better. Thus, error estimates for the input data values belonging to summer campaign were calculated according to method proposed by Polissar *et al.* (1998). Uncertainty matrix was constructed with the computed error estimates. There were episodic periods resulting in very high concentrations during summer campaign. The error estimates for these days were multiplied by 50 in order to down-weight these outliers in PMF2 run.

Application of the Model

PMF2 was computed using the data and uncertainty matrices generated for the summer data set. Model was run with different number of factors. Rules explained in Section 2.7.1 were applied to determine the optimum number of sources (factors) that provided the optimum solution. PMF2 runs using number of factors 3, 4, 5, 6 and 7 yielded calculated Q values of 4399, 3658, 3113, 2524 and 1973, respectively. Theoretical Q value for the input data was 3478.

The model solution for 7 factors resulted a calculated Q value of about 2 times lower than the theoretical value. Calculated Q value for 3 factors solution was very high and the resulting source profiles were not explainable. Solution for the number of factors 4 had the calculated Q value that was the closest to theoretical Q value. However, computed source profiles for number of factors 4 solution were not explainable. Therefore, 3, 4 and 7 factor solutions were excluded from the evaluation.

The effect of rotation on model fit was assessed by utilizing different FPEAK values. PMF2 was run with 5 factors and FPEAK values ranging from -1.0 to 1.0. Model runs with FPEAK values of -1.0, -0.5, -0.1, 0.0, 0.1, 0.5, 0.7 and 1.0 yielded calculated Q values of 3415, 3173, 3112, 3113, 3109, 3176, 3230, and 3289, respectively. FPEAK values of ±1.0 did not result in significant change in Q value and computed source profiles. The calculated Q value increased by the increase in the absolute value of FPEAK. FPEAK value of -0.5 resulted in a slight change in source profiles. Except for one source profile, all the source profiles were explainable. Similar performance test was also performed for the 6 factor model. Different FPEAK values did not result in significant change in calculated Q value and source profiles while running PMF2 with 6 factors. FPEAK values did not result in significant change in scaled residual errors. FPEAK value of zero was accepted as the optimum rotation value.

FKEY function was used for the 6 factors solution. Paatero (1998) indicates that when a priori knowledge tells that a certain factor element should be zero or very small, the pulling down operation is controlled by the function FKEY in PMF2. All the source profiles for the 6 factors solutions were explainable but the toluene concentration in the solvent profile was extremely high. Concentration of the toluene was pulled down in this profile by utilizing different FKEY values of 3, 5 and 8. FKEY value of 5 provided a better solvent profile. However, slight changes in other profiles were also observed. At the end, 5 factor model was selected as the optimum that provided most explainable source profiles and the best model performance parameters.

Results of the Model

PMF2 analysis, with the application of the robust mode resulted in five sources that explained variation in the VOC data generated at the residential site during summer campaign. Factors identified by PMF2 are interpreted qualitatively by evaluating source profiles, time variations in source contributions and EV that were generated by the model. Source profiles are also compared with the profiles available in the literature and the profiles generated in this study for a quantitative interpretation of the sources. Each factor is interpreted separately in the following paragraphs.

Factor 1

The source profile, EV and source contribution plots generated for Factor 1 are shown in Figure 5.18. Accompanying the factor, individual error estimates are also computed for all elements in the factor and shown in the figure. Source contributions are averaged over sampling sessions. Source profile plot for Factor 1 shows that isoprene and n-pentane are the most abundant species in this factor. EV plot demonstrates that Factor 1 explains greater than 80% of the variance in isoprene concentration indicating that factor 1 is the main source of isoprene measured at the residential site during summer campaign. Isoprene is a very well known marker for biogenic emissions (Watson *et al.*, 2001). Source contributions indicate that contribution of this factor is the highest during daytime and the lowest during nighttime sessions. This pattern indicates the relation between sunlight and emission from Factor 1, which agrees with the sunlight dependence of emissions from plants. Standard deviations of source contributions are the lowest during nighttime session. It is obvious that Factor 1 is associated with biogenic emissions. Factor 1 is identified as ***biogenic emission*** source.

Factor 2

Results of the PMF2 run for Factor 2 are presented in Figure 5.19. Source profile plot generated for Factor 2 indicates that toluene is the most abundant compound in this factor. Concentration of toluene in Factor 2 is the highest of all source profiles for all factors.

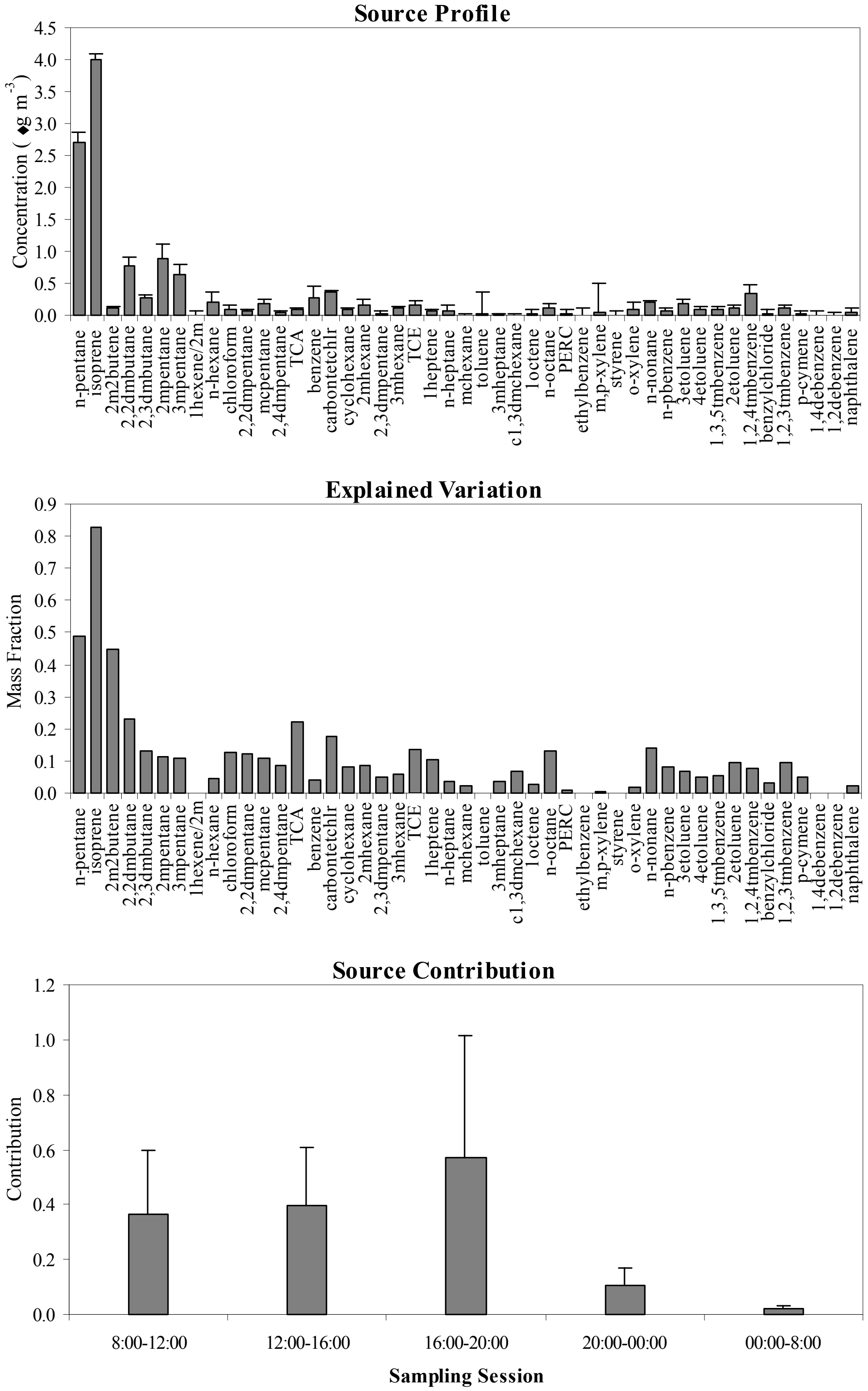


Figure 5.18. PMF2 results for Factor 1-residential site, summer 2003.

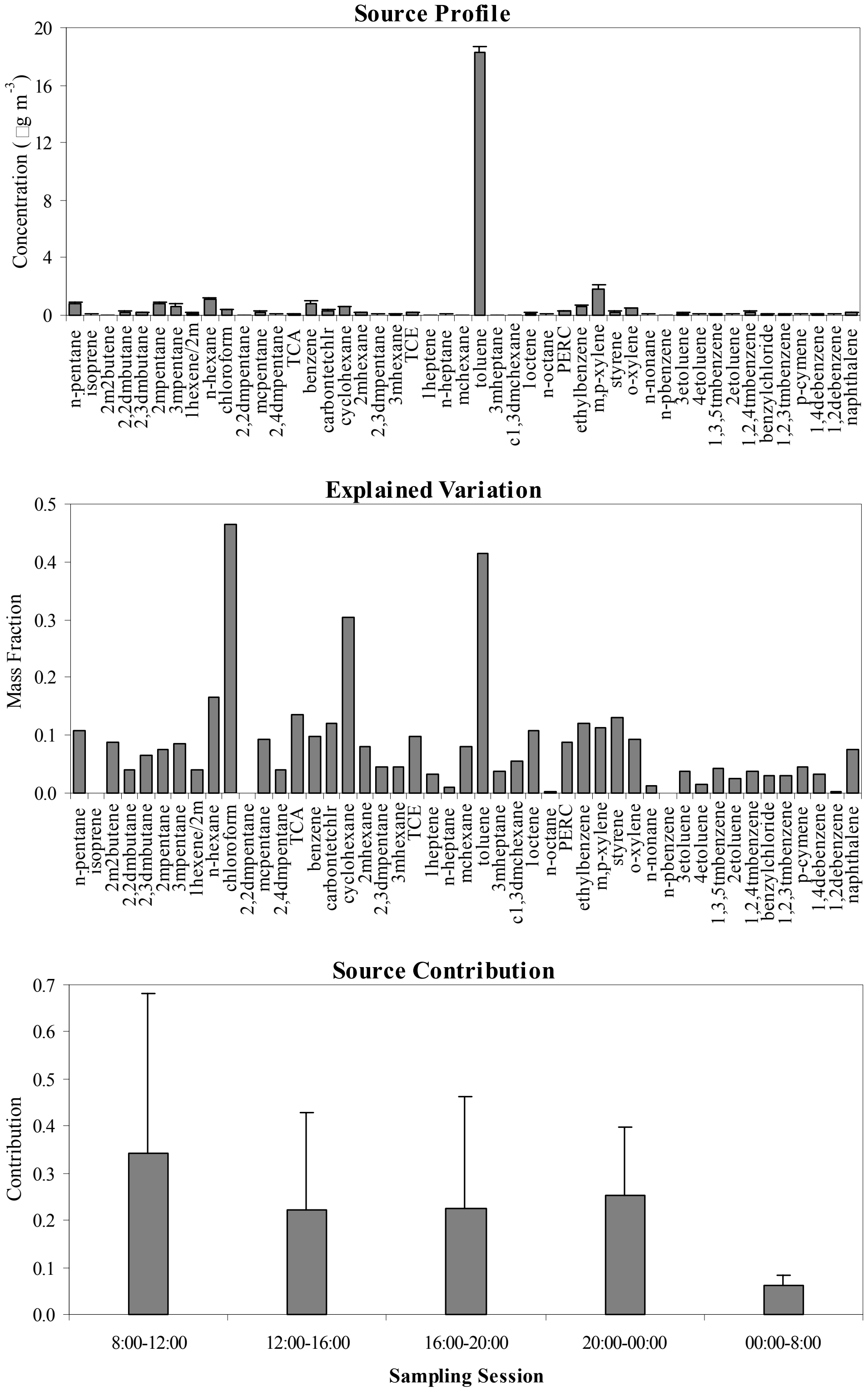


Figure 5.19. PMF2 results for Factor 2-residential site, summer 2003.

EV plot shows that greater than 30% of variances in chloroform, toluene and cyclohexane concentrations are explained by Factor 2. Source contributions indicate that the contribution of this source is the highest during morning session. The standard deviation of source contribution for morning session is also the highest. Source contribution and its standard deviation for Factor 2 are almost negligible during night session.

Source profile for Factor 2 is compared with the profiles available in the literature to identify the source accurately. Among various profiles used in comparison, Factor 2 shows the best fit with architectural coating profiles. The source profile for Factor 2 together with two other source profiles, for architectural coatings, obtained from the literature are shown in Figure 5.20.

Paint-1 is a paint solvent profile generated for Seoul, South Korea by Na *et al.* (2004). Paint-1 profile is composite of four major paints used in Seoul that were urethane, varnish, archryl and thinner. Aromatics accounted for 95% of paint solvents and alkanes accounted for the rest. Toluene (63%) is the most abundant component in paint-1 profile, followed by m&p-xylene (19%) and o-xylene (8%). Contribution of benzene is about 1%.

Paint-2 is an architectural coating profile generated for the U.S.A. by Scheff *et al.* (1989). This profile is composite of solvent-based coating, thinning and cleanup solvent, and water-based coating. Toluene (78%) is the most abundant component in paint-2 profile followed by o-xylene (9%) and m&p-xylene (8%). Contribution of benzene is only about 0.3%. Scheff *et al.* (1989) also provided a water-based coating profile. Contribution of aromatic compounds including toluene, m&p-xylene and o-xylene are almost negligible in water-based coatings.

Source profile for Factor 2 shows a similar pattern with the architectural coating profiles available in the literature. On the other hand, paint-1 and paint-2 profiles provide the best fit with Factor 2.

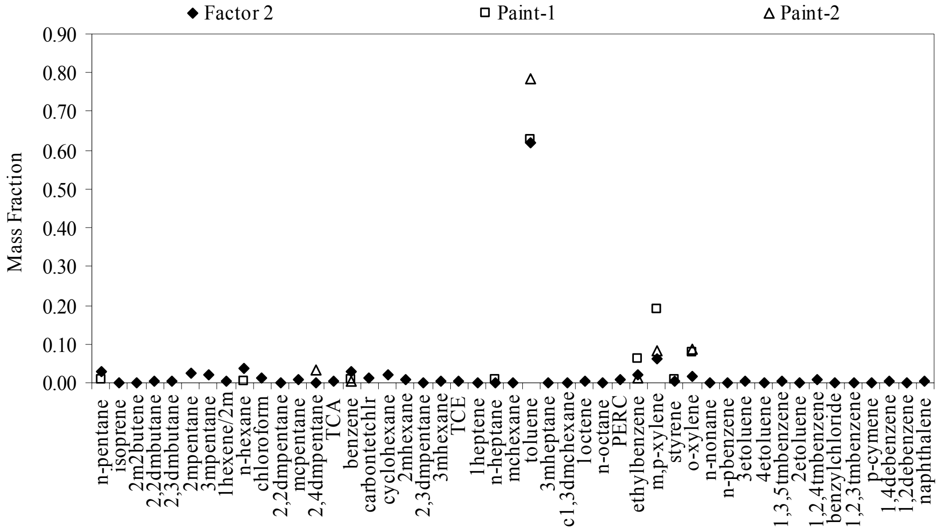


Figure 5.20. Comparison of the source profile for Factor 2 with the profiles available in the literature.

Contributions of toluene, m&p-xylene and o-xylene are 62%, 6% and 2% in the source profile for Factor 2, respectively. Abundance of aromatic compounds in source profile for Factor 2 indicates that Factor 2 is ***solvent-based architectural coating*** source rather than water-based coating.

Factor 3

Source profile, EV and source contribution plots for Factor 3 are shown in Figure 5.21. Toluene, m&p-xylene, benzene and 2-methylpentane are among the most abundant compounds in the source profile. Light hydrocarbons have higher concentrations than heavy hydrocarbons in the source profile for Factor 3. Abundance of BTEX compounds and the source profile pattern indicate that this profile could be associated with light duty motor vehicle emissions. EV plot demonstrate that Factor 3 explains large fractions of variances in concentrations of most of the traffic related species.

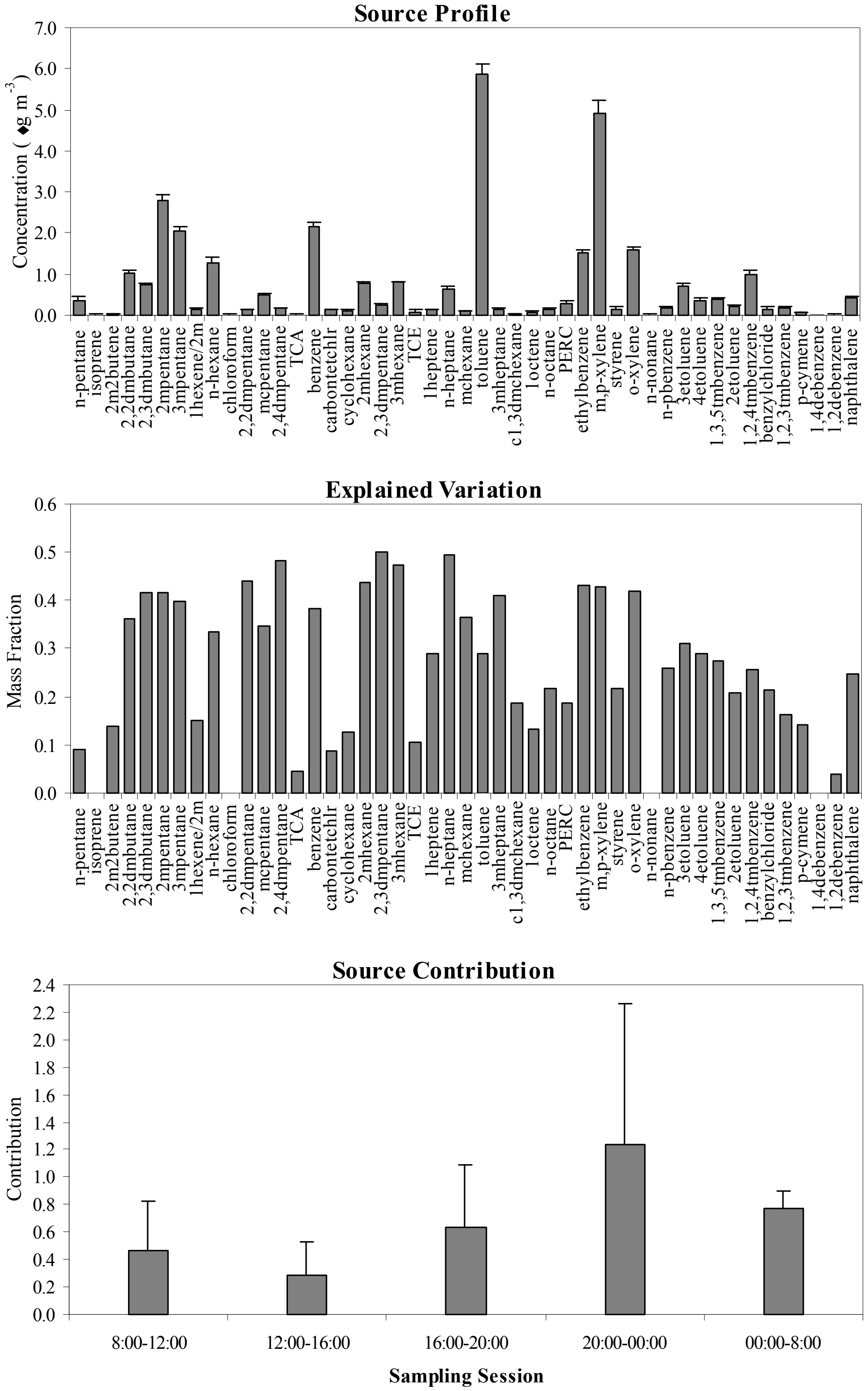


Figure 5.21. PMF2 results for Factor 3-residential site, summer 2003.

Source contributions averaged over sampling sessions show a well-defined diurnal variation, which is typical for traffic emissions with high contributions during morning and evening rush hours and low contribution during noon session. The highest contribution for Factor 3 is observed during evening session. The standard deviation of the contribution was also the highest during evening session. The traffic is usually busy resulting a high traffic load even during night session during summer weekends in Ankara.

The highest contribution observed during night session might also be partly due to two episodic periods observed in the dataset coinciding night sessions as described in Section 4.1. Factor 3 is identified as ***motor vehicle exhaust***. Further comparison with the profiles generated in this study is done in order to identify source accurately.

The selected profiles generated in Ankara campaign together with source profile for Factor 3 are shown in Figure 5.22(a). Unleaded gasoline, running vehicle exhaust and evaporative + exhaust profiles show a good fit to Factor 3 profile. On the other hand, headspace diesel and diesel profiles result in a very poor fit with Factor 3 profile. Evaporative + exhaust profile shows the best fit to source profile for Factor 3 as can be seen from the correlation plot given in Figure 5.22(b). Consequently, Factor 3 is identified as ***LDV exhaust and evaporative*** source.

Factor 4

Results of the PMF2 run for Factor 4 are shown in Figure 5.23. Source profiles are plotted together with computed standard deviations. Carbon tetrachloride, benzene, PERC are among the most abundant compounds in the source profile for Factor 4. EV plot shows that carbon tetrachloride, PERC, TCA and TCE are the compounds that are mostly explained in this factor.

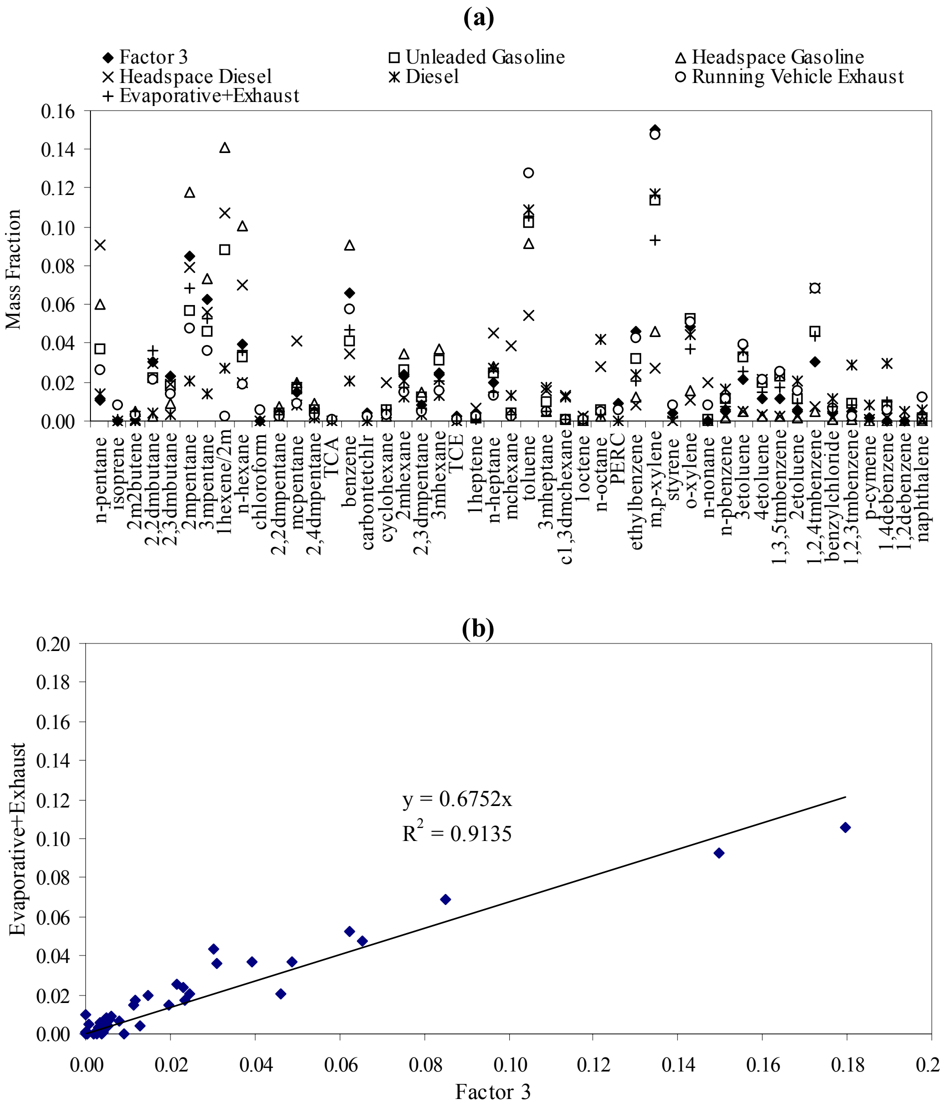


Figure 5.22. Comparison of the source profiles, (a) selected normalized source profiles generated in this study and profile for factor 3; (b) correlation between evaporative+exhaust and Factor 3 source profiles.

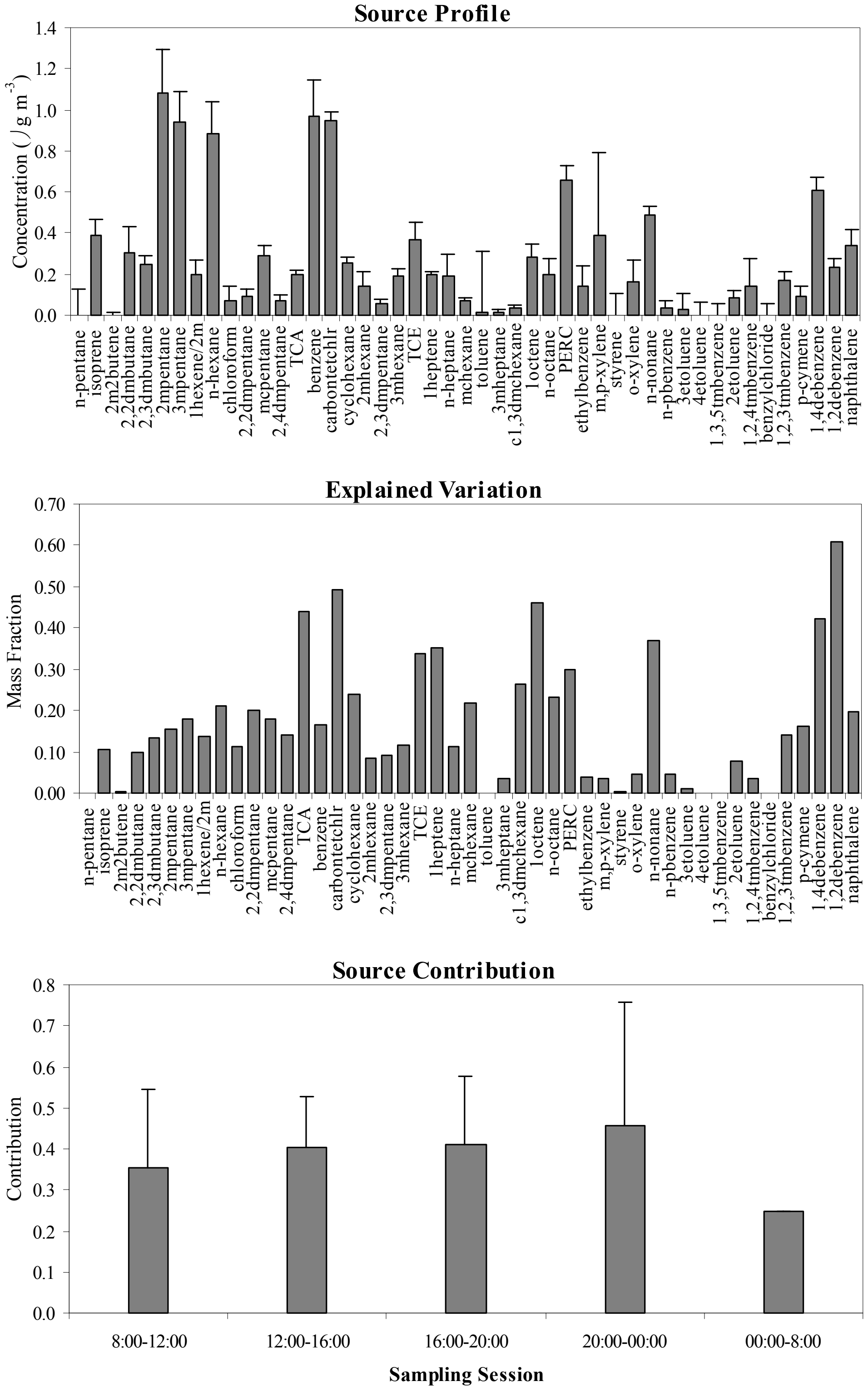


Figure 5.23. PMF2 results for Factor 4-residential site, summer 2003.

Carbon tetrachloride, TCA and TCE are commonly used in industrial processes, however, most likely sources for human exposure to these compounds are household cleaners and polishes (Nazaroff and Weschler, 2004). Utilization of these compounds in different sectors is discussed in detail in the previous section. The PERC is a very well known marker for dry cleaning (Scheff *et al.*, 1989; Watson *et al.*, 2001).

The source contribution plot shows that Factor 4 does not present a significant diurnal pattern except for the night session. The source contribution profile reveals a very similar pattern with that observed for Factor 2 of winter PMF2 solution except for the night session. The decrease in the source contribution during night session could be due to share of PERC in the summer profile. PERC is associated with dry cleaning activities and most of the dry cleaners work until 22:00. Factor 4 is identified as a ***solvent*** source.

Factor 5

The results of PMF2 run plotted for Factor are shown in Figure 5.24. Toluene, m&p-xylene, 1,2,4-trimethylbenzene and benzene are the most abundant compounds in the source profile for Factor 5. Heavy hydrocarbons have higher concentrations than light hydrocarbons. EV plot shows that Factor 5 explains variations in most of the heavy hydrocarbons. Source contributions indicate a diurnal variation that is very similar to that observed for Factor 3. Higher source contributions during morning and evening rush hours than noon hours are observed. The highest contributions observed during evening session could be due to different traffic pattern observed in summer season as suggested for Factor 3. Factor 5 is interpreted as motor vehicle exhaust source that is mostly influenced by diesel emissions. Further comparison is performed with the profiles developed in this study.

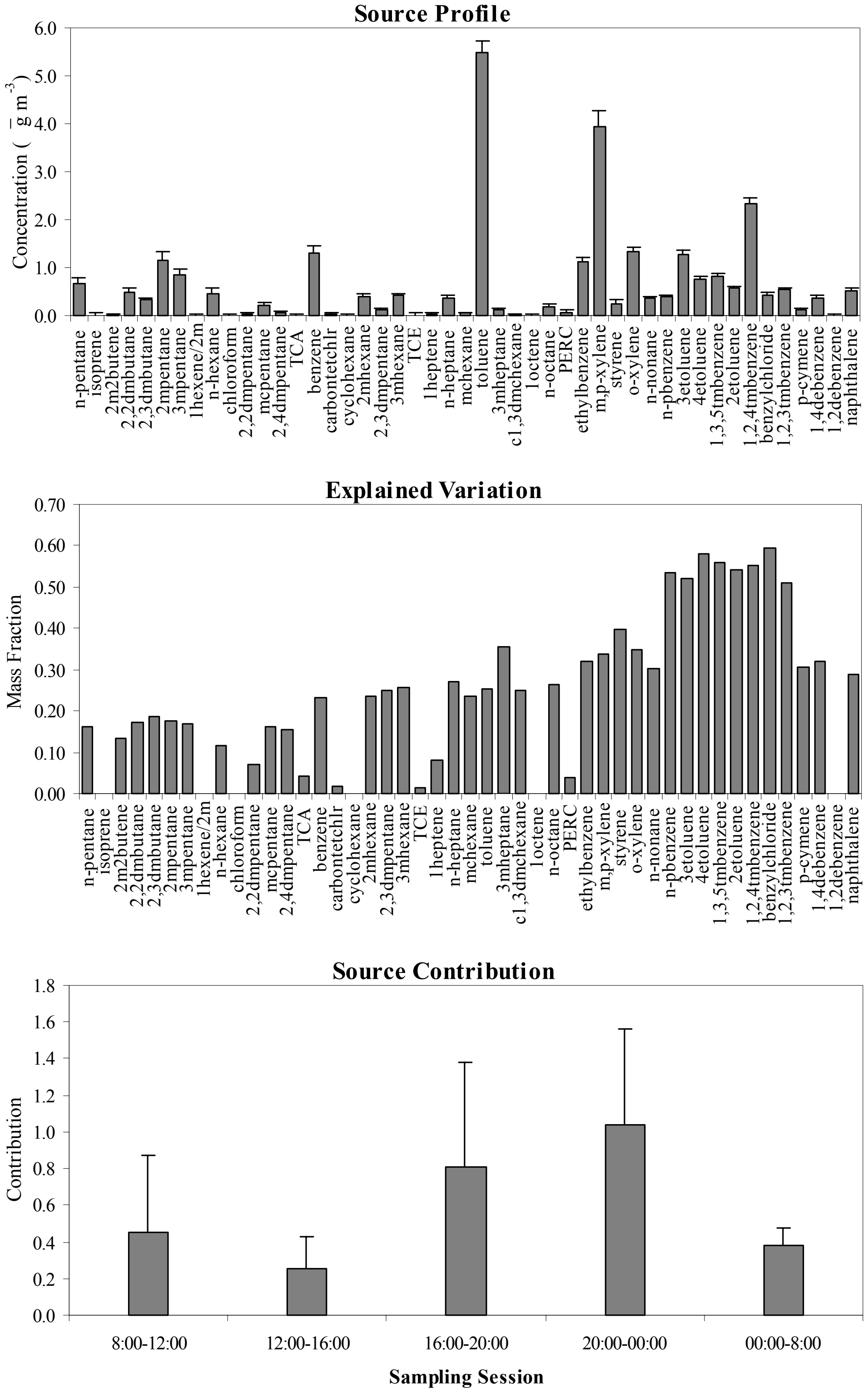


Figure 5.24. PMF2 results for Factor 5-residential site, summer 2003.

The unleaded gasoline, headspace gasoline, diesel, headspace diesel, running vehicle exhaust, evaporative+exhaust source profiles generated in this study together with source profile for Factor 5 are shown in Figure 5.25(a). Headspace gasoline and headspace diesel profiles result in very poor fit with Factor 5 profile. Evaporative+exhaust profile also does not have the same composition with factor 5. However, running vehicle exhaust and diesel profiles exhibit a good fit with Factor 5. The correlation plot in Figure 5.25(b) shows that there is a very good correlation ($R^2 = 0.91$) with the profiles generated for running vehicle exhaust and profile computed for Factor 5. Therefore, Factor 5 is identified as ***running vehicle exhaust strongly influenced by diesel emissions***.

Source Contribution Estimates

Linear regression between the modeled and measured VOC data was performed in order to test the performance of the PMF2 run and to compute source contribution estimates for each resolved factor. LR between the model-predicted and measured total VOC concentration data generated at the residential station during summer campaign is shown in Figure 5.26.

The model results reveal a very good fit with the measured VOC data. LR resulted in R^2 value of 0.99 with intercept of 1.07. Thus, it is shown that the resolved sources by PMF2 effectively reproduce the measured values and account for most of the variation in the total VOC concentrations. Ratio of the modeled to measured total VOC concentration is 0.95 indicating that the PMF2 solution is very close to measured data.

The source contribution estimates are also calculated for each factor. The percent contribution of each factor to total VOCs is determined by dividing the modeled concentration for each factor by the total modeled concentration. LR is used to quantitatively apportion the mass contributions among the resolved sources.

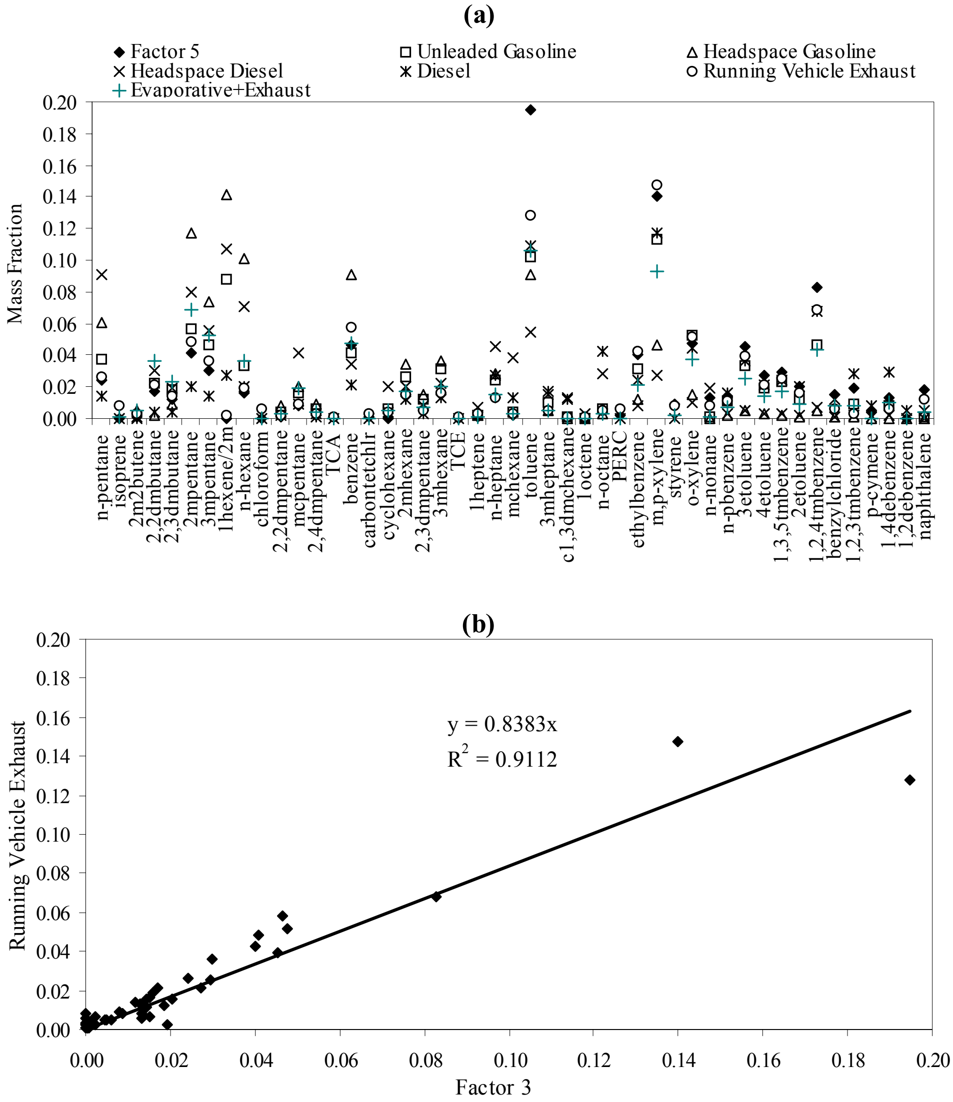


Figure 5.25. Comparison of the source profiles, (a) selected normalized source profiles generated in this study and profile for Factor 5; (b) correlation between running vehicle exhaust and Factor 5 source profiles.

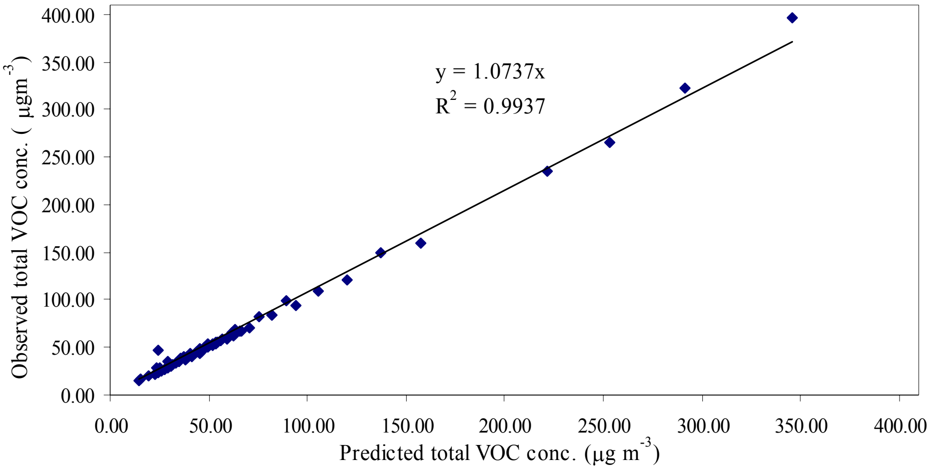


Figure 5.26. Observed versus predicted VOC concentration.

The average source contribution estimates (SCE) of each factor to the measured total VOC concentration are presented in Table 5.12. LDV exhaust and evaporative (42%) and running vehicle exhaust (30%) sources contribute most of the VOC emissions observed at the residential station during summer campaign. Architectural coating is the third most abundant source with 12% contribution. Biogenic emissions and solvent use account for 9% and 8% of the total VOC concentration, respectively.

On the average, the motor vehicle related sources contribute to 72% of the total VOC concentration. The solvent related sources including solvent use and the architectural coating result in about 20% contribution.

Motor vehicles are the major source of VOCs measured at the residential station during summer campaign. PMF2 runs also successfully resolved biogenic emission source that is effective during summer campaign.

Table 5.12. Source contribution estimates for residential station during summer campaign.

Factor No	**Source**	**% SCE**
1	Biogenic emissions	8.75
2	Architectural coating	12.11
3	LDV exhaust and evaporative	41.77
4	Solvent use	7.66
5	Running vehicle exhaust (diesel emission dominating)	29.71

Model Performance Parameters

One of the advantages of PMF2 is to provide performance evaluation tools such as goodness of fit (i.e., Q) value and scaled residuals. Q value was inspected to decide on the optimum number of factors. PMF2 solution with 5 factors resulted in a calculated Q value of 3113 that was about 10% lower than the theoretical Q value. This indicated a good fit that can also be seen from the result of the LR analysis.

Scaled residual errors were also inspected. Most of the scaled residuals are between -2.0 and 2.0 with a random distribution of positive and negative values. The frequency distributions of scaled residual errors for selected compounds for convenience are shown in Figure 5.27.

5.1.3.3 Background Station Winter Campaign

Input parameters

Ambient air samples collected at the background station were analyzed by PMF2 in order to resolve sources of VOCs. A total of 91 VOC species were detected at the background station. The campaigns conducted in summer and winter yielded a total number of 27 and 91 data points, respectively. The number of data points collected in the summer does not provide the degree of freedom that is required by PMF2 run. Therefore, the model was run only for the winter data set.

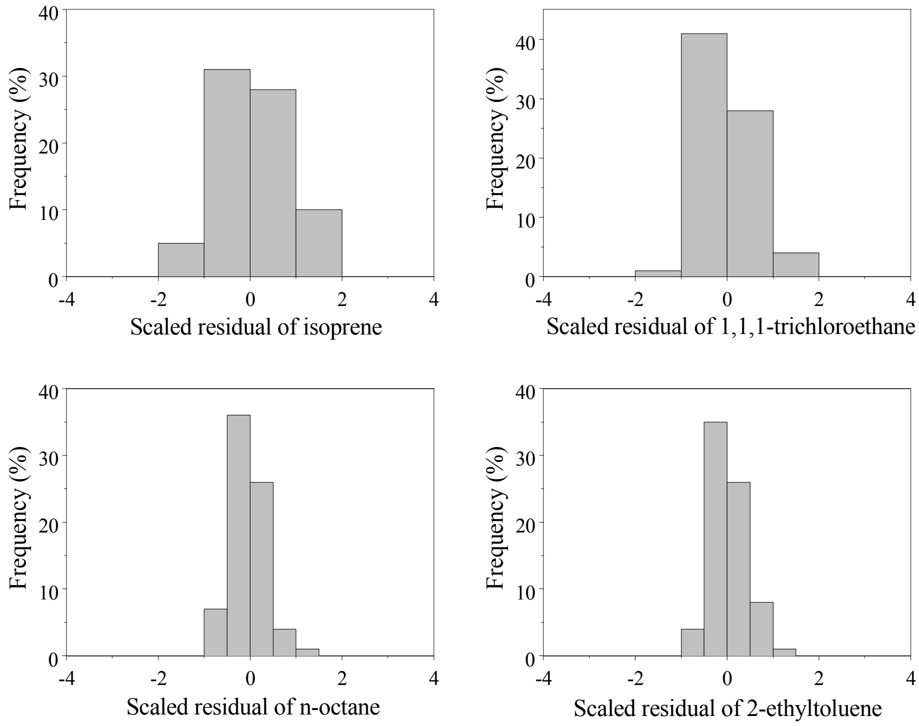


Figure 5.27. Frequency distribution plots for scaled residual errors.

Input data were pretreated for missing and BDL values. There were 54 and 38 compounds in the data set with more than or equal to 50% and 70% of the detected data points, respectively. The 50% was selected as the cut point. 1-hexene/2-methyl-1-pente was observed in the dataset at more than 46% of the time. This compound was also included in the data set since it was a critical component of the vehicle emissions.

The dataset was also inspected for the bad variables. A total of 12 compounds had S/N values of below 0.2 and thus they were excluded from the dataset. BDL values were replaced with half of the MDL and missing values were replaced with median values for the remaining compounds. Input matrix was constructed with 43 compounds and 91 data points collected at the background station. Uncertainty matrix was constructed with the error estimates computed by the method proposed Polissar *et al.* (1998).

Application of the Model

PMF2 was run utilizing data and uncertainty matrices constructed as described in the previous section. The model was applied under different initial conditions in order to determine the optimum solution. Number of factors was changed in each run to determine the optimum number of sources. Rules explained in Section 2.7.1 were applied to decide on the optimum number of sources that provide the optimum solution. PMF2 runs using number of factors 3, 4 and 5 resulted in calculated Q values of 2904, 2388 and 1987, respectively. Theoretical Q value for the input data set was 3913. Number of factors 5 resulted in the lowest Q value that was about 2 times lower than the theoretical Q value. PMF2 run utilizing number of factor 3 resulted in the closest Q value to the theoretical Q value. However, neither 3 factors nor 5 factors yielded explainable source profiles. Therefore, PMF2 solution with number of factors 4 was accepted as the optimum solution.

Effect of rotation on the model performance in terms of factor profiles, scales residuals and calculated Q value was investigated. FPEAK tool was applied using values ranging from -1.0 to 1.0 to test different rotations. PMF2 runs with 4 factors and FPEAK values of -1.0, -0.5, -0.1, 0.0, 0.1, 0.5, and 1.0 yielded calculated Q values of 2783, 2451, 2391, 2387, 2388, 2442, and 2592, respectively. Calculated Q value increased with the increase in the FPEAK value. Source profiles did not change for FPEAK values of 0.1 and -0.1. There was a significant change in source profiles for the higher FPEAK values. Resulting source profiles were not explainable and different FPEAK values did not result in significant change in distribution of scaled residuals. Therefore, FPEAK value of zero that provided explainable source profiles and acceptable distributions of scaled residuals were selected. FKEY tool was not used.

Scaled residuals were re-inspected for each compound for the optimum PMF2 solution with FPEAK=0.0 and number of factors of 4. For the compounds having scaled residuals beyond ±2 limit value, the input data matrix was re-inspected and the uncertainty values were increased by a factor of 2 for the outlier data points. There were only few compounds for which estimated errors were adjusted to down-weight outlier values.

Results of the Model

PMF2 analysis with the application of robust mode resolved four sources that explained variation in the VOC data generated at the background station during winter campaign. Factors resolved by PMF2 were interpreted qualitatively by evaluating source profiles, time variations in source contributions and explained variations that were generated by the model. Source profiles were also compared with the profiles available in the literature and the profiles generated in this study for a quantitative identification of the sources. Each factor is interpreted separately in the following paragraphs.

Factor 1

The source profile, EV and source contribution plots generated for Factor 1 are shown in Figure 5.28. Benzene and toluene are among the most abundant species in the source profile. Abundance of light hydrocarbons is significant and concentrations of heavy hydrocarbons are almost negligible. EV plot indicates that this source explains variation in most of the compounds that are related to motor vehicle emissions.

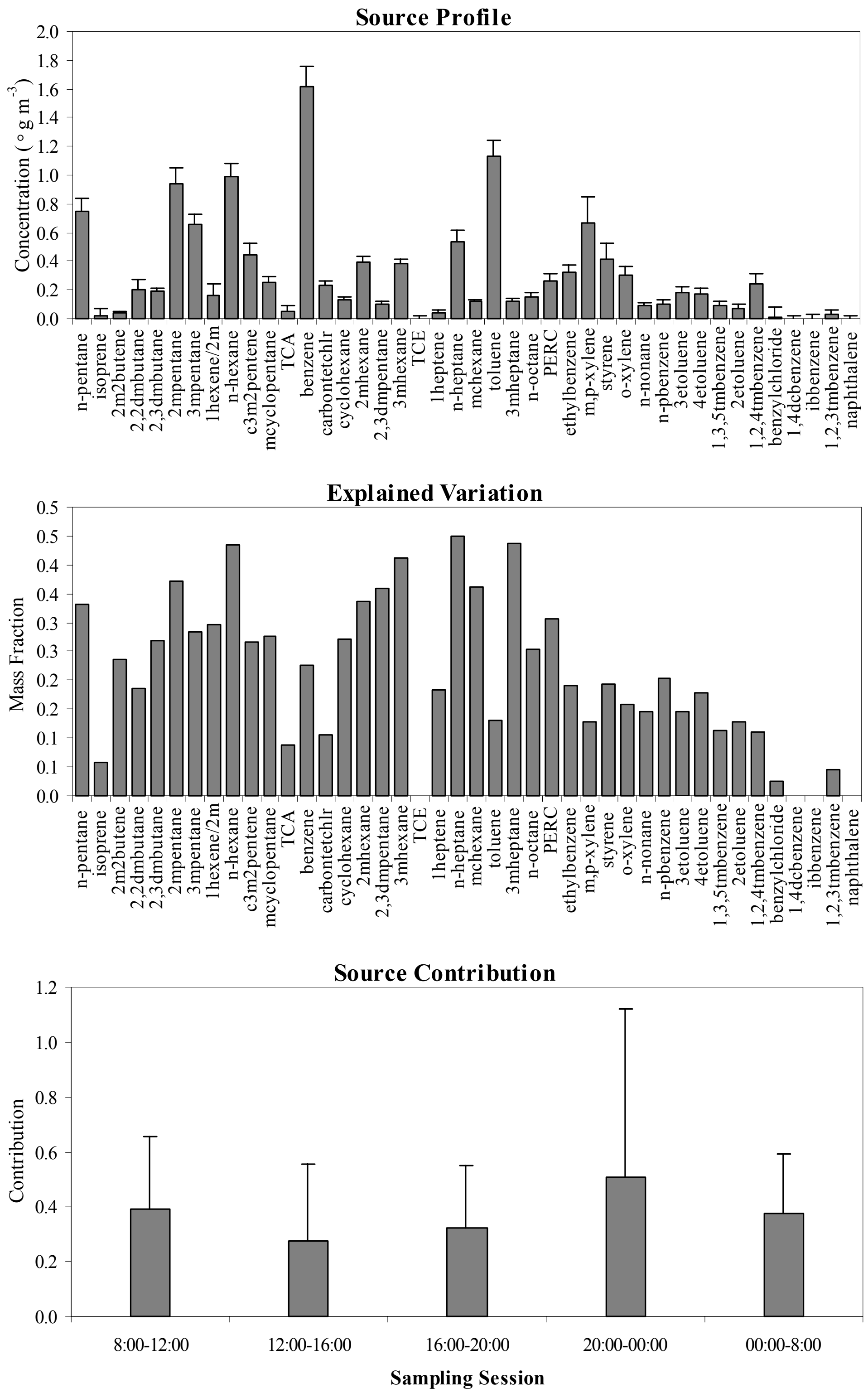


Figure 5.28. PMF2 results for Factor 1-background site, winter 2004.

Source profile for Factor 1 has a similar pattern with that observed for Factor 1 computed for the residential station during winter campaign. However, relative abundance and concentrations of certain compounds in both profiles are different. Source contribution plot shown in Figure 5.28 also indicates similarities to source contribution plot of Factor 1 generated for the residential station during winter campaign. However, there seems to be a delay in the contribution plot of Factor 1 generated for the background station for one session. The highest contribution is observed during afternoon session at the residential station, however, the highest contribution is observed during evening session at the background station. The background station was located in a suburban area in the Middle East Technical University campus (see Section 3.1). Therefore, few local sources and polluted air masses transported from the city center are expected to influence VOC concentrations measured at the background station, as discussed in the previous section. Factor 1 is interpreted as ***aged motor vehicle emission source***. Further assessment is done by evaluating relationship between atmospheric lifetimes and changes in the abundances of individual species.

The correlation plot between source profiles of Factor 1 generated for the background station and Factor 1 generated for the residential station is shown in Figure 5.29. As can be seen from the correlation plot, most of the compounds have higher concentration at the residential site than at the background site. There are only few compounds that have high concentrations at the background site. The decrease in the concentration of most of the compounds at the background site could be due to short atmospheric residence times of these compounds. Thus, the air mass traveled from city center to the background site could be considered "aged". Such transport probably takes approximately 1-2 hours, which is enough for the depletion of reactive VOCs in the profile.

The rate constants and lifetimes of hydrocarbons that are associated with motor vehicle emissions with respect to their reactivity against hydroxyl (OH) radical are shown in Table 5.13. There are four major routes for decomposition of VOCs in the atmosphere as discussed in Section 2.2, including photolysis, attack by OH, NO_3 radicals and O_3. Some VOCs react significantly with O_3 and/or degrade by thermal decomposition or photolysis, however, removal by reaction with O_3, or due to photolysis, can be estimated to be much less than 1% of the OH removal rate for most VOCs (Lu, 1996; Atkinson, 2000). Therefore, decomposition of VOCs with HO radical attack is considered as the removal mechanism for VOCs in Ankara.

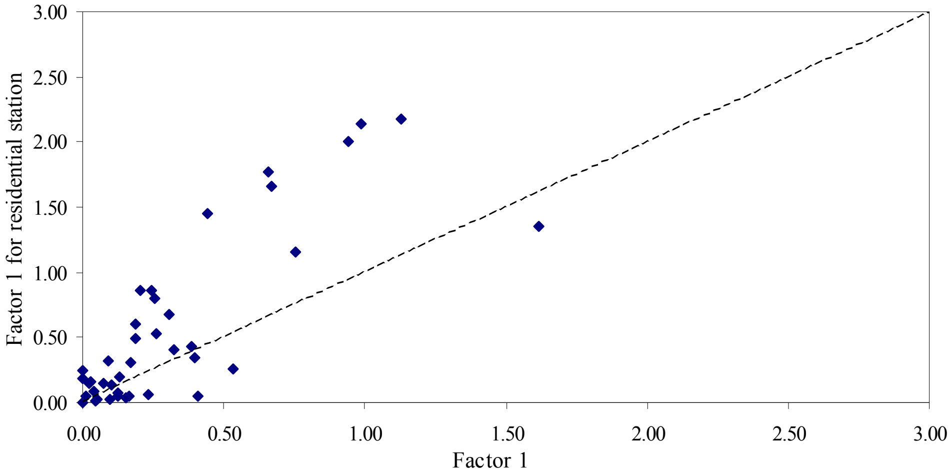


Figure 5.29. Source profiles of Factor 1 computed for background and residential stations.

Kinetic and mechanisms of the gas phase reactions of the OH radical with VOCs have been reviewed and evaluated by Atkinson (1985; 1990). Rate constants were also recommended for VOCs for which experimental data did not exists. Rate constants provided in Table 5.13 are obtained from Atkinson (1989; 1990) and Lu (1996). The reactions are assumed to be of second order with reactant lifetime of $\tau=1/k[OH]$. The OH concentration of $5x10^6$ molecule cm^{-3} (Finlayson-Pitts and Pitts, 1986) is used to calculate life times that are given in Table 5.13.

Table 5.13. Rate constants and lifetimes of motor vehicle related compounds due to reaction with OH radicals.

Compound name	**Group**	**C-No**[a]	**Vapor pressure (Pa at 25 °C)**	**k_{OH} (cm^3 $molecule^{-1}$ s^{-1})**	**Life time (hr)**
Pentane	P	5	68400	3.35E-12	16.6
Isoprene	O	5	NA	1.01E-10	0.6[b]
2-methyl-2-butene	O	5	62143	1.08E-10	0.5
2,2-dimethylbutane	P	6	42600	1.61E-12	34.6
2,3-dimethylbutane	P	6	32010	6.30E-12	8.8
2-methylpentane	P	6	28200	5.60E-12	9.9
3-methylpentane	P	6	25300	5.70E-12	9.7
1-hexene	O	6	26000	5.14E-11	1.1
2-methyl-1-pentene	O	6	24800	3.70E-11	1.5
Hexane	P	6	20200	5.61E-12	9.9
c-3-methyl-2-pentene	O	6	NA	NA	NA
Methylcyclopentane	P	6	18300	NA	NA
Benzene	A	6	12700	1.23E-12	45.2
Cyclohexane	P	6	12700	6.75E-12	8.2
2-methylhexane	P	7	8780	6.79E-12	8.2[b]
2,3-dimethylpentane	P	7	9180	4.87E-12	11.4[b]
3-methylhexane	P	7	8210	7.16E-12	7.8[b]
1-heptene	O	7	7510	4.00E-11	1.4
Heptane	P	7	6110	7.15E-12	7.8
Methylcyclohexane	P	7	6180	1.04E-11	5.3
Toluene	A	7	3800	7.09E-12	7.8
3-methylheptane	P	7	2600	5.70E-12	9.7[b]
Octane	P	8	1800	7.19E-12	7.7
Ethylbenzene	A	8	1270	7.10E-12	7.8
m-xylene	A	8	1100	2.36E-11	2.4
p-xylene	A	8	1170	1.43E-11	3.9
Styrene	A	8	NA	5.80E-11	1[b]
o-xylene	A	8	1170	1.37E-11	4.1
Nonane	P	9	571	1.02E-11	5.4
n-propylbenzene	A	9	450	6.00E-12	9.3
3-ethyltoluene	A	9	NA	NA	NA
4-ethyltoluene	A	9	NA	NA	NA
1,3,5-trimethylbenzene	A	9	325	5.75E-11	1.0
2-ethyltoluene	A	9	NA	NA	NA
1,2,4-trimethylbenzene	A	9	270	3.25E-11	1.7
iso-butylbenzene	A	10	250	NA	NA
1,2,3-trimethylbenzene	A	9	200	3.27E-11	1.7
Naphthalene	A	10	134	2.16E-11	2.6

[a] *Carbon number*

[b] *Source: Lu, 1996*

Paraffins are saturated hydrocarbons. Thus, they are stable in the atmosphere resulting in long atmospheric lifetimes. Olefins and aromatics, on the other hand, are unsaturated hydrocarbons and they are unstable in the atmosphere (Sawyer and McCartery. 1978). All of the olefins have life times much shorter than that of paraffins as can be seen from Table 5.13. Aromatics, except benzene, have comparable or shorter lifetimes than paraffins. Benzene has the longest atmospheric lifetime, which is approximately 45 hours.

Figure 5.29 is reevaluated considering the reactivity data provided in Table 5.13. Benzene has almost the same concentration at both stations and it is due to its very long atmospheric lifetime. On the other hand, 1-hexene has higher concentrations at the background site despite its very short atmospheric residence time (i.e., 1 hr). Increase in 1-hexene concentrations associated with the degradation of the paraffins or aromatics, as olefins are known as the end product of reaction between paraffins or aromatics and OH radicals. TCA, TCE, carbontetrachloride and styrene have also fairly high concentrations at the background site. Among these compounds, TCA, TCE and carbontetrachloride have very long atmospheric lifetimes as indicated in the previous sections. Therefore, the higher concentrations of these compounds observed at the background site is due to their long residence time and local sources. These compounds are used at the research laboratories located in the METU. Styrene has short lifetime in the atmosphere (i.e., 1 hr), however, it is used in the laboratories at the METU campus and especially at the laboratories located in the Department of Metallurgical Engineering where the background station was located (in one of the laboratories in the Department of Metallurgical Engineering, styrene was being used to dissolve foam, which probably is distributed in whole building through ventilation system). The high styrene concentrations are observed at the background site as indicated in Section 4.1. Therefore, although its atmospheric residence time is short, styrene concentrations are higher at the background station owing to sources of styrene within the METU campus. There are few other compounds with higher concentrations at the background site probably due to similar reasons.

Most of the paraffins and aromatics have higher concentrations at the residential site than at the background site. For example, toluene and m&p-xylene have short life times of about 8-hrs and 3-hrs, respectively. Therefore, toluene and m&p-xylene concentrations computed at the residential station decrease significantly when they reach to the background station due to decomposition via atmospheric reactions. Light hydrocarbons that are mostly associated with paraffins in this dataset have atmospheric residence times of about 10-hrs. They also show lower concentrations at the background station indicating that these compounds are also participated in atmospheric reactions. Heavy hydrocarbons mostly included aromatics have short atmospheric residence times. For example, atmospheric residence times of o-xylene, 1,2,4-trimethylbenzene and naphthalene are 4-hrs, 2-hrs and 3-hrs, respectively. Concentrations of these compounds observed at the background site are about three times lower than those are observed at the residential site. There is only one paraffin (i.e., heptane) that has slightly higher concentrations observed at the background site. This could be due to local sources of this compound, as discussed previously for styrene. Since the concentration of heptane in the atmosphere is fairly low (i.e., about 0.5 $\mu g\ m^{-3}$), its contribution to total VOC levels is not expected to be significant.

Nelson and Quigley (1983) declared that m&p-xylene to ethylbenzene (mpX:E) ratio is used in the literature to estimate hydrocarbon age in ambient atmosphere. They conducted a series of field campaign and smog chamber studies to investigate mpX:E ratio for different VOC sources, urban atmosphere and simulated urban atmosphere. It was found that m&p-xylene and ethylbenzene occur in significant concentrations and constant relative proportions in the major anthropogenic sources of VOCs and they disappear from the atmosphere at markedly different rates by photochemical reaction (i.e., τ_{mpX}=3 hr, τ_{Eb}=8 hr). Consequently, mpX:E decrease as the air parcel containing these gases ages in the atmosphere. The ratio changes between 3.5 and 4.0 at most of the VOC sources. However, ratio decrease with aging time and reaches to a stable value of 2.0 within few hours under photochemical reactions simulated in smog chamber.

The mpX:E ratio was investigated for Factor 1 profiles of the background and residential stations together with profiles generated for several VOC sources in this study. The mpX:E ratio is 4.03 in the Factor 1 profile computed for the residential station, which is typical for fresh emissions. The mpX:E ratios for the unleaded gasoline, leaded gasoline, and running vehicle exhaust are 3.57, 3.94 and 4.27, respectively. For the Factor 1 profile computed for the background station, however, the mpX:E ratio is 2.08. The mpX:E ratios calculated for the residential station and source profiles developed in this study are similar indicating that the LDV exhaust emissions observed at the residential station is resulted from fresh emissions. The LDV exhaust emissions observed at the background station, however, are aged owing to its low mpX:E ratio.

Source profile generated for Factor 1 is also compared with the motor vehicle related source profiles developed in this study. The comparison yields similar outcomes as indicated in the previous paragraphs. Atmospheric lifetime analysis for individual compounds, comparison with profile of Factor 1 generated for the residential station and mpX:E ratio analysis indicates that Factor 1 is an aged or transported profile. Different temporal pattern in source contribution is also supported this result. Consequently, Factor 1 is identified as ***transported LDV exhaust*** profile.

Factor 2

Results of the PMF2 run for Factor 2 are shown in Figure 5.30. Source profile plot generated for Factor 2 reveals that carbon tetrachloride, 1,4-dichlorobenzene, benzene, styrene and isobutyl benzene are the most abundant compounds in this profile.

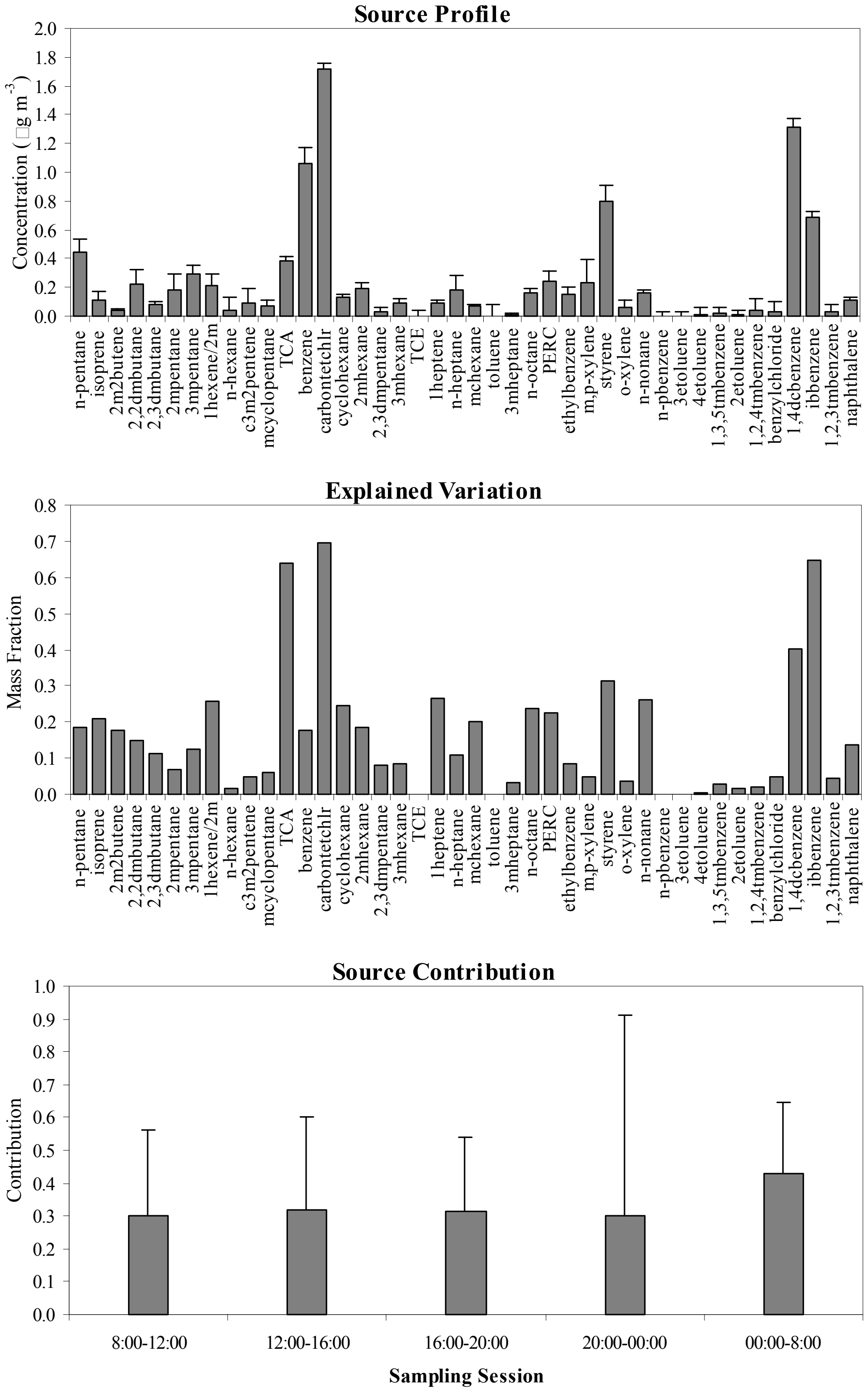


Figure 5.30. PMF2 results for Factor 2-background site, winter 2004.

EV plot shows that Factor 2 explains most of the variances in TCA, carbon tetrachloride and isobutylbenzene concentrations measured at the background station during winter campaign. As it is described in the previous sections, TCA and carbon tetrachloride are used in industrial applications as solvent and in household products such as cleaning products and polishes (Nazaroff and Weschler, 2004). Styrene and 1,4-dichlorobenzene are also used as solvent. Source contribution plot for this factor does not show a significant diurnal variation.

Factor 2 is identified as ***solvent use*** source. The possible sources of solvent could be the household cleaners and solvent use in small enterprises within the city. An additional source at the background station could be the use of solvent in laboratories within the METU campus.

Factor 3

Source profile, EV and source contribution plots generated for Factor 3 are shown in Figure 5.31. Toluene, m&p-xylene and benzene are the most abundant compounds in the source profile. Concentrations of the remaining compounds are almost negligible. Absence of many hydrocarbons associated with motor vehicle emissions indicates that Factor 3 is not a motor vehicle related source. EV plot shows that TCE and toluene are the compounds that are mostly explained in this factor. There is a slight diurnal change in source contributions with the lowest contributions observed during night session.

Source profile generated for Factor 3 is compared with the profiles available in the literature. The profile generated by Kubica *et al.* (2004) for coal combustion in small residential appliances in Poland provides the best fit to the modeled source profile for Factor 3. All the species except pentane fit with the Factor 3 profile. The source profiles for coal combustion-1 generated by Kubica *et al.* (2004) and Factor 3 excluding pentane are shown in Figure 5.32.

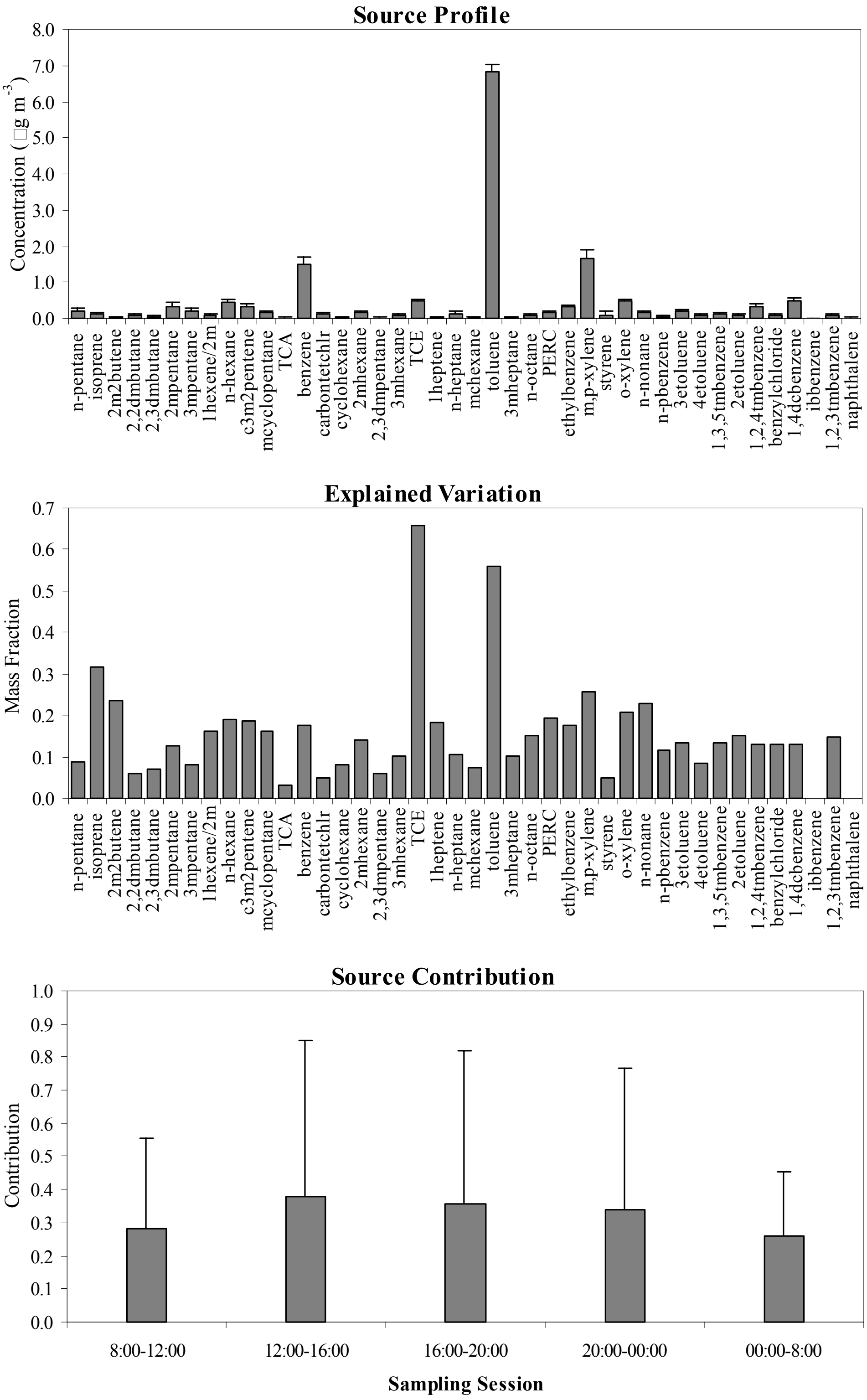


Figure 5.31. PMF2 results for Factor 3-background site, winter 2004.

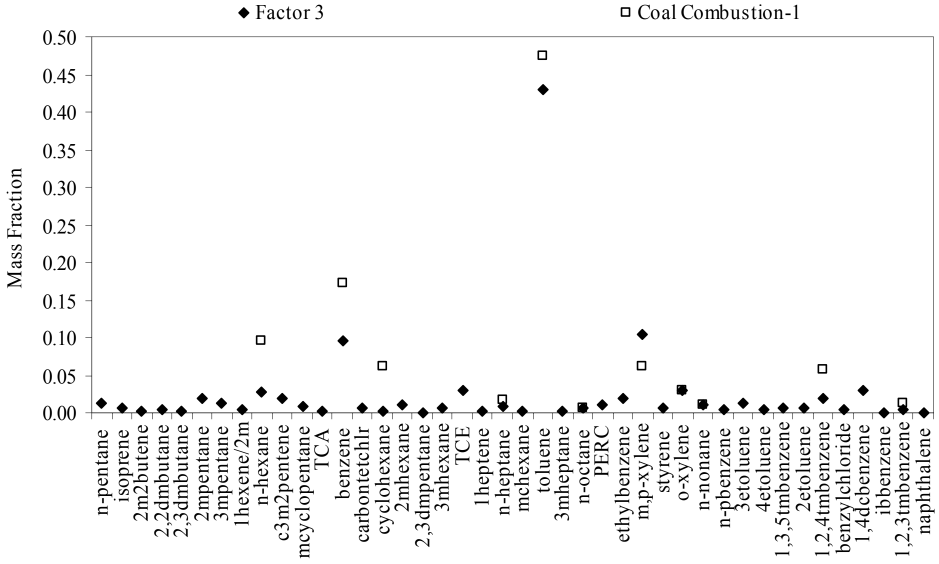


Figure 5.32. Source profiles of Factor 3 and coal combustion.

Correlation between these two profiles are also investigated and found that the correlation is very good with R^2=0.91 and intercept of 1.12. Consequently Factor 3 is identified as ***coal combustion for residential heating***.

Diurnal pattern observed in Factor 3 scores, where lowest concentrations are observed during nighttime does not agree with typical diurnal pattern expected for emissions from coal combustion, which should be higher during night time owing to extensive heating of residents at extreme cold night period in Ankara. However, it should be noted that heating pattern at the University is different from the pattern in the city. University is extensively heated during daytime, but at night heating is reduced, as number of people living in the campus is very limited. This pattern suggests lower concentrations of coal related VOCs at night. When this pattern is coupled to transport from polluted regions in the city, which is higher at night, can explain observed lack of temporal variation in Factor 3 scores.

As indicated in previous sections, coal accounts for about 60% of the fuels used for residential heating in Ankara. Residential heating source is successfully resolved by PMF2 for the VOC data collected at both background and residential stations during winter campaign.

Factor 4

Results of the PMF2 run for Factor 4 are presented in Figure 5.33. Figure provides source profile and source contribution plots together with their uncertainties and EV plot. Source contributions are averaged over sessions. Toluene, m&p-xylene, benzene and 1,2,4-trimethylbenzene are the most abundant species in the source profile. BTEX compounds are known as the marker for motor vehicle exhaust as indicated in the previous paragraphs.

EV plot shows that this source explained variances in concentrations of many of the hydrocarbons, but EV values are higher for heavy hydrocarbons than EV values of light hydrocarbons. Factor 4 is interpreted as motor vehicle emission. Further comparison with the profiles generated in this study and the profiles available in the literature is conducted to identify the source accurately.

Selected source profiles generated during Ankara campaign together with modeled source profile for Factor 4 are shown in Figure 5.34. Normalized source profiles for unleaded gasoline, leaded gasoline, diesel, running vehicle exhaust and cold start, that is generated during Ankara campaign, and for Factor 4 are shown in Figrue 5.34(a). Running vehicle exhaust shows a very similar pattern to that of Factor 4. Figure 5.34(b) shows correlation between normalized source profiles of running vehicle exhaust and Factor 4. The correlation is very good with R^2=0.93 and intercept of 0.96. It is clear that Factor 4 is a running vehicle exhaust source.

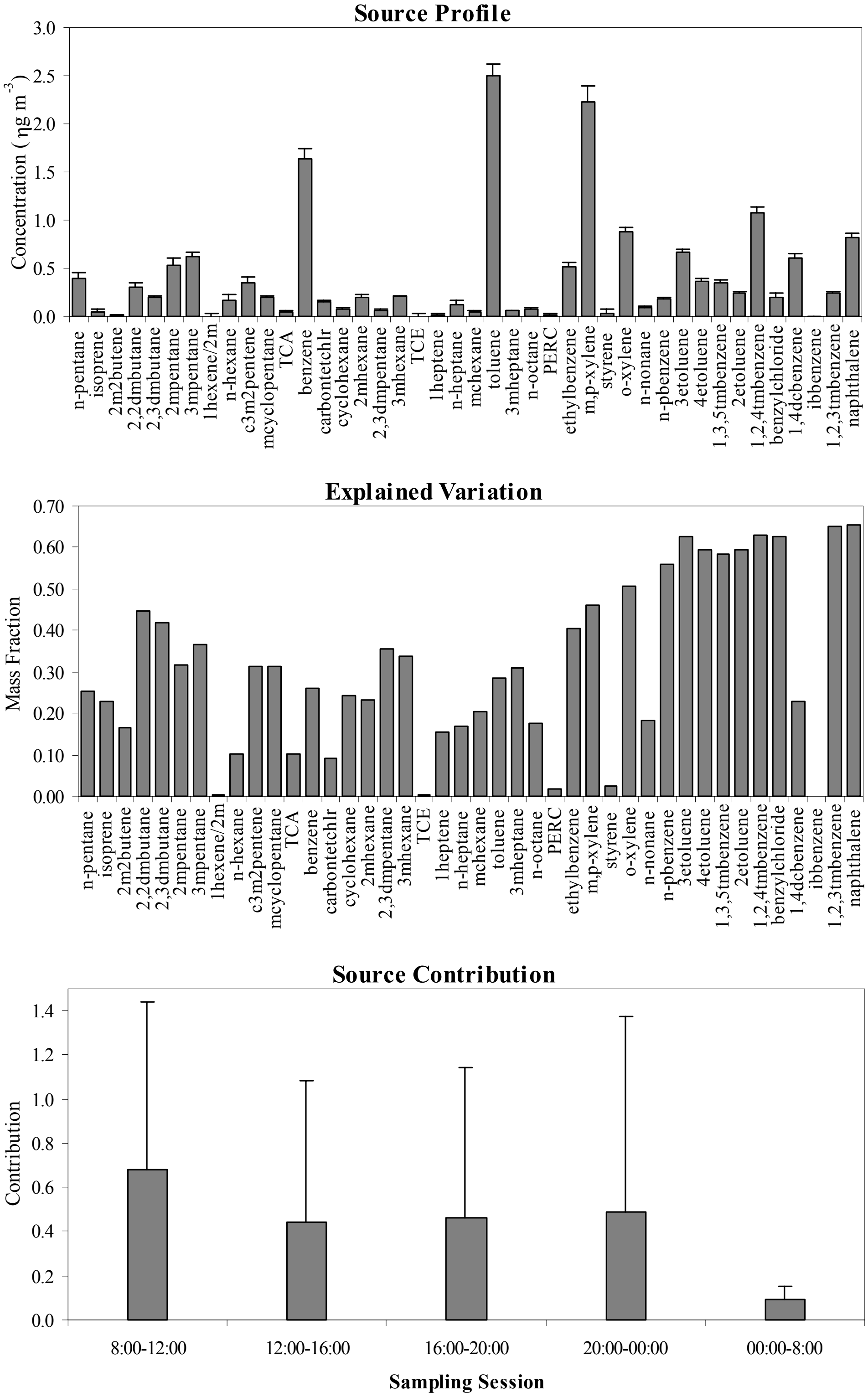


Figure 5.33. PMF2 results for Factor 4-background site, winter 2004.

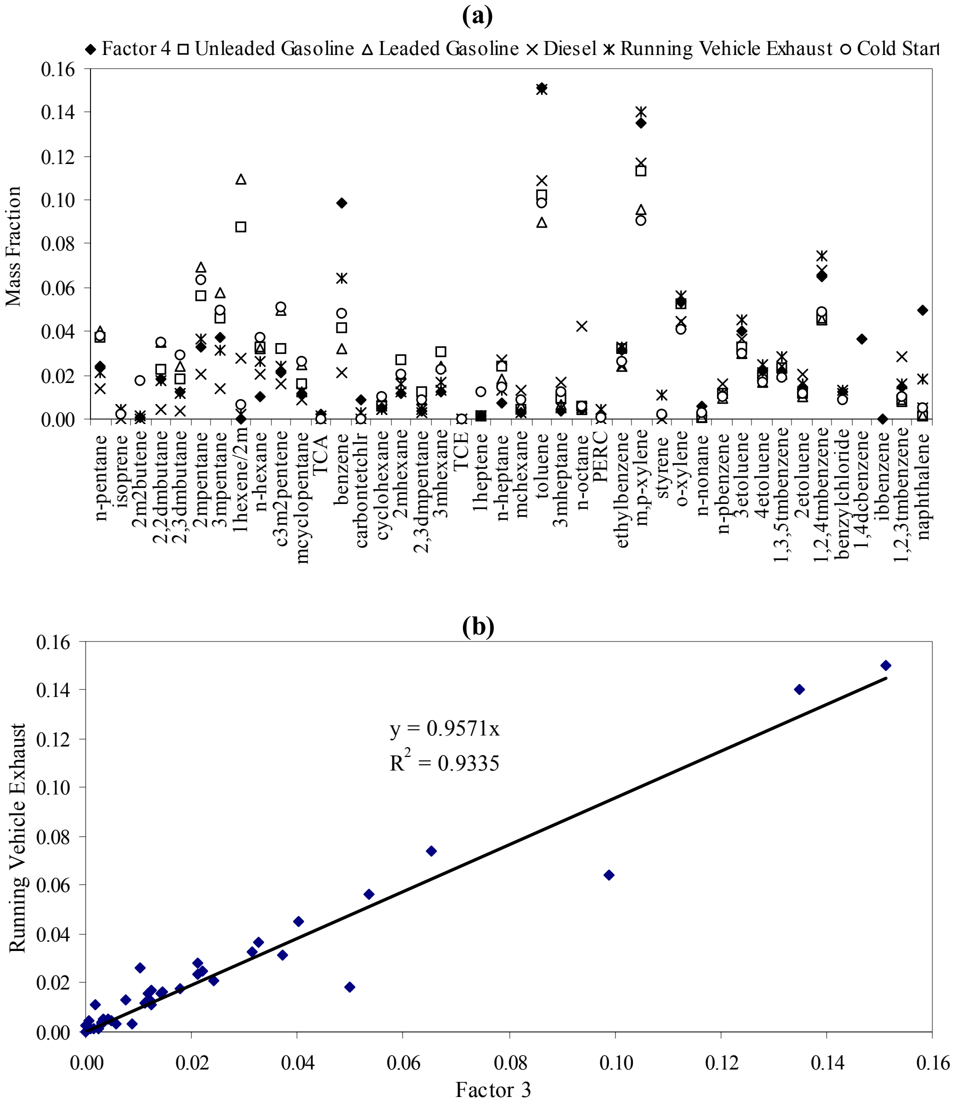


Figure 5.34. Comparison of the source profiles, (a) selected normalized source profiles generated in this study and profile for Factor 4; (b) correlation between running vehicle exhaust and Factor 4 source profiles.

Factor 4 is also compared with the source profiles available in the literature. The source profiles used in Section 5.1.3.1 were used for the comparison and similar results are observed. Most of the profiles available in the literature have poor correlation with profile for Factor 4, except Tunnel-1 profile generated by Conner *et al.* (1995). This result indicates that motor vehicle emissions generated in Ankara have a distinct pattern, and use of literature profiles in receptor modeling will produce results with very high uncertainty.

There is a diurnal variation in the source contributions computed for Factor 4. The highest and the lowest source contributions are observed during morning and night sessions, respectively. There is not a significant change in source contributions during noon, afternoon, and evening sessions. There is a high traffic flow throughout the day within the METU campus since significant number of students and employees own cars. Source profile, which shows a non-disturbed pattern, variations in source contributions, and mpX:E ratio show that Factor 4 represent a fresh emission source. Factor 4 is identified as ***running vehicle exhaust emission associated mostly with local sources***.

Source Contribution Estimates

Linear regression was used to regress the modeled total VOC concentration against the measured total VOC concentrations. LR helped ascertain the optimal number of factors and also to apportion sources.

LR between the model-predicted and the measured total VOC concentrations are shown in Figure 5.35. R-squared values and the ratios of the modeled to measured concentrations were examined to determine how well the regression model fit the measured data for total VOCs. LR resulted in R^2 value of 0.99 with intercept of 1.02. These results indicated that the resolved sources by PMF2 effectively reproduced the measured values and accounted for most of the variation in the total VOC concentration. Ratio of the modeled to the measured total VOC concentration was 0.97 indicating that predicted and measured concentrations are every close to each other.

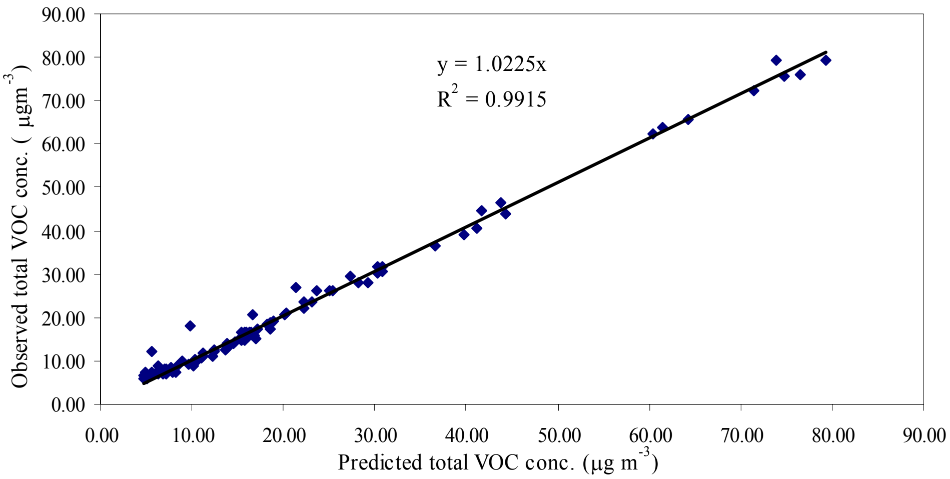


Figure 5.35. Observed versus predicted VOC concentration.

The SCE of individual factors were also calculated. The average SCE values of each factor to the measured total VOC concentration are shown in Table 5.14. Residential heating has the second highest contribution with a SCE value of 25%. The share of residential heating observed at the residential station during winter campaign is higher than that is observed at the background station. It is simply due to the location of the background station that is located on a suburban area with relatively few residences. Running vehicle exhaust contributes the most accounting for 39% of the total VOC concentration measured at background station during winter campaign. There is an increase in the share of running vehicle exhaust emissions observed at the background station relative to that is observed at the residential station. This is a relative increase resulting from the decrease in the share of residential heating. Transported LDV exhaust and solvent use have the SCE values of 21% and 15%, respectively.

On the average, motor vehicle related sources contribute to 60% of the total VOC concentration. Thus, motor vehicles and residential heating are the major sources of VOCs measured at the background site in Ankara during winter campaign.

Table 5.14. Source contribution estimates calculated for background station during winter campaign.

Factor No	Source	% SCE
1	Transported LDV exhaust	20.82
2	Solvent use	14.77
3	Residential heating	25.23
4	Running vehicle exhaust (HDV)	39.18

Model Performance Parameters

Model performance was evaluated by inspecting Q value and distribution of scaled residuals. Q value was inspected to decide on the optimum number of factors. Minimum Q value that is the closest to the theoretical Q value indicated a better fit of the model to measured data. PMF2 solution with 4 factors resulted in a calculated Q value of 2858 that was about 27% lower than the theoretical Q value.

Scaled residual errors were also inspected. Most of the scaled residuals were between -2.0 and 2.0 with a random distribution of positive and negative values. The frequency distributions of scaled residual errors only for selected compounds for convenience Figure 5.36.

5.1.4. Summary of Findings

PMF2 applications for the data collected at residential station during summer and winter campaigns and for the data collected at background station during winter campaign were successful to resolve and quantify VOC sources observed at these stations. There are a total of 7 sources emitting VOCs in Ankara during summer and winter seasons. The sources and their contributions observed at stations in Ankara at different seasons are summarized in Table 5.15.

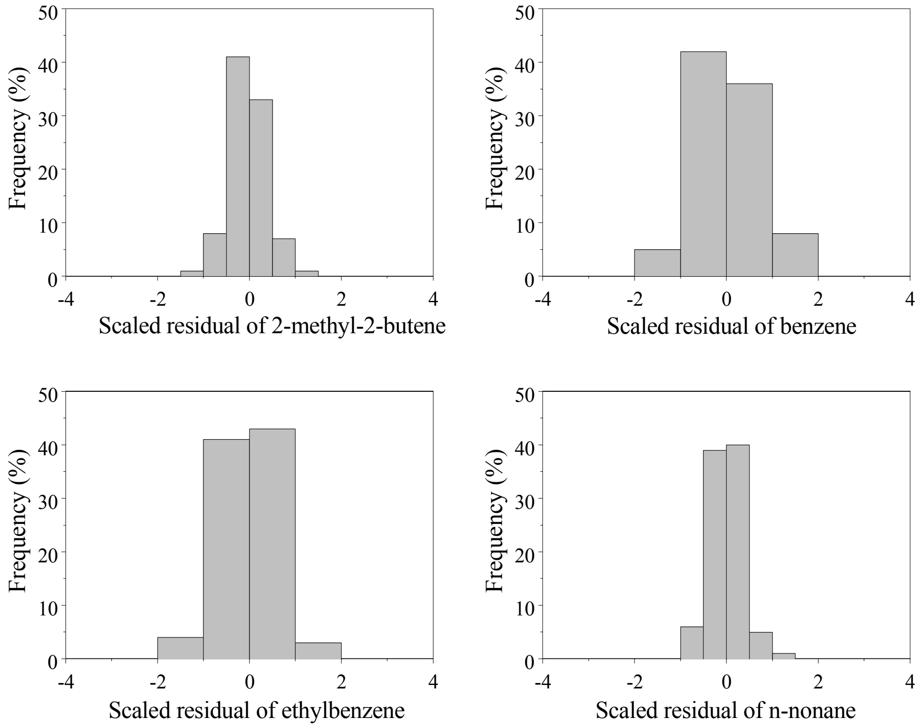


Figure 5.36. Frequency distribution plot for scaled residual errors.

Table 5.15. Summary of VOC sources and source contribution estimates calculated for Ankara stations.

VOC Source	**Residential**		**Background**
	Winter SCE (%)	**Summer SCE (%)**	**Winter SCE (%)**
LDV exhaust (gasoline)	21.84	41.77	
HDV exhaust (diesel)	34.14	29.71	39.18
Solvent use	12.48	7.66	14.77
Residential heating	31.54		25.23
Biogenic emissions		8.75	
Architectural coating		12.11	
Transported LDV exhaust			20.82

Although their composition changes slightly, LDV exhaust, HDV exhaust and solvent use profiles are common sources observed at all stations and seasons. LDV exhaust source, however, is a transported emission rather than fresh emission at background site during winter campaign. Residential heating is an important VOC source in Ankara during winter campaign. Biogenic emissions and architectural coating sources, for both emissions are temperature dependent, contribute to VOC concentrations during summer, but not in winter. On the average, motor vehicle related emission is the most important VOC sources in Ankara accounting for about 60% during winter and 70% during summer.

There are two weaknesses in the source apportionment part of the study; (i) the LPG, which is used both in vehicles and for heating is not identified as a separate source, and (ii) evaporative emissions appeared as mixed with the exhaust in some of the factors. Both of these are due to sampling protocol used in this study. This study aimed at determining diurnal and seasonal variations in VOC concentrations. Thus samples were collected onto Tenax + Carbopack B adsorption tubes as these sorbents provide sample collection for longer durations (e.g., 4-hr used in this study) without a significant breakthrough. However, these sorbents collect VOCs with five and higher C-number. Consequently, VOCs with less than five C, thus propane (C-3) that is marker for LPG and acetylene (C-2) that is marker for gasoline combustion, are not included in Ankara study (they are collected at Ottawa).

5.1.5. Comparison of Receptor Models

In this study, a new generation receptor model namely PMF was used for source apportionment. Conventional Factor Analysis (CFA) is one of the first generation receptor models used in atmospheric research for many years. In this study, PMF results were compared with that calculated by CFA for the VOC data measure at residential station during winter campaign.

The purpose of CFA is to describe the covariance relationships among variables in terms of a few underlying but unobservable random quantities called factors. Basically, the factor model is motivated by the argument of whether the variables can be grouped by their correlations. CFA provides preliminary information about the possible sources that may influence the sampling location and separates the elements into factors, which represents source profiles (Hopke, 1991).

CFA calculates factor loading and factor score values that are similar to EV and source contribution values calculated by PMF. Factor loading in CFA is correlation coefficients (between 0 and 1) for each compound with particular factor. Factor loading values normalized in each factor are provided in Figure 5.37 for comparison with EV values calculated by PMF and Table 5.16 presents original factor loading values.

CFA calculation resolved five VOC sources. On the other hand, PMF resolved four VOC sources. Comparison of the normalized EV values calculated by CFA (see Figure 5.37) and EV values calculated by PMF (see Figure 5.8, Figure 5.10, Figure 5.11, Figure 5.14) yields that Factor 1 calculated by CFA is LDV exhaust and residential heating sources. These sources are resolved by PMF but they are not resolved by CFA. Factor 2 in Figure 5.37 explains variation in heavy hydrocarbons. Halogenated compounds are not explained in this factor. This factor is very similar to EV plot of HDV exhaust source profile calculated by PMF. Thus, Factor 2 of CFA is identified as HDV exhaust source.

There is only one solvent source identified by PMF. This source explains most of the variation in halogenated compounds and especially chloroform, TCA, CCl_4 and PERC. CFA, however, resolved three different solvent sources. Factor 3, 4 and 5 of CFA explain variation in PERC, TCA+CCl_4 and chloroform, respectively. The comparison of the factors resolved by CFA and PMF are summarized in Table 5.16.

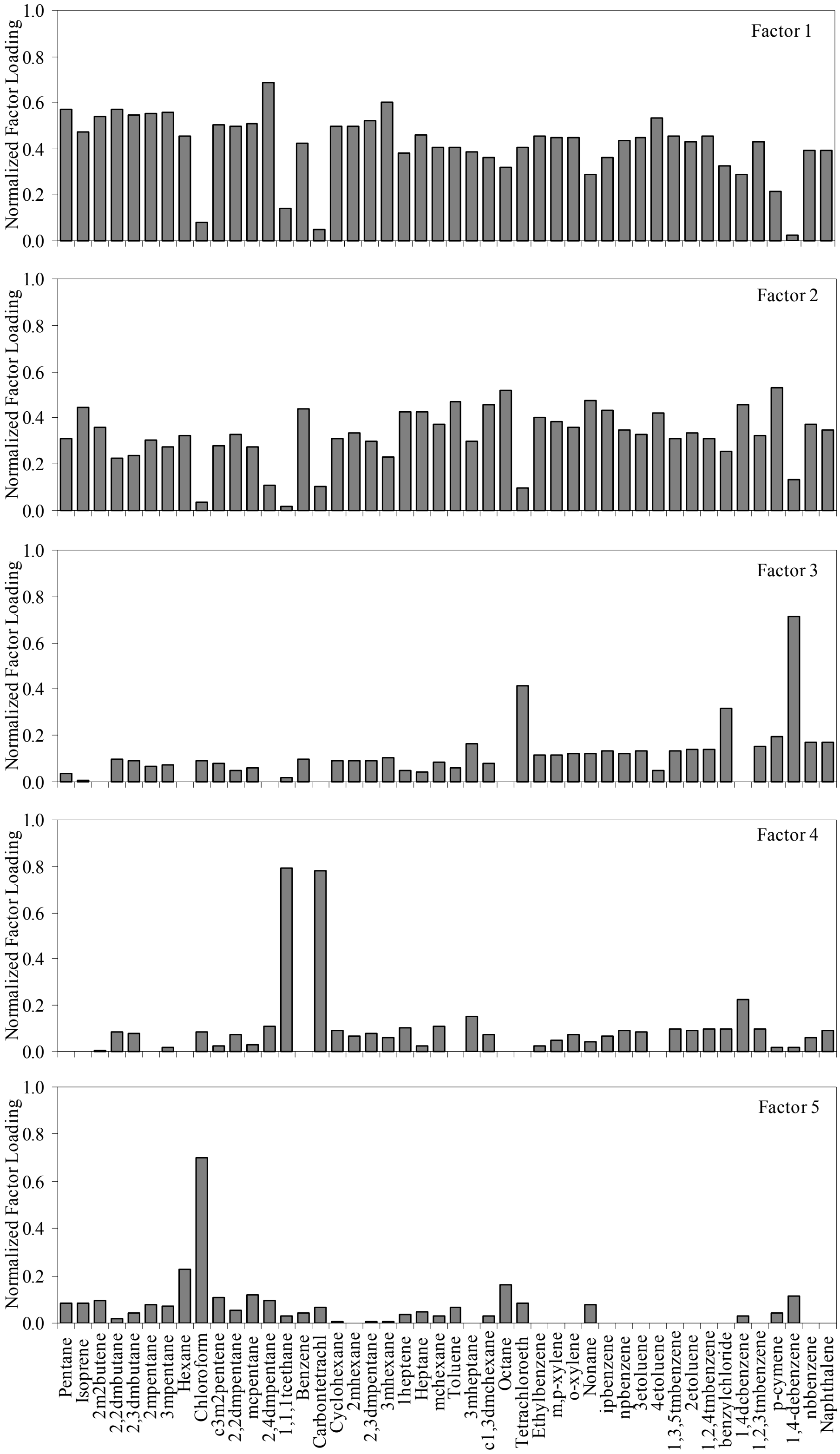


Figure 5.37. Results of the CFA for normalized factor loadings.

Table 5.16. Results of CFA analysis.

Variable	**Factor1**	**Factor2**	**Factor3**	**Factor4**	**Factor5**	**Communality**
Pentane	0.84	0.46	0.05		0.12	0.94
Isoprene	0.69	0.65	0.01		0.12	0.92
2-methyl-2-butene	0.76	0.50		0.01	0.13	0.84
2,2-dimethylbutane	0.88	0.35	0.15	0.13	0.03	0.94
2,3-dimethylbutane	0.88	0.39	0.15	0.13	0.07	0.97
2-methylpentane	0.85	0.47	0.10		0.12	0.98
3-methylpentane	0.87	0.43	0.11	0.03	0.11	0.97
Hexane	0.70	0.50	0.00		0.35	0.88
Chloroform	0.10	0.05	0.12	0.11	0.89	0.84
c-3-methyl-2-pentene	0.83	0.46	0.13	0.04	0.18	0.95
2,2-dimethylpentane	0.77	0.51	0.08	0.11	0.08	0.88
Methylcyclopentane	0.84	0.45	0.10	0.05	0.20	0.95
2,4-dimethylpentane	0.89	0.14		0.14	0.12	0.86
1,1,1-trichloroethane	0.15	0.02	0.02	0.84	0.03	0.73
Benzene	0.65	0.67	0.15		0.06	0.91
Carbontetrachloride	0.06	0.12		0.91	0.08	0.85
Cyclohexane	0.80	0.50	0.15	0.15	0.01	0.94
2-methylhexane	0.80	0.54	0.15	0.11		0.97
2,3-dimethylpentane	0.84	0.48	0.15	0.13	0.01	0.99
3-methylhexane	0.89	0.34	0.15	0.09	0.01	0.95
1-heptene	0.62	0.70	0.08	0.17	0.06	0.91
Heptane	0.69	0.64	0.06	0.04	0.07	0.89
Methylcyclohexane	0.70	0.64	0.15	0.19	0.05	0.96
Toluene	0.60	0.70	0.09		0.10	0.89
3-methylheptane	0.67	0.52	0.29	0.26		0.87
c-1,3-dimethylcyclohexane	0.60	0.75	0.13	0.12	0.05	0.95
Octane	0.32	0.52			0.16	0.62
Tetrachloroethene	0.53	0.13	0.54		0.11	0.64
Ethylbenzene	0.73	0.64	0.19	0.04	0.00	0.98
m,p-xylene	0.73	0.63	0.19	0.08		0.98
o-xylene	0.75	0.60	0.21	0.12		0.99
Nonane	0.49	0.81	0.21	0.07	0.13	0.95
iso-propylbenzene	0.57	0.68	0.21	0.11		0.84
n-propylbenzene	0.74	0.59	0.21	0.16		0.96
3-ethyltoluene	0.76	0.56	0.23	0.15		0.98
4-ethyltoluene	0.75	0.59	0.07		0.00	0.92
1,3,5-trimethylbenzene	0.78	0.53	0.23	0.17		0.97
2-ethyltoluene	0.74	0.58	0.24	0.16		0.98
1,2,4-trimethylbenzene	0.78	0.53	0.24	0.17		0.97
benzyl chloride	0.49	0.38	0.48	0.15		0.65
1,4-dichlorobenzene	0.42	0.66		0.33	0.04	0.73
1,2,3-trimethylbenzene	0.75	0.56	0.26	0.17		0.97
p-cymene	0.33	0.81	0.30	0.03	0.06	0.86
1,4-diethylbenzene	0.03	0.15	0.81	0.02	0.13	0.70
n-butylbenzene	0.66	0.62	0.29	0.10	0.00	0.92
Naphthalene	0.66	0.58	0.29	0.15		0.89

Table 5.17. Comparison of the factors resolved with CFA and PMF.

Factor number		**Factor name**
FA	**PMF**	
1	1+4	Residential heating + LDV exhaust
2	3	HDV exhaust
3	2	Solvent use (PERC)
4	2	Solvent use (TCA, CCl_4)
5	2	Solvent use (Chloroform)

Diurnal variation in the factor scores in CFA and source contributions in PMF was also compared. The factor scores calculated by CFA for each sampling sessions are shown in Figure 5.38. Comparison of Figure 5.38 for Factor 1 with Figure 5.8 and Figure 5.14 shows that the diurnal variation in source contributions is similar in CFA and PMF. For the Factor 2 of CFA, the diurnal variations are similar to that of PMF except night session (see Figure 5.11 for PMF results). During the night session PMF calculated the lowest contributions whereas CFA calculated the highest contributions. Diurnal variation in the source contributions for Factor 3, 4 and 5 are different than the diurnal variation in the source contributions for solvent source calculated by PMF (see Figure 5.10 for PMF result). The average factor scores for three solvent sources resolved by CFA, however, have similar diurnal variation with that of PMF.

The CFA does not calculate source contributions. Thus the SCE values calculated by PMF are not compared with CFA. The factor loadings calculated by CFA are not in concentration units and thus it is not possible to compare them with the source profiles available in the literature. The source profiles calculated by PMF make the identification of sources easier. The factor loadings calculated by CFA, however, are difficult to interpret to identify sources as the many VOC sources have common abundant compounds.

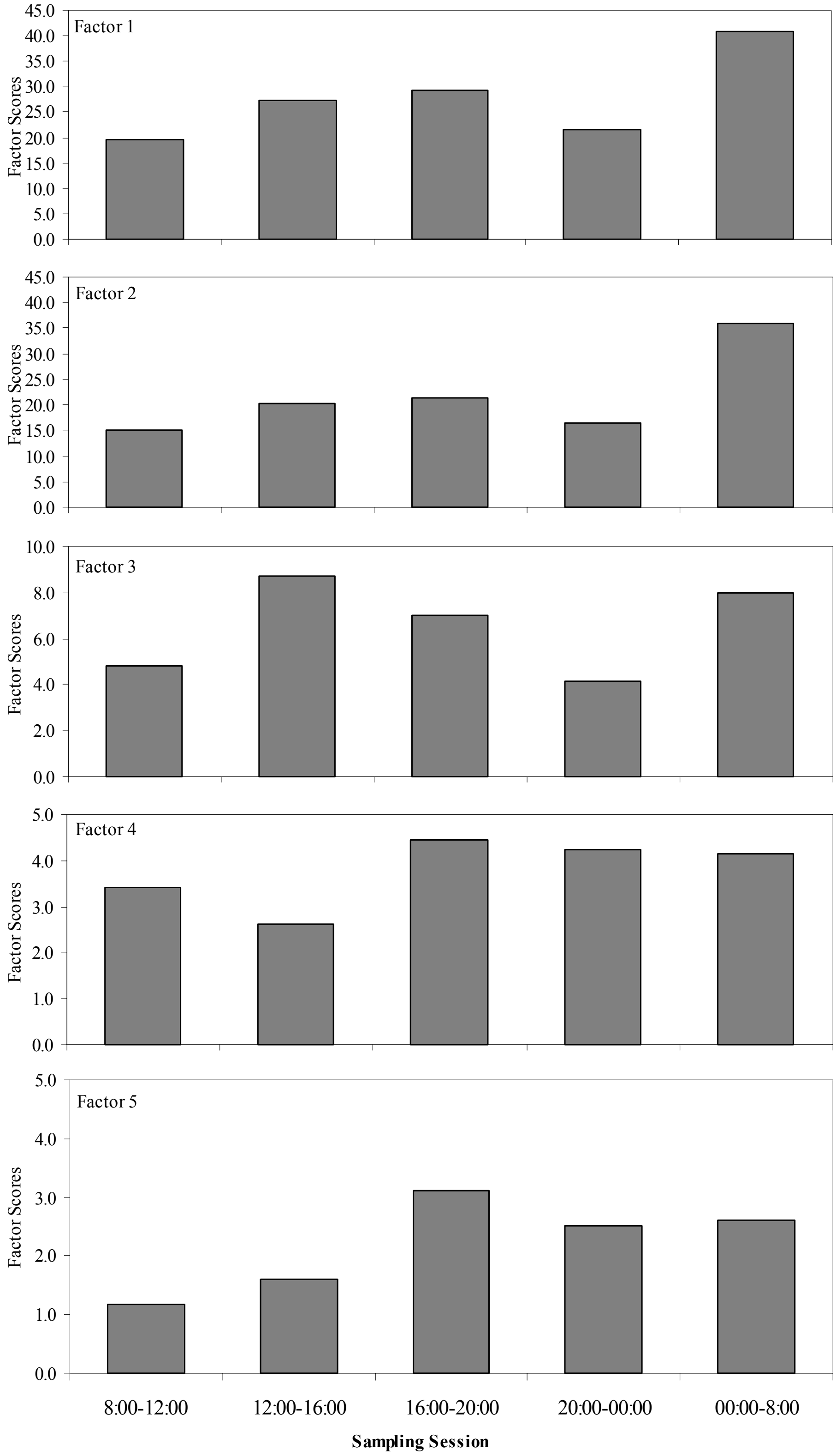


Figure 5.38. Diurnal variations in the factor scores calculated by CFA.

In conclusion, the results of the CFA and PMF to identify four VOC sources observed at residential station during winter campaign are comparable. The differences in the results of both methods were due to differences in model algorithms and model fundamentals. The strengths and weaknesses of CFA and PMF receptor models are shown in Table 5.18.

Table 5.18. Strengths and weaknesses of CFA and PMF.

CFA	
Strength	**Weakness**
• Identify major source types and relate secondary components to source via correlations or covariances. • Sensitive to the influence of unknown and/or minor sources. • Easier to optimize and run	• Sensitive to extreme values in the data set. • Vectors or components are usually related to broad source types as opposed to specific categories or sources • Many subjective rather than objective decision and interpretations of eigenvectors as source • Need to use empirical rotation to identify and clarify the resulting factors.
PMF	
Strength	**Weakness**
• Provides source contribution estimates to each sample. • Requires uncertainty estimates of ambient measurements. Can handle missing or BDL data. • Weight species concentrations by their analytical precision. • Constrained to non-negative species concentrations or source contributions. • Provides solution evaluation tools (e.g., Q, R^2). • Derives source profiles from ambient measurements as they would appear at the receptor.	• Need to determine number of retained sources. • Requires knowledge of source profiles or existing profiles to verify the representativeness of calculated source profiles and uncertainties of source contributions.

5.2. Ottawa Campaign

5.2.1. Positive Matrix Factorization

Input Parameters

Ambient concentrations of 163 VOCs were measured at the nose-level station located on Slater Street in Ottawa during winter and summer campaigns. There were a total of 18 and 49 data measured during summer and winter campaigns, respectively. As the data collected during summer campaign was not many, the PMF analysis was performed only for the winter data set.

The VOC data was inspected for missing values and found that 31 compounds have less than 30% missing values. There were 11 compounds having less than 50% but higher than 30% missing value. The minimum number of compounds that provide the high abundance in the data set was selected to provide a high degree of freedom. The compounds that have low abundance but are important to determine sources such as 1,3-butadiene, isobutene, nonane were also included in the data set. There were few heavy hydrocarbons in the final list thus organic carbon (OC) and elemental carbon (EC) were also included in the data set.

Secondly, S/N ratio was inspected to identify “bad” variables and found that none of the compounds were “bad” variables. A total of 34 compounds were processed to replace missing and BDL values with the proper input values as described in the previous sections. The input data matrix was constructed with the pretreated 34 compounds and a total of 49 data points.

Error estimates for the input data values were computed using the error model (EM) -14 built in PMF2. Three different C3 values, 0.10, 0.05 and 0.01, were used during calculations. PMF2 was run with different number of factors and different C3 values. Error estimates were also calculated according to method proposed by Polissar *et al.* (1998). Uncertainty matrix was constructed and used in the PMF2 run. Model was run with different number of factors. The model fit was better when using the uncertainty matrix calculated by Polissar *et al.* (1998) than that was calculated by PMF2 algorithms.

Application of the Model

Determination of the number of factors (i.e., sources) is the critical step in PMF2. Four rules discussed in Section 2.7.1 were utilized in order to select the optimum number of sources that provided the optimum solution. PMF2 runs using number of factors 3, 4 and 5 yielded calculated Q values of 1753, 1424 and 1082, respectively. Model runs with 5 factors yielded the lowest calculated Q value that is approximately 1.5 times lower than the theoretical Q value (i.e., 1598). Three factors solution had the closest calculated Q value to the theoretical Q value and thus it was selected as the optimum solution.

Effect of transformation on the model performance in terms of factor profiles, scaled residuals and calculated Q value was investigated. FPEAK tool was applied using values ranging between -1.0 and 1.0 to test different rotations. PMF2 runs with 3 factors and FPEAK values of –1.0, -0.5, -0.1, 0.0, 0.1, 0.5, and 1.0 yielded calculated Q values of 1782, 1768, 1809, 1753, 1753, 1755 and 1890, respectively. The FPEAK value of zero resulted in the closest Q value to the theoretical one. In addition, considering the physical meaning of the resolved sources and the distribution of the scaled residuals, the FPEAK value was finally set equal to zero.

Scaled residuals were re-inspected for individual compounds at each output file that was resulted in utilizing the model with input settings of FPEAK=0.0 and number of factors 3. For the compounds having scaled residuals beyond ±2 limit value, input data matrix was re-inspected and the uncertainty values were increased for the outlier data points.

Results of the Model

PMF2 analysis, with the application of robust mode resulted in three factors (i.e., sources) that explain variation in the VOC data generated at nose-level station during winter campaign. Factors identified by PMF2 are interpreted qualitatively by evaluating source profiles, time variations in source contributions and EV that were generated by the model. The source profiles are used as the final criteria for source identification. EV profiles are provided for reference only. Source profiles are also compared with the profiles available in the literature for a quantitative interpretation of the sources. Each factor is interpreted separately in the following paragraphs.

Factor 1

The source profile, EV and source contribution plots generated for Factor 1 are shown in Figure 5.39. Accompanying the factor, individual error estimates are also computed for all of the factor elements. Error estimates are also shown in Figure 5.39 together with factor profiles. Source contributions are averaged over each sampling sessions, namely morning (7:30-9:30), noon (11:30-13:30), afternoon (15:30-17:30).

Ethylene, hydrocarbons ranging between C3 and C4 and toluene are the abundant species in the source profile for Factor 1. Acetylene is also among the abundant species in this profile. Acetylene is formed by the combustion of gasoline thus it is commonly used as the marker for gasoline vehicle exhaust (Derwent *et al.*, 1995; Broderick and Marnane, 2002). Ethylene to acetylene ratio is higher than one indicating that this profile is a gasoline vehicle exhaust source as indicated by Doskey *et al.* (1992). EV plot shows that this source explains variation in most of the hydrocarbons except EC and heavy hydrocarbons. Source contributions shown in Figure 5.39 indicate a diurnal variation with a high contribution during evening rush hour and a decreasing contribution through morning session.

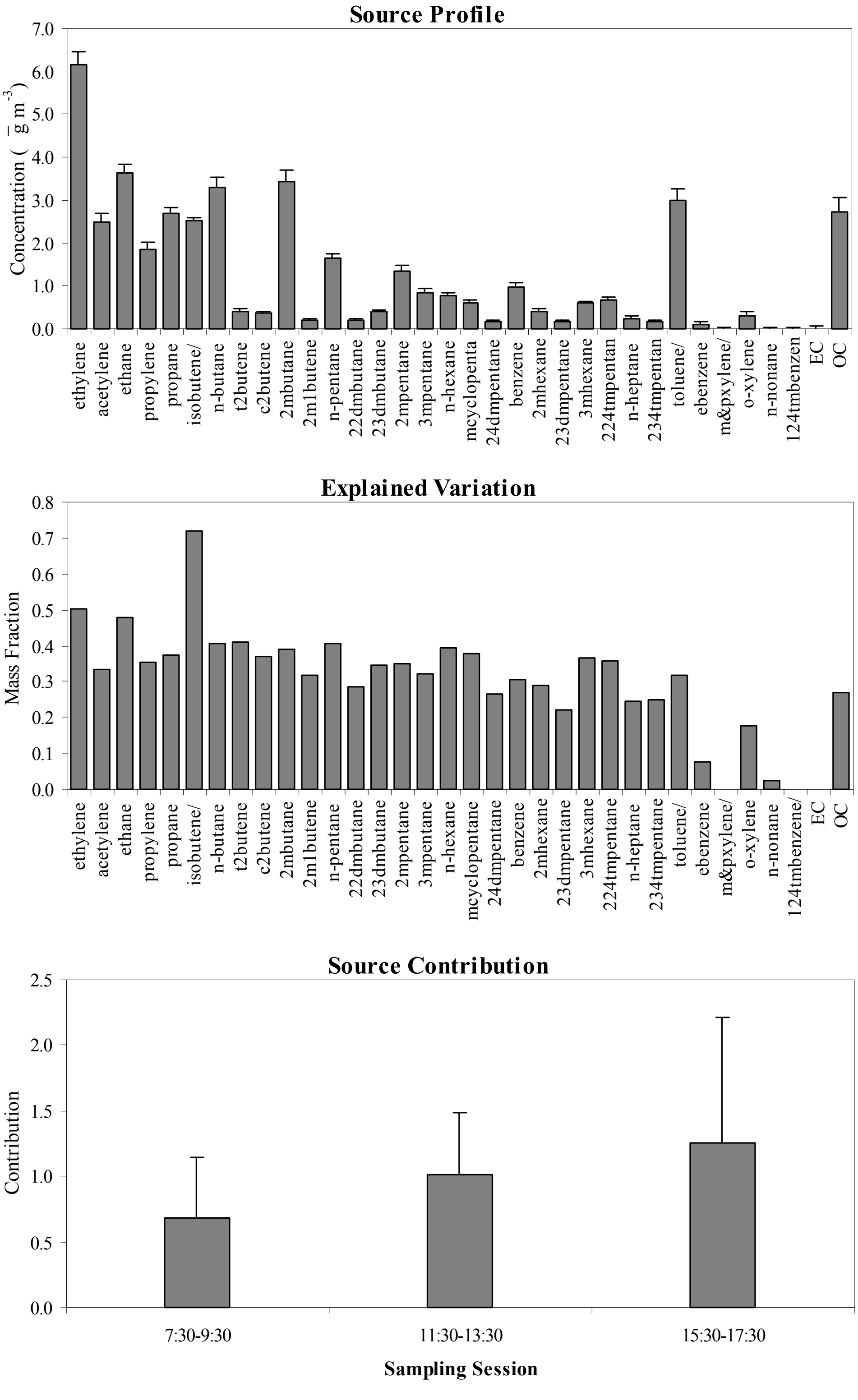


Figure 5.39. PMF2 results for Factor1.

Diurnal variation in the source contributions observed for this factor is similar to traffic pattern (see Section 4.2.1). This factor is interpreted as LDV exhaust. Further comparison with the profiles available in the literature is conducted to identify the source accurately.

The profile generated by PMF is compared with the profiles available in the literature, SPECIATE database and the profiles generated by ERMD during the Ottawa campaign. ERMD profiles were generated by dynamometer tests on a passenger car and a bus for emissions at different stages of driving such as cold start, idle and hot start. The comparison of the source profile for Factor 1 with the hot start LDV exhaust profile generated by ERMD is shown in Figure 5.40. The ERMD hot-start profile provides the best fit with the Factor 1 profile. For these reasons, Factor 1 is identified as the ***LDV exhaust source***.

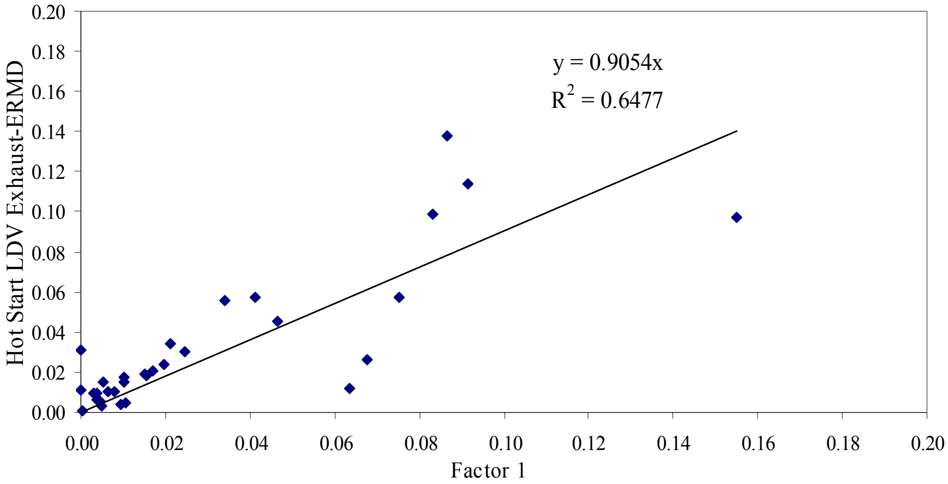


Figure 5.40. Correlation between hot start and Factor 1 profiles.

Factor 2

Results of the PMF2 run are plotted for Factor 2 in Figure 5.41. Source profile plot generated for Factor 2 indicates that ethylene, ethane, propane and OC are the dominating species in this factor.

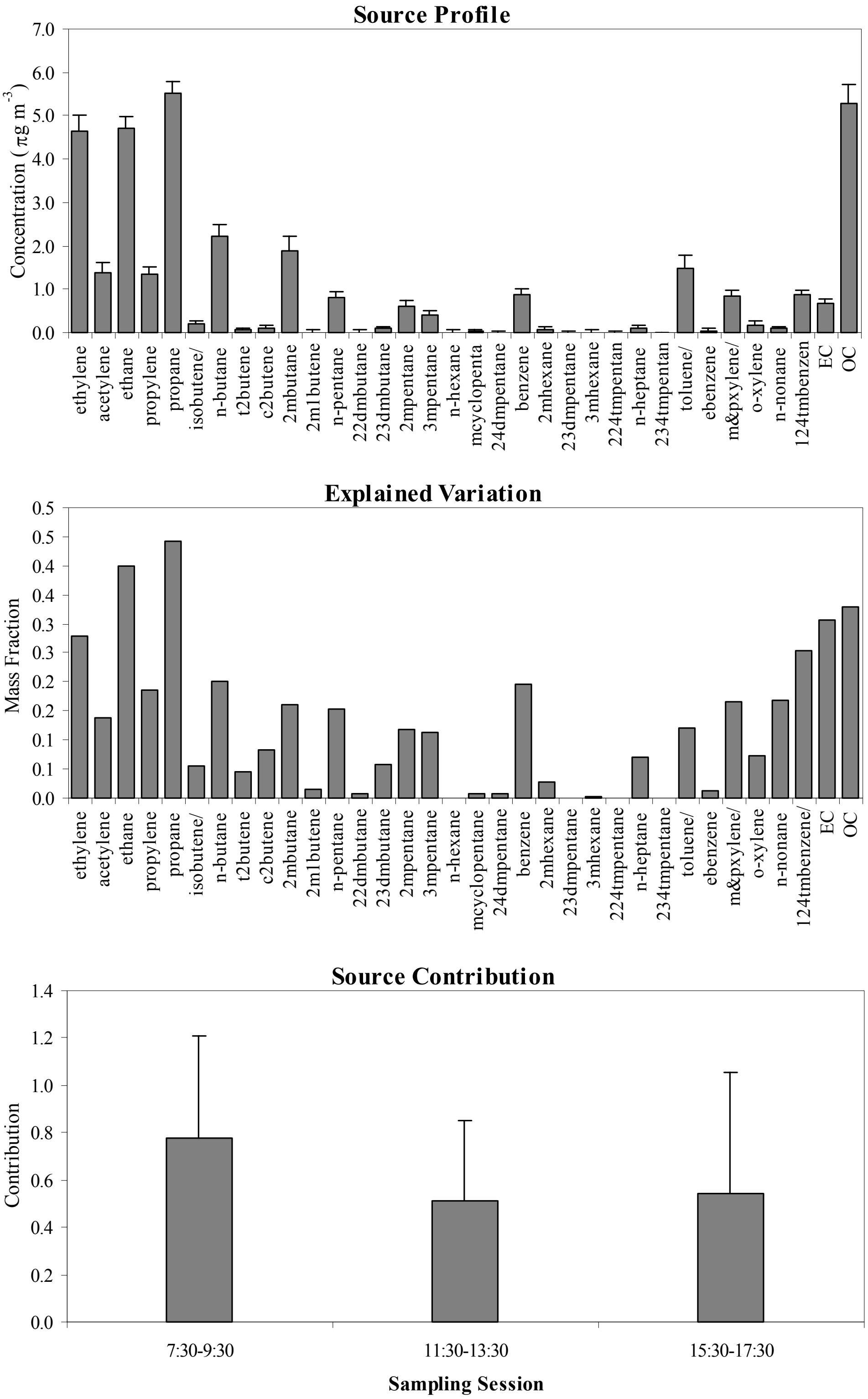


Figure 5.41. PMF2 results for Factor2.

EC has also contribution in the profile of Factor 2. The EV plot shows that Factor 2 explains variation in the OC and EC most. EC is a major component of diesel exhaust, contributing approximately 50% to 85% of diesel particulate mass, depending on engine technology, fuel type, duty cycle, engine lubrication oil consumption and state of engine maintenance (EPA, 2002). EC is directly emitted whereas OC is both directly emitted and formed through atmospheric oxidation of reactive organic gases and subsequent gas-to-particle conversion processes (Douglas *et al.*, 1994; Yu *et al.*, 2004).

Source contribution of the Factor 2 shows a diurnal variation with the highest contribution observed during morning session and lowest contribution during noon session. This pattern is very similar to diurnal pattern of the number of buses recorded on the Slater Street. The buses have the contributions of 16%, 7% and 13% during morning, noon and afternoon sessions, respectively. According to these findings Factor 2 is interpreted as HDV exhaust profile. The high abundance of propane in this factor is explained by unresolved LPG and HDV exhaust profiles depicted in Factor 2. Therefore, Factor 2 is identified as ***LPG and HDV exhaust source***.

Factor 3

The source profile, EV and source contribution plots generated for Factor 3 are shown in Figure 5.42. Toluene, acetylene, m,p-xylene and 2-methyl-butane are the most abundant species in source profile of Factor 3. Ethylene has very low abundance. Ethylene to acetylene ratio is less than one indicating cold start LDV exhaust emission (Doskey *et al.*, 1992). EV plot shows that Factor 3 explains variation in most of the compounds except propane, isobutene, ethane and ethylene. Source contribution plot shows a diurnal variation with the highest contribution during evening session. This source contribution pattern is similar to that obtained for Factor 1. However, the contribution during the evening session is more pronounced for Factor 3.

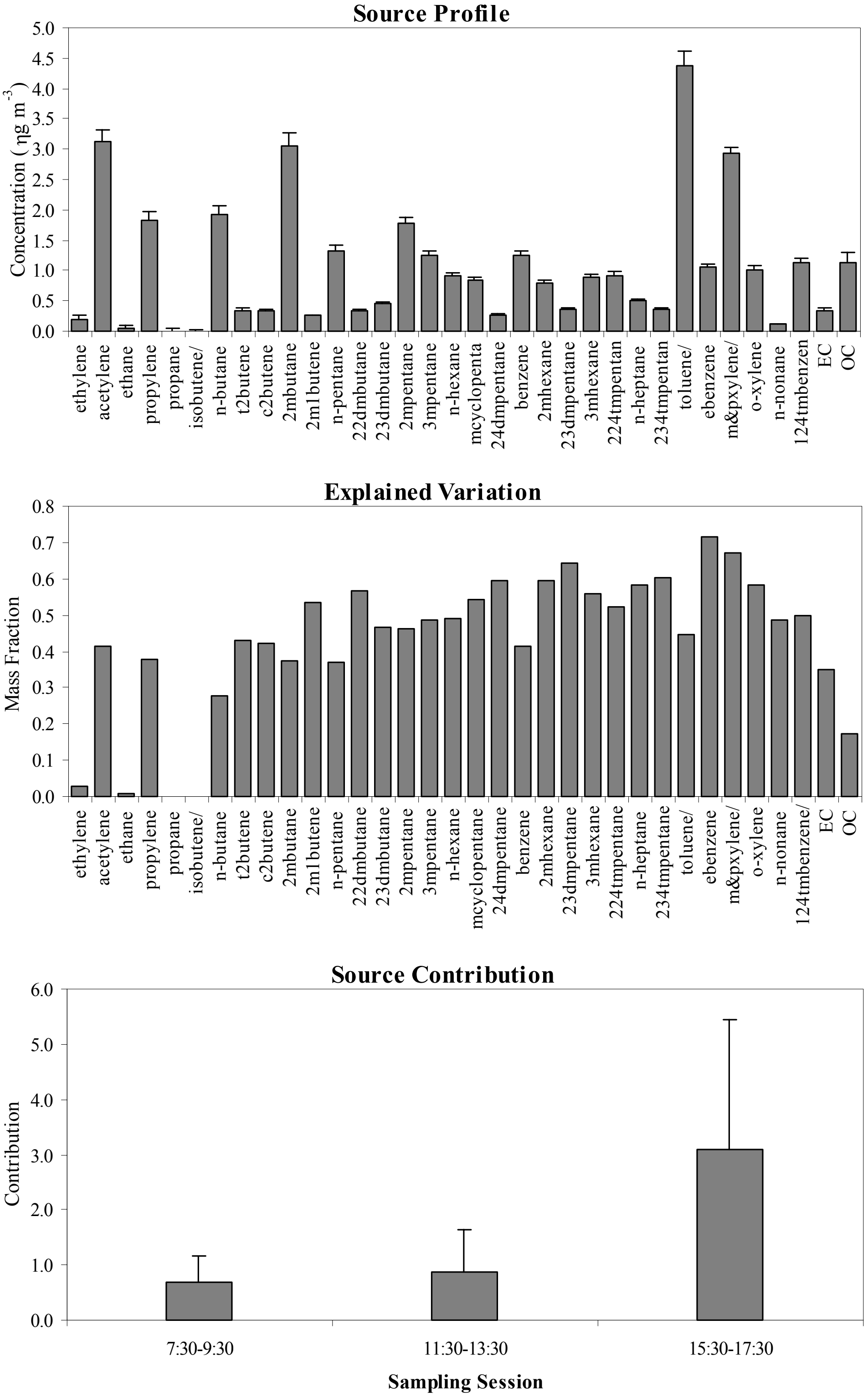


Figure 5.42. PMF2 results for Factor3.

The source contribution pattern is similar to traffic pattern as explained earlier. The very high evening contribution could be due to high abundance of cold start emissions during this session. The passenger cars parked in the city center left the city during evening rush hour resulting in significant cold start emission. The Factor 3 is interpreted as cold start LDV exhaust.

The source profile calculated for Factor 3 was compared with the profiles available in the literature, SPECIATE database and ERMD source profiles. The best correlation is obtained between cold start LDV exhaust profile generated by ERMD and Factor 3 profile (see Figure 5.43). The correlation coefficient is 0.95 and intercept is 0.92. Therefore, Factor 3 is identified as ***cold start LDV exhaust*** source.

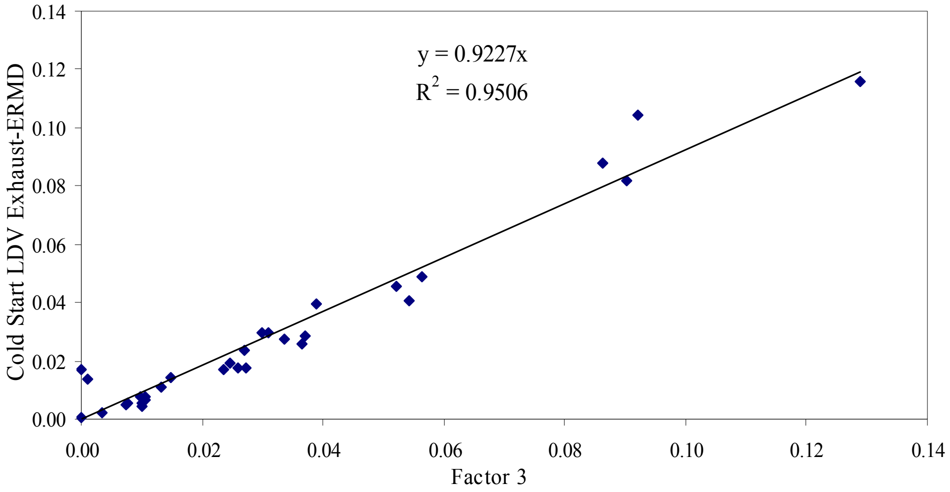


Figure 5.43. Correlation between cold start and Factor 3 profiles

Source Contribution Estimates

Linear regression was used to regress the modeled total VOC concentrations against the measured total VOC concentrations. LR helped ascertain the optimal number of factors and apportion source contributions. LR between the model-predicted and measured total VOC concentrations is shown in Figure 5.44. R-squared values and the ratios of the modeled to measured concentrations are examined to determine how well the regression model fit the measured data for total VOCs. LR resulted in R^2 value of 0.98 with intercept of 1.06. These results indicate that the resolved sources by PMF2 effectively reproduce the measured values and accounted for most of the variance in the total VOC concentration. Ratio of the modeled to measured total VOC concentrations is 0.94 indicating that the PMF2 solution have excellent agreement with measured results.

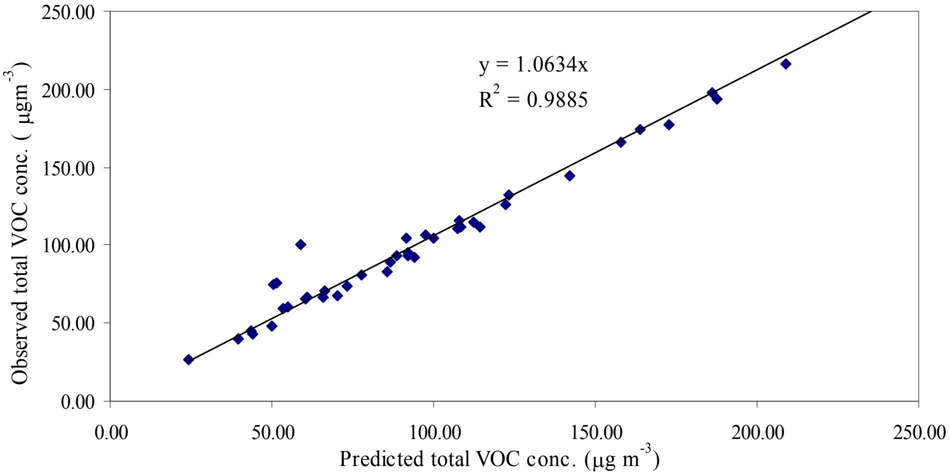


Figure 5.44. Observed versus predicted VOC concentrations.

The percent contribution of each factor to total VOCs was also determined. Regression was used to quantitatively apportion the mass contributions among the resolved sources. The average source contribution estimates (SCE) of each factor to the measured total VOC concentration are shown in Table 5.19.

Cold start and LDV exhaust sources contribute the most totally accounting for about 83% of total VOC concentration measured at nose-level station during winter campaign. HDV exhaust and LPG sources account for about 18% of VOC concentrations. The high contribution of the LDV sources is expected since the vehicle count data show very high contribution of LDVs at the measurement site. The important point here is the higher contribution of cold start emissions to LDV sources.

Table 5.19. Source contribution estimates for nose-level station during winter campaign.

Factor No	Source	% SCE
1	LDV exhaust	35.58
2	HDV exhaust + LPG	17.72
3	Cold start LDV exhaust	46.70

Model Performance Parameters

One of the advantages of PMF2 is to provide performance evaluation tools such as goodness of fit value (i.e., Q) and scaled residuals. Q value was inspected to decide on the optimum number of factors. Minimum Q value that is the closest to the theoretical Q value indicates a better fit of the model to measured data. PMF2 solution with three factors resulted in a calculated Q value of 1753 that was about 9% higher than the theoretical Q value. This indicates a good fit that can also be seen from the result of the LR analysis.

Scaled residual errors were also inspected. Most of the scaled residuals were between -2.0 and 2.0 with a random distribution of positive and negative values. The frequency distributions of scaled residual errors only for selected compounds for convenience are shown in Figure 5.45.

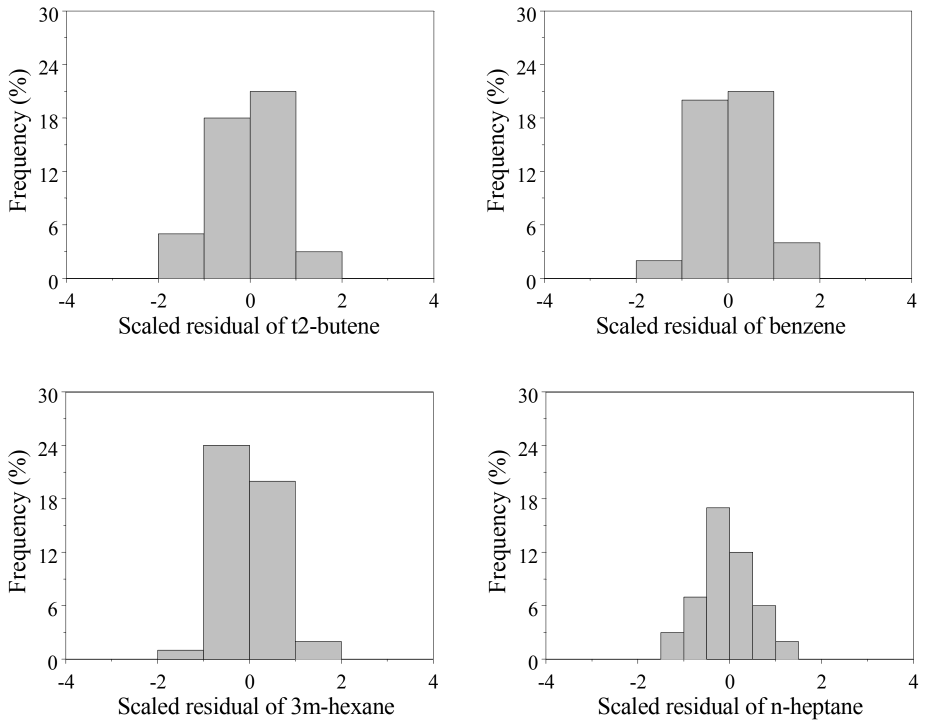


Figure 5.45. Frequency distribution plot for scaled residual errors.

5.2.2. Comparison of Receptor Models

In this study, a new generation receptor model namely PMF was used for source apportionment. However, since PMF powerful, but only recently developed tool of receptor modeling, its comparison with other, well-established receptor modeling tools can be useful to reveal its strengths and weaknesses. Positive matrix factorization results of Ankara study was compared with the results of factor analysis performed on the same data set. In this part of the study, PMF results from Ottawa study are compared with another receptor modeling tool, namely, chemical mass balances (CMB). Results are discussed in following paragraphs.

The CMB receptor model uses the chemical and physical characteristics of gases and particles measured at source and receptor to identify the presence of and to quantify source contributions to pollutants measured at receptor (Hopke, 1991). The CMB consists of a least squares solution to a set of linear equations which expresses each receptor concentration of a chemical specie as a linear sum of products of source compositions and source contributions (Hopke, 1991; Fujita *et al.*, 1994). Detailed information on CMB are provided in Chapter 2.

5.2.2.1 CMB Application

In this study, CMB version 8.0 developed for US EPA was used for the source apportionment of VOC concentrations measured at nose-level station during Ottawa winter and summer campaigns. Receptor profiles for which descriptive statistics were provided in Section 4.2 were utilized as input to the model. Source profiles available in the literature, SPECIATE database and profiles developed by ERMD during Ottawa campaign were evaluated and used as input to the model.

The VOCs emitted from mobile and stationary sources in an urban atmosphere. Stationary sources include solvent use (painting, printing, surface coating, dry cleaning, etc.), industrial activities (organic chemistry, petrochemical plants, food industry, iron and steel industry, etc.), waste processing plants, combustion and agriculture (UN ECE, 1991). Mobile sources are motor vehicles. The recent research demonstrated that about 50% of VOCs measured in urban atmosphere emitted by motor vehicles (US EPA, 1993; Conner *et al.*, 1995; Fujita *et al.*, 1995; Rappengluck and Fabian, 1999, Thijsse *et al.*, 1999; Watson *et al.*, 2001). Gasoline vehicles compose majority of motor vehicle emissions in urban atmosphere (UN ECE, 1991).

Ottawa is the capital city and majority of the government offices locates in this city. Industrial facilities located in or near Ottawa are negligible. In this study, 30 source profiles including motor vehicle sources and solvent use were used in preliminary CMB runs. The results of these runs were evaluated and a total of 18 source profiles that provided a better fit to the measured data selected to be used in the second set of model runs. Source categories of these source profiles were gasoline vehicle exhaust, diesel vehicle exhaust, whole gasoline, printing, and liquefied petroleum gas (LPG). Solvent source composition changes with region according to active legislations. In this study solvent profiles available in the literature for different part of the world did not provide a good fit to Ottawa data. Thus, solvent use source profile was not used in the second step. The second set of runs was conducted under different combinations of source profiles and fitting species. The results demonstrated that 8 source profiles out of 18 provided a better fit to the VOC data measured during summer and winter campaigns. The source profiles used in the final set of CMB runs are given in Table 5.20. The motor vehicle source profiles generated by ERMD provided better fit to the measured concentrations. Summer grade whole gasoline profile was obtained from CPPI (1994).

Table 5.20. Source profiles used in the CMB modeling.

Abbreviation	**Source profile name**	**Source**
PRNT1	Printing	SPECIATE
LPG01	Liquefied petroleum gas	SPECIATE
WGASS	Ottawa summer grade whole gasoline	Literature
BAG22C	Gasoline vehicle exhaust, FTP2 at 20 °C	ERMD
BAG11C	Gasoline vehicle exhaust, FTP1 (cold start) at -10 °C	ERMD
BAG31C	Gasoline vehicle exhaust, FTP3 (hot start) at -10 °C	ERMD
DN20	Diesel vehicle exhaust at 20 °C	ERMD
DN-10	Diesel vehicle exhaust at -10 °C	ERMD

5.2.2.2 CMB Results

The CMB model calculates contribution of each source together with model performance parameters. The final CMB model runs performed for each sampling session and each season resulted in the SCE values depicted in Figure 5.46 anf Figure 5.47 for winter and summer seasons, respectively. Gasoline vehicle exhaust emissions that accounted for about 90% of the VOC concentrations measured at nose-level station are estimated as the major VOC source during winter campaign. Diesel vehicle exhaust and LPG are also estimated to contribute VOC concentrations measured during winter campaign.

Cold start and hot start gasoline vehicle exhaust contributions show significant diurnal variation. Cold start source contributions denoted by BAG11C in the Figure 5.46 show an increasing trend from morning to afternoon session. On the contrary, contribution of hot start emission denoted by BAG31C shows a decreasing trend from morning to afternoon session. City center is mainly occupied by office buildings and commercial stores. People drive to the city center during morning session, park their cars and leave the center during afternoon rush hour. Therefore, cold start emissions contributes the most during afternoon session and hot start emissions contributes during morning session.

Total contributions of the gasoline vehicle exhaust emissions calculated during winter season are 82%, 87% and 95% during morning, noon and afternoon sessions, respectively. This diurnal trend is similar to diurnal trend for LDV traffic counts recorded at Slater Street during winter campaign.

Diesel vehicle exhaust emission has the highest estimated contribution during morning and lowest contribution during afternoon session. This pattern is similar to diurnal pattern of the number of buses recorded on the Slater Street. The buses have the contributions of 16% and 13% during morning and afternoon sessions, respectively. Contribution of LPG source also shows a decreasing trend from morning to afternoon session. Motor vehicle exhaust and whole gasoline are estimated as the major VOC sources during summer campaign as can be seen from Figure 5.47.

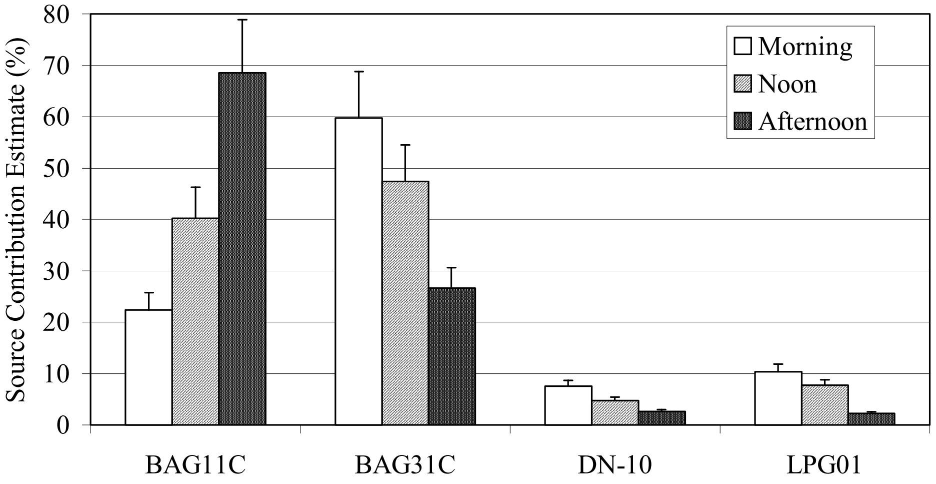


Figure 5.46. SCE values calculated for winter campaign.

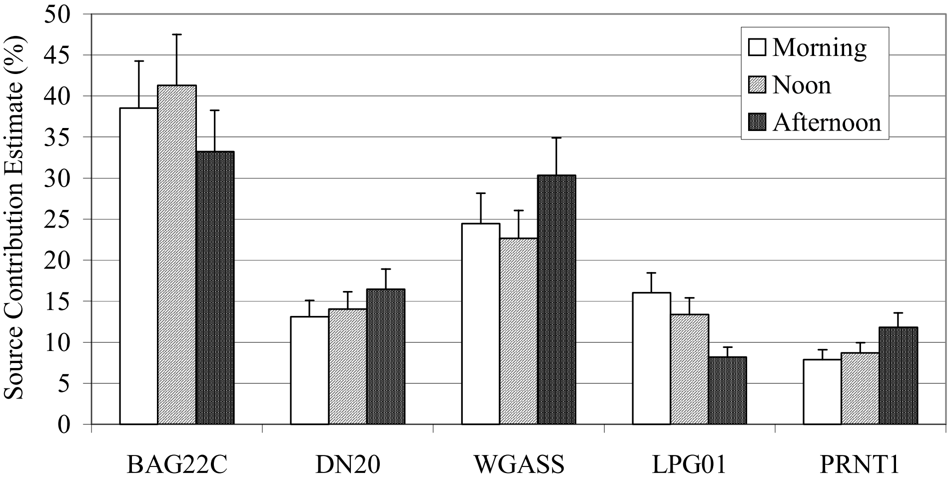


Figure 5.47. SCE values calculated for summer campaign.

Printing is also a source of VOCs that is distinguished during summer campaign. Gasoline vehicle exhaust that is denoted as BAG22C source profile estimated to contribute the most during noon and the least during the evening session. Higher SCE value calculated for noon session than for morning session is excepted since the number of vehicles is higher during noon session.

The SCE values calculated for afternoon session are lower although the number of vehicles is higher. This decrease in the SCE value could be a relative decrease in afternoon session that is associated with the significant increase in the SCE value of whole gasoline source. As the ambient temperatures are higher, cold start emissions are not distinguished during summer campaign.

Diesel vehicle emissions show a diurnal variation that is close to diurnal variation observed in vehicle numbers. Whole gasoline and printing sources estimated to contribute most during afternoon sessions when the temperatures are high. Both of these sources are evaporative sources. LPG use has a similar diurnal pattern as that is observed during winter campaign.

Seasonal variation in the estimated sources contributing the VOC concentrations measured at nose-level station is shown in Figure 5.48. The estimated contributions of gasoline vehicle exhaust, diesel vehicle exhaust, and LPG are 91%, 4% and 5%, respectively during the winter season. During the summer season, the estimated contributions of gasoline vehicle exhaust, diesel vehicle exhaust, whole gasoline, LPG and printing are 34%, 16%, 28%, 13% and 10%, respectively. Motor vehicle emissions are estimated to contribute about 95% and 50% of the measured VOC concentrations during winter and summer seasons, respectively. Residents start using bicycle and motorcycles during summer season and number of passenger cars decreases during this season.

Whole gasoline emissions have the second highest estimated contributions during summer season. Estimated contributions from whole gasoline and printing sources calculated for the summer season is related with the evaporation of these emissions during warmer summer season.

Model performance parameters are evaluated both for winter and summer solutions. The R^2 value was higher than 0.85, χ^2 value was lower than 1.5, t-stat value was higher than 2.0, and more than 85% of the total VOC mass was explained with the solutions at 95% confidence interval. Calculated and measured VOC concentrations are very close to each other. A typical comparison is given in Figure 5.49. The ratio of the measured to calculated VOC mass was between 0.8 and 1.2 for all the solutions.

PMF and CMB receptor models were utilized to estimate contribution of sources to the VOC concentrations measured at nose-level station during winter campaign. Both CMB and PMF provide quantitative estimates of the source contributions. In the CMB analysis, source profiles are provided whereas in PMF, the source profiles are estimated. Both CMB and PMF are employing least square fitting, but there are some important difference in how the underlying error structures are modeled and how many unknowns are being estimated. CMB analysis is done on a sample-by-sample basis and thus there can be errors in the estimated source contributions because of the variations that can occur in the source profiles. PMF uses all of the data and thus, estimates the average source profile over the time interval during which samples were acquired. Thus, there are some similarities in the process and the outcome, but there are also some important differences in what is being estimated, the input data that is required, and the estimates of the uncertainties in the calculated values.

5.2.2.3 Comparison of PMF and CMB results

The estimated source contributions calculated by both model are shown in Table 5.21. Both model identified four VOC sources. HDV and LPG sources were identified but not resolved in PMF model.

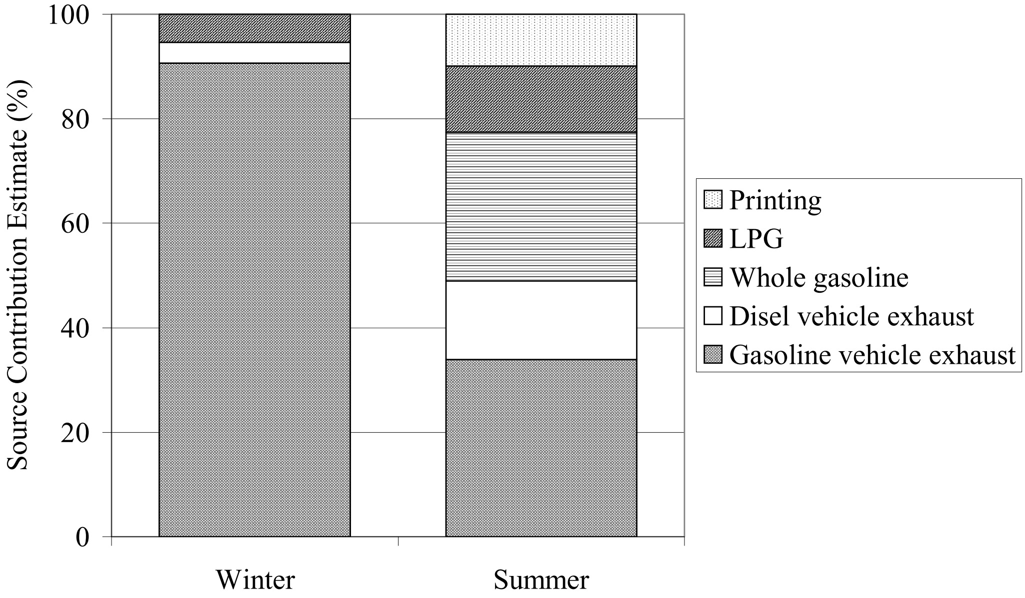


Figure 5.48. Seasonal variation in the estimated source contributions.

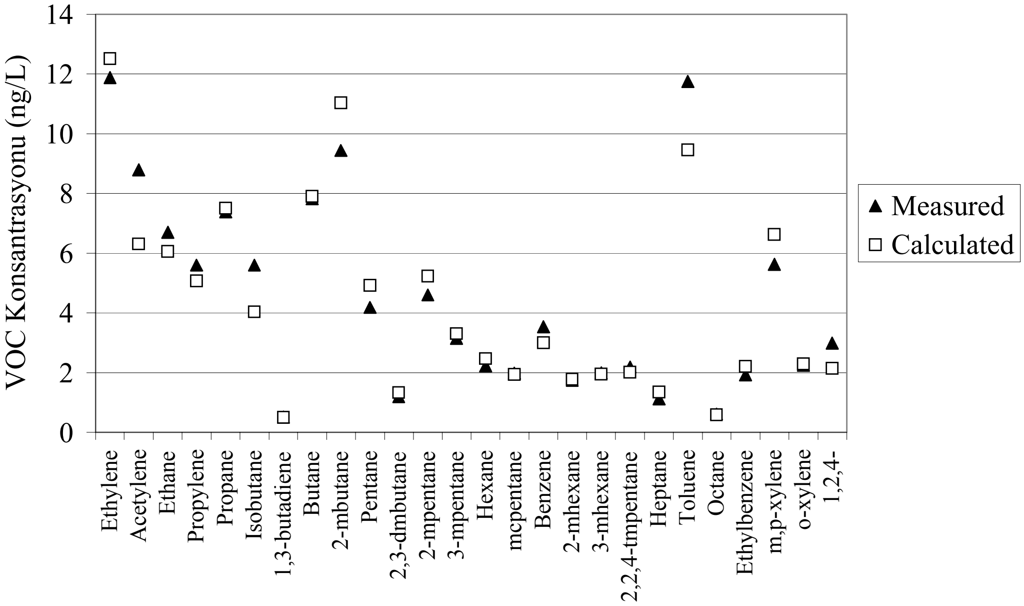


Figure 5.49. Comparison of the calculated and measured VOC concentrations.

The SCE values for CMB were presented in the table as the average of all session. Cold start LDV exhaust source contribution values calculated by the models are very close to each other (i.e., 6% deviation). The diurnal source contribution pattern for PMF (see Figure 5.42) and CMB (see Figure 5.46) are identical indicating an increasing contribution from morning to afternoon session. Estimated contributions for LDV exhaust emissions calculated by the models are different. The CMB estimates LDV contribution to total VOC mass 25% higher than that found by PMF. The diurnal variation in the source contributions for PMF (see Figure 5.39) and CMB (see Figure 5.46) are also different. The total average contributions of HDV exhaust and LPG sources calculated by CMB are about 34% lower than that are calculated by PMF. The diurnal variations in the source contributions, however, are the same for both models showing a decreasing contribution from morning to afternoon sessions.

Table 5.21. Comparison of source contributions calculated by PMF and CMB.

Source	**PMF (% SCE)**	**CMB (% SCE)**
Cold start LDV exhaust	46.70	43.72
LDV exhaust	35.58	44.60
HDV exhaust + LPG	17.72	11.68

The PMF and CMB models identified the same VOC sources although PMF did not resolve HDV and LPG sources. The SCE values calculated by the models show some differences. These differences might be due to differences in the model algorithms and model applications. In the CMB model, SCE values are calculated for individual sampling sessions and average of those values are presented in this section. In the PMF model, however, the input data file consists of all the sessions and model calculates the SCE values for the whole data set.

The overall model performances are good to estimate the major and the minor VOC sources.

5.3. Comparison of Ankara and Ottawa Campaigns

PMF receptor model was applied to both Ankara and Ottawa data. Sources of VOC emissions in these cities were resolved by PMF as discussed in previous sections. Source contributions estimated during winter campaign of Ankara and Ottawa are compared in Table 5.22.

Table 5.22. %SCE values estimated during Ankara and Ottawa winter campaigns.

Source	**Ankara**		**Ottawa**
	Residential	**Background**	**Roadside**
LDV Exhaust	21.84		35.58
HDV exhaust (+ LPG)[a]	34.14	39.18	17.72
Solvent use	12.48	14.77	
Residential heating	31.54	25.23	
Transported LDV exhaust		20.82	
Cold start LDV exhaust			46.70

[a] *LPG source together with HDV exhaust is valid for Ottawa roadside results.*

Motor vehicle related emissions contribute about 60% at both residential and background stations in Ankara whereas they contribute more than 85% in Ottawa. Traffic emissions are the major source in Ottawa whereas there are additional major sources in Ankara.

Cold start LDV exhaust source was resolved in Ottawa as acetylene and ethylene were among the target species. Exhaust emissions mostly influenced by diesel vehicles contribute more in Ankara than in Ottawa. Poor inspection and maintenance of most of HDVs in Ankara is the main reason for their increased contributions to VOC concentrations. As discussed in previous sections, even smaller number of HDVs than LDVs result in more emission in Ankara. In Ottawa, however, there are strict regulations that control HDV emissions.

Coal combustion for residential heating is not recognized in Ottawa while it has an important share in Ankara during winter. Natural gas and electricity are used in Ottawa for residential heating whereas coal combustion has still a significant contribution resulting in elevated VOC concentrations in Ankara. Solvent use does not contribute to VOC concentrations measured in Ottawa as the target compound list has limited halogenated compounds.

CHAPTER 6

SUMMARY OF RESULTS

6.1. Ankara Campaign

Ambient measurements of VOCs were conducted at three different locations in Ankara, namely roadside, residential and background stations. Samples were collected five times a day for two months in summer and two months in winter seasons of the year 2003 and 2004. Samples were also collected in a roadway tunnel and an underground garage in order to generate source profiles associated with motor vehicle emissions. Fuel samples were also collected and analyzed to generate several fuel profiles specific to Ankara. Indoor measurements of speciated VOCs were also performed for the first time in Turkey.

A sampling and analytical method to measure VOCs in Ankara atmosphere was developed, implemented and evaluated, demonstrating high efficiency and reliability. Sampling with sorbent tubes followed by a thermal desorption and. gas chromatography with mass selective detector provided a very high sensitivity.

The data was investigated for temporal and spatial variations and sources of VOCs in Ankara. Toluene was the most abundant compound that was followed by m&p-xylene and benzene at all ambient sites. The World Health Organization provides international guideline values for several VOCs. However, there are no national or international regulatory limit values or thresholds for the ambient concentrations of VOCs except for benzene. The EC Directive 2000/69/EC sets annual average benzene concentrations to 5 μg m^{-3} considering that benzene is a known human carcinogen. Average benzene concentrations measured at the residential and background sites complied with the EC limit value although very high short-term concentrations were observed at these two sites. Average benzene concentrations measured at the roadside station, however, did not comply with the EC limit value. Benzene concentrations were more than 10 times higher than the EC limit value at the roadside station. At all sites aromatic compounds resulted in the highest concentration followed by paraffins, halogenated compounds and olefins. Concentrations of the olefins were the lowest at all sites due to their high reactivity in the atmosphere.

Most of the VOCs measured at the roadside and background stations showed seasonal variation whereas concentrations measured at the residential station did not show significant seasonal variations in 90% confidence interval. Seasonal variations are shown to be influenced by meteorological conditions and emission patterns. Concentrations measured at the roadside station were higher during winter than in summer as the number of emission sources increased and meteorological conditions that contributed to poor atmospheric dispersion prevailed in winter. The background station that was located on a sub-urban area was influenced mostly by distant emission sources. Concentrations measured in summer were slightly higher than in winter at this station.

Evaluation of the daily variation in the data set helped to identify pollution episodes. Weekday to weekend variation in the data was also evaluated. Weekday variation showed seasonal and spatial variability. Weekday concentrations were significantly higher during winter season at the roadside and residential stations indicating influence of traffic emissions at these stations. The vehicle counts were also higher at the roadside and residential stations during weekday than at weekend. During the summer season, there was no significant variation in weekday and weekend concentrations measured at the roadside station whereas higher weekday concentrations were observed at the residential station. Vehicle count data did not show significant weekday to weekend variation in summer explaining this fact observed at the roadside station which was heavily influenced by traffic emissions. A variation that was contrary to traffic count data observed at the residential station pointed out to an additional source of VOCs measured at the residential station. The weekday to weekend variation observed at the background station indicated that this station was influenced by both nearby traffic emissions and distant VOC sources.

Diurnal variation in the VOC data showed that concentrations of most of the VOCs were influenced by emission patterns and meteorological conditions. VOCs mostly emitted from motor vehicle sources, such as BTEX compounds, resulted in morning and afternoon peaks as the vehicle count also reached its peak numbers. Concentrations of these compounds were the lowest during noon sessions as meteorological conditions shown to enhance atmospheric dispersion during noontime. Low nighttime concentrations were observed due to decrease in the number of emission sources. Biogenic compounds such as isoprene, however, showed a different diurnal pattern that was affected by the sunlight hours that affected the emission rate.

Data for the criteria pollutants were obtained from the Ministry of Health and evaluated for temporal variability. It was shown that NO_x data had similar temporal variation with VOC data generated in this study. Noontime ozone peaks and higher ozone concentrations observed in summer are thus consistent with observations in other airsheds where photochemical reactions give rise to high ozone levels. Daily average O_3 concentrations reported by the Ministry of Health exceeded the WHO limit values almost all the time. In a study conducted in Ankara (MATRA, 2004) O_3 concentrations were shown to increase from more polluted city center to less populated and less polluted borders of the city. This is also consistent with observations in Ottawa and other urban centers due to the scavenging of O_3 by NO, which is the dominant portion of NOx in fresh combustion emissions. As the photochemical reactions between VOCs and NO_x take some time to occur, higher O_3 concentrations are observed where the polluted and aged air masses are transported to the less populated borders of the city. Therefore it is critical to monitor O_3 and its precursors (VOC and NO_x) continuously in different sections of the city and take measures to control levels of O_3 precursors.

Investigation of temporal variation in pollutants provided information on the possible emission sources. Evaluation of the spatial variations showed that the VOC concentrations were the highest at the roadside station and the lowest at the background station. A decrease in concentrations with an increase in distance from emission source was due to the high reactivity of most of the VOCs in atmosphere. Indoor measurements showed that concentrations measured at the residential home were higher than the office and outdoor concentrations. Naphthalene was among the most abundant compounds measured at the residential home indicating potential use of mothball that is a common practice in Turkey. Solvent-based compounds were abundant in office air. Indoor campaign included limited number of data but the results were important to point out that detailed measurements should be conducted to assess the health risks that could arise from exposure to VOCs in indoor environments.

A concentration weighted, wind-based surface trajectory analysis was developed in this study. Back trajectories of air masses are traditionally used to apportion the source regions to the measured concentrations at receptors. This method yields valuable results for the rural air quality studies where long-range transport can be distinguished from the local sources. For the studies that are conducted in urban microenvironments, however, contributions of the source regions cannot be assigned by using traditional methods used for back trajectories of air masses. Concentrations measured in urban microenvironments depend more strongly on local emissions from both natural and anthropogenic sources. The new method developed in this study is based on generation of back trajectories of surface wind that blows within the city borders. The method uses pollutant concentration measured at a receptor and frequencies of occurrence of wind sectors to apportion source regions to predefined wind sectors. This new method was applied to VOC data measured at the residential and background stations. The results proved that the new method was successful to identify and quantify source regions in an urban atmosphere.

Source profiles are essential components of receptor modeling for source apportionment. VOC source profiles have been developed for many urban areas of the U.S.A., Canada, Japan, and EU countries but comparable data is non-existent in Turkey. Source profiles from a variety of sources and a wide range of VOCs were developed in this study as the first steps towards establishing a database that can be used in source apportionment studies in Turkey. The source categories for which the emission profiles are generated include running vehicle exhaust, cold-start, hot-soak (evaporative), whole gasoline, headspace gasoline, whole diesel and headspace diesel. The profiles generated in this study were also compared with the profiles available in the literature. The comparison showed that the profiles generated in this study displayed different characteristics from those reported in the literature. Therefore, it is crucial to develop source profiles specific to a region and utilize those profiles in receptor modeling. The profiles developed in this study are considered significant in providing new information to the literature on VOC emission profiles, which included a variety of sources and conditions, and a wide range of compounds, for Ankara. Most of these profiles can be readily applied in other regions of Turkey as well, although some region specific characteristics may be expected for gasoline profiles due to the differences in refineries supplying different regions.

Contribution and type of VOC sources determined by PMF showed seasonality both due to emission activities and meteorological conditions. Motor vehicle exhaust emissions, however, were the major sources influencing the ambient VOC concentrations measured in Ankara both during winter and summer seasons. Therefore, an air quality management plan prepared for Ankara should include mitigation measures to decrease VOC emissions from motor vehicles. The mitigation measures should consider tailpipe treatment technologies (e.g., three way catalysts), preventive actions (e.g., reformulated gasoline, alternative fuels, fuel cells) and traffic regulations (e.g., promoting public transport, signalization, constructing bicycle ways, etc.).

Residential heating contributed significantly to ambient VOC concentrations measured during winter in Ankara. This was mostly associated with the coal combustion used in residential heating at more than 60% of the homes in Ankara. Residential heating was not reported as a significant VOC source in USA, Canada and Western Europe. However, it was reported to contribute VOC emissions in Eastern Europe (e.g., Poland) and China in significant quantities. It should be noted that, coal combustion in Ankara is the common mode of residential heating only in low-income districts of the city. Residential coal combustion emissions will likely continue to be a significant source for at least some of the VOCs for the foreseeable future.

Solvent use was identified as one of the VOC sources affecting ambient concentrations in Ankara both in summer and winter with the most dominant source possibly being architectural coatings during summer season. The source profile of architectural coating indicated that solvent-based paints have significant contribution during summer. Toluene was the major solvent used in paints. A regulation to limit levels and types of VOCs in solvents used in different sectors should be developed in Turkey. Biogenic sources had a minor contribution to VOC levels during summer season in Ankara.

Regression analysis was used in final identification of the source profiles generated by PMF. Utilization of different source profiles available in the literature and profiles generated in this study specific to Ankara and Turkey showed that the best regression fits were obtained by using the profiles generated in this study. This study demonstrated that source profiles are unique for each country due to differences in emission characteristics and active legislations.

Thus, it is critical to use source profiles specific to the country where they will be used.

CFA receptor model was also applied to Ankara data to compare the performances of different receptor models. CFA does not calculate source contribution estimates but is useful for qualitative identification of sources affecting a given receptor site. Factor scores and factor loadings generated by PMF and CFA were compared. CFA resolved five VOC sources whereas PMF resolved four. CFA resolved three separate solvent sources whereas PMF resolved one solvent source that is identical to sum of the three sources resolved by CFA. On the other hand, CFA did not resolve residential heating and LDV exhaust sources while PMF identified these sources. Factor scores calculated by both models showed similarities. In conclusion, CFA and PMF receptor models showed similar results. The differences were due to differences in model algorithms and input parameters.

Benzene, that is a known human carcinogen, was emitted both from motor vehicle exhaust and solvent sources. A control plan on benzene emissions should include measures to reduce benzene in both of these sources. Ambient levels of two ozone depleting substances namely 1,1,1-trichloroethane and carbon tetrachloride were measured for the first time in Turkey. Production and consumption of ODSs were banned in Turkey as Turkey ratified Montreal Protocol. Statistical analysis on the concentration data showed that both of these substances showed temporal variations indicating sources still exist for these substances in Ankara. ODSs should be monitored in Turkey and illegal usage of these substances should be stopped.

6.2. Ottawa Campaign

A field campaign was conducted at Ottawa, Canada in order to investigate ambient levels and sources of air toxics at different microenvironments and at extreme ambient temperatures. Air samples were collected at two roadside stations and during commuting inside a passenger car and buses in the winter and summer of 2000.

Many VOCs and carbonyl compounds listed in the Priority Substance List (PSL) 1 and 2 of Health Canada and Hazardous Air Pollutants (HAP) list of Clean Air Act were selected for analyses. Ethylene was the most abundant compound at the nose-level roadside station. 2-methyl-butane, toluene, propane and ethane were the next most abundant compounds. The VOC pattern (i.e., relative abundances of light and heavy hydrocarbons) at any location is determined by abundances of sources contributing to these groups. The dominant abundance of light hydrocarbons was observed at the roadside station, which is strongly influenced by gasoline-powered vehicles according to traffic count data, as these light hydrocarbons originated from gasoline powered cars and evaporative emissions.

Evaluation of the seasonal variations showed that for most compounds measured at nose-level station, winter concentrations were higher than or comparable to their concentrations measured in summer campaign. Better mixing of the atmosphere due to prevailing unstable conditions, increased rate of photochemical reactions and decrease in emission sources are factors that can contribute to lower VOC concentrations measured during summer season. The VOC data showed a diurnal variation with comparable concentrations in the morning and noon periods, and higher concentrations in the afternoon sampling period. This observed difference in concentrations is consistent with the higher number of vehicles in the street during afternoon hours and the receptor modeling, which indicated that most of the VOCs measured at the nose-level station were emitted from motor vehicle sources.

Evaluation of the spatial variations showed that concentrations measured at the rooftop roadside station (10 m high) were higher than those measured at the nose-level roadside station (1.5 m high) during both summer and winter seasons. In-vehicle concentrations were much higher than ambient concentrations indicating the importance of in-vehicle exposure studies. When comparing in-car and in-bus data, concentrations were comparable during summer as the vehicles were ventilated during commuting. During the winter season, in-car concentrations of VOCs were much higher than in-bus concentrations.

Formaldehyde was the most abundant atmospheric aldehyde, followed by acetaldehyde at the roadside station during both summer and winter campaigns. There was a clear diurnal trend in formaldehyde and acetaldehyde concentrations. The highest concentrations were measured in afternoon samples and lowest concentrations were measured in morning samples. This trend was consistent in both winter and summer sampling campaigns. This diurnal pattern was expected, because carbonyl compounds are key compounds of photochemically generated air pollution (Christensen *et al.*, 2000). Higher concentrations of these compounds in the afternoon hours were also observed by other researchers (Christensen *et al.*, 2000; Viskari *et al.*, 2000).

PMF receptor model was applied to estimate sources and source contributions. Four VOC sources were identified. Cold start and LDV exhaust sources contributed the most accounting for about 82% of the total VOC concentration measured at the nose-level station during winter campaign. HDV exhaust and LPG sources accounted for about 18% of the VOC concentrations. The high contribution of the LDV sources was expected since the vehicle count data showed very high contribution of LDVs at the measurement site. The important point here was the higher contribution of the cold start mode in the emissions from LDVs.

CMB receptor model was also applied and the results were compared. The sources and their contribution were similar in both models. CMB also estimated source contribution of four sources that were cold start LDV exhaust, LDV exhaust, HDV exhaust and LPG use. The model gave the best results with the source profiles generated for Ottawa. The CMB model provides timely resolved source contribution estimates whereas PMF model provides average source contribution estimate values. The differences were due to differences in model algorithms and input data requirements.

6.3. Comparison of Ankara and Ottawa Results

The comparison of the results of these two cities demonstrated the influence of control measures on ambient levels and sources of VOCs observed in different urban atmospheres. Ankara and Ottawa campaigns were carried out to determine levels and sources of air toxics in urban atmosphere in different microenvironments. Both studies had similar strategy to conduct measurements hourly and seasonally to evaluate diurnal and seasonal variation in air toxic concentrations. Traffic counts according to source categories and meteorological data were recorded and effect of these parameters on ambient concentrations was investigated. The receptor modeling was applied to both data to identify and quantify VOC sources.

Ankara and Ottawa showed some similar characteristic in emission sources. In both cities emissions associated with industrial sources were negligible and motor vehicles were the major sources of VOCs. Comparison of the results of two cities provides useful information on the differences in levels and sources of VOCs in these cities and underlying factors. Emission characteristic that is determined by active legislations and control strategies is the major factor resulting in differences. Regulatory emissions control has been well adopted in Ottawa for over a decade whereas Turkey currently lacks implementation of emission control regulations for VOCs.

At comparable roadside stations, the VOC concentrations measured in Ankara were about 1.5 times higher for paraffins and about 2.5 times higher for aromatics than the concentrations measured in Ottawa. On the other hand, traffic density is a factor of two higher at Ottawa. Thus emission factors for road traffic in Ankara can be as high as 5 times comparable emission factors in Ottawa. Because traffic intensity is increasing rapidly in Turkish cities, toxic VOC concentrations will be unacceptably high in very near future, unless necessary precautions are taken to avoid this. Higher aromatic content of the Turkish gasoline is one of the reasons for the observed situation. In both cities motor vehicle emissions were the major source of VOCs. Therefore, lower ambient concentrations observed in Ottawa than in Ankara was mostly due to stringent legislations and enforcement on motor vehicle emissions and fuel compositions that are currently used in Canada.

Comparison of the PMF results for Ankara and Ottawa showed that motor vehicle related emissions contribute more than 85% in Ottawa whereas they contribute about 60% in Ankara to measured VOC concentrations. Traffic emissions are the major source in Ottawa whereas there are additional sources in Ankara. Residential heating was a major VOC source during winter season in Ankara whereas it was not identified in Ottawa even as a minor source. HDV emissions were minor in Ottawa as their number is less than LDVs. In Ankara, however, although the number of HDVs is less than LDVs, their emissions are shown to influence ambient concentrations the most. This was due to poor inspection and maintenance of especially public transportation buses and minibuses in Ankara. Therefore, a VOC management plan for Ankara must include measures to control VOC emissions from HDVs, especially public transport vehicles.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1. Conclusions

This study aimed at providing a thorough understanding of temporal and spatial variations of VOCs and underlying factors in different microenvironments in two different urban atmospheres, with different degrees of regulatory enforcement. The VOC data were collected in field campaigns conducted in Ankara, Turkey, and Ottawa, Canada over the years 2000-2004. Insight into the sources of VOCs in different urban atmospheres was sought by using three commonly used receptor models. In addition, a new method to estimate the contribution of sources from wind sectors in urban atmosphere was developed and implemented. The comparison of the results of these two cities demonstrated the influence of control measures on ambient levels and sources of VOCs observed in different urban atmospheres.

The key conclusions of the study in terms of the observed levels of VOCs, the interpretation of these observations, and the implications for regulatory action can be summarized in the following points:

- Motor vehicles are the most abundant VOC sources with about 60% and 95% contributions to ambient levels in Ankara and Ottawa, respectively. Residential heating (31%) during winter season, biogenic (9%) and architectural coating (12%) emissions during summer season and solvent use (about 12%) emissions are the next abundant VOC sources in Ankara.

- Ambient levels of VOCs measured in both cities showed temporal variations. Diurnal and weekday to weekend variations are consistent with traffic pattern for most of the compounds as the motor vehicles are dominating sources. Exceptions such as isoprene and TCA are emitted from biogenic and solvent use sources. Concentrations are higher in winter than in summer due to elevated emissions and meteorological conditions that suppress atmospheric mixing. In Ottawa, data show spatial variations with higher in-vehicle concentrations than ambient concentrations. Higher nose-level concentrations than roof-top concentrations are also observed in Ottawa, indicating influence of vertical mixing.
- VOC levels in Ankara exceed EU levels and they are about factor of two higher than that are measured in Ottawa. However, the number of vehicles recorded in Ottawa is about factor of two higher than in Ankara. This is mainly due to regulatory emissions control that has been well adopted in Ottawa for over a decade whereas Turkey currently lacks implementation of emission control regulations for VOCs. Considering the rapid increase in number of motor vehicles in Ankara, severe problems might be expected in future if implementation of regulations fails.
- Given the levels observed in Ankara that exceed EU criteria, regulatory action is required. Given the identification of sources, any regulatory action must include measures aimed at the transportation sector.

This study is the first of its kind performed in Turkey; 1) to investigate ambient levels and sources of speciated VOCs that include a wide range of compounds, and 2) to measure ambient speciated VOC levels for extended periods of time in different microenvironments and urban atmospheres. The receptor modeling performed in this thesis is also the first source apportionment study implemented for VOCs in Turkey. In short, it is believed that this study pioneers the research on organic pollutants in Turkey.

7.2. Recommendations for Future Research

Following recommendations are provided for future research that will be conducted in Turkey:

- Continuous measurements of VOCs and NO_x in Ankara should be performed as more data provide better resolution in evaluation of temporal variations.
- Similar studies to determine levels and sources of VOCs should be conducted in different regions of Turkey.
- Ambient VOC measurements should be conducted at hot spot regions where VOC emitting industries such as refineries and petrochemical manufacturing, located in Turkey.
- A VOC emission inventory should be prepared for each city in Turkey.
- Research on development of source profiles for various VOC source categories should increase.
- The measurements should also include VOC with < 5 carbon atoms. This can allow characterization of natural and LPG leaks, both of which are widely used in Turkey.
- Since it looks like toxic effects of VOCs will continue to be an ever increasing problem in Turkish cities in the near future, studies directed public exposure to VOCs and health risks associated with VOC's are needed.
- This study provided preliminary data on indoor levels of VOCs and showed that indoor levels are higher than outdoor levels, more systematic screening statistically significant number of households, offices and particularly schools is necessary. These measurements should also include exposure and health risk assessment components

REFERENCES

Anderson, M.J., Daly, E.P., Miller, S.L., Milford, J.B., 2002. “Source Apportionment Of Exposures To Volatile Organic Compounds: II. Application Of Receptor Models To TEAM Study Data”, *Atmospheric Environment*, Vol. 36, pp. 3643–3658.

Anderson, M.J., Miller, S.L., and Milford, J.B., 2001. “Source apportionment of exposure to toxic volatile organic compounds using positive matrix factorization”, *Journal of Exposure Analysis and Environmental Epidomiology*, Vol. 11, pp. 295-307.

Anfossi, D., Sandroni, S., and Viarengo, S., 1991. “Tropospheric ozone in the nineteenth century: the Moncalieri series”, *J. Geophys. Res.*, Vol. 96, pp. 17349-17352.

Anttila, P., Paatero, P., Tapper, U., and Jarvinen, O., 1995. “Application of positive matrix factorization to source apportionment: results of a study of bulk deposition chemistry in Finland”, *Atmospheric Environment*, Vol. 29, pp. 1705-1718.

Atkinson, R., 1985. "Kintetics and mechanism of gas phase reaction of hydroxy radicals with organic compounds under atmospheric conditions", Chem. Rev., Vol. 85, pp.69-201.

Atkinson, R., 1990. "Gas phase troposheric chemistry of organic compounds: a review", Atmospheric Environment, Vol. 24A, Iss. 1,pp.1-41

Atkinson, R., 2000. “Atmospheric chemistry of VOCs and NOx”, *Atmospheric Environment*, Vol. 34, pp. 2063-2101.

AAS, 2004. Austrian Academy of Science, Clean Air Commission, http://www.oeaw.ac.at/krl/, accessed on December 2004.

ATSDR, 1995. “Fact Sheet for Carbon Tetrachloride”, prepared by U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, Atlanta, GA.

Bi, X., Sheng, G., Peng, P., Chen, Y., Zhang, A., and Fu, J., 2003. “Distribution of particulate and vapor phase n-alkanes and polycyclic aromatic hydrocarbons un urban atmosphere of Guangzhou, China”, *Atmospheric Environment*, Vol. 37, pp. 289-298.

Borbon, A., Fontaine, H., Veillerot, m., Locoge, N., Galloo, J.C., and Guillermo, R., 2001. “An investigation into the traffic-related fraction of isoprene at an urban location”, *Atmospheric Environment*, Vol. 35, pp. 3749-3760.

Borbon, A., Locoge, N., Veillerot, M., Galloo, J.C., and Guillermo, R., 2002. “Characterisation of NMHCs in a French urban atmosphere: overview of the main sources”, *The Science of the total environment*, vol. 292, pp. 177-191.

Bowman, F.M., and Seinfeld, J.H., 1994. “Ozone productivity of atmospheric organics”, *J. Geophys. Res.*, Vol. 99, pp. 5309-5324.

Broderick, B.M., and Marnane, I.S., 2002. “A comparison of the C2-C9 hydrocarbon composition of vehicle fuels and urban air in Dublin, Ireland”, *Atmospheric Environment*, Vol. 36, pp. 975-986.

Cadle, S.H., Gorse, R.A., Bailey, B.K., and Lawson. D.R., 2000. “Real-world vehicle emissions: a summary of the ninth coordinating research council on-road vehicle emissions workshop”, *J. Air and Waste Management Association*, Vol. 50, pp., 278-291.

Calabrese, E.J., and Kenyon, E.M., 1991. Air toxic and risk assessment, Lewis Publishers Inc., Michigan, U.S.A.

Carter, W.P.L., 1994. “Development of Ozone Reactivity Scales for Volatile Organic Compounds**”,** *J. of the Air and Waste Management Association*, vol. 44, pp. 881-899.

Carter, W.P.L., and Atkinson, R., 1987. “An experimental study of incremental hydrocarbon reactivity”, *Environ. Sci. Technol.*, Vol. 21, pp. 670-679.

Carter, W.P.L., and Atkinson, R., 1989. “Computer modeling study of incremental hydrocarbon reactivity”, *Environ. Sci. Technol.*, Vol. 23, pp. 864-880.

CCME, 1997. “Canadian 1996 NOx/VOC science assessment- Ground-level ozone and its precursors, 1980-1993”, Report of the data analysis working group, *required by* Canadian Council of Ministers of the Environment, ISBN 1-896997-00-7.

Çetin, E., Odabaşı, M., Seyfioğlu, R., 2003. “Ambient volatile organic compound (VOC) concentrations around a petrochemical complex and a petroleum refinery”, *The Science of the Total Environment*, Vol. 312, pp. 103-112.

Chan, C.C., Ozkaynak, H., Spengler, J.D., and Sheldon, L., 1991a. “Driver exposure to volatile organic compounds, CO, ozone, and NO_2 under different driving conditions”, *Environmental Science and Technology*, Vol. 25, pp.964-972.

Chan, C.C., Spengler, J.D., Ozkaynak, H., and Lefkopolou, M., 1991b. “Commuter exposure to VOCs in Boston Massachusetts”, *Journal of Air Waste Management Association*, Vol. 41, pp.1549-1600.

Chan, C.Y., Chan L.Y., Wang, X.M., Liu, Y.M., Lee, S.C., Zou, S.C., Sheng, G.Y., and Fu, J.M., 2002. “Volatile Organic Compounds in Roadside Microenvironments of Metropolitan Hong Kong”, *Atmospheric Environment*, *Vol. 36, pp. 2039-2047*.

Chan, Y.C., Simpson, R.W., Mctainsh, G.H., Vowles, P.D., Cohen, D.D., Bailey, G.M., 1999. “Source apportionment of PM2.5 and PM10 aerosols in Brisbane (Australia) by receptor modeling”, *Atmospheric Environment*, Vol. 33, pp. 3251-3268.

Christensen, C.S., Skov, H., Nielsen, T., and Lohse, C., 2000. “Temporal variation of carbonyl compound concentrations at a semi-rural site in Denmark”, *Atmospheric Environment*, Vol. 34, pp. 287-296.

Chueinta, W., Hopke, P.K., Paatero, P., 2000. "Investigation Of Sources Of Atmospheric Aerosol At Urban And Suburban Residential Areas In Thailand By Positive Matrix Factorization", *Atmospheric Environment, Vol.* 34, pp. 3319-3329.

Ciccioli, P., Brancaleoni, E., and Frattoni, M., 1999. "Reactive hydrocarbons in atmosphere at urban and regional scales", in *Reactive hydrocarbons in the atmosphere*, Ed. Hewitt, C.N., Academic Press, USA, pp. 160-201.

Ciccioli, P., Cecinato, A., Brancaleoni, E., Frattoni, M., 1992. "Use of carbon adsorption traps combines with high-resolution gas chromatography –mass spectrometry for the analysis of polar and non-polar C4-C14 volatile organic compounds involved in photochemical smog formation', *J. High Resolute. Chromatogr. Commun,.* Vol. 15, pp. 75-84.

Conner, T.L., Lonneman, W.A., and Seila, R.L., 1995. "Transportation Related Volatile Hydrocarbon Source Profiles Measured in Atlanta", *Journal of the Air & Waste Management Association*, Vol. 45, pp. 383-394.

CORINAIR, 1999. EMEP/CORINAIR Emission Inventory Guidebook, European Environment Agency, Denmark.

CPPI, 1994. "Canadian Summer and Winter Gasolines", prepared by Alberta Research Council for Canadian Petroleum Products Institute, CPPI Report No. 94-5.

De Never, N., 1995. "Air Pollution Control Engineering", McGraw Hill, Inc., New York, U.S.A., ISBN 0-070113273-2.

Derwent, R G; Davies, T J; Delaney, M; Dollard, G J; Field, R A; Dumitrean, P; Nason, P D; Jones, B M R; Pepler, S A., 2000. "Analysis and interpretation of the continuous hourly monitoring data for 26 C2-C8 hydrocarbons at 12 United Kingdom sites during 1996", Atmospheric Environment, v.34, n.2, p.297-312.

Derwent, R.G., 1999. "Reactive hydrocarbons and photochemical air pollution", in *Reactive hydrocarbons in the atmosphere*, Ed. Hewitt, C.N., Academic Press, USA, pp. 267-289.

Derwent, R.G., Jenkin, M.e., Saunders, S.M., and Pilling, M.J., 1998. "Photochemical ozone creation potentials for organic compounds in northwest Europe calculated with a master chemical mechanism", *Atmospheric Environment*, Vol. 32, pp.

Derwent, R.G., Middleton D.R., Field R.A., Goldstone M.E., Lester J.N., and Perry R., 1995. "Analysis and Interpretation of Air Quality Data from an Urban Roadside Location in Central London Over the Period from July 1991 to July 1992", Atmospheric Environment, Vol. 29, Iss. 8, pp. 923-946.

Dimitriades, B., 1999. "Scientific basis of an improved EPA policy on control of organic emissions for ambient ozone reduction", J. Air & Waste Manage. Assoc., Vol. 49, pp. 831-838.

Dodge, M.C., 1977. "Combined use of modeling techniques and smog chamber data to derive ozone-precursor relationship", Vol II, *Ed.* Dimitriades, B., EPA-600/3-77-001b, 881.

Doskey, P.V., Fukui, Y., Sultan, M., Maghraby, A.A., and Taher, A., 1999. “Source profiles for non-methane organic compounds in the atmosphere of Cairo, Egypt”, *J. of Air and Waste Management Association*, Vol. 49, pp. 814-822.

Doskey, P.V., Porter, J.A., Scheff, P.A., 1992. “Source fingerprints for volatile non-methane hydrocarbons”, *J. Air&Waste Management Association*, Vol. 42, pp. 1437-1445.

Duffy, B.L., and Nelson, P.F., 1997. “Exposure to emissions of 1,3-butadiene and benzene in the cabins of moving motor vehicles and busses in Sydney, Australia”, *Atmospheric Environment*, Vol. 31, No. 23, pp. 3877-3885.

EC, 2004. “A Federal Agenda for Reduction of Emissions of Volatile Organic Compounds from Consumer and Commercial Products”, Environment Canada, http://www.ec.gc.ca/nopp/DOCS/notices/voc/en/supportDoc_p4.cfm, accessed on March 2004.

EEA, 2003. “Europe’s environment: the 3rd assessment”, European Environment Agency, Copenhagen, p 122.

EPA, 2002. “Health Assessment Document for Diesel Engine Exhaust”, prepared by U.S. Environmental Protection Agency, Office of Research and Development, National Center for Environmental Assessment, Washington Office, Washington, DC, EPA/600/8-90/057F.

ETC, 1999. “Standard Operation Procedures Method No 4.1/1/M; Carbonyl compound analysis for vehicle emissions”, Environmental Technology Center, Environment Canada, Ottawa, CA.

Finlayson-Pitts B.J., and Pitts J.N., 1997. “Troposheric Air Pollution: Ozone, Airborne Toxics, Polycyclic Aromatic Hydrocarbons, and Particles”, *Science*, Vol. 276, pp. 1045-1052.

Finlayson-Pitts, B.J., and Pitts, J.N., 1986. “Atmospheric chemistry: Fundamentals and experimental techniques”, John Wiley and Sons, Inc., New York, USA.

Finlayson-Pitts, B.J., and Pitts, J.N., 1993. “Atmospheric Chemistry of Tropospheric Ozone Formation: Scientific and Regulatory Implications”, *Air and Waste Management*, 43, pp. 1091-1100.

Fraser, M.P., Cass, G.R., and Simoneit B.R.T., 1998. “Gas-Phase and Particle Phase Organic Compounds Emitted from Motor Vehicle Traffic in a Los Angeles Roadway Tunnel*”, Environmental Science and Technology*, Vol. 32, pp. 2051-2060.

Fujita, E.M., Watson, J.G., Chow, J.C., and Magliano, K.L., 1995. “Receptor Model and Emission Inventory Source Apportionments of Nonmethane Organic Gases in California’s San Joaquin Valley and San Francisco Bay Area”, *Atmospheric Environment*, Vol. 29, Issue 21, pp. 3019-3035.

Fujita, E.M., Watson, J.G., Chow, J.C., Lu, Z., 1994. “Validation of the Chemical Mass Balance Receptor Model Applied to Hydrocarbon Source Apportionment in the Southern

California Air Quality Study", *Environmental Science and Technology*, Vol. 28, Iss. 9, pp.1633-1649.

Gee, I.L., and Sollars, C.J., 1998. "Ambient air levels of volatile organic compounds in Latin American and Asian cities", *Chemosphere*, Vol. 36, pp. 2497-2506.

Gertler A.W., Fujita E.M., Pierson W. R., and Wittorff D.N., 1996. "Apportionment of NMHC Tailpipe vs Non-Tailpipe Emissions in the Fort McHenry and Tuscarora Mountain Tunnels", *Atmospheric Environment*, Vol. 30, Iss. 12, pp. 2297-2305.

Gwilliam, K., Kojima, M., and Johnson, T., 2004. Reducing air pollution from urban transport. The World Bank Publication.

Hammerie, R.H., Siegl, W.O., Herrmann, H.M., Wenclawiak, B.W., 1995. "A method for the speciation of diesel fuel and the semi-volatile hydrocarbon percentage of diesel-fueled vehicle exhaust emissions", SAE Paper No. 952353, Society of Automotive Engineers.

Harley R.A., Hannigan M.P., and Cass G.R., 1992. "Respeciation of Organic Gas Emissions and the Detection of Excess Unburned Gasoline in the Atmosphere", *Environmental Science and Technology*, Vol. 26, Iss. 12, pp. 2395-2408.

Harper, M., 2000. "Sorbent trapping of volatile organic compounds from air-Review", *Journal of Chromatography*, Vol. 885. pp.129-151

Hedberg, E., Gidhagen, L., Johansson, C., 2005. "Source Contributions To PM10 Andarsenic Concentrations In Central Chile Using Positive Matrix Factorization", *Atmospheric Environment*, Vol. 39, pp. 549–561.

Henry, R.C., 1987. "Current factor analysis receptor models are ill-posed", *Atmospheric Environment*, Vol.21, pp. 1815-1820.

Hester, R.E. and Harrison, R.M., 1998. Air pollution and health, The Royal Society of Chemistry, UK.

Hidy, G.M., and Friendlander, S.K., 1972. "The nature of the Los Angeles Aerosol", 2nd IUPPA Clean Air Congress, Washington DC, USA.

Ho, K.F., Lee, S.C., Guo, H., and Tsai, W.Y., 2004. "Seasonal and diurnal variations of volatile organic compounds (VOCs) in the atmosphere of Hong Kong", *The Science of the Total Environment*, Vol. 322, pp. 155-166.

Hopke, P.K., 1991. Receptor Modeling for Air Quality Management, Data Handling in Science and Technology Vol. 7, Advisory Editors Vandeginste, B.G.M., and Kvalheim, O.M., Elsevier Publishers, Netherlands, pp. 83.

Hopke, P.K., 2003. "Recent developments in receptor modeling", *Journal of Chemometrics*, Vol. 17, pp. 255-265.

Huang, S., Rahn, K.A., Arimoto, R., 1999. "Testing and optimizing two-factor-analysis techniques on aerosol at Narragansett, Rhode Island", *Atmospheric Environment*, Vol. 33, pp. 2169-2185.

Huber, P.J., 1981. “Robust statistics”, John Wiley and Sons, Inc., New York.

JICOP, 1991. “Manual for reductions in the use of ozone depleting substances”, prepared by *Japan Industrial Conference for Ozone Layer Protection*, Second Edition, Tokyo.

Jo, W.K., and Park, K.H., 1999. “Commuter exposure to volatile organic compounds under different driving conditions”, *Atmospheric Environment*, Vol. 33, pp. 409-417.

Jorquera, H., Rappengluck, B., 2004. “Receptor Modeling Of Ambient VOC At Santiago, Chile”, *Atmospheric Environment*, Vol. 38, pp. 4243–4263.

Kendall, P., 1993. “Outdoor Air Quality in Toronto: Issues and Concerns”, City of Toronto Department of Public Health, Canada.

Khan, F.I. and Ghoshal, A.K., 2000. “Removal of volatile organic compounds from polluted air”, *Journal of Loss Prevention*, Vol. 13, pp. 527-545.

Kim, E., Hopke, P.K., Edgerton, E.S., 2004. “Improving Source Identification Of Atlanta Aerosol Using Temperature Resolved Carbon Fractions In Positive Matrix Factorization”, *Atmospheric Environment*, Vol. 38, pp. 3349–3362.

Kim, E., Hopke, P.K., Paatero, P., Edgerton, E.S., 2003. “Incorporation Of Parametric Factors Into Multilinear Receptor Model Studies Of Atlanta Aerosol”, *Atmospheric Environment*, Vol. 37, pp. 5009–5021.

Kneip, T.J., Kelinman, M.T., and Eisenbud, M., 1973. “Relative contribution of emission sources to the total airborne particulates in New York City”, 3rd IUPPA Clean Air Congress, New York City, USA.

Kourtidis, K.A., Ziomas, I., Zerefos, C., Kosmidis, E., Symeonidis, P., Christophilopoulos, E., Karathanassis, S., Mploutsos, A., 2002. “Benzene, toluene, ozone, NO_2 and SO_2 measurements in an urban street canyon Thessaloniki, Greece”, *Atmospheric Environment*, Vol. 36, pp. 5355-5364.

Kubica, K., Dilara, P., and Paradiz, B., 2004. “Toxic emissions from solid fuel combustion in small residential appliances”, *Proceedings* of 6th international conference on Emission Monitoring CEM 2004, 9-11 June, Milan, Italy.

Kuntasal, G. and Chang, T.Y., 1987. “Trends and relationships of O_3, NO_x and HC in the South Coast Air Basin of California”, *JAPCA J of Air and Waste Management Association*, Vol. 37, Iss. 10, pp. 1158-1163.

Lawrimore, J.H. and Aneja, V.P., 1997. “A Chemical Mass Balance Analysis of Nonmethane Hydrocarbon Emissions in North Carolina”, *Chemosphere*, Vol. 35, Issue 11, pp. 2751-2765.

Lee, E., Chan, C.K., Paatero, P., 1999. “Application of positive matrix factorization in source apportionment of particulate pollutants in Hong Kong”, *Atmospheric Environment*, Vol. 33, pp. 3201-3212.

Lee, S.C., Chiu, M.Y., Ho, K.F., Zou, S.C., and Wang, X., 2002. "Volatile organic compounds (VOCs) in urban atmosphere of Hong Kong", Chemosphere, Vol. 48, pp. 375-382.

Leung, P.L., and Harrison, R.M., 1999. "Roadside and in-vehicle concentrations of monoaromatic hydrocarbons", *Atmospheric Environment*, Vol. 33, pp. 191-204.

Li, Z., Hopke, P.K., Husain, L., Qureshi, S., Dutkiewicz, V.A., Schwab, J.J., Drewnick, F., Demerjian, K.L., 2004. "Sources Of Fine Particle Composition In New York City", *Atmospheric Environment*, Vol. 38, pp. 6521–6529.

Liu, W., Hopke, P.K., Han, Y.J., Yi, S.M., Holsen, T.M., Cybart, S., Kozlowski, K., Milligan, M., 2003. "Application Of Receptor Modeling To Atmospheric Constituents At Potsdam And Stockton, NY", *Atmospheric Environment*, Vol. 37, pp. 4997–5007.

Lonneman, W.A., Sella, R.L., Meeks, S.A., 1986. "Non-methane organic composition in the Lincoln tunnel", *Environmental Science and Technology*, Vol. 20, pp. 790-796.

Lowenthal, D.H., Zielinska, B., Chow, J.C., Watson, J.G., Gautam, M., Ferguson, D.H., Neuroth, G.R., Stevens, K.D., 1994. "Characterization of heavy-duty diesel vehicle emissions", *Atmospheric Environment*, Vol. 28, pp. 731-743.

Lu, Z., 1996. "Temporal and spatial analysis of VOC source contributions for southeast Texas", Ph.D. thesis, University of Nevada, Reno, U.S.A., December 1996.

Mackay, D., Ying Shiu, W., Ching Ma, K., 1992a. "Illustrated handbook of physico-chemical properties and environmental fate for organic chemicals-Volume I: Monoaromatic Hydrocarbons, Chlorobenzenes and PCBs", Lewis publishers, Inc., USA.

Mackay, D., Ying Shiu, W., Ching Ma, K., 1992b. "Illustrated handbook of physico-chemical properties and environmental fate for organic chemicals-Volume II: Volatile Organic Chemicals", Lewis publishers, Inc., USA.

Main, H.H., Hurwitt, S.B., Roberts, P.T., 1999. "Spatial and temporal characteristics of California PAMS and long-term trends site VOC data (1990-1997)", prepared for U.S. EPA, NC, U.S.A.

Mastral, A.M., Callen., M.S., Lopez, J.M., Murillo, R., Garcia, T., and Navarro, M.V., 2003. "Critical review on atmospheric PAH. Assessment of reported data in the Mediterranean basin", *Fuel Processing Technologies*, Vol. 80, pp. 183-193.

MATRA, 2004. "Preliminary assessment of ambient air quality for the Ankara metropolitan area", Prepared for Dutch Matra Pre-Accession Projects Program, Agency for International Business and Cooperation, MAT02/TR/9/2.

McLaren, R., Gertler, A., Wittorff, D.N., Belzer, W., Dann, T., and Singleton, D.L., 1996. "Real–World Measurements of Exhaust and Evaporative Emissions in the Cassiar Tunnel Predicted by Chemical Mass Balance Modelling", *Environmental Science and Technology*, Vol. 30, pp. 3001-3009.

McLaren, R; Singleton, D L; Lai, J Y K; Khouw, B; Singer, E; Wu, Z; Niki, H., 1996. "Analysis of motor vehicle sources and their contribution to ambient hydrocarbon distributions at urban sites in Toronto during the Southern Ontario oxidants study", *Atmospheric Environment*, Vol.30, pp. 2219-2232.

McNair, L., Russel, A., Odman, M.T., 1992. *J. Air & Waste Manag. Assoc.*, Vol. 42, pp. 174-178.

Miller S.L., Anderson, M.J., Daly, E.P., Milford, J.B., 2002. "Source Apportionment Of Exposures To Volatile Organic Compounds. I. Evaluation Of Receptor Models Using Simulated Exposure Data", *Atmospheric Environment*, Vol. 36, pp. 3629–3641.

Mitchum, R.K., 1991. "Instrumental Analysis of Pollutants", Elsevier Applied Science, Hewitt C.N. *(editor)*, USA.

Motallebi, N., 1999. "Wintertime PM2.5 and PM10 source apportionment at Sacramento, California", *J. Air and Waste Management Association*, Vol. 49, pp. 25-34.

Müezzinoğlu, A., Odabaşı, M., and Onat, L., 2001. " Volatile organic compounds in the air of Izmir, Turkey", *Atmospheric Environment*, Vol.35, pp.753-760.

Mugica, V., Vega, E., Arriaga, J.L., Ruiz, M.E., 1998. "Determination of motor vehicle profiles for non-methane organic compounds in the Mexico City metropolitan area", *Journal of the Air and Waste Management Association*, Vol. 48, pp. 1060-1068.

Na, K., Kim, Y.P., Moon, I., Moon, K.C., 2004. "Chemical composition of major VOC emission sources in the Seoul atmosphere", *Chemosphere*, Vol. 55, pp. 585-594.

Na, K., Kim, Y.P., Moon, K.C., 2002. "Seasonal variation of the C2-C9 hydrocarbons concentrations and compositions emitted from motor vehicles in a Seoul tunnel", *Atmospheric Environment*, Vol. 36, pp. 1969-1978.

Nazaroff, W.W., Weschler, C.J., 2004. "Cleaning products and air fresheners: exposure to primary and secondary air pollutants", *Atmospheric Environment*, Vol. 38, pp. 2841-2865.

Nelson, P.F., and Quigley, S.M., 1983. "The m&p-xylene:ethylbenzene ratio. A technique fro estimating hydrocarbon age in ambient atmosphere", *Atmospheric Environment*, Vol. 17, Iss. 3, pp. 659-662.

Novamann, 1994. "Commuter exposure to vehicle related air pollutants", a report prepared for Health Canada, Novamann International, Toronto, Canada.

Oğuz, Ö., 2001. "Innovative Technologies in Protection of Ozone Layer", Proceeding of *IV. National Conference of Turkish Chamber of Environmental Engineers*, September 7-10, İçel, Turkey.

Ollivon, D., Blanchoud, H., Motelay-Massei, A., and Garban, 2002. "Atmospheric deposition of PAHs to an urban site, Paris, France", *Atmospheric Environment*, Vol. 36, pp. 2891-2900.

Önoğlu, İ. And Atımtay, A., 2002. "Ankara'da kullanılan binek otomobillerin egzos emisyonlarının değerlendirilmesi", *Proceedings of the I. National Environmental Problems Symposium*, Erzurum, Turkey.

Owega, S., Khan, B.U.Z., Dsouza, R., Evans, G.J., Fila, M., Jervis, R.E., 2004. "Receptor modeling of Toronto PM2.5 Characterized by aerosol Laser Ablation Mass Spectrometry", Environmental Science and Technology, Vol. 38, pp. 5712-5720.

Paatero, P. and Juntto, S., 1994. "Analysis of daily precipitation data by positive matrix factorization", *Environmetrics*, Vol. 5, pp. 127-144.

Paatero, P., 1998. User's Guide for Positive Matrix Factorization programs PMF2 and PMF3, Helsinki, Finland.

Paatero, P., and Tapper, U., 1994. "Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values", *Environmetrics*, Vol. 5, pp. 111-126.

Paatero, P., Hopke, P.K., 2003. "Discarding or downweighting high-noise variables in factor analytical models", Analytica Chimica Acta, Vol., 490, pp. 277-289.

Paatero, P., Hopke, P.K., Begum, B.A., Biswas, S.K., 2005. "A graphical diagnostic method for assessing the rotation in factor analytical models of atmospheric pollution", *Atmospheric Environment*, Vol. 39, pp. 193-201.

Paatero, P., Hopke, P.K., Song, X.H., Ramadan, Z., 2002. "Understanding and controlling rotations in factor analytic models", *Chemometrics And Intelligent Laboratory Systems*, Vol. 60, pp. 253– 264.

Paterson, K.G., Sagady, J.L., Hooper, D.L., Bertman, S.B., Carroll, M.A., and Shepson, P.B., 1999. "Analysis of air quality data using positive matrix factorization", *Environmental Science and Technology*, Vol. 33, pp. 635-641.

Patnaik, P., 1997. Handbook of Environmental Analysis-Chemical pollutants in air, water, soil and solid wastes, Lewis Publishers, CRC Press Inc., New York, USA, pp. 24.

Pierson, W.R., Gertler, A.W., Bradow, R.L., 1990. "Comparison of the SCAQS tunnel study with other on-road vehicle emission data", *Journal of the Air and Waste Management Association*, Vol. 40, pp. 1495-1504.

Polissar, A.V., Hopke, P.K., Malm, WC, and Sisler, J.F., 1996. "The ratio of aerosol optical absorption coefficients to sulfur concentrations, as an indicator of smoke from forest fires when sampling in polar regions", *Atmospheric Environment*, Vol. 30, pp. 1147-1157.

Polissar, A.V., Hopke, P.K., Malm, WC, and Sisler, J.F., 1998. "Atmospheric aerosol over Alaska: 2. Elemental composition and sources", *Journal of Geophysical Research*, Vol. 103, pp. 19045-19057.

Polissar, A.V., Hopke, P.K., Paatero, P., Kaufman, Y.J., Hall, D.K., Bodhaine, B.A., Dutton, E.G., and Harris, J.M., 1999. "The aerosol at Barrow Alaska: long-term trends and source locations", *Atmospheric Environment*, Vol. 33, pp. 2441-2458.

Polissar, A.V., Hopke, P.K., Poirot, R.L., 2001b. "Atmospheric Aerosol Over Vermont: Chemical Composition And Sources", *Environ. Sci. Technol.*, Vol. 35, pp. 4604-4621.

Polissar, A.V., Hopke, P.K., Poirot, R.L., Wishinski, P.R., 2001a. “Comparative Application Of Multiple Receptor Methods To Identify Aerosol Sources In Northern Vermont”, *Environ. Sci. Technol.*, Vol. 35, pp. 4622-4636.

Qin, Y., Oduyemi, K., Chan, L.Y., 2002, “Comparative Testing Of PMF And CFA Models” *Chemometrics And Intelligent Laboratory Systems*, Vol. 61, pp. 75– 87.

Rappengluck, B., and Fabian, P., 1999. “Nonmethane hydrocarbons (NMHC) in the Greater Munich Area/Germany”, *Atmospheric Environment*, Vol. 33, Issue 23, pp. 3843-3857.

Rappengluck, B., Fabian, P., Kalabokas, P., Viras, L.G., and Ziomas, I.C., 1998. “Quasi-continuous measurements of non-methane hydrocarbons (NMHC) in the greater Athens area during MEDCAPHOT-TRACE”, *Atmospheric Environment*, Vol. 32, pp. 2103-2121.

Reid, R.C., Prausnitz, J.M., Poling, B.E., 1998. The properties of gases and liquids, Fourth edition, McGraw-Hill, New York.

Russel, A., Milord, J., Bergin, M.S., McBride, S., McNair, L., Yang, Y., Stockwell, W.R.T., and Croes, B., 1995. “Urban ozone control and atmospheric chemistry of organic gases”, *Science*, Vol. 269, pp. 491-495.

Sagebiel J.C., Zielinska B., Pierson W.R., and Gertler A.W., 1996. “Real-World Emissions and Calculated Reactivities of Organic Species from Motor Vehicles”, *Atmospheric Environment*, Vol. 30, Iss. 12, pp. 2287-2296.

Sather, M.E., Kemp, M.G., Yarbrough, J.W., Kinsella, C., Vanichchagorn, M., and Hazlett, J., 1997. “Analysis of 1995 Speciated Volatile Organic Compound Data in the South Central U.S.”, *Proceedings of the Air and Waste Management Association’s 90th annual Meeting and Exhibition*, Toronto, Canada.

Sawyer, C.N., and McCarty, P.L., 1978. Chemistry for environmental engineering, Third edition, McGraw Hill, Inc., New York.

Sawyer, R.F., Harley, R.A., Cadle, S.H., Norbeck, J.M., Slott, R., Bravo, H.A., 2000. “Mobile sources critical review: 1998 NARSTO assessment”. *Atmospheric Environment*, 34, pp. 2161-2181.

Schauer, J.J., Rodge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., and Simoneit, B.R.T., 1996. “Source apportionment of airborne particulate matter using organic compounds as tracers”, *Atmospheric Environment*, Vol. 30, pp. 3837-3855.

Scheff, P.A., Wadden, R.A., Kenski, D.M., Chung, J., and Wolff, G., 1996. “Receptor model evaluation of the southern Michigan ozone study ambient NMOC measurements”, *J. Air and Waste Management Association*, Vol. 46, pp. 1048-1057.

Scheff, P.A., Wadden, R.S., Bates, B.A., Aronian, P.F., 1989. “Source fingerprints for receptor modeling of volatile organics”, *JAPCA*, Vol. 39, pp. 469-478.

Seinfeld and Pandis, 1998. Atmospheric chemistry and physics from Air Pollution to Climate Change, John Wiley & Sons, Inc., New York.

Sigsby, J.E., Tejada, S., Ray, W., Lang, J.M., Duncan, J.W., 1987. "Volatile organic compound emissions from 46 in-use passanger cars", *Env. Sci, technol.*, Vol. 21, pp. 466.

Singer, B.C., Kirchestetter, T.W., Harley, R.A., Kendall, G.R.,, Hesson, M., 1999. “A fuel-based approach to estimating motor vehicle cold-start emissions”, *J. of Air & Waste Management Association*, Vol. 49, pp. 125-135.

Song, X.H., Polissar A.V., Hopke, P.K., 2001. “Sources Of Fine Particle Composition In The Northeastern US”, *Atmospheric Environment*, Vol. 35, pp. 5277–5286.

Stump, F., Tejada, S., Ray, W., Dropkin, D., Black, F., Snow, R., Crews, W., Siudak, P., Davis, C.O., Carter, P., 1990. “The influence of ambient temperature on tailpipe emissions from 1985 to 1987 model year light-duty gasoline motor vehicles”, *Atmospheric Environmen*t, Vol. 24A, pp. 2105-2112.

Thijsse, T.R., Oss, R.F.V., and Lenschow, P., 1999. “Determination of Source Contributions to Ambient Volatile Organic Compound Concentrations in Berlin”, *Journal of the Air & Waste Management Association*, Vol. 49, pp. 1394-1404.

TÜPRAŞ, 2003. Annual production report for the year 2003. Prepared by Turkish Petroleum Refineries Inc., Turkey.

Turner, D.B., 1994. “Atmospheric dispersion estimates”, Lewis publishers, London.

UN ECE, 1991. “Protocol to the 1979 Convention on Long-Range Transboundary Air Pollution Concerning the Control of Emissions of Volatile Organic Compounds or their transboundary fluxes”, United Nations Economic Commission for Europe, Geneva, Switzerland, ECE/EB.AIR/30.

Üner, D.Ö., Akay, G., Erişmiş, B., 2000. “Egzos gazlarından kaynaklamam hıdrokarbon emisyonlarının analizi ve değerlendirilmesi”, *Proceedings of the Air Pollution and Combustion VI National Symposium,*

UNFCCC, 2005. United Nations Framework Convention of Climate Change, http://unfccc.int, accessed on January 2005.

USEPA, 1986. “Air quality criteria for photochemical oxidants”, Vol. 2-5, US Environmental Protection Agency, Environmental Criteria and Assessment Office, EPA-600/8-84/020d, e, and f. Research Triangle Park, Raleigh, NC.

USEPA, 1993. “Motor Vehicle Related Air Toxics Study”, U.S. Environmental Protection Agency, Office of mobile sources, Office of Air and Radiation: Ann Arbor, MI.

USEPA, 1997a. “Compendium Method TO 15- Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS)”, Center for Environmental Research Information Office of Research and Development, U.S. Environmental Protection Agency Cincinnati, OH.

USEPA, 1997b. “Method TO-17; Determination of VOCs in Ambient Air using Active Sampling onto Sorbent Tubes”, Center for Environmental Research Information, Ohio.

USEPA, 1999. “Spatial and temporal characteristics of California PAMS and Long-term trend site VOC data (1990-1997)”, Final report STI-998241-1883-FR, US EPA Research Triangle Park, NC.

USEPA, 2005. US Environmental Protection Agency Air Toxics Division, http://www.epa.gov, accessed on January 2005.

Vega, E., Mugica, V., Carmona, R., and Valencia, E., 2000. “Hydrocarbon source apportionment in Mexico City using the chemical mass balance receptor model”, *Atmospheric Environment*, Vol.34, pp. 4121-4129.

Viskari, E.L., Vartiainen, M., Pasanen, P., 2000. “Seasonal and diurnal variation in formaldehyde and acetaldehyde concentrations along a highway in Eastern Finland”, *Atmospheric Environment*, Vol. 34, pp. 917-923.

Volz, A., and Kely, D., 1988. “Evaluation of the montsouris series of ozone measurements made in the nineteenth century”, *Nature*, Vol. 332, pp. 240-242.

Wadden, R.A., Uno, I., Wakamatsu, S., 1986. “Source discrimination of short-term hydrocarbon samples measured aloft”, *Environmental Science and Technology*, Vol. 20, pp. 473-483.

Watson, J.G., 1984. “Overview of receptor model principles”, *J. of Air Pollution Control Association*, Vol. 34, pp. 620-623.

Watson, J.G., Chow, J.C., and Fujita, E.M., 2001. “Review of volatile organic compounds source apportionment by chemical mass balance”, *Atmospheric Environment*, Vol. 35, pp. 1567–1584.

Watson, J.G., Chow, J.C., Lu, Z., Fujita, E.M., Lowenthal, D.H., Lawson, D.R., Ashbaugh, L.L., 1994. “Chemical mass balance source apportionment of PM10 during the southern California air quality study”, *Aerosol Science and Technology*, Vol. 21, pp. 1-36.

Watson, J.G., Cooper, J.A., Huntzicker, J.J., 1984. “The effective variance weighted for least squares calculations applied to the mass balance receptor model”, Atmospheric Environment, Vol. 18, Iss. 7, pp. 1347-1355.

Watson, J.G., Robinson, N.F., Fujita, E.M., Chow, J.C., Pace, T.G., Lewis, C. and Coulter, T., 1998. “CMB8 Applications and Validation Protocol for PM2.5 and VOCs”, Desert Research Institute, Doc. No: 1808.2D1.

Weisel, C.P., Lawryk, N.S., and Lioy, P.J., 1992. “Exposure to emissionsfrom gasoline within automobile cabins”, *Journal of Experimental analysis Environmental Epidomiology*, Vol. 2, pp. 79-96.

Winchester, J.W., and Nifong, G.D., 1971. “Water pollution in Lake Michigan by trace elements from aerosol fallout”, Water, Air and Soil Pollution, Vol. 1, pp. 50-64.

Xie, Y.L., Hopke, P.K., Paatero, P., Barrie, L.A., and Li, S.M., 1999. “Identification of source nature and seasonal variations of Arctic aerosol by positive matrix factorization”, *Journal of Atmospheric Science*, Vol. 56, pp. 249-260.

Yang, Y., Stockwel, W.R., and Milford, J.B., 1995. "Uncertainties in incremental reactivities of volatile organic compounds", *Environ. Sci. Technol.*, Vol. 29, pp. 1336-1345.

Yu, S., Dennis, R.L., Bahve, P.V., Eder, B.K., 2004. "Primary and secondary organic aerosols over the United States: estimates on the basis of observed organic carbon (OC) and elemental carbon (EC), and air quality modeled primary OC/EC ratios", *Atmospheric Environment*, Vol. 38, pp. 5257-5268.

Yu, T.Y., Lin, Y.C., and Chang, L.F.W., 2000. "Optimized combinations of abatement strategies for urban mobile sources", *Chemosphere*, Vol. 41, pp. 399-407.

Zhao, W., Hopke, P.K., 2004. "Source Apportionment For Ambient Particles In The San Gorgonio Wilderness", *Atmospheric Environment*, Vol. 38, pp. 5901–5910.

Zhao, W., Hopke, P.K., and Karl, T., 2004. "Source identification of volatile organic compounds in Houston, Texas", *Environmental Science and Technology*, Vol. 38, Iss. 5, pp. 1338-1347.

APPENDIX A

CUSTOM DESIGNED AND MANUFACTURED PARTS

A.1. Coding and Explanation of the Custom Designed Parts

SIS Short Path Thermal Desorption system used in this study has parts in British Units; however, many other parts in Turkey are in International System of Units (SI). Therefore, adopters to connect parts in two different unit systems were designed. Designed adaptors and several other parts are depicted in Figure A.1.

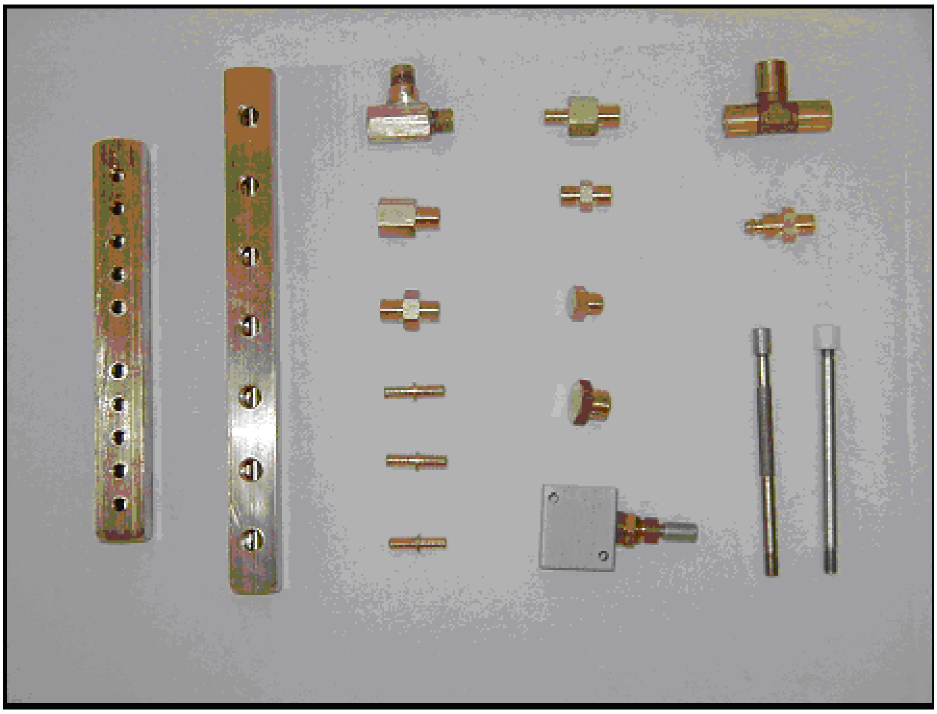


Figure A.1. Samples of custom designed parts.

All the parts are made of brass material. Stainless steel is a more durable, but it is very difficult to process and stainless steel is expensive compared to brass. Brass is easy to process and it can be heated up to 300 °C with no deformation, and it is relatively inexpensive. Table A.1 presents coding and explanation of custom designed and produced parts.

Table A.1. Custom designed and produced parts.

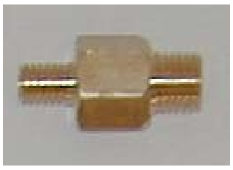
	Code Number : VOC 001 *Name:* Two sided fitting *Explanation:* Both sides have outer screw threads in SI units. Inner sides have screw threads that are suitable to fit SIS thermal desorption tubes. This part was produced by processing inner surface of commercial R1/8 fittings to fit thermal desorption tubes. *Places to use:* Almost in all systems as connecting part.
	Code Number : VOC 002 *Name:* Small Swagelock male connector *Explanation:* Left side shown on the figure has screw threads to allow connection of 1/8 inch swagelock nut. Thus the inner surface has angled to allow swagelock ferrule to fit. Right side of this part has outer screw threads of R1/8 that is suitable to connect parts commercially available in Turkey. *Places to use:* It is mainly used in gas distribution system of conditioning oven. It connects N_2 gas inlet to gas distribution structure. It can be used in all places where a connection to 1/8 inch swagelock is required.
	Code Number : VOC 003 *Name:* Large Swagelock female connector *Explanation:* Inner surface of the left side shown on the figure has R1/8 screw threads. Right side on the figure is suitable to connect large swagelock of 1/4 inch in size. It has screw threads in SI system and angled inner surface. *Places to use:* All the places where MFCs are used.
	Code Number : VOC 004 *Name:* Large Swagelock male connector *Explanation:* Left side shown on the figure has suitable inner and outer surfaces that will allow connection of large swagelock of 1/4 inch in size. Right side is a R1/8 fitting. *Places to use:* All the places where MFCs are used.

Table A.1. Custom designed and produced parts (*Continued*).

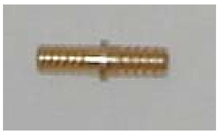
	Code Number : VOC 005 *Name:* Pipe connector (thin) *Explanation:* Both sides have the same diameter. It has conical surfaces in one direction that prevent pipe to easily remove. *Places to use:* Places where two same diameter pipes are connected. Outer diameter is small that will allow connection of digital flowmeter pipe.
	Code Number : VOC 006 *Name:* Pipe connector (thick) *Explanation:* Both sides have the same diameter. It has conical surfaces in one direction that prevent pipe to easily remove. *Places to use:* Places where two same diameter pipes are connected. Outer diameter is large that will allow connection of MFC and sampling pump tubing.
	Code Number : VOC 007 *Name:* Pipe connector (thin-thick sided) *Explanation:* One side is thick and other side has thin in diameter. *Places to use:* Where MFC and Digital Flow meter are required to use together, as connection part between two different tubings in diameter.
	Code Number : VOC 008 *Name:* T part for gas phase calibration standard injection *Explanation:* Left side shown on the figure has inner screw threads that are suitable to connect SIS desorption tubes. Top part is suitable for 1/4 inch swagelock connection but does not have angled inner surface for ferrule. Right side is suitable to connect a 1/4inch swagelock with ferrule. *Places to use:* To load gas phase calibration and internal standards to SIS desorption tubes.
	Code Number : VOC 009 *Name:* Sampling apparatus with multiple inlet *Explanation:* It provides connection of seven SIS desorption tubes at the same time for sampling. Holes in the brass block are suitable to connect R1/8 standard fittings. One end of the block has opening that is suitable to connect R1/8 fitting so that connection to other system parts or addition to system can be achieved. *Places to use:* During multiple sample collection.

Table A.1. Custom designed and produced parts (*Continued*).

	Code Number : VOC 010 *Name:* Gas distribution structure of conditioning oven *Explanation:* It provides distribution of ultra pure N_2 gas through GLT desorption tubes during conditioning. It is capable of connecting 10 tubes at the same time. Holes on the brass block have screw threads that are suitable to connect SIS tubes. On the backside of the brass block there is an opening suitable to connect part VOC002. *Places to use:* Conditioning oven.

A.2. Conditioning Oven

A conditioning oven was designed and manufactured to operate at high temperatures in extended periods in order to condition the tubes prior to sampling and to clean contaminated parts and tubes. The conditioning oven consists of four parts: i) iron oven, ii) temperature programming and control system, iii) gas distribution and control system, and iv) cabinet.

The iron oven includes tube beds and resistances. The dimension of the iron oven is 8 cm (width), 17 cm (length) and 4.5 cm (height) and there are 10 tube beds with 7 of them with 6 mm in diameter and 3 of them with 7 mm in diameter. The 7 mm diameter beds are prepared for the original stainless steel tubes and the other beds ware prepared for the newly manufactured tubes. The oven has a moving top cover made of iron. On outer surfaces of the top and bottom iron blocks, beds of approximately 7 mm in depth were prepared. These beds are used to place resistances. A 400-Watt resistance column placed both at the top and bottom bed of the oven provided the necessary 350^oC operating temperature. Resistance cables were covered with a heat resistant silk jacket. The heat insulation of the iron body from the surrounding is provided with a thick Ytong material.

Temperature of the oven is programmed and controlled by thermostat system that consists of three parts: digital programming panel, thermocouple, and conductor. A notched opening is available at the bottom of the oven for thermocouple connection. The thermocouple is placed in the middle of the bottom cover in order to monitor average temperature of the iron blocks during the operation of the oven. Thermocouple is directly connected to the digital panel. The thermostat can hold up to 1200ºC and consumes about 4 watts of power and it can be programmed to a desired temperature. The oven temperature and the programmed temperature can be monitored continuously on the digital screen. Actual temperature inside stainless steel sampling tubes can be monitored and conditioning oven can be calibrated for desired conditioning temperatures.

Gas distribution and control system consists of brass distribution channel, brass tubing, MFC, pressurized high purity nitrogen gas, gas regulators and brass connectors. While the tubes are heated in the conditioning oven, pure nitrogen gas must be passed through the tubes with a constant flow rate to flush the desorbed contaminants. High purity nitrogen gas released from pressurized cylinder passes through a hydrocarbon/oxygen trap to remove residue of any contaminants in the carrier gas before entering into system. The nitrogen gas then passes through a MFC where a constant flow rate throughout operation within the system is adjusted and controlled. The carrier gas flowing through a brass tube is then distributed to each multisorbent adsorption tube that is attached to distribution system made of brass material. The flow rate at each tube can be monitored and adjusted using a digital flow meter prior to conditioning.

A cabinet is designed to insulate the apparatus that reaches to high temperatures for safety reasons and to exhaust the waste gases from the laboratory air. The warnings signs were posted on the oven. The cabinet is 75 cm in length, 50 cm in width and 53 cm in height. The cabinet is made of a polyamide material to resist high temperatures. The front panel windows are made of hard PVC. Some contamination could be released to the laboratory atmosphere during the conditioning of the tubes. In order to discharge these contaminated exhaust, an aluminum pipe is connected to the opening at the top of the cabinet and connected to a spiral type fan. The suction rate of the fan is 450 m^3 per hour.

A.3. Gas Phase Standard Loading Apparatus

A specially designed apparatus shown in Figure A.2 was used to inject gaseous phase calibration and internal standards to thermal desorption tubes. This apparatus was prepared using 1/4 inch swagelock nut, custom made connectors and adaptors. A septum was placed within the 1/4 inch swagelock nut and the nut was placed onto part number VOC008. The gas phase standards are injected into the system using a gas tight syringe supplied by Hamilton (Hamilton Company, NV, U.S.A.) flow of high purity nitrogen gas at a constant rate is supplied to the system during injection of the standards as a carrier gas. The high purity nitrogen gas passes through a hydrocarbon and oxygen trap before entering into system. A MFC is used to provide constant flow rate of the carrier gas.

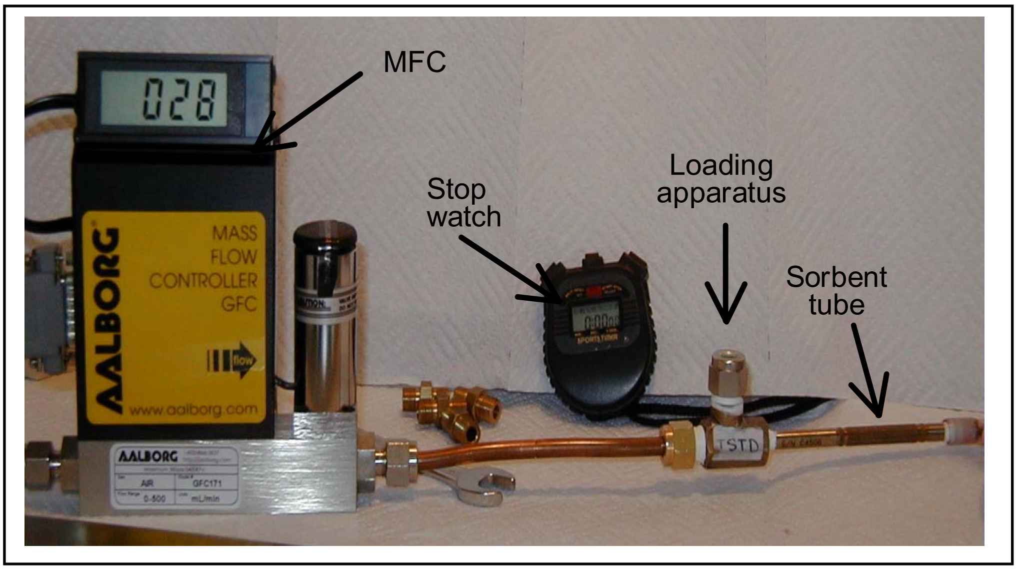


Figure A.2. Gas phase standard loading aparatus.

APPENDIX B

DESCRIPTIVE STATISTICS

Table B.1. Statistical summary of VOC data measured at residential stat
Summer 2003 (all sessions, N=75; conc. in μg m^{-3}).

No	Target Analytes	Median	Min.	Max.	Mean	Stdev.	% Detected
1	Pentane	1.79	0.24	21.19	2.55	3.24	100
2	Isoprene	1.47	0.08	8.88	1.83	1.33	100
3	c-2-pentene	0.06	0.01	0.42	0.08	0.08	56
4	2-methyl-2-butene	0.08	0.03	1.61	0.15	0.25	87
5	2,2-dimethylbutane	1.07	0.14	13.64	1.67	2.02	100
6	t-1,2-dichloroethene	NA	NA	NA	NA	NA	0
7	3-methyl-1-pentene	0.15	0.10	0.25	0.15	0.05	15
8	2,3-dimethylbutane	0.73	0.24	8.43	1.11	1.30	100
9	t-4-methyl-2-pentene	0.05	0.01	0.12	0.05	0.03	47
10	2-methylpentane	2.66	0.91	27.34	4.01	4.40	100
11	c-4-methyl-2-pentene	0.03	0.01	0.17	0.05	0.04	44
12	3-methylpentane	2.06	0.70	20.11	3.02	3.19	100
13	1-hexene/2-methyl-1-p	0.13	0.05	8.18	0.76	1.71	93
14	c-1,2-dichloroethene	NA	NA	NA	NA	NA	0
15	Hexane	1.50	0.43	11.04	2.10	1.86	100
16	Chloroform	0.10	BDL	1.22	0.15	0.19	92
17	t-2-hexene	0.04	0.01	0.24	0.08	0.07	15
18	c-2-hexene	0.03	0.01	0.15	0.05	0.04	20
19	c-3-methyl-2-pentene	0.45	0.17	1.81	0.54	0.34	48
20	2,2-dimethylpentane	0.13	0.04	1.11	0.19	0.20	92
21	1,2-dichloroethane	0.04	0.01	0.19	0.06	0.05	21
22	Methylcyclopentane	0.57	0.16	4.95	0.80	0.81	100
23	2,4-dimethylpentane	0.17	BDL	1.58	0.23	0.26	97
24	1,1,1-trichloroethane	0.16	0.07	0.33	0.16	0.05	100
25	2,2,3-trimethylbutane	0.03	0.01	0.14	0.04	0.04	44
26	1-methylcyclopentene	0.02	0.01	0.21	0.03	0.04	65
27	Benzene	2.20	0.68	23.50	3.34	3.77	100
28	Carbontetrachloride	0.69	0.29	1.48	0.70	0.21	100
29	Cyclohexane	0.34	0.07	2.20	0.46	0.40	97
30	2-methylhexane	0.71	0.04	7.59	1.05	1.23	100
31	2,3-dimethylpentane	0.21	0.06	2.77	0.35	0.44	100
32	3-methylhexane	0.66	0.18	7.93	1.06	1.30	100
33	Dibromomethane	0.01	0.01	0.01	0.01	BDL	12
34	1,2-dichloropropane	0.02	0.01	0.05	0.02	0.01	16
35	Trichloroethene	0.15	0.04	0.75	0.22	0.18	100

Table B.1. *(Continued).*

No	Target Analytes	Median	Min.	Max.	Mean	Stdev.	% Detected
36	1-heptene	0.20	0.07	1.27	0.25	0.20	99
37	2,2,4-trimethylpentane	0.05	0.02	0.20	0.07	0.05	19
38	Heptane	0.55	0.16	6.39	0.86	1.04	100
39	c-3-heptene	0.03	0.01	0.13	0.04	0.03	24
40	t-2-heptene	0.02	0.01	0.09	0.03	0.03	9
41	c-2-heptene	0.02	0.01	0.08	0.03	0.02	12
42	c-1,3-dichloropropene	NA	NA	NA	NA	NA	0
43	2,2-dimethylhexane	0.12	0.03	0.16	0.10	0.06	7
44	Methylcyclohexane	0.11	0.04	1.22	0.18	0.22	100
45	2,5-dimethylhexane	0.04	0.00	0.43	0.06	0.07	69
46	2,4-dimethylhexane	0.07	0.03	0.74	0.12	0.13	75
47	t-1,3-dichloropropene	NA	NA	NA	NA	NA	0
48	Bromotrichloromethan	NA	NA	NA	NA	NA	0
49	2,3,4-trimethylpentane	0.95	0.02	3.24	1.03	0.95	52
50	Toluene	9.81	2.87	52.17	12.32	9.52	100
51	1-methylcyclohexene	0.02	0.01	0.03	0.02	0.01	9
52	Dibromochloromethan	0.01	0.01	0.01	0.01	0.00	4
53	3-methylheptane	0.14	0.04	1.87	0.25	0.36	100
54	c-1,3-dimethylcyclohex	0.04	0.01	0.35	0.06	0.07	91
55	t-1,4-dimethylcyclohex	0.02	0.01	0.18	0.03	0.03	79
56	1,2-dibromoethane	0.01	0.01	0.05	0.02	0.02	16
57	2,2,5-trimethylhexane	0.40	0.03	0.89	0.40	0.30	12
58	1-octene	0.18	0.05	0.55	0.19	0.08	93
59	Octane	0.25	0.09	2.12	0.37	0.36	100
60	t-2-octene	0.04	0.02	0.52	0.08	0.10	37
61	t-1,2-dimethylcyclohex	0.02	0.01	0.12	0.03	0.03	35
62	Tetrachloroethene	0.46	0.08	7.27	0.82	1.10	100
63	c-1,4/t-1,3-dimethylcyc	0.02	0.01	0.13	0.03	0.03	36
64	Chlorobenzene	0.01	BDL	0.04	0.01	0.01	53
65	Ethylbenzene	1.35	0.41	14.25	2.18	2.62	100
66	m,p-xylene	4.40	1.43	49.49	7.23	8.91	100
67	Bromoform	0.01	0.01	0.02	0.01	BDL	41
68	Styrene	0.18	0.03	2.12	0.30	0.41	100
69	1,1,2,2-tetrachloroetha	0.05	0.01	0.19	0.07	0.06	15
70	o-xylene	1.40	0.49	17.22	2.42	3.04	100
71	Nonane	0.47	0.04	3.08	0.63	0.55	100
72	iso-propylbenzene	0.07	0.02	0.86	0.12	0.15	100
73	n-propylbenzene	0.29	0.07	3.92	0.50	0.68	99
74	3-ethyltoluene	0.93	0.19	12.96	1.64	2.26	99
75	4-ethyltoluene	0.52	0.05	6.68	0.89	1.17	99
76	1,3,5-trimethylbenzene	0.56	0.10	8.64	1.01	1.47	100
77	2-ethyltoluene	0.41	0.05	5.15	0.69	0.90	100
78	1,2,4-trimethylbenzene	1.65	0.02	21.71	2.80	3.80	100
79	benzyl chloride	0.29	BDL	2.73	0.38	0.41	80
80	iso-butylbenzene	0.03	0.01	0.76	0.09	0.14	89
81	sec-butylbenzene	0.06	0.02	0.67	0.10	0.12	80

Table B.1. *(Continued).*

No	Target Analytes	Median	Min.	Max.	Mean	Stdev.	% Detected
82	1,2,3-trimethylbenzene	0.45	0.12	5.32	0.74	0.95	96
83	p-cymene	0.11	0.03	2.44	0.22	0.37	100
84	1,2-dichlorobenzene	0.01	0.01	0.03	0.01	0.01	5
85	1,4-diethylbenzene	0.42	0.03	6.41	0.74	1.12	83
86	n-butylbenzene	0.14	0.01	1.24	0.20	0.24	91
87	1,2-diethylbenzene	0.07	0.01	0.63	0.12	0.13	88
88	1,2,4-trichlorobenzene	0.01	BDL	0.02	0.01	BDL	29
89	Naphthalene	0.67	0.03	9.93	1.24	1.93	100
90	Hexachlorobutadiene	NA	NA	NA	NA	NA	0
91	Hexylbenzene	0.04	0.02	0.04	0.03	0.01	7
	Total VOC	46.77	15.23	403.63	66.35	66.69	100

Table B.2. Statistical summary of VOC data measured at residential stat
Winter 2004 (all sessions, N=94; conc. in μg m^{-3}).

No	Target Analytes	Median	Min.	Max.	Mean	Stdev.	% Detected
1	Pentane	1.25	0.34	7.12	1.56	1.11	100
2	Isoprene	0.19	0.06	0.98	0.24	0.19	97
3	c-2-pentene	0.04	0.01	0.35	0.05	0.05	87
4	2-methyl-2-butene	0.09	0.03	0.56	0.12	0.10	97
5	2,2-dimethylbutane	0.62	0.13	4.82	0.84	0.71	100
6	t-1,2-dichloroethene	NA	NA	NA	NA	NA	0
7	3-methyl-1-pentene	0.07	0.07	0.07	0.07	NA	1
8	2,3-dimethylbutane	0.47	0.14	3.42	0.63	0.49	100
9	t-4-methyl-2-pentene	0.03	0.01	0.08	0.03	0.02	36
10	2-methylpentane	1.72	0.44	9.51	2.12	1.52	100
11	c-4-methyl-2-pentene	0.03	0.01	0.09	0.03	0.02	39
12	3-methylpentane	1.47	0.45	8.09	1.81	1.25	99
13	1-hexene/2-methyl-1-p	0.16	BDL	4.56	0.38	0.80	86
14	c-1,2-dichloroethene	NA	NA	NA	NA	NA	0
15	Hexane	1.34	0.19	6.09	1.67	1.21	100
16	Chloroform	0.11	BDL	1.06	0.15	0.16	90
17	t-2-hexene	0.04	0.02	0.13	0.05	0.03	18
18	c-2-hexene	0.03	0.01	0.11	0.04	0.02	32
19	c-3-methyl-2-pentene	1.31	0.37	7.09	1.55	1.08	99
20	2,2-dimethylpentane	0.09	0.02	0.54	0.11	0.08	94
21	1,2-dichloroethane	0.05	0.04	0.10	0.06	0.02	12
22	Methylcyclopentane	0.72	0.19	3.46	0.83	0.55	100
23	2,4-dimethylpentane	0.10	0.03	0.53	0.12	0.08	97
24	1,1,1-trichloroethane	0.18	0.10	0.39	0.18	0.05	100
25	2,2,3-trimethylbutane	0.04	0.01	0.27	0.07	0.07	14
26	1-methylcyclopentene	0.03	0.01	0.27	0.04	0.04	95
27	Benzene	3.78	1.12	19.07	5.19	3.77	100
28	Carbontetrachloride	0.76	0.41	1.25	0.73	0.17	100
29	Cyclohexane	0.25	0.09	1.36	0.30	0.20	97
30	2-methylhexane	0.59	0.15	3.06	0.75	0.49	99
31	2,3-dimethylpentane	0.16	0.03	1.06	0.22	0.16	98
32	3-methylhexane	0.60	0.18	3.38	0.76	0.53	96
33	Dibromomethane	0.04	0.04	0.04	0.04	NA	1
34	1,2-dichloropropane	0.02	0.01	0.05	0.02	0.01	9
35	Trichloroethene	0.18	0.04	3.11	0.33	0.47	72
36	1-heptene	0.08	0.03	0.41	0.10	0.06	94
37	2,2,4-trimethylpentane	0.06	0.02	0.21	0.06	0.04	23
38	Heptane	0.55	0.11	2.48	0.67	0.46	100
39	c-3-heptene	0.05	0.01	0.23	0.06	0.05	39
40	t-2-heptene	0.02	0.01	0.11	0.03	0.02	26
41	c-2-heptene	0.06	0.01	0.26	0.07	0.04	37
42	c-1,3-dichloropropene	NA	NA	NA	NA	NA	0
43	2,2-dimethylhexane	0.01	BDL	0.01	0.01	0.00	4
44	Methylcyclohexane	0.14	0.03	0.93	0.19	0.14	100
45	2,5-dimethylhexane	0.04	BDL	0.19	0.04	0.03	76
46	2,4-dimethylhexane	0.08	0.02	0.38	0.09	0.06	79

Table B.2. *(Continued).*

No	Target Analytes	Median	Min.	Max.	Mean	Stdev.	% Detected
47	t-1,3-dichloropropene	NA	NA	NA	NA	NA	0
48	Bromotrichloromethan	NA	NA	NA	NA	NA	0
49	2,3,4-trimethylpentane	0.02	BDL	3.09	0.18	0.61	78
50	Toluene	6.72	1.19	50.08	10.70	10.94	100
51	1-methylcyclohexene	0.06	0.03	0.09	0.06	0.02	6
52	Dibromochloromethan	BDL	BDL	0.00	BDL	NA	1
53	3-methylheptane	0.16	0.03	1.23	0.22	0.18	94
54	c-1,3-dimethylcyclohex	0.03	0.01	0.25	0.05	0.04	98
55	t-1,4-dimethylcyclohex	0.02	BDL	0.13	0.03	0.02	97
56	1,2-dibromoethane	0.01	0.01	0.03	0.01	0.01	17
57	2,2,5-trimethylhexane	0.23	0.12	0.31	0.22	0.07	6
58	1-octene	0.10	BDL	0.50	0.12	0.07	89
59	Octane	0.22	0.07	7.50	0.37	0.77	99
60	t-2-octene	0.04	0.03	0.43	0.12	0.16	9
61	t-1,2-dimethylcyclohex	0.02	0.01	0.06	0.02	0.01	17
62	Tetrachloroethene	0.30	0.09	6.04	0.66	1.02	100
63	c-1,4/t-1,3-dimethylcyc	0.02	0.01	0.09	0.03	0.02	31
64	Chlorobenzene	0.01	BDL	0.05	0.01	0.01	62
65	Ethylbenzene	0.96	0.12	6.19	1.35	1.06	100
66	m,p-xylene	3.94	0.55	27.13	5.50	4.53	100
67	Bromoform	0.02	0.01	0.03	0.02	0.00	100
68	Styrene	0.62	0.02	3.36	0.89	0.81	86
69	1,1,2,2-tetrachloroetha	0.04	0.01	0.08	0.04	0.03	11
70	o-xylene	1.58	0.22	10.56	2.09	1.70	100
71	Nonane	0.23	0.08	1.75	0.35	0.32	100
72	iso-propylbenzene	0.08	0.03	0.64	0.12	0.10	98
73	n-propylbenzene	0.33	0.05	2.35	0.46	0.37	100
74	3-ethyltoluene	1.11	0.15	8.12	1.52	1.26	100
75	4-ethyltoluene	0.62	0.09	4.43	0.88	0.79	100
76	1,3,5-trimethylbenzene	0.65	0.09	5.20	0.91	0.79	100
77	2-ethyltoluene	0.40	0.06	3.16	0.57	0.49	100
78	1,2,4-trimethylbenzene	1.83	0.27	14.01	2.49	2.11	100
79	benzyl chloride	0.31	0.00	1.62	0.40	0.31	99
80	1,4-dichlorobenzene	1.10	0.38	5.63	1.47	0.93	100
81	iso-butylbenzene	0.02	0.01	0.64	0.04	0.07	99
82	sec-butylbenzene	0.04	0.01	0.33	0.06	0.06	89
83	1,2,3-trimethylbenzene	0.39	0.07	3.16	0.55	0.48	99
84	p-cymene	0.06	0.02	0.42	0.09	0.08	100
85	1,2-dichlorobenzene	BDL	BDL	0.01	0.00	0.00	9
86	1,4-diethylbenzene	0.05	0.01	2.56	0.16	0.33	86
87	n-butylbenzene	0.08	0.02	0.68	0.12	0.11	94
88	1,2,4-trichlorobenzene	BDL	BDL	0.01	BDL	0.00	18
89	Naphthalene	1.14	0.20	9.47	1.62	1.49	100
90	Hexachlorobutadiene	NA	NA	NA	NA	NA	0
91	Hexylbenzene	0.05	0.03	0.06	0.05	0.02	3
	Total VOC	40.94	10.89	249.16	55.38	42.70	100

Table B.3. Statistical summary of VOC data measured at background st
Summer 2003 (all sessions, N=27; conc. in μg m^{-3}).

No	Target Analytes	Median	Min.	Max.	Mean	Stdev.	% Detected
1	Pentane	0.43	0.21	2.08	0.60	0.45	100
2	Isoprene	0.47	0.18	1.87	0.64	0.42	96
3	c-2-pentene	0.04	0.04	0.07	0.04	0.01	22
4	2-methyl-2-butene	0.04	0.03	0.10	0.05	0.02	30
5	2,2-dimethylbutane	0.43	0.18	0.99	0.48	0.21	89
6	t-1,2-dichloroethene	NA	NA	NA	NA	NA	0
7	3-methyl-1-pentene	0.67	0.67	0.67	0.67	NA	4
8	2,3-dimethylbutane	0.33	0.13	0.70	0.35	0.15	100
9	t-4-methyl-2-pentene	0.03	0.01	0.07	0.03	0.02	56
10	2-methylpentane	1.40	0.74	2.49	1.47	0.52	100
11	c-4-methyl-2-pentene	0.04	0.03	0.10	0.05	0.03	22
12	3-methylpentane	1.09	0.51	2.13	1.21	0.46	100
13	1-hexene/2-methyl-1-p	0.26	0.09	0.50	0.27	0.13	89
14	c-1,2-dichloroethene	NA	NA	NA	NA	NA	0
15	Hexane	1.03	0.55	2.15	1.16	0.48	100
16	Chloroform	0.11	BDL	0.64	0.16	0.16	96
17	t-2-hexene	0.03	0.02	0.07	0.04	0.02	15
18	c-2-hexene	NA	NA	NA	NA	NA	0
19	c-3-methyl-2-pentene	0.46	0.21	1.22	0.55	0.31	63
20	2,2-dimethylpentane	0.07	0.04	0.13	0.07	0.03	59
21	1,2-dichloroethane	NA	NA	NA	NA	NA	0
22	Methylcyclopentane	0.36	0.18	1.16	0.44	0.26	100
23	2,4-dimethylpentane	0.08	0.04	0.21	0.09	0.04	89
24	1,1,1-trichloroethane	0.14	0.09	0.34	0.17	0.07	100
25	2,2,3-trimethylbutane	0.03	0.02	0.05	0.03	0.02	15
26	1-methylcyclopentene	0.01	0.01	0.01	0.01	NA	4
27	Benzene	1.70	0.60	2.91	1.70	0.63	100
28	Carbontetrachloride	1.71	0.77	3.83	1.79	0.81	100
29	Cyclohexane	0.15	0.07	0.38	0.17	0.09	89
30	2-methylhexane	0.49	0.03	1.41	0.59	0.30	96
31	2,3-dimethylpentane	0.10	0.07	0.29	0.13	0.06	93
32	3-methylhexane	0.41	0.22	1.02	0.43	0.19	100
33	Dibromomethane	0.01	0.01	0.02	0.01	0.00	11
34	1,2-dichloropropane	NA	NA	NA	NA	NA	0
35	Trichloroethene	0.10	0.04	0.36	0.10	0.06	100
36	1-heptene	0.21	0.05	0.64	0.25	0.16	85
37	2,2,4-trimethylpentane	0.06	0.03	0.08	0.06	0.02	11
38	Heptane	0.50	0.28	1.07	0.52	0.20	100
39	c-3-heptene	0.04	0.02	0.05	0.03	0.01	22
40	t-2-heptene	0.03	0.02	0.05	0.03	0.01	44
41	c-2-heptene	0.05	0.03	0.05	0.04	0.01	15
42	c-1,3-dichloropropene	NA	NA	NA	NA	NA	0
43	2,2-dimethylhexane	0.03	0.01	0.05	0.03	0.02	15
44	Methylcyclohexane	0.11	0.06	0.21	0.11	0.03	100
45	2,5-dimethylhexane	0.03	0.01	0.04	0.03	0.01	33
46	2,4-dimethylhexane	0.06	0.02	0.07	0.05	0.02	26

Table B.3. *(Continued).*

No	Target Analytes	Median	Min.	Max.	Mean	Stdev.	% Detected
47	t-1,3-dichloropropene	NA	NA	NA	NA	NA	0
48	Bromotrichloromethan	NA	NA	NA	NA	NA	0
49	2,3,4-trimethylpentane	1.64	0.22	3.91	1.67	0.85	59
50	Toluene	7.69	2.27	20.43	8.62	3.96	100
51	1-methylcyclohexene	NA	NA	NA	NA	NA	0
52	Dibromochloromethan	0.01	0.01	0.01	0.01	NA	4
53	3-methylheptane	0.09	0.04	0.23	0.10	0.04	81
54	c-1,3-dimethylcyclohex	0.03	0.01	0.03	0.02	0.01	37
55	t-1,4-dimethylcyclohex	0.01	0.01	0.03	0.02	0.01	33
56	1,2-dibromoethane	NA	NA	NA	NA	NA	0
57	2,2,5-trimethylhexane	0.39	0.39	0.39	0.39	NA	4
58	1-octene	0.17	0.05	0.50	0.23	0.12	78
59	Octane	0.20	0.06	0.52	0.23	0.11	93
60	t-2-octene	0.04	0.02	0.30	0.08	0.11	22
61	t-1,2-dimethylcyclohex	0.02	0.02	0.02	0.02	NA	4
62	Tetrachloroethene	0.18	0.05	0.41	0.20	0.09	100
63	c-1,4/t-1,3-dimethylcyc	NA	NA	NA	NA	NA	0
64	Chlorobenzene	0.02	BDL	0.05	0.02	0.01	85
65	Ethylbenzene	0.80	0.32	1.88	0.86	0.36	100
66	m,p-xylene	1.97	0.94	5.75	2.29	1.14	100
67	Bromoform	0.02	0.01	0.05	0.02	0.01	59
68	Styrene	0.13	0.04	0.28	0.14	0.07	100
69	1,1,2,2-tetrachloroetha	0.05	0.02	0.08	0.05	0.05	7
70	o-xylene	0.65	0.29	1.99	0.76	0.39	100
71	Nonane	0.33	0.03	0.67	0.33	0.17	96
72	iso-propylbenzene	0.05	0.02	0.13	0.05	0.02	78
73	n-propylbenzene	0.14	0.02	0.43	0.16	0.09	93
74	3-ethyltoluene	0.36	0.04	1.27	0.45	0.29	93
75	4-ethyltoluene	0.22	0.02	0.74	0.26	0.16	93
76	1,3,5-trimethylbenzene	0.18	0.02	0.63	0.23	0.17	93
77	2-ethyltoluene	0.18	0.02	0.56	0.20	0.12	93
78	1,2,4-trimethylbenzene	0.60	0.03	2.02	0.71	0.49	96
79	benzyl chloride	0.14	0.01	0.34	0.15	0.14	22
80	iso-butylbenzene	0.68	0.02	1.72	0.66	0.46	85
81	sec-butylbenzene	0.03	0.01	0.05	0.03	0.01	52
82	1,2,3-trimethylbenzene	0.17	BDL	0.49	0.20	0.14	59
83	p-cymene	0.08	0.02	0.43	0.09	0.08	93
84	1,2-dichlorobenzene	0.01	0.01	0.01	0.01	0.00	7
85	1,4-diethylbenzene	0.30	0.10	0.40	0.26	0.12	33
86	n-butylbenzene	0.07	0.02	0.14	0.07	0.03	85
87	1,2-diethylbenzene	0.16	0.03	0.42	0.20	0.15	59
88	1,2,4-trichlorobenzene	0.01	BDL	0.02	0.01	0.00	30
89	Naphthalene	0.24	0.01	0.92	0.29	0.20	96
90	Hexachlorobutadiene	NA	NA	NA	NA	NA	0
91	Hexylbenzene	NA	NA	NA	NA	NA	0
	Total VOC	29.55	12.71	49.81	31.22	10.11	100

Table B.4. Statistical summary of VOC data measured at background st
Winter 2004 (all sessions, N=85; conc. in $\mu g\ m^{-3}$).

No	Target Analytes	Median	Min.	Max.	Mean	Stdev.	% Detected
1	Pentane	0.59	0.13	2.30	0.70	0.49	93
2	Isoprene	0.09	0.02	0.41	0.12	0.09	68
3	c-2-pentene	0.03	0.01	0.09	0.04	0.02	30
4	2-methyl-2-butene	0.04	0.02	0.15	0.05	0.03	58
5	2,2-dimethylbutane	0.24	0.04	1.25	0.34	0.29	78
6	t-1,2-dichloroethene	NA	NA	NA	NA	NA	0
7	3-methyl-1-pentene	NA	NA	NA	NA	NA	0
8	2,3-dimethylbutane	0.15	0.03	0.91	0.23	0.20	88
9	t-4-methyl-2-pentene	0.02	0.01	0.05	0.02	0.01	21
10	2-methylpentane	0.51	0.07	2.96	0.78	0.68	93
11	c-4-methyl-2-pentene	0.01	BDL	0.05	0.02	0.01	21
12	3-methylpentane	0.54	0.07	2.93	0.76	0.64	87
13	1-hexene/2-methyl-1-p	0.12	0.04	2.51	0.19	0.37	46
14	c-1,2-dichloroethene	NA	NA	NA	NA	NA	0
15	Hexane	0.51	BDL	5.11	0.73	0.78	88
16	Chloroform	0.22	0.01	4.91	0.62	1.05	53
17	t-2-hexene	0.04	0.02	0.05	0.03	0.01	4
18	c-2-hexene	0.02	0.01	0.05	0.02	0.01	13
19	c-3-methyl-2-pentene	0.32	BDL	2.49	0.51	0.54	88
20	2,2-dimethylpentane	0.04	0.01	0.17	0.04	0.03	62
21	1,2-dichloroethane	0.05	0.02	0.11	0.05	0.02	59
22	Methylcyclopentane	0.18	BDL	1.37	0.28	0.29	89
23	2,4-dimethylpentane	0.04	BDL	0.21	0.05	0.05	78
24	1,1,1-trichloroethane	0.17	0.10	0.28	0.17	0.04	99
25	2,2,3-trimethylbutane	0.01	BDL	0.07	0.01	0.01	22
26	1-methylcyclopentene	0.01	BDL	0.07	0.02	0.01	43
27	Benzene	1.66	0.39	11.10	2.42	2.10	100
28	Carbontetrachloride	0.75	0.42	1.22	0.74	0.19	100
29	Cyclohexane	0.12	0.02	0.51	0.14	0.11	92
30	2-methylhexane	0.33	0.07	1.28	0.39	0.28	84
31	2,3-dimethylpentane	0.07	0.01	0.33	0.09	0.07	80
32	3-methylhexane	0.32	0.11	1.10	0.41	0.27	59
33	Dibromomethane	0.05	0.04	0.06	0.05	0.01	2
34	1,2-dichloropropane	0.02	0.01	0.08	0.02	0.01	40
35	Trichloroethene	0.11	0.04	2.24	0.21	0.35	55
36	1-heptene	0.06	0.02	0.22	0.08	0.04	65
37	2,2,4-trimethylpentane	0.05	0.01	0.11	0.05	0.03	14
38	Heptane	0.28	0.06	1.45	0.35	0.27	93
39	c-3-heptene	0.02	0.01	0.08	0.03	0.02	8
40	t-2-heptene	0.01	0.01	0.06	0.02	0.02	13
41	c-2-heptene	0.03	0.01	0.16	0.05	0.04	19
42	c-1,3-dichloropropene	0.01	0.01	0.01	0.01	NA	1
43	2,2-dimethylhexane	NA	NA	NA	NA	NA	0
44	Methylcyclohexane	0.08	0.01	0.37	0.10	0.08	100
45	2,5-dimethylhexane	0.02	0.01	0.06	0.03	0.02	25
46	2,4-dimethylhexane	0.05	0.02	0.13	0.06	0.03	29

Table B.4. *(Continued).*

No	**Target Analytes**	**Median**	**Min.**	**Max.**	**Mean**	**Stdev.**	**% Detected**
47	t-1,3-dichloropropene	NA	NA	NA	NA	NA	0
48	Bromotrichloromethan	0.02	0.02	0.02	0.02	NA	1
49	2,3,4-trimethylpentane	0.02	BDL	0.97	0.17	0.30	31
50	Toluene	2.67	0.21	18.81	3.95	4.37	100
51	1-methylcyclohexene	0.01	0.01	0.01	0.01	NA	1
52	Dibromochloromethan	0.00	BDL	0.00	BDL	0.00	3
53	3-methylheptane	0.08	0.01	0.35	0.10	0.08	75
54	c-1,3-dimethylcyclohex	0.02	BDL	0.08	0.03	0.02	69
55	t-1,4-dimethylcyclohex	0.01	BDL	0.04	0.02	0.01	62
56	1,2-dibromoethane	0.01	BDL	0.01	0.01	0.00	3
57	2,2,5-trimethylhexane	0.24	0.09	0.50	0.29	0.17	7
58	1-octene	0.11	0.04	0.48	0.12	0.08	54
59	Octane	0.16	0.03	0.80	0.18	0.13	90
60	t-2-octene	0.04	0.01	0.15	0.06	0.05	15
61	t-1,2-dimethylcyclohex	0.02	0.01	0.03	0.02	0.00	8
62	Tetrachloroethene	0.16	0.04	1.15	0.20	0.16	100
63	c-1,4/t-1,3-dimethylcyc	0.01	0.01	0.03	0.02	0.01	10
64	Chlorobenzene	0.01	0.01	0.05	0.01	0.01	71
65	Ethylbenzene	0.36	0.05	2.19	0.55	0.53	100
66	m,p-xylene	1.30	0.03	9.33	1.98	2.15	100
67	Bromoform	0.02	0.01	0.07	0.02	0.01	99
68	Styrene	0.44	0.02	7.63	0.73	1.11	69
69	1,1,2,2-tetrachloroetha	0.02	0.01	0.08	0.03	0.02	10
70	o-xylene	0.46	0.01	3.58	0.73	0.81	100
71	Nonane	0.17	0.04	0.94	0.20	0.17	98
72	iso-propylbenzene	0.04	BDL	0.20	0.05	0.04	78
73	n-propylbenzene	0.10	0.01	0.79	0.15	0.17	100
74	3-ethyltoluene	0.24	0.01	2.56	0.46	0.56	100
75	4-ethyltoluene	0.14	BDL	1.55	0.27	0.33	100
76	1,3,5-trimethylbenzene	0.14	BDL	1.59	0.25	0.31	100
77	2-ethyltoluene	0.10	0.01	0.94	0.18	0.21	100
78	1,2,4-trimethylbenzene	0.40	0.01	4.22	0.73	0.90	100
79	benzyl chloride	0.18	0.05	0.78	0.24	0.19	51
80	1,4-dichlorobenzene	0.77	0.02	4.71	1.01	0.80	96
81	iso-butylbenzene	0.05	0.01	0.65	0.17	0.19	90
82	sec-butylbenzene	0.02	BDL	0.08	0.03	0.02	46
83	1,2,3-trimethylbenzene	0.16	0.04	0.92	0.23	0.21	69
84	p-cymene	0.03	0.01	0.14	0.04	0.03	98
85	1,2-dichlorobenzene	NA	NA	NA	NA	NA	0
86	1,4-diethylbenzene	0.08	0.01	0.77	0.13	0.14	66
87	n-butylbenzene	0.04	0.01	0.19	0.05	0.04	65
88	1,2,4-trichlorobenzene	NA	NA	NA	NA	NA	0
89	Naphthalene	0.22	0.02	4.25	0.56	0.78	99
90	Hexachlorobutadiene	NA	NA	NA	NA	NA	0
91	Hexylbenzene	0.03	0.02	0.05	0.03	0.02	2
	Total VOC	16.57	2.59	80.98	22.02	19.39	100

Table B.5. Statistical summary of VOC data measured at roadside statio
Summer 2003 (all sessions, N=23; conc. in $\mu g\ m^{-3}$).

No	Target Analytes	Median	Min.	Max.	Mean	Stdev.	% Detected
1	Pentane	2.85	0.65	11.32	3.57	2.47	100
2	Isoprene	0.83	0.08	3.58	1.07	0.82	100
3	c-2-pentene	0.09	0.02	0.49	0.11	0.10	91
4	2-methyl-2-butene	0.23	0.05	0.85	0.27	0.20	100
5	2,2-dimethylbutane	1.99	0.32	6.75	2.38	1.66	100
6	t-1,2-dichloroethene	NA	NA	NA	NA	NA	0
7	3-methyl-1-pentene	NA	NA	NA	NA	NA	0
8	2,3-dimethylbutane	1.20	0.24	4.14	1.46	0.98	100
9	t-4-methyl-2-pentene	0.03	0.01	0.11	0.04	0.03	78
10	2-methylpentane	4.26	0.95	13.41	5.03	3.19	100
11	c-4-methyl-2-pentene	0.03	0.01	0.10	0.04	0.02	65
12	3-methylpentane	3.28	0.78	10.43	3.83	2.41	100
13	1-hexene/2-methyl-1-p	0.21	0.08	14.79	1.10	3.22	96
14	c-1,2-dichloroethene	NA	NA	NA	NA	NA	0
15	Hexane	1.89	0.59	5.10	2.19	1.24	100
16	Chloroform	0.09	0.03	0.22	0.10	0.05	100
17	t-2-hexene	0.05	0.02	0.13	0.06	0.03	43
18	c-2-hexene	0.03	0.02	0.08	0.04	0.02	57
19	c-3-methyl-2-pentene	0.75	0.16	1.86	0.83	0.48	61
20	2,2-dimethylpentane	0.21	0.05	0.80	0.25	0.18	100
21	1,2-dichloroethane	0.05	0.05	0.05	0.05	NA	4
22	Methylcyclopentane	0.83	0.28	2.69	1.02	0.63	100
23	2,4-dimethylpentane	0.26	0.07	0.88	0.33	0.21	100
24	1,1,1-trichloroethane	0.21	0.09	0.34	0.21	0.05	100
25	2,2,3-trimethylbutane	0.03	0.02	0.09	0.04	0.02	48
26	1-methylcyclopentene	0.04	0.01	0.12	0.05	0.03	78
27	Benzene	5.15	1.29	13.53	5.75	3.28	100
28	Carbontetrachloride	0.78	0.42	1.27	0.80	0.18	100
29	Cyclohexane	0.36	0.12	1.06	0.42	0.25	100
30	2-methylhexane	1.43	0.40	3.83	1.64	1.00	100
31	2,3-dimethylpentane	0.45	0.11	1.60	0.59	0.40	100
32	3-methylhexane	1.42	0.35	4.33	1.76	1.12	100
33	Dibromomethane	0.01	0.01	0.02	0.01	0.00	22
34	1,2-dichloropropane	0.02	0.01	0.02	0.02	0.00	9
35	Trichloroethene	0.19	0.07	0.41	0.20	0.11	100
36	1-heptene	0.28	0.09	0.64	0.31	0.15	100
37	2,2,4-trimethylpentane	0.04	0.02	0.07	0.04	0.02	17
38	Heptane	1.28	0.33	3.51	1.39	0.79	100
39	c-3-heptene	0.04	0.02	0.14	0.06	0.04	39
40	t-2-heptene	0.04	0.04	0.04	0.04	NA	4
41	c-2-heptene	0.02	0.01	0.05	0.03	0.01	22
42	c-1,3-dichloropropene	NA	NA	NA	NA	NA	0
43	2,2-dimethylhexane	0.13	0.13	0.13	0.13	0.00	9
44	Methylcyclohexane	0.27	0.13	0.81	0.29	0.17	100
45	2,5-dimethylhexane	0.08	0.03	0.25	0.09	0.05	96
46	2,4-dimethylhexane	0.15	0.06	0.45	0.18	0.10	96

Table B.5. *(Continued).*

No	Target Analytes	Median	Min.	Max.	Mean	Stdev.	% Detected
47	t-1,3-dichloropropene	NA	NA	NA	NA	NA	0
48	Bromotrichloromethan	NA	NA	NA	NA	NA	0
49	2,3,4-trimethylpentane	0.05	0.02	7.67	1.25	2.29	83
50	Toluene	12.41	3.30	57.14	17.41	12.73	100
51	1-methylcyclohexene	0.01	BDL	0.03	0.01	0.01	30
52	Dibromochloromethan	NA	NA	NA	NA	NA	0
53	3-methylheptane	0.41	0.11	1.39	0.48	0.31	100
54	c-1,3-dimethylcyclohex	0.08	BDL	0.22	0.08	0.05	96
55	t-1,4-dimethylcyclohex	0.04	0.02	0.11	0.04	0.02	96
56	1,2-dibromoethane	0.01	0.00	0.03	0.01	0.01	30
57	2,2,5-trimethylhexane	0.07	0.01	0.13	0.07	0.09	9
58	1-octene	0.19	0.06	0.29	0.18	0.06	70
59	Octane	0.50	0.21	1.00	0.50	0.21	96
60	t-2-octene	0.07	0.05	0.16	0.08	0.05	17
61	t-1,2-dimethylcyclohex	0.02	0.01	0.07	0.03	0.02	48
62	Tetrachloroethene	1.91	0.20	90.22	13.38	24.43	100
63	c-1,4/t-1,3-dimethylcyc	0.02	0.01	0.07	0.03	0.02	57
64	Chlorobenzene	0.01	0.01	0.03	0.01	0.01	70
65	Ethylbenzene	3.71	1.40	12.78	4.32	2.72	100
66	m,p-xylene	11.07	4.12	39.37	13.82	8.85	100
67	Bromoform	0.02	0.01	0.02	0.02	0.00	48
68	Styrene	0.48	0.08	2.22	0.65	0.51	100
69	1,1,2,2-tetrachloroetha	0.12	0.12	0.12	0.12	NA	4
70	o-xylene	3.87	0.86	11.44	4.80	2.98	100
71	Nonane	0.51	0.04	1.17	0.51	0.24	100
72	iso-propylbenzene	0.18	0.08	0.49	0.20	0.11	96
73	n-propylbenzene	0.73	0.01	2.00	0.85	0.53	100
74	3-ethyltoluene	2.61	0.01	7.44	3.04	1.95	100
75	4-ethyltoluene	1.41	0.01	3.78	1.61	0.99	100
76	1,3,5-trimethylbenzene	1.62	0.01	4.96	1.92	1.27	100
77	2-ethyltoluene	1.00	0.29	2.87	1.19	0.68	96
78	1,2,4-trimethylbenzene	4.35	0.03	12.34	5.03	3.16	100
79	benzyl chloride	0.56	0.04	1.71	0.62	0.56	87
80	iso-butylbenzene	0.05	0.02	0.12	0.06	0.03	96
81	sec-butylbenzene	0.09	0.04	0.22	0.09	0.04	78
82	1,2,3-trimethylbenzene	0.96	0.02	2.84	1.10	0.68	100
83	p-cymene	0.13	0.03	0.61	0.16	0.12	100
84	1,2-dichlorobenzene	NA	NA	NA	NA	NA	0
85	1,4-diethylbenzene	0.42	0.04	2.94	0.71	0.78	87
86	n-butylbenzene	0.21	0.08	0.59	0.23	0.12	96
87	1,2-diethylbenzene	0.07	0.04	0.19	0.08	0.03	91
88	1,2,4-trichlorobenzene	NA	NA	NA	NA	NA	0
89	Naphthalene	1.00	0.03	2.38	1.12	0.56	100
90	Hexachlorobutadiene	NA	NA	NA	NA	NA	0
91	Hexylbenzene	NA	NA	NA	NA	NA	0
	Total VOC	92.33	40.85	276.59	111.93	66.76	100

Table B.6. Statistical summary of VOC data measured at roadside statio
Winter 2004 (all sessions, N=27; conc. in $\mu g\ m^{-3}$).

No	Target Analytes	Median	Min.	Max.	Mean	Stdev.	% Detected
1	Pentane	4.18	0.72	20.65	5.61	5.12	100
2	Isoprene	0.53	0.08	3.84	0.78	0.91	96
3	c-2-pentene	0.10	0.03	0.81	0.16	0.18	93
4	2-methyl-2-butene	0.28	0.04	1.87	0.40	0.43	100
5	2,2-dimethylbutane	1.84	0.27	9.87	2.67	2.47	100
6	t-1,2-dichloroethene	NA	NA	NA	NA	NA	0
7	3-methyl-1-pentene	0.14	0.08	0.19	0.14	0.07	7
8	2,3-dimethylbutane	1.34	0.16	7.31	1.99	1.87	100
9	t-4-methyl-2-pentene	0.04	0.02	0.22	0.06	0.06	63
10	2-methylpentane	3.88	0.57	25.68	6.39	6.39	100
11	c-4-methyl-2-pentene	0.05	BDL	0.25	0.07	0.07	63
12	3-methylpentane	3.02	0.50	18.47	5.03	4.65	100
13	1-hexene/2-methyl-1-p	0.34	0.16	2.35	0.56	0.60	74
14	c-1,2-dichloroethene	NA	NA	NA	NA	NA	0
15	Hexane	2.83	0.41	14.92	4.06	3.71	100
16	Chloroform	0.27	0.02	1.53	0.43	0.38	100
17	t-2-hexene	0.11	0.05	0.39	0.17	0.13	33
18	c-2-hexene	0.06	0.02	0.43	0.11	0.12	67
19	c-3-methyl-2-pentene	2.70	0.44	15.85	4.06	3.88	100
20	2,2-dimethylpentane	0.21	0.03	1.30	0.33	0.32	100
21	1,2-dichloroethane	0.07	0.07	0.07	0.07	NA	4
22	Methylcyclopentane	1.45	0.24	8.06	2.16	2.00	100
23	2,4-dimethylpentane	0.30	0.04	1.96	0.50	0.52	96
24	1,1,1-trichloroethane	0.38	0.26	0.58	0.38	0.07	100
25	2,2,3-trimethylbutane	0.02	BDL	0.05	0.02	0.01	22
26	1-methylcyclopentene	0.07	0.01	0.77	0.13	0.19	96
27	Benzene	7.24	1.56	58.85	12.64	13.47	100
28	Carbontetrachloride	1.54	1.07	1.82	1.51	0.20	100
29	Cyclohexane	0.59	0.10	3.55	0.87	0.92	89
30	2-methylhexane	1.75	0.32	8.07	2.51	2.05	96
31	2,3-dimethylpentane	0.52	0.07	2.87	0.80	0.73	100
32	3-methylhexane	1.74	0.25	8.68	2.57	2.22	100
33	Dibromomethane	NA	NA	NA	NA	NA	0
34	1,2-dichloropropane	0.03	0.03	0.03	0.03	NA	4
35	Trichloroethene	0.43	0.09	2.59	0.73	0.82	37
36	1-heptene	0.22	0.09	1.18	0.31	0.29	96
37	2,2,4-trimethylpentane	0.47	0.39	0.66	0.51	0.14	11
38	Heptane	1.68	0.24	7.52	2.15	1.80	100
39	c-3-heptene	0.15	0.03	0.32	0.17	0.11	26
40	t-2-heptene	0.05	0.03	0.22	0.09	0.07	37
41	c-2-heptene	0.12	0.08	0.65	0.20	0.19	52
42	c-1,3-dichloropropene	NA	NA	NA	NA	NA	0
43	2,2-dimethylhexane	NA	NA	NA	NA	NA	0
44	Methylcyclohexane	0.42	0.09	2.60	0.63	0.68	100
45	2,5-dimethylhexane	0.12	0.05	0.50	0.15	0.13	85
46	2,4-dimethylhexane	0.25	0.09	1.04	0.33	0.27	81

Table B.6. *(Continued).*

No	Target Analytes	Median	Min.	Max.	Mean	Stdev.	% Detected
47	t-1,3-dichloropropene	NA	NA	NA	NA	NA	0
48	Bromotrichloromethan	NA	NA	NA	NA	NA	0
49	2,3,4-trimethylpentane	0.05	0.02	0.25	0.07	0.07	67
50	Toluene	14.73	2.20	108.82	25.23	26.30	100
51	1-methylcyclohexene	0.21	0.19	0.22	0.21	0.03	7
52	Dibromochloromethan	0.01	0.01	0.01	0.01	NA	4
53	3-methylheptane	0.49	0.07	2.95	0.80	0.76	100
54	c-1,3-dimethylcyclohex	0.11	0.02	0.73	0.17	0.20	100
55	t-1,4-dimethylcyclohex	0.06	0.01	0.36	0.09	0.10	100
56	1,2-dibromoethane	0.03	0.01	0.06	0.03	0.02	30
57	2,2,5-trimethylhexane	0.73	0.68	0.77	0.73	0.06	7
58	1-octene	0.30	0.09	1.20	0.37	0.25	96
59	Octane	0.65	0.14	3.76	0.92	0.94	100
60	t-2-octene	0.05	0.02	0.23	0.09	0.08	30
61	t-1,2-dimethylcyclohex	0.05	0.02	0.23	0.09	0.08	37
62	Tetrachloroethene	3.30	0.32	106.38	9.08	20.87	100
63	c-1,4/t-1,3-dimethylcyc	0.05	0.02	0.25	0.08	0.07	56
64	Chlorobenzene	0.03	0.01	0.08	0.03	0.03	15
65	Ethylbenzene	2.94	0.39	16.12	4.28	3.82	100
66	m,p-xylene	13.06	1.71	69.26	18.44	16.35	100
67	Bromoform	0.03	0.02	0.04	0.03	0.01	93
68	Styrene	0.84	0.07	7.34	1.48	1.72	100
69	1,1,2,2-tetrachloroetha	0.11	0.05	0.15	0.10	0.05	15
70	o-xylene	5.01	0.62	27.44	7.36	6.56	100
71	Nonane	0.53	0.14	5.51	1.04	1.48	100
72	iso-propylbenzene	0.22	0.03	1.57	0.36	0.38	100
73	n-propylbenzene	1.02	0.12	5.90	1.55	1.42	100
74	3-ethyltoluene	3.89	0.44	21.23	5.66	5.01	100
75	4-ethyltoluene	2.09	0.23	11.56	3.05	2.72	100
76	1,3,5-trimethylbenzene	2.48	0.26	13.93	3.65	3.31	100
77	2-ethyltoluene	1.37	0.15	8.23	2.08	1.96	100
78	1,2,4-trimethylbenzene	6.58	0.74	35.64	9.54	8.48	100
79	benzyl chloride	1.12	0.14	5.64	1.55	1.27	100
80	1,4-dichlorobenzene	4.91	0.89	25.77	6.38	5.41	100
81	iso-butylbenzene	0.07	0.01	0.47	0.11	0.12	100
82	sec-butylbenzene	0.11	0.02	0.75	0.18	0.20	89
83	1,2,3-trimethylbenzene	1.37	0.17	8.22	2.09	1.98	100
84	p-cymene	0.11	0.03	1.39	0.22	0.33	100
85	1,2-dichlorobenzene	0.01	0.01	0.01	0.01	0.00	15
86	1,4-diethylbenzene	0.07	BDL	3.74	0.35	0.78	96
87	n-butylbenzene	0.27	0.03	1.76	0.42	0.43	100
88	1,2,4-trichlorobenzene	0.01	0.01	0.57	0.12	0.25	19
89	Naphthalene	2.17	0.39	25.42	4.01	5.53	100
90	Hexachlorobutadiene	NA	NA	NA	NA	NA	0
91	Hexylbenzene	0.33	0.33	0.33	0.33	NA	4
	Total VOC	109.61	31.35	634.82	171.09	150.88	100

CURRICULUM VITAE

PERSONAL INFORMATION

Surname, Name: Oğuz Kuntasal, Öznur
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Date of Birth: 1976

EDUCATION

Degree	*Institution*	*Year of Graduation*
M.S.	METU Environmental Engineering	1999
B.S.	METU Environmental Engineering	1997

WORK EXPERIENCE

Year	*Place*	*Enrollment*
1997-2005	METU Department of Environmental Engineering	Teaching Assistant
Jan-Sep 2000	Carleton University, Canada	Research Project Staff
Jan-Mar 2001	Japan International Cooperation Agency, Japan	Technical Trainee

AWARDS

Year	*Institution*	*Award*
2005	World Meteorological Organization (WMO)	Travel award
2001	International Union of Air Pollution Prevention and Environmental Protection Associations (IUAPPA) and the International Academy of Science	Thomas Kuhn Honor Pin
2001	Japan International Cooperation Agency (JICA)	JICA fellow
2000	Scientific and Technical Research Council of Turkey (TÜBİTAK)	NATO A-2
1998	WARSAW98 Organization Committee	Student Travel Award

CERTIFICATES

January-March 2001, "Seminar on Policy Implementation and Alternative Technologies Concerning Ozone Layer Protection", organized by *Japan International Cooperation Agency (JICA)* under the International Cooperation Program of the Government of Japan, Tokyo, Japan.

PUBLICATIONS

A. Refereed Journal Articles

1. Oğuz, Ö., Karman, D., Wang, D., Tuncel, S.G., Tuncel, G., "Determination of Volatile Organic Compounds in Different Microenvironments by Multibed Adsorption and Short-Path Thermal Desorption Followed by GC-MS Analysis", *Journal of Chromatography A* (accepted for publication).
2. Oğuz, Ö., Karman, D., Tuncel, G., 2003. "Measurement of Traffic Related Toxic Air Pollutants in an Urban Atmosphere", *Water, Air and Soil Pollution: Focus*, Volume 3, Nos. 5-6, pp. 175-192.

C. Proceedings

C.1. National Conferences

1. Oğuz, Ö., Tuncel, G., and Karman, D., 2003. "Source Apportionment of Organic Air Pollutants by Receptor Modelling Technique", Proceedings of the *2nd National Symposium on Environmental Pollution Control,* October 22-24, METU, Ankara, Turkey, pp. 121-128.
2. Oğuz, Ö., Tuncel, G., Karman, D., 2001. "Levels and Seasonal Variations of Traffic Related Volatile and Semivolatile Organic Compounds", Proceeding of the *IV. National Conference of Turkish Chamber of Environmental Engineers*, September 7-10, İçel, Turkey, pp. 495-503.
3. Oğuz, Ö., 2001. "Innovative Technologies in Protection of Ozone Layer", Proceeding of *IV. National Conference of Turkish Chamber of Environmental Engineers*, September 7-10, İçel, Turkey.

C.2. International Conferences

1. Oğuz Kuntasal, Ö., Karman, D., Tuncel, G., 2005. "Source Apportionment of Urban Volatile Organic Compounds (VOCs) Using Chemical Mass Balance Receptor Model", Proceedings of the *5th International Conference on Urban Air Quality*, March 29-31, Valencia, Spain, pp. 112-115.
2. Oğuz Kuntasal, Ö., Karman, D., Tuncel, S.G., Tuncel, G., 2004. "Determination of Volatile Organic Compounds in Ambient Air by Multibed Adsorption/Short Path Thermal Desorption-GC/MS", Proceedings of the *4th Aegean Analytical Chemistry Days*, September 29 - October 3, Kuşadası, Turkey.
3. Oğuz Kuntasal, Ö., Karman, D., Tuncel, G., 2004. "Comparison Of Volatile Organic Compounds In A Regulated And A Nonregulated City Atmosphere", Proceedings of the *13th World Clean Air and Environmental Protection Congress and Exhibition*, August 22-27, London, UK.
4. Oğuz Kuntasal, Ö., Karman, D., Tuncel, S.G., Tuncel, G., 2004. "Characterization Of Toxic Air Pollutants At a Residential Site in Ankara, Turkey", Proceedings of the *Air & Waste Management Association's 97th Annual Conference and Exhibition,* June 22-25, Indianapolis, IN, USA.
5. Oğuz, Ö., Orhan, A.S., Karman, D., Tuncel, G., 2003. "Volatile Organic Compounds in the Ankara Atmosphere", Abstract book of the *12th International Symposium on Environmental Pollution and Its Impact on Life in the Mediterranean Region, Appropriate Solutions for Environmental Problems in Emerging Economies*, October 4-8, Antalya, Turkey, pp. 311.
6. Oğuz, Ö., Yurteri, C., and Tuncel, G., 2003. "Modeling Plume Rise and Dispersion of Power Plant Flue Gases Through Cooling Towers", accepted for presentation at the *26th NATO/CCMS International Technical Meeting on Air Pollution and its Application*, 26-30 May, İstanbul, Turkey, pp.512-514.

7. Girgin, S., Ünlü, K., Taşel, E., Tokmak Cangir, B., Tokcaer, E., Oğuz, Ö., Dilek, F.B., and Yetiş, U., 2002, "Geographical Information Systems on Development of the Environmental Emergency Response Plans", Proceedings of the *International Conference on Environmental Problems of the Mediterranean Region*, 12-15 April, Lefkoşa, Northern Cyprus.
8. Oğuz, Ö., Gökçay, C.F., Sürücü, G., and Yetiş, Ü., 2002. "Assessment of Disaster Emergency Plans Minimize Environmental Risk of Disasters", Proceedings of the *International Conference on Environmental Problems of the Mediterranean Region*, 12-15 April, Lefkoşa, Northern Cyprus.
9. Oğuz, Ö., Tuncel, G., and Karman, D., 2002. "Volatile Organics in an Urban Atmosphere", Proceedings of the *EUROTRAC-2 Symposium 2002 Transport and Chemical Transformation in the Troposphere*, March 11-15, Garmisch-Partenkirchen, Germany, pp. GUEST51(1-4).
10. Karman, D., Oğuz, Ö., Akay, G., and Graham, L.A., 2002. "The Ottawa Micro-Environment Database for Motor Vehicle Related Air Pollutants", Abstract of the *Toxic Substance Research Initiative National Conference*, March 5-8, Ottawa, Canada, pp. 95.
11. Karman, D., Tuncel, G., Graham, L.A., Oğuz, Ö., 2002. "Spatial Variations in the Concentrations of Motor Vehicle Related Organic Air Pollutants in Ottawa", Abstract of the *Toxic Substance Research Initiative National Conference*, March 5-8, Ottawa, Canada, pp. 96.
12. Oğuz, Ö., Gökçay, C.F., Sürücü, G., and Yetiş, U., 2001. "A Model Disaster Emergency Plan for the Marmara Region to Minimize Environmental Risk of Disasters", Proceedings of the *TUBITAK-INERIS Joint Seminar on Major Industrial Risk Prevention and Implementation of the Seveso II Directive*, October 9-12, Gebze, Turkey.
13. Girgin, S., Ünlü, K., Taşel, E., Tokmak Cangir, B., Tokcaer, E., Oğuz, Ö., Dilek, F.B., and Yetiş, U., "Implementation of Geographical Information System on Development of the Environmental Emergency Response Plan for Marmara Region", Proceedings of the *TUBITAK-INERIS Joint Seminar on Major Industrial Risk Prevention and Implementation of the Seveso II Directive,* October 9-12, Gebze, Turkey.
14. Oğuz, Ö., Tuncel, G., Karman, D., 2001. "Measurement of Traffic Related Toxic Air Pollutants in an Urban Atmosphere", Proceedings of the *2nd International Symposium on Air Quality Management at Urban, Regional and Global Scales*, September 25-28, İstanbul, Turkey, pp. 608-615.
15. Karman, D., Oğuz, Ö, Akay, G., and Graham, L.A., 2001. "Measurement of Air Toxics in the Cabins of Commuter Vehicles Under Summer and Winter Conditions in Ottawa, Canada", Proceedings of the *11th CRC On-Road Vehicle Emissions Workshop*, March 26-28, San Diego, California.
16. Karman, D., Noseworthy, L., Graham, L.A., and Oğuz, Ö., 2000. "Motor Vehicle Related Air Toxic Measurements Along an Urban Street", Proceedings of the *International Symposium on the Measurement of Toxic and Related Air Pollutants*, the Air & Waste Management Association's Annual Meeting and Specialty Conference, PA, USA.
17. Oğuz, Ö., Tuncel, G., and Yurteri, C., 1998. "Assessment of Air Quality Impacts of the Afşin-Elbistan Series", Proceedings of *the Fourth International Symposium and Exhibition on Environmental Contamination in Central and Eastern Europe (WARSAW'98)*, Warsaw, Poland, pp. 340.