DETERMINATION OF SOURCE APPORTIONMENT OF VOLATILE ORGANIC COMPOUNDS IN ANKARA

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ABSTRACT

DETERMINATION OF SOURCE APPORTIONMENT OF VOLATILE ORGANIC COMPOUNDS IN ANKARA

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In this study, ambient concentrations of fifty-one volatile organic compounds (VOCs) were measured to determine their current level, emission sources and contributions in both urban and suburban atmosphere of Ankara. Two sampling stations were established in Ankara, one in Ankara University (AU), Faculty of Agriculture, other in Middle East Technical University (METU). AU stations is for representing the urban atmosphere while METU represents suburban atmosphere. In these stations with canister sampling, between January 2013 and September 2015 for METU and between June 2014 and September 2015 for AU, VOCs were collected by 24-hour period. By using GC-FID technique, concentrations of VOCs were determined in gathered 559 canister samples.

Mean VOC concentrations ranged between 0.09 µg m^{-3} (cis-2-pentene) and 24.76 µg m^{-3} (toluene) with average benzene concentration of 2.1 µg m^{-3} in AU while 0.06 µg m^{-3} (cis-2-pentene) and 10.09 µg m^{-3} (toluene) with average benzene concentration of 1.4 µg m^{-3} in METU. During sampling period, the annual limit of 5 µg m^{-3} for benzene was exceeded twenty five times in urban station and fifteen times in suburban station.

Comparison study was applied to measured concentrations with: other cities in Turkey and cities around the world. Episodic changes, weekday – weekend changes and seasonal changes were examined. In addition, relationship between meteorological parameters and the measured concentrations were discussed.

Finally, source apportionment study was conducted using PMF. Six different factors were identified in both stations, namely gasoline exhaust, diesel exhaust, industrial evaporation, solvent, gasoline evaporation and asphalt pavement. Gasoline exhaust factor had the highest contribution to total VOC mass in both stations (38% at each station). At urban station, gasoline evaporation and asphalt pavement activities contributions were approximately 23% each. Contribution of remaining factors (solvent, industrial evaporation, diesel) was <10%. At suburban station gasoline evaporation factor was the second highest contributor (19%), which was followed by industrial evaporation (13%), diesel (11%) and solvent (10%) factors.

Keywords: Ankara, VOC, atmosphere, receptor modeling, PMF

ÖZ

ANKARA’DA UÇUCU ORGANİK BİLEŞİKLERİN KAYNAK KATKI PAYLARININ BELİRLENMESİ

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Yüksek Lisans, Çevre Mühendisliği Bölümü

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Bu çalışmada, Ankara'nın hem kentsel hem de kırsal atmosferinde elli bir adet uçucu organik bileşiğin (UOB) mevcut düzeyi, emisyon kaynakları ve katkılarını belirlemek için ortam konsantrasyonları ölçülmüştür. Biri Ankara Üniversitesi, Ziraat Fakültesi yerleşkesinde, diğeri ise Orta Doğu Teknik Üniversitesi yerleşkesinde olmak üzere iki istasyon kurulmuştur. Ankara Üniversitesinde bulunan istasyon kentsel alanı temsil ederken ODTÜ istasyonu kırsal alanı temsil etmektedir. Bu istasyonlarda, kanister örneklemesi ile, ODTÜ’de Ocak 2013 - Eylül 2015 ve Ankara Üniversitesinde Haziran 2014 - Eylül 2015 tarihleri arasında, 24 saatlik sürelerle UOB örnekleri toplanmıştır. Toplanan yaklaşık 559 örnekte, GC-FID tekniği kullanılarak, elli beş organik bileşiğin konsantrasyonları belirlenmiştir.

Ortalama UOB konsantrasyonları Ankara Üniversitesinde 0.09 μg m^{-3} (cis-2-penten) - 24.76 μg m^{-3} (tolüen) aralığında ve ortalama benzen konsantrasyonu 1.4 μg m^{-3} olarak ölçülürken, ODTÜ’de en düşük 0.06 μg m^{-3} (cis-2-penten) ve en yüksek 10.09

µg m^{-3} (tolüen) olmak üzere ortalama benzen konsantrasyonu 1.4 µg m^{-3} olarak ölçülmüştür. Benzen konsantrasyonları, kırsal alanda 15 kez; kentsel alanda ise 25 kez limit değer olan 5 µg m^{-3} değerinin üzerinde ölçülmüştür.

Ölçülen UOB konsantrasyonları Türkiye'deki ve dünyadaki diğer şehirlerde yapılan çalışmalarla karşılaştırılmıştır. Episodik değişiklikler, hafta içi - hafta sonu değişiklikleri ve mevsimsel değişiklikler incelenmiştir. Buna ek olarak meteorolojik parametreler ile ölçülen konsantrasyonlar arasındaki ilişki üzerinde durulmuştur.

Son olarak, Pozitif Matriks Faktorizasyonu (PMF) kullanılarak bir kaynak tahmini çalışması yürütülmüş ve her iki istasyonda da 6 farklı kaynak tanımlanmıştır (benzinli egzoz, dizel egzoz, endüstriyel buharlaşma, solvent, benzin buharlaşması ve asfalt). Her iki istasyonda toplam VOC kütlesine en fazla katkıda bulunan kaynak benzinli araç egzoz faktörüdür (her istasyonda% 38). Kentsel istasyonda, benzin buharlaşması ve asfalt kaldırım faaliyetleri katkıları her biri için yaklaşık %23'tür. Geri kalan kaynakların (solvent, endüstriyel buharlaşma, dizel) katkısı <% 10'dur. Kırsal istasyonda benzin buharlaşma faktörü (%19) ikinci en yüksek katkıyı yapmıştır (%19). Bunu endüstriyel buharlaşma (%13), dizel (%11) ve solvent (%10) faktörleri izlemektedir.

Anahtar Kelimeler: Ankara, UOB, atmosfer, reseptör modellemesi, PMF

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To my family

TABLE OF CONTENTS

ÖZ vii
ACKNOWLEDGEMENTS ix
TABLE OF CONTENTS xi
LIST OF FIGURES xiv
LIST OF TABLES xvii
LIST OF ABBREVIATIONS xviii

CHAPTERS

1 INTRODUCTION 1
  1.1 Purpose of the Study 2
  1.2 Layout of the Study 2
2 LITERATURE REWIEV 3
  2.1 Volatile Organic Compounds 3
  2.2 Sources of Volatile Organic Compounds 4
  2.3 Effects of Volatile Organic Compounds 5
  2.4 VOC Emission Control Regulations 7
    2.4.1 National Regulations 7
    2.4.2 Regulations around the World 8
      2.4.2.1 EuropeanUnion 8
      2.4.2.2 U.S. Environmental Protection Agency (U.S. EPA) 9
      2.4.2.3 EnvironmentCanada 10
  2.5 Source Apportionment 10
    2.5.1 Positive Matrix Factorization 12
  2.6 Source Apportionment Studies around the World 13
3 MATERIAL AND METHODS 17
  3.1 Study Area 17
    3.1.1 Ankara University, Faculty of Agriculture Campus 17

3.1.2 Middle East Technical University, Environmental Engineering Department 18
3.2 Sampling Schedule 19
3.3 Sampling Methodology 19
3.3.1 Preparation of Samples for Analysis 20
3.4 Analytical Methodology 22
3.4.1 Target Volatile Organic Compounds 22
3.4.2 Analyses of Samples 23
3.4.3 Parameters 24
3.5 Quality Assurance / Quality Control (QA/QC) Studies 26
3.5.1 Calibration of the instrument, detection limits and field blanks 26
3.5.2 Analytical System QA/QC Procedure 31
3.5.3 Precision of Sampling Kit and Analysis 31
3.6 Positive Matrix Factorization (PMF) 37
4 RESULTS AND DISCUSSION 41
4.1 General Data 41
4.1.1 Summary Statistics of VOCs at AU and METU Stations 41
4.1.2 Frequency Distributions at AU and METU Stations 42
4.2 Comparison with Literature 51
4.2.1 Comparison of Data in This Study and Other Cities in Turkey 51
4.2.2 Comparison of Data in This Study and Other Cities around the World 55
4.3 Temporal Variations in VOC Concentrations 57
4.3.1 Episodic Variations in VOC Concentrations at AU and METU Stations 57
4.3.2 Weekday – Weekend Variations in VOC concentrations at AU and METU Stations 68
4.3.3 Long – term (seasonal) Variations in VOC Concentrations at AU and METU Stations 70
4.3.4 Year – to – Year Variations in VOC Concentration at AU and METU Station 78

4.4 Dependence of Measured Concentrations of VOCs on Local Meteorology 82
4.4.1 Effect of Temperature 82
4.4.2 Effect of Wind Speed 86
4.4.3 Effect of Mixing Height 86
4.4.4 Effect of Ventilation Coefficient 90
4.5 Sources contributing to VOC compositions 93
4.5.1 PMF Results at METU Station 93
4.5.2 PMF Results at AU Station 104
5 CONCLUSION AND FUTURE WORK 119
REFERENCES 123

LIST OF FIGURES

Figure 3.1 AU and METU stations on Ankara map 18
Figure 3.2: Sampling Stations 19
Figure 3.3: Canister and sampling kit 20
Figure 3.4: Canister cleaning system 21
Figure 3.5: Analytical system 24
Figure 3.6: Sample chromatogram 25
Figure 3.7: Chromatogram of 600 ml standard gas mixture analysis 28
Figure 3.8 Calibration curves for some VOCs (Uzunpınar, 2015) 29
Figure 3.9: Precision of sampling kit 34
Figure 3.10: Precision of analysis for BTEX compounds 35
Figure 4.1 Frequency distributions of BTEX at AU 49
Figure 4.2 : Frequency distributions of BTEX at METU 50
Figure 4.3: Comparison of BTEX concentrations measured at urban and suburban stations in this study with BTEX concentrations reported for other cities in Turkey 53
Figure 4.4: Episodic variations in concentrations of selected VOCs at AU and METU stations 59
Figure 4.5: Coefficient of variation (relative standard deviation) of measured VOCs at two stations 60
Figure 4.6: Percent contribution of episodes on average concentrations of VOCs at AU and METU stations 67
Figure 4.7: Weekday, weekend concentrations and WD-to-WE concentration ratios of VOCs at AU and METU stations 69
Figure 4.8: Winter-to-summer concentration ratios of VOCs at AU and METU stations 73
Figure 4.9: VOCs, which show well-defined seasonal patterns at AU and METU stations 76

Figure 4.10: VOCs, which do not show well-defined seasonal patterns at AU and METU stations 77
Figure 4.11: Long-term changes in concentrations of VOCs in Ankara atmosphere 81
Figure 4.12: Variation of BTEX compounds with temperature at urban and suburban stations 84
Figure 4.13: Elements that shows increasing concentrations at high temperatures in both stations 85
Figure 4.14: Dependence of VOC concentrations at urban and suburban stations on wind speed 87
Figure 4.15: Wind frequency distribution during sampling campaigns 88
Figure 4.16: Variation of VOC concentrations with mixing height: VOC that decrease with mixing height 89
Figure 4.17: Variation of VOC concentrations with mixing height: VOC that does not vary with mixing height 90
Figure 4.18: Variation of VOC concentration with ventilation coefficient: VOCs with concentrations decreasing with VC 92
Figure 4.19: Variation of VOC concentration with ventilation coefficient: VOCs with concentrations independent of VC 92
Figure 4.20: Factor 1 diagnostic figures at METU station 98
Figure 4.21: Factor 2 diagnostic figures at METU station 99
Figure 4.22: Factor 3 diagnostic figures at METU station 100
Figure 4.23: Factor 4 diagnostic figures at METU station 101
Figure 4.24: Factor 5 diagnostic figures at METU station 102
Figure 4.25: Factor 6 diagnostic figures at METU station 103
Figure 4.26: Factor 1 diagnostic figures at AU station 109
Figure 4.27: Factor 2 diagnostic figures at AU station 110
Figure 4.28: Comparison of compositions of gasoline evaporation factors generated at urban and suburban stations 111
Figure 4.29: Comparison of compositions of asphalt profile generated in this work with asphalt profile found in Bursa study 111

Figure 4.30: Factor 3 diagnostic figures at AU station 112
Figure 4.31: Factor 4 diagnostic figures at AU station 113
Figure 4.32: Factor 5 diagnostic figures at AU station 114
Figure 4.33: Comparison of compositions of industrial evaporation factors generated at urban and suburban stations 115
Figure 4.34: Comparison of compositions of diesel profiles generated at urban and suburban stations 115
Figure 4.35: Factor 6 diagnostic figures at AU station 116
Figure 4.36: Comparison of compositions of gasoline exhaust profiles generated at urban and suburban stations 117
Figure 4.37: Contribution of factors to total VOC concentrations at urban and suburban stations 118

LIST OF TABLES

Table 3.1: Target VOCs (Uzunpinar, 2015) 22
Table 3.2: Thermal desorber parameters (Uzunpınar, 2015) 25
Table 3.3: GC column and oven properties (Uzunpınar, 2015) 26
Table 3.4: R^2 values for calibration of each compound (Uzunpınar, 2015) 29
Table 3.5: Average and median field blank values and method detection limits 32
Table 3.6: Calibration check results (Uzunpınar, 2015) 36
Table 4.1: Summary statistics of data at AU station 43
Table 4.2: Summary statistics of data at METU station 46
Table 4.3: BTEX Mean concentrations (µg /m^3) in this work and corresponding concentrations reported in other cities in Tukey 54
Table 4.4: BTEX concentrations (mean) measured in this study and corresponding concentrations reported for other cities around world 56
Table 4.5: Baseline concentration values of VOCs calculated using different definitions 65
Table 4.6: Average and baseline concentrations (µg/m^3) of VOCs at AU and METU stations 65
Table 4.7: Summer and Winter Concentrations (µg/m^3) of Measured VOCs at AU Station 71
Table 4.8: Variation of VOC median concentrations (µg/m^3) between 2003 and 2015 in Ankara 80
Table 4.9: Factor loadings at METU station (µg/m^3) 93
Table 4.10: Factor loadings at AU station (µg/m^3) 104

LIST OF ABBREVIATIONS

APCS: Absolute Principal Component Scores

AU: Ankara University

AVOC: Anthropogenic Volatile Organic Compounds

BTEX: Benzene, Toluene, Ethylbenzene, Xylenes

BVOC: Biogenic Volatile Organic Compounds

CV: Coefficient of Variation

CMB: Chemical Mass Balance

EDGAR: Emissions Database for Global Atmospheric Research

ENVE: Environmental Engineering

EU: European Union

FA: Factor Analysis

GC/FID: Gas Chromatography/Flame Ionization Research

GC/MS: Gas Chromatography/Mass Spectrometry

LPG: Liquefied Petroleum Gas

METU: Middle East Technical University

MH: Mixing Height

NMHC: Non-methane Hydrocarbons

PAH: Polycyclic Aromatic Hydrocarbons

PAMS: Photochemical Assessment Monitoring Stations

PCA: Principle Components Analysis

PM: Particulate Matter

PMF: Positive Matrix Factorization

RSD: Relative Standard Deviation

SD: Standard Deviation

S/W: Summer/Winter

U.S.EPA: United States Environmental Agency

VC: Ventilation Coefficient

VOC: Volatile Organic Compound

WD/WE: Weekday/Weekend

WHO: World Health Organization

WS: Wind Speed

CHAPTER 1

INTRODUCTION

Volatile organic compounds (VOCs) have many definitions by different institutions but they are quite similar to each other. According to the definition of Environment Canada, VOCs are organic compounds, which contain one or more carbon atoms with high vapor pressures and evaporate readily to the atmosphere. Also, according to U.S. EPA, VOCs are described as any carbon containing compounds whose vapor pressure is greater than 10^{-1} torr under normal conditions, except carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, ammonium carbonate.

VOCs have a plenty of sources and have major effects on human health and the environment. For that reason, determination, quantification and source apportionment of VOCs in the atmosphere are very essential.

Identification of sources of VOCs allows prioritizing those sources that contribute most significantly to exposures, and target subpopulations with elevated exposure levels. Very little is known about the health effects of individual compounds, however, and still less about sources of these compounds that contribute to daily exposures. In addition, although exposure to several of these pollutants has been associated with adverse health effects and, in spite of VOC studies; little was known about exposure levels of these compounds (Edwards et al., 2001).

Thanks to studies like this one, the exposure levels, sources and health effects of VOC concentrations have identified. Accordingly, the need for reduction of VOC concentration has been demonstrated and legal regulations related this issue have been adopted.

1.1 Purpose of the Study

The purposes of this study are listed below:

- To determine long term trends in VOC concentrations between 2005 and 2015,
- To observe differences between suburban and urban atmosphere of Ankara in terms of VOC,
- To understand temporal and spatial variations in VOC concentrations and factors causing the variability,
- To understand sources of VOCs that are responsible from observed levels in urban and suburban Ankara atmosphere.

1.2 Layout of the Study

In Chapter 2, typical features of volatile organic compounds are briefly explained. Also, information about sources of and effects of VOCs are given. Furthermore, VOC emission control legislations in terms of national and international regulations are provided. Finally, source apportionment methodology and related studies conducted around the world are mentioned briefly.

In Chapter 3, study areas are introduced and information about sampling time is given. After that, sampling and analytical methodologies are mentioned. Finally, PMF and the application of the software in this study is explained.

In Chapter 4, descriptive statistics of data obtained in this study are given. Then, data in this study are compared with previous studies in Turkey and around the world. Temporal variations in VOC concentration are mentioned. Moreover, the relationship between meteorology and the results are discussed. Finally, result of the source apportionment study with PMF are provided and discussed in detail.

In Chapter 5, the whole study is clarified briefly and suggestions for future studies are given.

CHAPTER 2

LITERATURE REWIEV

2.1 Volatile Organic Compounds

Volatile organic compounds (VOCs) can be defined as carbon-based chemicals with high vapor pressure at room temperature; i.e., greater than 0.01 kPa at 20 °C (Goodman et al., 2017). VOCs are moving freely between water and air phases due to their physical and chemical properties. Since they have low boiling points they can easily evaporate at room temperature. As they have mobility, VOCs can be found everywhere in the environment.

Tremendous amounts of VOCs are released into atmosphere from different kinds of sources such as vehicle exhaust, solvent usage, agriculture, gasoline evaporation and natural gas usage. Most of the VOCs pose a risk to human health and adverse effects on the environment. Therefore, investigating the processes influencing the concentration and distribution of VOCs is crucial (Rathbun, 2000; Yurdakul, 2014; Kim et al., 2017). In addition, VOCs are important because they take a part in photochemical reactions in atmosphere, which leads to ozone formation (U.S.EPA, 2014). Accordingly, the nations of the world have limited the emissions of VOCs in order to eliminate these adverse effects on both human and the environment.

In order to be more specific about VOCs, sources, effects and legislations of VOCs will be mentioned in the next sections. In addition, source apportionment technique and studies related to VOCs will be discussed.

2.2 Sources of Volatile Organic Compounds

VOCs in the atmosphere can be released by diverse sources and they can be reviewed under two headings as natural sources and anthropogenic sources.

Volatile organic compounds that are emitted from vegetation are called as biogenic volatile organic compounds (BVOC). Emissions of total biogenic organic volatile compounds are estimated as 1150 TgC per year. When BVOCs are released to the atmosphere, they start to be oxidized by ozone and form secondary pollutants.

Although the amount of BVOCs released into atmosphere are much higher than anthropogenic volatile organic compounds it is difficult to measure this amount due to diverse nature of source pathways. In addition, the biogenic sources are not seen as important as the anthropogenic ones. BVOCs include alkanes, alkenes, carbonyl groups, acids, esters, ethers, alcohols and isoprenoids (Loreto and Fares, 2013; Ahn et al., 2016). Leaves, flowers and roots, in other words, plant growth, development, reproduction and defense of plants produce BVOCs (Laothawornkitkul et al., 2009).

On the other hand, volatile organic compounds emitted from various human activities are called as anthropogenic volatile organic compounds (AVOC). Anthropogenic sources of volatile organic compounds can be categorized under four headlines according to USEPA's Report on Environment. The first one is fuel combustion. Fuel combustion includes emissions power plants and industrial, commercial, and institutional sources, in addition to residential heaters and boilers. The second one is other industrial processes, which involves chemical and metals production and petroleum refining. The third anthropogenic sources of VOCs are on-road vehicles, which contains cars, trucks, and motorcycles. The fourth and the last group of VOC sources are non-road vehicles and engines such as farm and construction equipment, chainsaws, boats, snowmobiles, and aircrafts.

In the recent years, among these anthropogenic sources, motor vehicle exhaust has become more important due to increasing urbanization (Han and Naeher, 2006). Also, fossil fuel combustions are the most outstanding AVOCs emissions source.

Technically, complete combustion of fossil fuels cannot occur and due to incomplete combustion, VOC concentrations are increasing (Friedrich and Obermeier, 1999).

Total AVOCs emissions are estimated as 142 TgC year^{-1} and some of AVOCs are regulated by national and international criteria (Ahn et al., 2016). 27 Tg/year of AVOCs are produced by industrial use of solvents and 4.09 Tg/year of them are caused by agricultural waste burning (EDGAR, 2008; Williams and Koppmann, 2007).

2.3 Effects of Volatile Organic Compounds

One of the most harmful air pollutants are volatile organic compounds. They can be easily evaporated and transported to atmosphere. VOCs have many pollution risks including photochemical ozone formation and its mutagenic and carcinogenic effects on human health (Ismail and Hameed, 2013). It is more logical to investigate the effects of VOCs under two headings as effects on human health and environment.

VOCs may lead to different health effects depending on the chemical characteristics. For example, formaldehyde inhalation could aggravate asthma symptoms (Casset et al., 2005) while exposure dosage to benzene is closely linked to childhood leukemia (Zhou et al., 2014). There are two types of health effects of VOCs, which are chronic and the acute ones. Chronic health effects are based on exposure to small amount of a compound over long time while acute health effects are based on single exposure to a high amount of a compound. For instance, recent studies have shown that chronic exposure to traffic-related, petrochemical, and chemical industry pollutants such as suspended particles, hydrocarbons, volatile organic compounds, ozone and NOx, are associated with adverse health effects such as, decreased lung function, increased respiratory morbidity, and increased mortality, especially in children (WHO, 2006). The most important issue about health effects of VOCs is their toxic and carcinogenic health effects at different exposure levels. VOCs are sorted incompliance with unknown health effects to extremely toxic or carcinogenic effects

(Ramírez, 2012). Usually, chronic health effects of VOCs are classified as either carcinogenic or non-carcinogenic. Non-carcinogenic effects are delineated as irritative, sensorial impacts, destruction in the liver, kidney and nervous system, asthma and other severe respiratory effects. According to World Health Organization (WHO), carcinogenic effects of VOCs appear generally in lung, blood, liver, kidney, respiratory system and biliary tract. For example, according to International Agency for Research Cancer, benzene is classified as one of the most important human carcinogen. (Ramírez, 2012).

There are three main concerns about effects of VOCs on environment namely, tropospheric photochemical ozone formation, stratospheric ozone depletion and effects on climate change. All of them will be mentioned briefly under three headings:

Tropospheric Photochemical Ozone Formation:

Tropospheric ozone, which is a secondary pollutant, is originated from VOCs with the presence of sunlight and nitrogen oxides. Not all VOCs contribute evenly to photochemical ozone formation. Some of them have higher tendency to form oxidants while some of them are unreactive. (Garzon et al., 2015; Derwent, 2015).

In a study conducted by Carter, six VOCs sensitive conditions were determined according to their reactivity potentials and impacts on O_3 formation and these conditions are called as Maximum Incremental Reactivity (MIR). In order to assess ozone production potential of a compound, MIR value of that compound is multiplied with its concentration. For example, MIR value of trans-2-butene is higher than to 10, which means more than 10 grams of ozone can be produced from 1 gram of trans-2-butene (Carter, 1994).

Stratospheric Ozone Depletion:

Volatile organic compounds have an indirect effect on stratospheric ozone depletion but its role is important. In the atmosphere, most of the organic compounds are in a steady state. In addition, they can play a role in tropospheric removal reactions and they can reach to the stratosphere. Particularly, bromine and chlorine groups containing organic compounds leads to hydroxyl radicals destruction and accordingly, ozone destroying processes are activated (Derwent, 1995).

Climate Change:

As mentioned above, volatile organic compounds are considered as ozone precursor and since ozone is a greenhouse gas, they indirectly affect climate change. Most of the volatile organic compounds are simply oxidized in the atmosphere. Still, during some metrological events, some VOCs accumulate in the troposphere. These accumulative and long-lived compounds are classified as radiative active gases. They absorb solar radiation, and stimulate ozone formation in free troposphere (Bek, 2015).

2.4 VOC Emission Control Regulations

In previous sections, sources and effects of volatile organic compounds were mentioned. Since they have various sources and many adverse effects on human health and the environment, there are some national regulations in order to control the VOC emissions. In this section, these regulations and regulations around the world will be summarized.

2.4.1 National Regulations

In Turkey, VOCs are mentioned in and regulated by three different regulations. First one is Air Quality Assessment and Management Regulation (AQAMR) which was forced in 2008 (MoEU, 2008). In AQAMR, there is a list for recommended VOCs to be monitored under ozone precursor measurements. In this list, there are thirty VOCs including benzene, toluene and other hydrocarbons excluding total methane. Among all compounds in the list, only benzene has a concentration limit, which is 5 µg/m^3 for annual average amount. The second one is Regulation on Control of Air Pollution

Originating from Industry which was forced in 2009 (MoEU, 2009). This regulation put air quality limits regarding petroleum rafineries, photochemical industries and fuel and petroleum storage plants. In addition, in this regulation there are parameters for some VOCs such as benzene, toluene, isopropyl, xylene and ethyl benzene. The third and the last regulation related to VOCs is Regulation on Exhaust Emissions Control and Gasoline and Diesel Fuel Quality which was forced in 2013 (MoEU, 2013). This regulation also put a limit on benzene for gasoline fuels.

2.4.2 Regulations around the World

VOCs are the concern of most of the developed and developing countries. In this section, especially regulations in European Union, United States and Canada will be mentioned since their approaches and regulations towards the environment and human health is abounding, strict and pioneer to the other countries.

2.4.2.1 European Union

In European Union (EU), there are plenty of directives related VOCs. Common purpose of these directives is to protect the human health and environment as well as pollution reduction measurements. Outstanding directives are listed as follows:

- European Parliament and Council Directive 94/63/EC on the control of volatile organic compound (VOC) emissions resulting from the storage of petrol and its distribution from terminals to service stations (European Commission, 1994)
- Directive 2000/69/EC of European Parliament and Council relating to limit values for Benzene and Carbon Monoxide in ambient air (European Commission, 2000)
- Directive 2001/81/EC of the European Parliament and Council on national emission ceilings for certain atmospheric pollutants (European Commission, 2001)

- Directive 2003/17/EC of the European Parliament and of Council relating to the quality of petrol and diesel fuels sets maximum concentrations of olefins, aromatics and benzene for gasoline fuel (European Commission, 2003)
- Directive 2004/42/CE of the European Parliament and of the Council on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain paints and varnishes and vehicle refinishing products (European Commission, 2004)
- Directive 2008/50/EC of European Parliament and Council on ambient air quality and cleaner air for Europe (European Commission, 2008)

Among these regulations, benzene is the only VOC with specific provision. Lower and upper assessment threshold limits for benzene are 2µg m^{-3} and 3 µg m^{-3}, respectively. In addition, limit value of benzene for human health is provided as 5 µg m^{-3}.

2.4.2.2 U.S. Environmental Protection Agency (U.S. EPA)

In the United States, the Clean Air Act authorizes the U.S. EPA for putting limitations to emissions of certain air polluters. States may have their own laws stricter than U.S. EPA but they are not allowed to have limits lower than the U.S. EPA.

Since VOCs are precursors of O_3, they are regulated in the scope of air quality standards regarding O_3. In order to reduce the VOC levels, National Ambient Air Quality Standards for Ground-Level Ozone appoint control actions and provide simulation results for O_3 according to changes in NOx and VOC concentrations. National Ambient Air Quality Standards for Ozone decide some VOC measurement protocols since VOCs are O_3 precursors. With these protocols, they are aiming to obtain better model results (U.S.EPA, 2008).

PAMS stations were established by the USEPA to determine levels of VOCs that are responsible for tropospheric ozone formation in the US. Volatile organic compounds and NOx were measured in all PAMS stations. First PAMS station was established in 1994 (U.S.EPA, 2014b). Non-methane hydrocarbons measured in PAMS stations include 55 compounds with carbon numbers C2 to C12. There are > 300 VOCs available in the atmosphere. Fifty-five of these that are measured at PAMS network are the ones that are expected to contribute tropospheric ozone formation.

In addition, with The Canada-United States Air Quality Agreement, United States had an agreement in order to reduce the emissions of specific pollutants for preventing the transboundary air pollution (Environment Canada, 1991).

2.4.2.3 Environment Canada

In Canada, some VOCs are the subgroup of Criteria Air Contaminants of Environment Canada. Environment Canada published some regulations for monitoring and the reduction of VOCs. Two direct regulations regarding VOCs, which are Volatile Organic Compound Concentration Limits for Architectural Coatings Regulations and Volatile organic Compound Concentration Limits for Automotive Refinishing Product Regulation, put limits to VOCs. In addition, Benzene in Gasoline Regulations is aiming to reduce benzene emissions form gasoline vehicles and put a limit to benzene in gasoline as 1.5% by volume (Environment Canada, 1997). Lastly, “Volatile Organic Compound Concentration Limits for Certain Products Regulation” regulates the 98 product categories by limiting the VOC concentrations (Environment Canada, 2008).

2.5 Source Apportionment

Source Apportionment is a method of deriving information about pollution sources and the amount of contributions to air pollution levels. For source apportionment studies, different models and approaches are used. There are two approaches to source apportionment studies as receptor-oriented and source-oriented models.

For source-oriented models, firstly profiles of sources should be known. Emissions from probable sources are followed and confirmation of the model is achieved by comparison between measured and predicted concentrations. Among these types of models Chemical Mass Balance (CMB) is the most known and used model in many studies (Bek, 2015). CMB has been applied to air quality problems over the last decades (U.S.EPA, 2016). CMB is applied to each data individually, rather than to all collected data and contribution of source types should be identified before the model run. There are six assumptions used in CMB model, which are;

- compositions of source emissions are constant over the period of ambient and source sampling,
- chemical species do not react with each other,
- all sources with a potential for significantly contributing to the receptor have been identified and have had their emissions characterized,
- the number of sources or source categories is less than or equal to the number of species,
- the source profiles are sufficiently different from one another,
- measurement uncertainties are random, uncorrelated, and normally distributed (Sosa et al., 2009; Watson et al., 2001).

In receptor-oriented models, there is no certain information about profiles of sources at the beginning. As an input to models, chemical measurements are used and according to these measurements source compositions are clarified. However, introductory knowledge about tracers is crucial for identification studies since there might be more than one source for one tracer. For that purpose, additional data e.g. pollution roses might be used (Doğan, 2013). Positive Matrix Factorization (PMF), Principle Component Analysis (PCA), Unmix and Factor Analysis (FA) are the mostly used receptor oriented models (Uzunpınar, 2015). In this study, for source apportionment of VOCs in the rural and urban Ankara atmosphere, Positive Matrix Factorization (PMF) was performed.

2.5.1 Positive Matrix Factorization

Positive Matrix Factorization (PMF) is one of the widely used advanced receptor-modeling algorithms, which solves (factor-analyses) problems using least square method without any source profile requirement (Paatero and Tapper, 1994). PMF is used not only for VOCs but also for 24-h PM 2.5, size resolved aerosol, toxic air compounds, and aerosol (Brown et al, 2007).

As stated in EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide, PMF is a multivariate factor analysis tool that breaks down a matrix of sample data into two matrices: factor contributions "G" and factor profiles "F". The user defines these factor profiles in order to identify the source types that might be contributing to the sample with measured source profile information, and emissions. Results are procured using the constraint that no sample can have somewhat contribution of negative sources. PMF works with sample concentration and uncertainty data.

The PMF model minimizes the objective function Q. Q is a critical parameter for PMF which derives factor contributions. Factor profiles and two versions of Q are displayed which are Q_{true}, and Q_{robust} for the model run. Q_{true} represents the goodness-of-fit parameter calculated including all points and Q_{robust} represents the goodness-of-fit parameter calculated excluding points not fit by the model, defined as samples for which the uncertainty-scaled residual is greater than 4.

Impact of data points with high-scaled residuals is measured by the difference between Q_{true} and Q_{robust}. These data points might be associated with peak impacts from sources, which are not always present during the sampling duration. Also, the uncertainties may be too high, which result in similar Q_{true} and Q_{robust} values since the residuals are scaled by the uncertainty. PMF needs multiple iterations of the underlying Multilinear Engine in order to help recognize the most optimal factor contributions and factor profiles. This factor profile is consistently adjusted using the gradient approach to chart the optimal path to the best-fit solution. The best solution is recognized by the minimum Q_{robust} value.

2.6 Source Apportionment Studies around the World

In the literature, there are many studies related to source apportionment of VOCs. As it was mentioned previous sections, different types of approaches and techniques were used for source apportionment studies around the world. In this section, some of these studies will be introduced.

Sosa et al. (2009) used CMB model for source apportionment of VOCs in southwestern area of Mexico City. Thirteen VOCs were measured at three stations: Gasoline refueling station (GC), a Condominium area (CA) and University Center for Atmospheric Sciences (CAS). Samples were collected with canisters and the quantification of VOCs concentration was done with GC - Flame Ionization Detector (GC-FID). CMB model results show that in CAS, LPG evaporation was the major source of VOCs with average contribution of 52% due to presence of LPG tanks on the building's roof. During early morning hours, temperature is rising and accordingly, evaporation of VOCs from the leaks of tanks and refilling activities are increasing. The second important dominant source o was vehicle exhaust with 25% contribution. Asphalt pavements, food cooking and solvents were the other sources with 14%, 5% and 3% contributions, respectively. Same trend was observed in CA. Important emission sources were LPG (42%), vehicle exhaust (28%), asphalt works (12%), food cooking (10%) and use of solvents (4%). In GC, the source contributions are quite different according to other two sites. It is important to note that at the GC, samples were taken so close to the ground level and the air was not well mixed, so that is why there is a great variation in the concentrations. At GC, most of the emissions were coming from fuel evaporation and gasoline from vehicles. Exhaust emission contribution (45%) was followed by LPG with 21% contribution and contribution of evaporative gasoline was found as 17%.

Another study with CMB was mentioned by Brown et al. (2007). In this study, PMF was applied for VOCs in two different sites namely Azusa and Hawthorne in Los Angeles, USA and the data were compared with CMB model results of previous studies. According to PMF, five and six factors were identified in Azusa and

Hawthorne, respectively. Four factors were identical in two sites which were evaporative emissions, liquid/unburned gasoline, motor vehicle exhaust and biogenic emissions. In Azusa, in addition to these factors, there was coating. On the other hand, in Hawthorne, natural gas and industrial processes were the two other factors. Comparing results from PMF with CMB, they were quite different possibly due different number of samples and time periods.

In Edmonton, Alberta, Canada, McCarthy et al. (2013) studied air samples for over seventy-seven VOCs in two sampling stations. One of the stations was in the downtown area (Central Site) and the other one was in the industrial area (East site). VOC concentrations reached highest values at East site. For source apportionment, PMF model was used and eleven factors including transportation combustion, industrial sources, biogenic sources, natural gas related sources and global background pollutants were identified. Transportation sources have higher contribution in Central site while industrial sources have higher contribution in East site. In East site, five independent industrial factors were classified. On the other hand, major contributing factors in Central site were diesel and gasoline combustion. At both sites, biogenic emissions and natural gas source were other important contributors.

Up to now, all examples were given from America continent. When it comes to Asia, in a study conducted in urban atmosphere, Taipei, Taiwan, source apportionment with PMF was applied to 24-h fine particulate matter ($PM_{2.5}$) and hourly collected VOCs. In PMF model, nine factors were determined including, natural gas/LPG leakage, solvent use/industrial process, contaminated marine aerosol, secondary aerosol/long-range transport, oil combustion, traffic related, evaporative gasoline emission, gasoline exhaust, and soil dust (Liao, 2017). The largest contribution was from solvent use for VOCs while secondary aerosol/long range transport for $PM_{2.5}$.

Another example study in Asia is source apportionment of VOCs in the suburban area of Beijing, China (Wang et al., 2016). Sampling site was chosen to represent a mixed residential environment, educational activities and traffic of suburban area.

Canisters were used for sampling and Gas Chromatography-Mass Spectrometry (GC-MS) was used to analyze samples. In this study, for source apportionment purpose,

PMF was applied as receptor model and according to output data of PMF, vehicle exhaust was the major emission source for both sampling periods. Three factors were described including source of LPG and natural gas, gasoline vapor and industrial production and vehicle exhaust.

The other study with PMF was chosen from Europe, France. Sauvage et al. (2009) used VOC concentrations measured between 1992 and 2002 from three different rural sampling sites for source apportionment study with PMF. Five similar factors were determined for three sites, which are evaporative sources, residential heating, vehicle exhaust, remote sources and biogenic sources. Evaporative sources were containing mainly ethane, propane, isopentane, n-pentane and n-butane. In addition, for remote sources ethane and propane were the predominant compounds. Since their reactivity is low, they are commonly associated with the contribution of old air masses carried towards the sampling sites.

In another example of source apportionment study in Europe, is from Belgrad, Serbia. In this study, 36 VOCs were measured with Proton Transfer Reaction Mass Spectrometer. Also, two receptor models which are PMF and Unmix were used and compared for source apportionment in an urban site. In both models, there were six factors. These six factors were listed as, traffic-related emissions, gasoline evaporations/oil refinery, petrochemical industry/biogenic emissions, aged plumes, solid fuel burning and local laboratory. The Unmix source profiles showed good correlation with the profiles obtained by PMF. Although both models have good performance in reproducing main factors affecting air quality, it might be hard to estimate which model provided the physically most reasonable results (Stojic et al., 2015).

Duodu et al. (2017) used both PMF receptor model and analyses/absolute principal component scores (PCA/APCS) receptor model for fifteen polycyclic aromatic hydrocarbons (PAHs) in Brisbane River sediment, Australia with the scope of source apportionment study. The quality of the PCA/APCS model was evaluated using the predicted PAH concentrations against the measured concentrations. Both, PCA/APCS and PMF concluded four identical factors of PAHs, namely gasoline emissions, diesel emissions, natural gas combustion and biomass burning. PCA/APCS and PMF analysis pointed out that vehicular emissions were the fundamental sources while biomass burning had temperate contribution.

CHAPTER 3

MATERIAL AND METHODS

3.1 Study Area

Ankara is the capital city of Turkey which has 5,346,518 residents according to last population census in 2016 (Turkish Statistical Institude, 2017). The dominant climatic type is continental and annual average temperature is 14 °C. Also, the city is located 890 m above the sea level and the surface area of the city is 26.897 km^2 (Turkish State Meteorological Service, 2016).

In this study, two sampling stations were established in Ankara, one of these stations was located at Ankara University, Faculty of Agriculture, and the other one was located at the METU Campus, behind the environmental engineering department.

3.1.1 Ankara University, Faculty of Agriculture Campus

One of the sampling stations was located in Ankara University, Faculty of Agriculture (AU) (39°57'24.74"N, 32°51'45.19"E). The location of AU station on Ankara map is depicted in Figure 3.1(a) and a picture of the station is depicted in Figure 3.2(a). The AU station represents urban atmosphere and thus referred to as “urban station” in this study since it was located in city center and close to main roads and possible pollution sources. The station was nearly 200 meters from Turgut Özal Boulevard, 380 m from Fatih Boulevard and even closer to Irfan Baştuğ Boulevard. It is also surrounded by dense settlement areas. Thus, AU station was a typical urban station. Potential sources of VOCs in this station are vehicle exhaust, gasoline evaporation, diesel, industrial and solvent emissions. VOC sampling was not the only sampling study in the station. Samples for trace element analysis, for analysis of secondary organic particles (SOP) were also collected. The station consisted of a platform with diameters 10m x 10m which is surrounded by a fence.

Figure 3.1 AU and METU stations on Ankara map

3.1.2 Middle East Technical University, Environmental Engineering Department

The other sampling station was located in Middle East Technical University, Environmental Engineering Department (METU) (39°53'12.19"N, 32°46'59.77"E), which is shown in Figure 3.1(b) and Figure 3.2(b). METU station is far from most major VOC sources, particularly from major roads with heavy traffic. Accordingly, the METU station represents suburban atmosphere and thus referred to as “suburban station” in this study. The distances between this site and Malazgirt Boulevard, Bilkent Boulevard and Eskişehir Highways are 1.3 km, 1.6 km and 2.4 km, respectively. Potential VOC sources in this station are similar to AU station which are, vehicle exhaust, gasoline evaporation, diesel, industrial and solvent emissions (Uzunpınar, 2015).

Figure 3.2: Sampling Stations

3.2 Sampling Schedule

Sampling in METU was started earlier than AU. Data collection was started in January, 2014 and ended in September, 2015 in METU. During this period, 323 daily samples were collected. The sampling in AU was started in June, 2014 and ended in September, 2015. In AU station, 236 daily samples were collected. During AU sampling period, there was a one month of gap in February, 2015 due to malfunction of flow controller in vacuum gage. After rectifying the fault, sampling was continued until September, 2015 without any interruption.

3.3 Sampling Methodology

Air samples for VOC analysis were collected into 6-L-capacity stainless steel SUMMA polished canisters using a RESTEK flow-controlled intake head. Both the canister and intake-head are shown in the Figure 3.3. There are different types of VOC samplers such as tedlar bags and sorbent tubes and they have different advantages and disadvantages relative to each other. Canister sampling is preferred in this study, since (1) wider range of hydrocarbons can be measured with canisters. Sorbents, on the other hand cannot collect light VOCs ($C < 5$ or at best $C < 4$) efficiently. (2) Multiple analysis is possible with canisters, whereas only one analysis can be performed with sorbent tubes.

Sampling head, which is nothing but a flow controller, was used to restrict the sample flow into canister at a requested level. Canister was first evacuated then, in the field, vacuum is released by slowly sucking air into the canister. Air intake rate was adjusted (with the flowmeter in the sampling head) to 2.8 – 3.5 ml min^{-1}. At this flow rate range vacuum is entirely released in 24 hours, which means ambient air is sucked into the canister, at the same flow-rate for 24 hours. Which, of course, means daily-sampling.

Figure 3.3: Canister and sampling kit

3.3.1 Preparation of Samples for Analysis

Sample processing in canister sampling consisted of three steps; (1) cleaning canister, (2) evacuation of canister for sampling and (3) pressuring canister after sampling. U.S.EPA method TO-14-A/15 (U.S.EPA, 1999a, 1999b) was followed to clean canisters. In the cleaning step, canisters were connected to the vacuum line, which is shown in Figure 3.4 and started coated with heating jackets. Then they are pressurized with humidified high-purity nitrogen to 10 inHg. Canister was allowed to stay under pressure for 30 minutes. After 30 minutes, canisters were evacuated to –27 inHg. This cycle (pressuring to 10 inHg and evacuation to -27 inHg) was repeated for three times. After final pressuring, canisters were evacuated to -27 inHg for sampling. Clean canisters were ready to be send to stations. According to TO-14-A/15, if concentration of VOCs were lower than 0.2 ppbv or lower than 10% of the background air concentrations, the canisters could be considered as clean. In order to test this criteria, after cleaning process, canisters were pressurized with dry nitrogen and analyzed for our target VOCs. This contamination check was performed from time-to-time.

Canisters were under slight vacuum (-5 inHg) when they were returned to laboratory after daily sampling. In the lab, they were pressurized with high purity dry nitrogen to atmospheric pressure level (14.7 psi) to be able to provide the gas flow into GC-FID system. Before starting, the analysis samples were waited approximately 1 hour in order to get homogenous sample distribution inside the canister.

Using this procedure 236 samples were collected at urban station. Since suburban station was started earlier, 323 samples were collected at the suburban site.

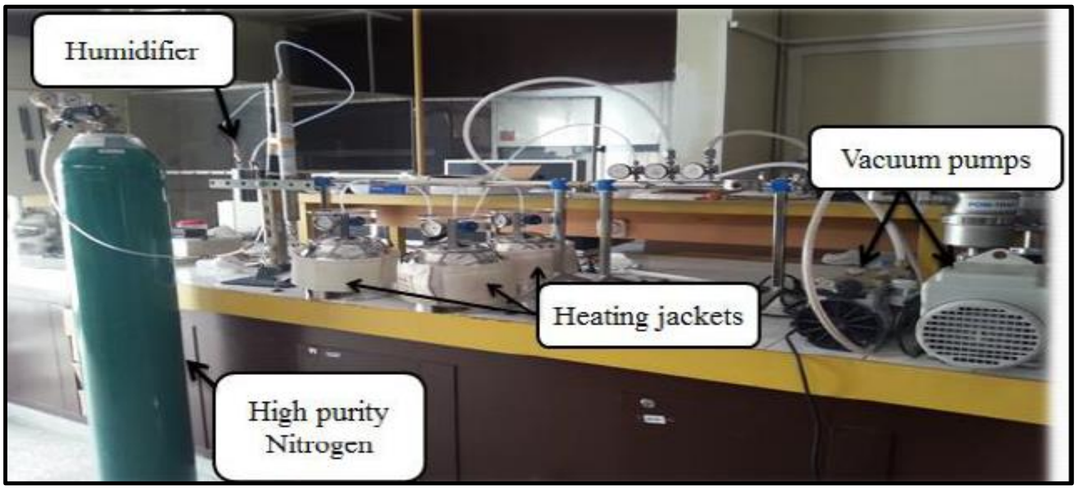


Figure 3.4: Canister cleaning system

3.4 Analytical Methodology

3.4.1 Target Volatile Organic Compounds

In study 51 out of 55 VOCs, which are routinely measured in Photochemical Assessment Monitoring Stations (PAMS) stations, which are operated by USEPA are measured. Fifty-one of 55 PAMS NMHCs are measured in this study. List of these 51 compounds are given in Table 3.1.

Table 3.1: Target VOCs (Uzunpinar, 2015)

Compounds	CAS No	Retention Time (min)	Boiling Point (^{0}C)
Ethane	74840	8.50	-88
Ethylene	74851	9.46	-104
Propane	74986	11.62	-42
Propylene	115071	12.94	-47.7
Isobutane	75285	13.65	-12
Acethylene	74862	14.55	-28
Trans - 2 - Butene	624646	16.69	1
1 - Butene	106989	16.99	-6.47
Cis-2-Butene	590181	17.59	3.7
Cyclopentane	287923	18.18	49.2
Isopentane	78784	19.10	28
n - Pentane	109660	19.89	36
Trans - 2 - Pentene	646048	22.51	37
1 - Pentene	109671	23.32	30
Cis-2- Pentene	627203	23.96	36-37
2,2-Dimethylbutane	75832	24.65	50
2,3-Dimethylbutane	79298	25.36	58
2-Methylpentane	107835	25.53	62
3-Methylpentane	96140	25.70	64
Isoprene	78795	27.26	34
n-Hexane	110543	13.84	68.95
2,4-Dimethylpentane	108087	15.33	80.5
Benzene	71432	16.58	80.1
Cyclohexane	110827	17.06	81
2-Methylhexane	591764	17.23	90
2,3-Dimethylpentane	590352	17.41	79.2
3-Methylhexane	589344	17.71	92

Table 3.1 cont'd: Target VOCs (Uzunpinar, 2015)

Compounds	CAS No	Retention Time (min)	Boiling Point (^{0}C)
2,2,4-Trimethylpentane	504841	18.48	99.24
n-Heptane	142825	18.91	98.42
Methylcyclohexane	108872	20.33	100.9
2,3,4-Trimethylpentane	565753	21.70	113.4
Toluene	108883	22.08	110.6
2-Methylheptane	592278	22.33	116
3-Methylheptane	589811	22.74	115
n-Octane	111659	24.00	125.7
Ethylbenzene	100414	26.82	136.2
p-Xylene	106423	27.23	138
Styrene	100425	28.12	145
o-Xylene	95476	28.35	144
Nonane	11842	28.73	151
Isopropylbenzene	98828	28.78	151
n-Propylbenzene	103651	31.14	159.2
m-Ethyltoluene	620144	31.40	158
1,3,5-Trimethylbenzene	108678	31.52	164.7
o-Ethyltoluene	611143	31.71	164
1,2,4-Trimethylbenzene	95636	32.28	169.4
n-Decane	124185	33.07	174
1,2,3-Trimethylbenzene	526738	34.19	176.1
p-Diethylbenzene	105055	35.40	184
n-Undecane	1120214	37.13	196
n-Dodecane	112403	41.56	216

3.4.2 Analyses of Samples

The GC-FID system used in this work consisted of three components. It includes an Agilent Model 6890 Gas chromatograph with two flame ionization detectors, a sampling system to collect air samples for short term on-line measurements (Air Server) and a thermal desorber (UNITY) to transfer samples from canister to GC. However, air server direct sampling system was not used in this work as measurements were not on-line. The analytical system is shown in Figure 3.5. There are two capillary columns in the GC. First one is an Agilent 123- 1063 DB-1-2 column which is connected to the first detector and the other one is Agilent 19091P-

S15 HP-PLOT Al_2O_3 column which is connected to the second detector. Column 1 is used to measure heavy hydrocarbons, while column 2 is used to measure light ones.

Figure 3.5: Analytical system

High-purity nitrogen gas was used as the mobile phase and hydrogen and dry air were used as fuel to ignite flame of FIDs. Analyses of each sample with GC – FID system took 46 minutes. Retention times of measured compounds are given in Table 3.1. During analysis, a peak occurs for each compound according to their retention time. A sample chromatogram is shown in Figure 3.6. Produced chromatograms were analyzed by ChemStation software for GC-FID system and areas of each compound for each standard volume were determined.

3.4.3 Parameters

GC – FID parameters were accessed from the studies which were conducted, by Kuntasal (2005), Yurdakul (2014) and Uzunpınar (2015) on temporal variations of VOCs in Ankara and Ottawa, Bursa and Ankara suburban atmospheres, respectively.

In Table 3.2, all the parameters for the Thermal Desorber are listed. Samples were collected for 25 minutes with flowrate of 20 ml min^{-1}. These two parameters were determined by examination of different flowrates and sampling times in order to obtain maximum sample volume that can be introduced to the system without exceeding the capacity of Air Server, which is 500 ml (Markes Int.Ltd., 2006).

After the examination, best results were detected at low flow rates and long sampling times. Trap temperature starts at -15°C for the quantification of ethane and acetylene, (Yurdakul, 2014) rises to 300°C. Also, GC-FID operational parameters are presented in Table 3.3. Oven temperature starts at 40°C and is held for 5 minutes. After that, temperature starts to rise with a rate of 5°C min^{-1} up to 195°C and is held for 10 minutes. A single sample analysis lasts 46 minutes.

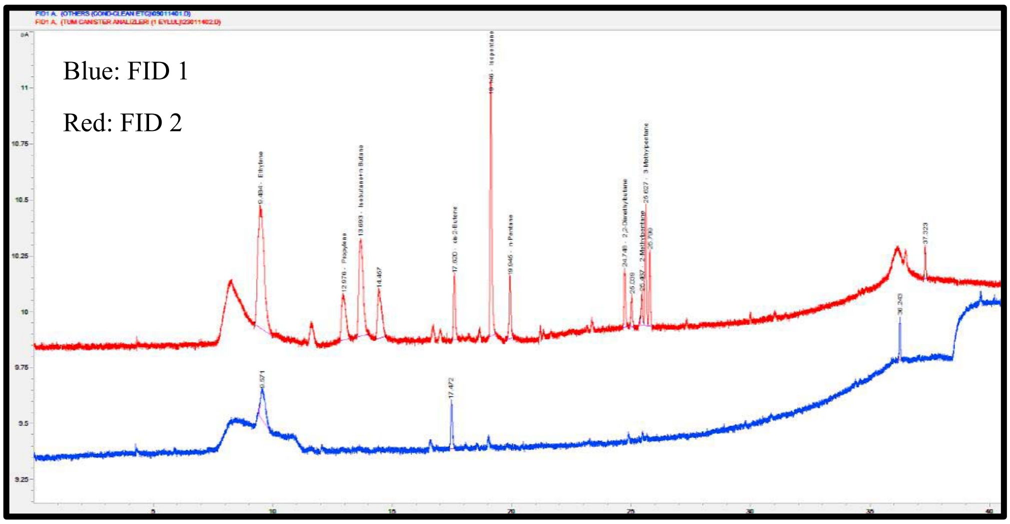


Figure 3.6: Sample chromatogram

Table 3.2: Thermal desorber parameters (Uzunpınar, 2015)

Thermal Desorber Parameters	
Prepurge Time (min)	1.0
Trap Purge Time (min)	1.0
Purge Flow Rate (ml/min)	20.0
Sample Time (min)	25.0
Sample Flow Rate (ml/min)	20.0
Sample Volume (ml)	500
Trap Low (°C)	-15
Trap High (°C)	300
Trap Hold (min)	3.0

Table 3.3: GC column and oven properties (Uzunpınar, 2015)

	Column 1	**Column 2**
Temperature (^{o}C)	30 - 325	-60 - 200
N_2 flow rate (ml/min)	2.8	5.2
Air flow rate (ml/min)	300	300
Hydrogen flow rate (ml/min)	30.0	30.0
Detector temperature (^{o}C)	300	300
Initial oven temperature (^{o}C)	40	
Hold (min)	5.0	
Ramp (^{o}C min^{-1})	5.0	
Final oven temperature (^{o}C)	195.0	
Hold (min)	10.0	
Total analysis time (min)	46.0	

3.5 Quality Assurance / Quality Control (QA/QC) Studies

3.5.1 Calibration of the instrument, detection limits and field blanks

Since QA/QC protocols used in our analytical system were discussed in detail earlier (Uzunpınar, 2015), only a brief description is provided in this section.

For the calibration of the analysis system, PAMS standard gas mixture with a concentration of 100 ppbv for each compound was used. In order to protect the analysis system from contamination, the gas mixture was diluted before calibration. For the preparation of diluted standard gas mixture, a cleaned canister was pressurized with dry high purity nitrogen up to -10 psi. Then, 240 ml of 100 ppbv standard gas mixture was injected to the pressurized canister and the canister was pressurized to 14.7 psi. Pressurized canister was waited for 24-hours to balance and obtain a homogeneous distribution. By means of this method, concentration of each compound was diminished to 2.1 ppbv according to the below calculations (RESTEK, 2010):

$$\text{Volume of Sample} = \frac{\text{Initial pressure} - \text{Final pressure}}{\text{Initial pressure}} * \text{Canister volume}$$

$$= \frac{-27-(-10)}{-27} * 6\text{L}$$

$$= 3.78\ \text{L}$$

<u>Standard injection;</u>

0.24 L/ 3.78 L = 0.063 (ratio of standard in volume of 1L)

0.063 * 100 ppb = 6.3 ppbv (concentration of the standard)

$$\text{Dilution factor} = \frac{\text{P(after dilution)} + \text{P(lab pressure)}}{\text{P(lab pressure)} - \text{P(before dilution)}}$$

$$= \frac{14.7 + 14.7}{14.7 - 10 * 0.491}$$

$$= 3.00$$

6.3 ppb/ 3.00 = 2.1 ppbv (final concentration of the standard gas mixture)

A six-point (100 ml, 200 ml, 300 ml, 400 ml, 500 ml and 600 ml) calibration was performed by injecting six different concentrations of target compounds to the GC (Figure 3.7). The calibration was checked in the beginning of every analysis day by injecting one of the mid-point standards.

Produced chromatograms were analyzed for GC-FID system. Calibration curves were drawn (Figure 3.8) by entering the areas and mass amounts of each compound for corresponding standard gas volume. (Uzunpınar, 2015).

During the generation of calibration curves correlations greater than 0.999 were achieved. Corresponding R^2 values are provided in Table 3.4.

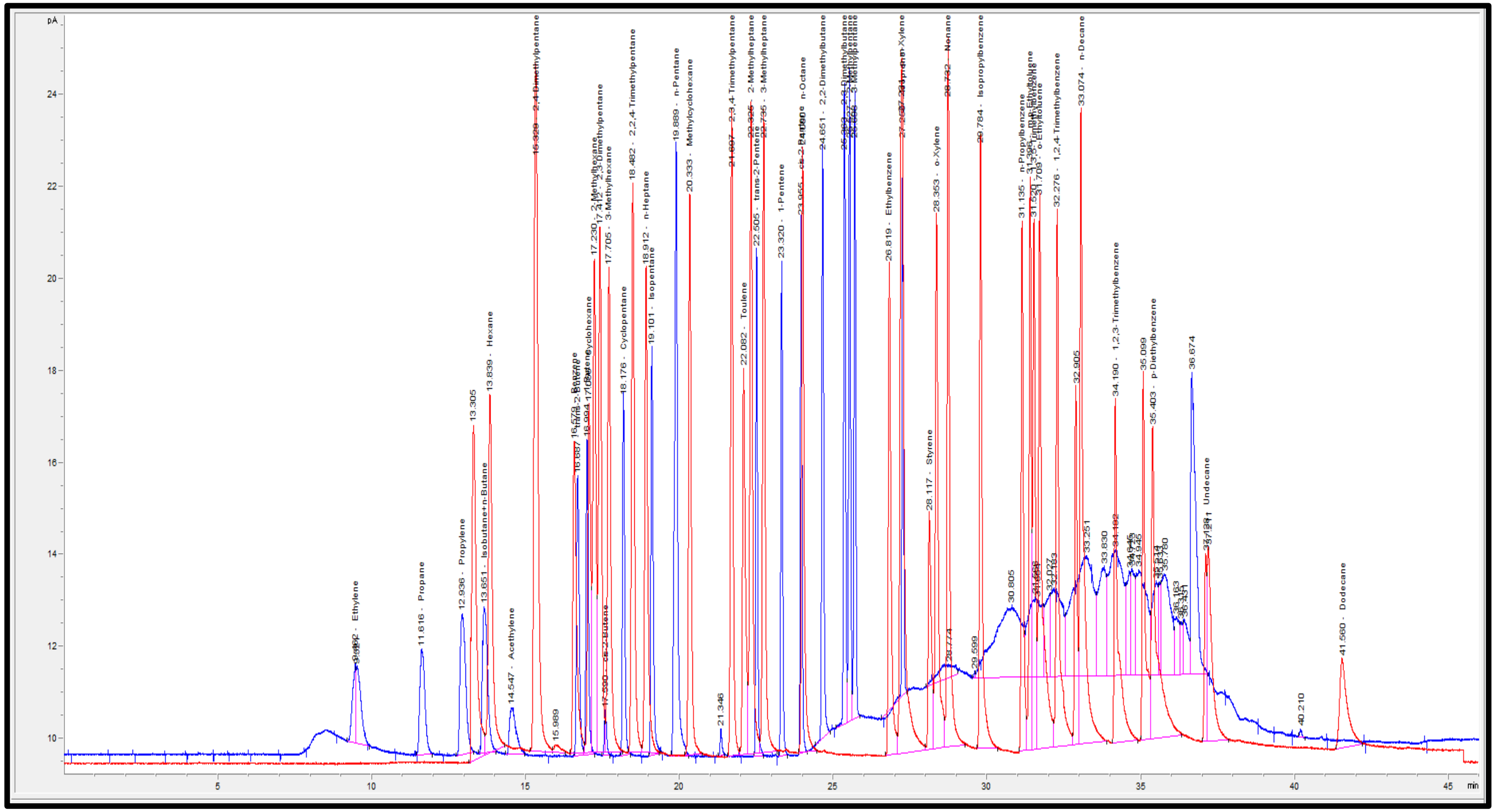


Figure 3.7: Chromatogram of 600 ml standard gas mixture analysis

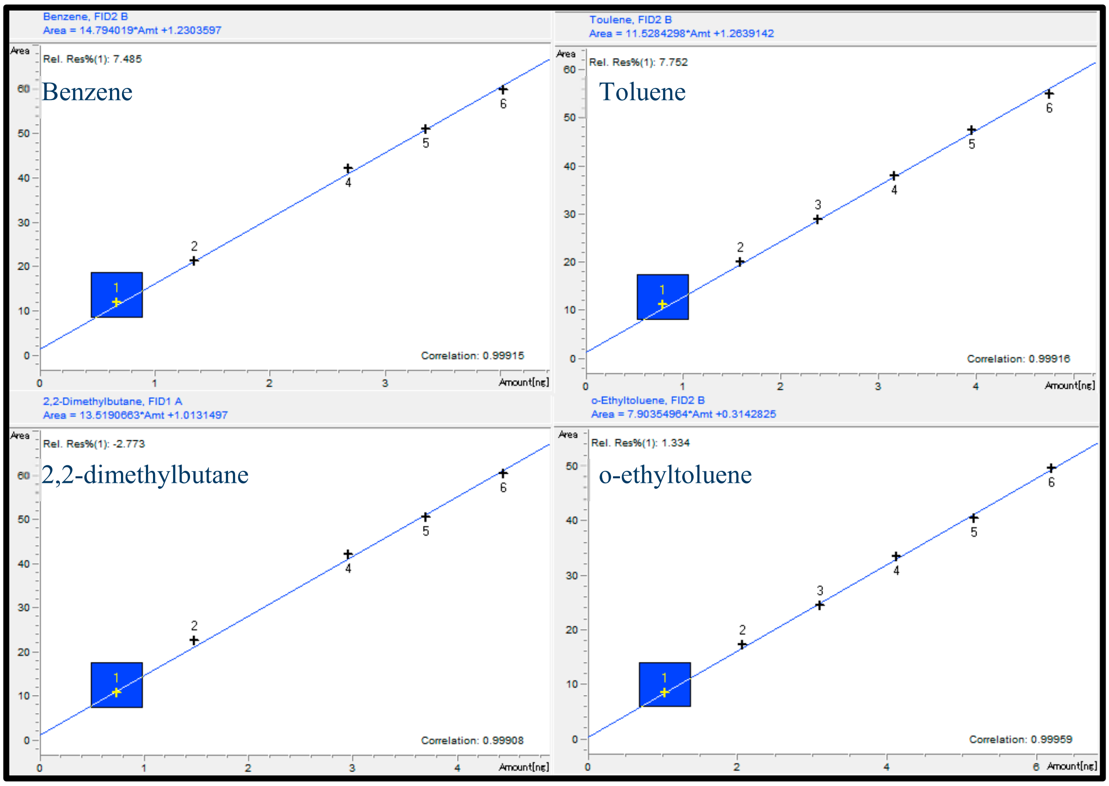


Figure 3.8 Calibration curves for some VOCs (Uzunpınar, 2015)

Table 3.4: R^2 values for calibration of each compound (Uzunpınar, 2015)

Compound	**R^2 value**
Ethane	0,99989
Ethylene	0,99965
Propane	0,99943
Propylene	0,99908
Isobutane - n-butane	0,99916
Acetylene	0,99916
Trans - 2 - Butene	0,99907
1 - Butene	0,99925
Cis-2-Butene	0,99955
Cyclopentane	0,99992
Isopentane	0,99904
n - Pentane	0,99915
Trans - 2 - Pentene	0,99910

Table 3.4 cont'd: R^2 values for calibration of each compound (Uzunpınar, 2015)

Compound	**R^2 value**
1 - Pentene	0,99970
Cis-2- Pentene	0,99903
2,2-Dimethylbutane	0,99908
2,3-Dimethylbutane	0,99907
2-Methylpentane	0,99953
3-Methylpentane	0,99901
Isoprene	0,99950
n-Hexane	0.99902
2,4-Dimethylpentane	0.99912
Benzene	0.99915
Cyclohexane	0.99930
2-Methylhexane	0.99911
2,3-Dimethylpentane	0.99924
3-Methylhexane	0.99911
2,2,4-Trimethylpentane	0.99905
n-Heptane	0.99912
Methylcyclohexane	0.99900
2,3,4-Trimethylpentane	0.99915
Toluene	0.99916
2-Methylheptane	0.99907
3-Methylheptane	0.99942
n-Octane	0.99912
Ethylbenzene	0.99911
m,p-Xylene	0.99929
Styrene	0.99900
o-Xylene	0.99930
Nonane	0.99909
Isopropylbenzene	0.99942
n-Propylbenzene	0.99968
m,p-Ethyltoluene	0.99921
1,3,5-Trimethylbenzene	0.99966
o-Ethyltoluene	0.99959
1,2,4-Trimethylbenzene	0.99901
n-Decane	0.99905
1,2,3-Trimethylbenzene	0.99910
p-Diethylbenzene	0.99977
n-Undecane	0.99960
n-Dodecane	0.99923

3.5.2 Analytical System QA/QC Procedure

Seven replicate measurements of minimum sample volume (100 ml) of standard gas that was used during the calibration phase were made and the standard deviations for each compound were calculated. Multiplication of standard deviations with corresponding student's t value, 3.14, gave the method detection limits (MDL), given in Table 3.5, for the target VOCs. MDL values of styrene, n-propylbenzene, m-ethyltoluene and 1,3,5-trimethylbenzene were not calculated. Corresponding values were obtained from Yurdakul (2014). Minimum amount was measured for cis-2-butene as 0.016 μg m^{-3}. Upper limit of the range was set by 2,3-dimethylpentane with a MDL of 0.212 μg m^{-3}.

Canisters were tested for leaks before starting the sampling. For that purpose, canisters were pressurized up to 30 psi. Then, final pressures were measured after 1 day and no change was observed in pressures.

In order to determine the field blanks, canisters were sent to the sampling field but returned to the laboratory without opening the valves for sampling. Total of 5 field blanks were collected and field blank analysis was made similar to the sample analysis. Minimum average blank concentration was measured as 0.01 ng for 1-butene, 2,3-dimethylbutane, 2-methylpentane, m,p-xylene and isopropylbenzene compounds. Maximum average blank concentration was 0.493 ng for cis-2-butene. Average and median blank values are presented in Table 3.5.

3.5.3 Precision of Sampling Kit and Analysis

Precision tests were performed by Uzunpınar (2015) for both sampling head and routine measurements. Precision of the sampling kit was determined by the simultaneous collection of four replicate daily samples. Simultaneous sampling was performed for three days (Figure 3.9). Standard deviations (SD) values were between 0.00 - 5.42 for the first day, 0.00 - 5.59 for the second day and 0.01 - 0.75 for the third day. In addition, relative standard deviations (RSD) were between 0.01 - 68.26

for the first day, 0.56 - 69.62 for the second day and 1.69 - 41.91 for the third day. Replicate precision is “the absolute value of the difference between analyses of canisters divided by their average value and expressed as a percentage” and required to be less than 25% according to U.S.EPA Method TO-15 (U.S.EPA, 1999b). For BTEX compounds, replicate precision values were between 7.80 and 23.20 for the first day, 3.09 and 11.19 for the second day and 0.49 and 15.97 for the third day. Therefore, replicate analyses were within the necessary range (Uzunpınar, 2015).

In order to determine the precision of analysis method and the analysis system, the same sample was analyzed three times. 500 ml of sample was introduced at each analysis. This method was repeated for four different sample canisters. SD varied between 0.001 for 2,4-dimethylpentane and 6.07 for isobutane. RSD varied between 0.62 for 2,4-dimethylpentane and 36.6 for isobutane (Uzunpınar, 2015).

Table 3.5: Average and median field blank values and method detection limits

Compounds	**Average (ng)**	**Median (ng)**	**MDL (µg m^{-3})**
Ethane	0.041	0.036	0.019
Ethylene	0.019	0.018	0.046
Propane	0.034	0.034	0.082
Propylene	0.019	0.02	0.050
Isobutane	0.031	0.032	0.097
Acethylene	0.019	0.019	0.049
Trans - 2 - Butene	0.032	0.031	0.074
1 - Butene	0.01	0.009	0.064
Cis-2-Butene	0.493	0.471	0.016
Cyclopentane	0.014	0.014	0.105
Isopentane	0.016	0.015	0.170
n - Pentane	0.011	0.01	0.115
Trans - 2 - Pentene	0.012	0.012	0.111
1 - Pentene	0.013	0.013	0.123
Cis-2- Pentene	0.014	0.014	0.146
2,2-Dimethylbutane	0.023	0.023	0.146
2-Methylpentane	0.01	0.01	0.145
3-Methylpentane	0.011	0.009	0.161

Table 3.5 cont'd: Average and median field blank values and method detection limits

Compounds	**Average (ng)**	**Median (ng)**	**MDL (µg m^{-3})**
Isoprene	0.011	0.012	0.157
n-Hexane	0.124	0.087	0.138
2,4-Dimethylpentane	0.009	0.007	0.094
Benzene	0.026	0.023	0.093
Cyclohexane	0.017	0.015	0.069
2-Methylhexane	0.011	0.009	0.109
2,3-Dimethylpentane	0.038	0.036	0.212
3-Methylhexane	0.04	0.037	0.089
2,2,4-Trimethylpentane	0.118	0.144	0.099
n-Heptane	0.027	0.022	0.073
Methylcyclohexane	0.018	0.016	0.120
2,3,4-Trimethylpentane	0.019	0.019	
Toluene	0.061	0.07	0.088
2-Methylheptane	0.022	0.019	0.133
3-Methylheptane	0.014	0.012	0.098
n-Octane	0.015	0.013	0.117
Ethylbenzene	0.018	0.017	0.089
p-Xylene	0.01	0.01	0.122
Styrene	0.045	0.034	0.051*
o-Xylene	0.025	0.024	0.102
Nonane	0.013	0.012	0.091
Isopropylbenzene	0.01	0.01	0.074
n-Propylbenzene	0.017	0.017	0.029*
m-Ethyltoluene	0.017	0.017	0.073*
1,3,5-Trimethylbenzene	0.021	0.02	0.073*
o-Ethyltoluene	0.025	0.025	0.538
1,2,4-Trimethylbenzene	0.13	0.135	0.094
n-Decane	0.045	0.036	0.137
1,2,3-Trimethylbenzene	0.042	0.04	0.089
m-Diethylbenzene	0.059	0.058	0.115
n-Undecane	0.046	0.042	0.110
n-Dodecane	0.173	0.164	0.106

*Yurdakul, 2014.

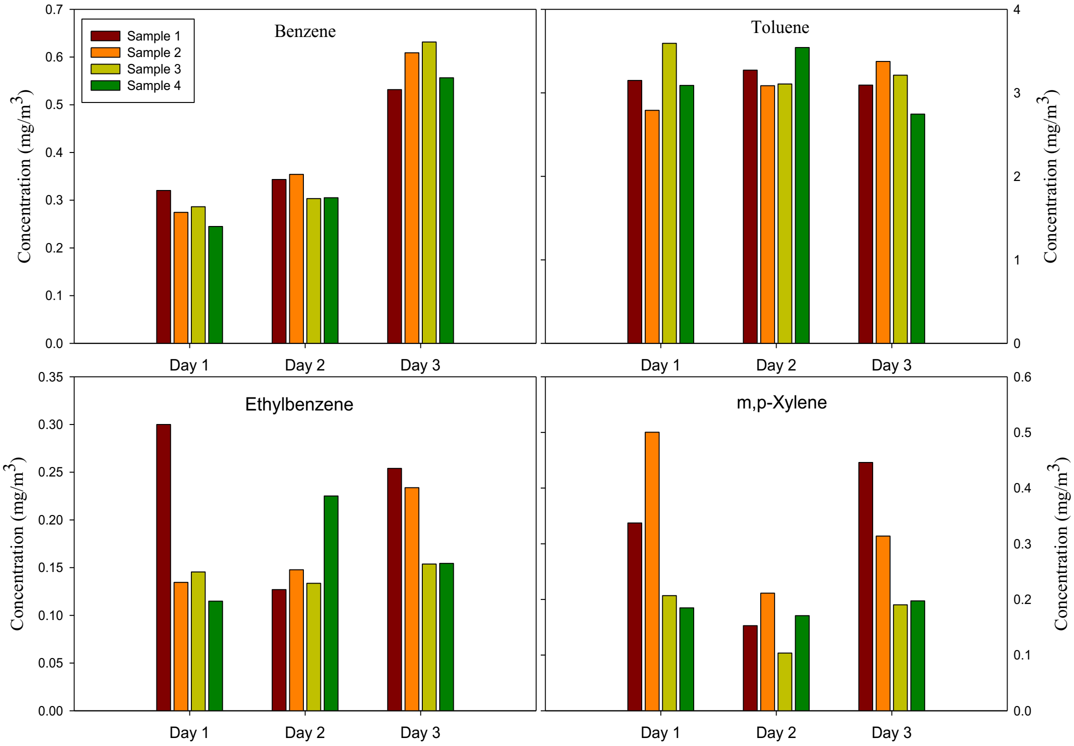


Figure 3.9: Precision of sampling kit

In Figure 3.10 precision analysis results for concentration variation for BTEX compounds are given. All compounds, except benzene, showed an increase during second analysis and started to decrease at third analysis. For BTEX compounds, precision values were between 3.69% and 16.71% for Canister 1, 0.54% and 17% for Canister 2, 5.88% and 23.33% t for Canister 3 and 0.11% and 4.96% for Canister 4. Precision values were lower than 25%, which is the limit of acceptable value (Uzunpınar, 2015).

To be able to check the stability of the calibration, standard gas analysis was performed between analyses. For the calibration check, 500 ml of standard gas was analyzed and results were compared with previous analyses. Due to the observation of concentration differences between analyses, new calibration was made in June, 2014. After the new calibration, calibration check results were similar.

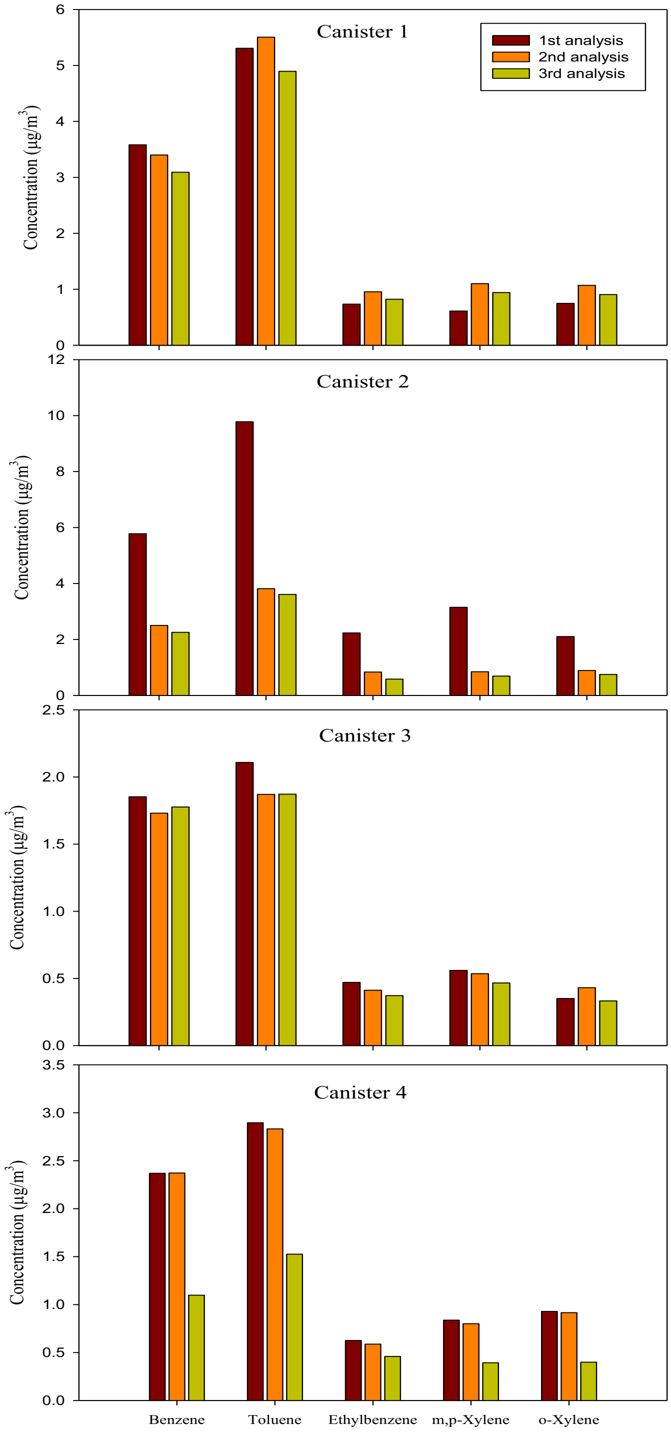


Figure 3.10: Precision of analysis for BTEX compounds

Table 3.6 shows the standard deviation and relative standard deviation results of calibration check analyses. SD values vary between 0.192 – 14.380 for benzene and m,p-xylene compounds. For RSD values, minimum value for benzene and maximum value for styrene compounds were calculated with a range of 0.426 – 28.604. Only RSD of styrene compound was above the 20% limit. According to EPA, calibration can still be accepted valid as long as the mean of the RSD values for all analytes is less than 20% (U.S.EPA, 1996). The mean of RSD values in Table 3.6 was calculated as 6.5. Therefore, new calibration was not needed.

Table 3.6: Calibration check results (Uzunpınar, 2015)

Compound	**Standard deviation**	**Relative Standard Deviation**
Ethane	0.987	2.911
Ethylene	1.933	5.742
Propane	1.272	6.084
Propylene	1.603	4.968
Isobutane	1.642	5.180
Acetylene	1.346	8.764
Trans - 2 - Butene	1.472	5.158
1-Butene	1.012	3.349
Cis-2-Butene	0.212	6.208
Cyclopentane	1.027	3.346
Isopentane	2.687	4.907
n - Pentane	2.811	3.827
Trans - 2 - Pentene	1.167	3.381
1-Pentene	1.040	3.060
Cis-2- Pentene	1.152	3.201
2,2-Dimethylbutane	1.475	3.040
2,3- Dimethylbutane	1.487	3.148
2-Methylpentane	2.038	3.903
3-Methylpentane	1.711	3.808
Isoprene	0.883	2.624
n-Hexane	0.234	0.435
2,4-Dimethylpentane	1.971	1.895

Table 3.6 cont'd: Calibration check results (Uzunpınar, 2015)

Compound	Standard deviation	Relative Standard Deviation
Benzene	0.192	0.426
Cyclohexane	0.642	1.702
2-Methyhexane	2.185	3.706
2,3-Dimethylpentane	3.169	5.171
3-Methylhexane	2.803	4.791
2,2,4-Trimethylpentane	3.334	5.293
n-Heptane	3.129	5.428
Methylcyclohexane	2.810	5.190
2,3,4-Trimethylpentane	3.184	5.316
Toluene	4.773	9.417
2-Methylheptane	3.897	5.808
3-Methylheptane	4.585	7.385
n-Octane	5.068	9.145
Ethylbenzene	6.552	14.798
m-Xylene	14.380	14.911
Styrene	4.701	28.604
o-Xylene	6.666	12.997
Nonane	4.616	7.381
Isopropylbenzene	4.462	8.340
n-Propylbenzene	5.236	14.483
m-Ethyltoluene	4.862	14.650
1,3,5-Trimethylbenzene	2.327	5.316
o-Ethyltoluene	0.433	0.691
1,2,4-Trimethylbenzene	6.367	12.939
n-Decane	9.402	11.423
1,2,3-Trimethylbenzene	2.509	6.670
m-Diethylbenzene	2.670	10.312
n-Undecane	1.864	4.949
n-Dodecane	0.872	5.705

3.6 Positive Matrix Factorization (PMF)

In this study, PMF study was conducted for determining source contribution to VOC concentrations measured in METU and AU stations.

For that purpose, EPA PMF 5.0 software was used. To be able to run the software, two input files were formed including concentrations and uncertainty values of target compounds. In input file, if the concentration of any compound is above its own detection limit it is used directly and its uncertainty value is calculated by adding its detection limit to a ratio of (0.05) concentration of that compound. On the other hand, if the concentration of any compound is below its own detection limit, the concentration data is replaced with half of its detection limit and for uncertainty, 5 / 6 of its detection limit is used. In addition, missing data are replaced with the geometric mean of the concentration of that compound (Yurdakul, 2014).

When the input files are formed, the second step is to decide the factor numbers. Difference between 'goodness of fit' parameters, Q values, is the main factor for deciding the factor number. After running specified numbers of factors, the software gives two Q values, which are Q_{true} and Q_{robust}. While Q_{true} represents the all points, Q_{robust} excludes points that cannot fit by model, which represents the ratio of uncertainty to scaled residual greater than 4. After that, by using equation below, $Q_{theoretical}$ is calculated:

$$Q_{theoretical} = nm - p\ (n + m\ ) \qquad \text{Equation (1)}$$

The values of m, n and p symbolize the amount of samples, number of target VOCs and the factor numbers, respectively. Q_{true}/Q_{robust} ratio should be lower than 1.5 according to U.S.EPA. In addition, $Q_{theoretical}$ should be not very different from Q_{robust} (Gupta and Kumar, 2011).

Q values are used to check performance of the PMF model. Also, 'signal to noise' (S/N) ratio is used in order to get accurate solution for each compound. Compounds are marked as 'weak' if the S/N ratio is between 0.5 – 1 and also marked as 'bad' if the ratio is smaller than 0.5. Whereas, S/N ratio is not sufficient by itself to determine whether the compound is 'weak' or 'bad'. In addition, if the observation occurrence of any compound is smaller than %35 they are marked as 'bad'. For to be sure, r^2 values are obtained for each compound. The compound is marked as 'bad' if the r^2 value of that compound is very low, which means the distribution of the compound is very poor and replacement amount is high. On the other hand, if the distribution of the compound is very poor but replacement amount is low, too, that compound is marked as 'weak' (Brown, et al., 2007). For AU station, 4 compounds (1-pentene, 3-methyheptane, isopropylbenzene, o-ethyltoluene) are marked as weak and 6 compounds (trans - 2 – pentene, cis-2-pentene, 2,3-dimethylpentane, methylcyclohexane, 2,3,4-trimethylpentene and 1,2,4-trimethylpentene) are marked as bad. Also, for METU station, 4 compounds (2,4-dimethylpentane, 3-methylheptane, n-Octane and isopropylbenzene) are marked as weak and 8 compounds (trans - 2 – pentene, 1 – pentene, cis-2- pentene, 2,3-dimethylpentane, methylcyclohexane, 2,3,4-trimethylpentane, o-ethyltoluene and 1,2,4-trimethylbenzene) are marked as bad.

After the PMF is run, three output data, which are F-loading, G-Scores and % Explained, are attained. F-loading is an indicator for factor profile and represents the distribution of compounds into factors. % Explained and F-loading data are used to describe the sources of VOCs. In addition, G-Score is used to represent the time dependent variation of the compounds.

To sum up, initially different factor numbers (from 6 to 8) were tried and all steps mentioned above were repeated. Then, best-fit factor number was selected for both stations, which is six. After running the PMF model with six factor, F-loading, G-scores and explained % values are obtained. All of the results regarding the PMF study for both stations will be given and discussed in Chapter 4.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 General Data

4.1.1 Summary Statistics of VOCs at AU and METU Stations

Summary statistics of this study for both AU and METU stations are given in Table 4.1 and Table 4.2, respectively. Tables include mean, median, geometric mean, range, number of data points, as well as 25th, 50th, 75th, 90th percentile values for each 51 non-methane hydrocarbons.

Mean values of measured hydrocarbons range between 0.09 µg m^{-3} for cis-2 -pentene and 24.76 µg m^{-3} for toluene in AU and from 0.06 µg m^{-3} to 10.09µg m^{-3} for the same compounds at suburban station, respectively. Median concentrations range between 0.02 µg m^{-3} (for cis-2-pentene) and 14.05 µg m^{-3} (for isobutene) in urban station and between 0.03 µg m^{-3} (for cis-2-pentene) and 5.31 µg m^{-3} (for isobutene) at METU station. Annual benzene concentration limit for European Commission is 5 µg m^{-3}. The same limit is also effective in Turkey. Average and median benzene concentrations are 2.10 µ /$^{-}$m^{3} and 0.84 µg m^{-3} in AU station and 1.41 µg m^{-3} and 0.64 µg m^{-3} in METU station indicating that existing standards were not exceeded in either stations.

Total number of samples for each compound were given under the column designated as N. The occurrence column, on the other hand gives percentage of occurrence for each compound in total number of sample collected. This ratio varies between 25% (for 2,3,4-trimethylpentane) and 100% (for 12 compounds which are ethylene, propane, propylene, isobutane, 1-butane, cyclopentane, isopentane, benzene, n-octane, p-xylene, nonane and 1,2,3 trimethylbenzene) at urban station and between 21% (cis-2-pentene) and 100% (for 11 compounds, which are ethane, propane, propylene, isobutene, 1-butene, isopentane, n-pentane, benzene, ethylbenzene, p-xylene and o-xylene) at suburban station.

4.1.2 Frequency Distributions at AU and METU Stations

Frequency distributions for all VOCs measured in this study were prepared. Chi-square test was used to test how well these histograms fit to lognormal distribution with 95% statistical confidence. In Figure 4.1 and Figure 4.2, frequency distributions of BTEX compounds were given for AU and METU stations, respectively. Although all BTEX compounds depicted right skewed distributions, chi-square test demonstrated that all of them are not log-normal. This is a key point that we see in all our atmospheric data sets. All parameters, organic and inorganic, show right skewed distributions. Observed distributions are not necessarily log-normal; however lognormal is the most frequently observed distribution. For example, distributions of ethylbenzene, toluene and benzene are right skewed and looks like lognormal. However, goodness-of the fit tests showed that distributions of ethylbenzene and toluene fits to “log-logistic” distribution with 95% confidence and benzene fits to an inverse Gaussian distribution in both stations. For other VOCs, there were other distribution types such as gamma, Wakebey and Birnbaum- Saunders. The variety of distribution types indicates that using median or geometric mean values is more representative according to arithmetic mean values. In this study, we first assumed that all parameters are log normally distributed and tested that assumption with chi-square goodness of the fit test. For the VOCs that that are not log normally distributed with 95%, other distributions were tested.

Table 4.1: Summary statistics of data at AU station

Compounds	**Mean**	**Median**	**Geo. Mean**	**Range**	**N**	**Occurrence**	**25th**	**50th**	**75th**	**90th**
Ethane	2.1±1.6	1.6	1.6	0.06-11.2	232	98%	0.94	1.6	2.8	4.3
Ethylene	6.5±7.5	4.1	4.3	0.31-80	236	100%	2.4	4.1	8.6	14
Propane	4.7±5.1	2.8	2.9	0.05-27	236	100%	1.5	2.7	5.7	12
Propylene	8.7±8.8	5.1	5.7	0.17-45	236	100%	3.2	5.1	10	22
Isobutane	24±4	14	15	0.35-123	236	100%	8.6	14.0	29	59
Acethylene	1.9±2.4	1.1	1.1	0.01-14	233	99%	0.55	1.1	2.2	4.3
Trans - 2 - Butene	0.42±0.36	0.31	0.29	0.003-1.9	231	98%	0.16	0.31	0.58	0.84
1 - Butene	0.67±0.72	0.40	0.44	0.03-4.0	236	100%	0.23	0.40	0.77	1.4
Cis-2-Butene	9.3±11	5.9	5.5	0.03-78	231	98%	2.9	5.9	11	20
Cyclopentane	0.38±0.90	0.22	0.22	0.01-13	235	100%	0.13	0.22	0.40	0.71
Isopentane	5.6±5.1	3.8	3.9	0.18-28	236	100%	2.1	3.8	6.9	12
n - Pentane	1.4±4.2	0.59	0.63	0.002-59	234	99%	0.30	0.59	1.2	2.8
Trans - 2 - Pentene	0.17±0.36	0.06	0.06	0.001-3.4	165	70%	0.02	0.06	0.16	0.45
1 - Pentene	0.25±0.30	0.15	0.14	0.002-1.8	214	91%	0.07	0.14	0.28	0.61
Cis-2- Pentene	0.09±0.20	0.02	0.03	0.002-1.2	61	26%	0.01	0.02	0.09	0.27
2,2-Dimethylbutane	0.75±0.66	0.53	0.50	0.002-3.3	218	92%	0.29	0.52	1.00	1.7
2,3-Dimethylbutane	0.53±0.74	0.32	0.32	0.01-8.1	229	97%	0.16	0.32	0.65	1.0

Table 4.1 cont'd: Summary statistics of data at AU station

Compounds	Mean	Median	Geo. Mean	Range	N	Occurrence	25th	50th	75th	90th
2-Methylpentane	1.7±1.7	1.1	1.1	0.03-10	234	99%	0.64	1.1	2.1	3.9
3-Methylpentane	0.84±0.88	0.54	0.54	0.03-5.4	232	98%	0.28	0.54	1.0	1.8
Isoprene	0.78±0.85	0.54	0.51	0.04-6.7	231	98%	0.27	0.54	0.94	1.8
n-Hexane	3.7±7.9	1.1	1.1	0.01-67	201	85%	0.43	1.1	3.5	8.5
2,4-Dimethylpentane	0.22±0.28	0.12	0.12	0.003-2.24	230	97%	0.07	0.12	0.23	0.57
Benzene	2.1±3.3	0.84	1.0	0.05-22	235	100%	0.47	0.84	1.9	5.8
Cyclohexane	0.28±0.79	0.12	0.13	0.001-11	202	86%	0.06	0.12	0.29	0.56
2-Methylhexane	0.45±0.63	0.22	0.22	0.01-4.3	221	94%	0.09	0.22	0.51	1.2
2,3-Dimethylpentane	0.30±0.35	0.16	0.16	0.005-1.9	177	75%	0.07	0.16	0.37	0.80
3-Methylhexane	1.4±1.0	1.1	1.1	0.04-5.3	227	96%	0.66	1.1	1.8	2.7
2,2,4-Trimethylpentane	1.3±2.0	0.45	0.45	0.01-13	106	45%	0.18	0.44	1.8	3.8
n-Heptane	0.60±1.7	0.32	0.31	0.005-25	230	97%	0.16	0.32	0.58	1.1
Methylcyclohexane	0.15±0.21	0.08	0.07	0.001-1.4	187	79%	0.03	0.08	0.16	0.32
2,3,4-Trimethylpentane	1.2±8.6	0.03	0.03	0.0004-66	59	25%	0.01	0.03	0.07	0.15
Toluene	25±45	9.1	10	0.51-375	232	98%	4.6	9.1	20	59
2-Methylheptane	0.49±0.78	0.28	0.27	0.01-6.6	218	92%	0.14	0.28	0.51	1.0
3-Methylheptane	0.19±0.29	0.09	0.08	0.002-1.9	205	87%	0.04	0.09	0.20	0.50

Table 4.1 cont’d : Summary statistics of data at AU station

Compounds	**Mean**	**Median**	**Geo. Mean**	**Range**	**N**	**Occurrence**	**25th**	**50th**	**75th**	**90th**
n-Octane	0.31±0.52	0.16	0.18	0.01-5.5	235	100%	0.10	0.16	0.30	0.67
Ethylbenzene	1.6±2.6	0.70	0.79	0.002-21	234	99%	0.35	0.70	1.6	3.8
p-Xylene	2.6±4.1	1.2	1.3	0.05-29	235	100%	0.57	1.2	2.5	6
Styrene	1.9±4.1	0.56	0.53	0.01-28	213	90%	0.18	0.56	1.5	4.1
o-Xylene	1.8±2.6	0.86	0.94	0.04-16	233	99%	0.41	0.86	1.8	3.9
Nonane	0.53±0.71	0.30	0.32	0.02-6.9	236	100%	0.16	0.30	0.61	1.2
Isopropylbenzene	0.23±0.68	0.09	0.09	0.002-8.2	199	84%	0.04	0.09	0.20	0.44
n-Propylbenzene	0.56±2.5	0.13	0.14	0.001-27	207	88%	0.05	0.13	0.26	0.79
m-Ethyltoluene	0.54±0.91	0.23	0.24	0.001-6.2	205	87%	0.10	0.23	0.51	1.2
1,3,5-Trimethylbenzene	1.3±1.9	0.62	0.58	0.01-16	231	98%	0.24	0.62	1.3	3.1
o-Ethyltoluene	0.74±1.8	0.25	0.24	0.002-16	214	91%	0.11	0.25	0.62	1.5
1,2,4-Trimethylbenzene	2.1±2. 6	1.2	0.94	0.01-14	62	26%	0.40	1.1	3.2	4.6
n-Decane	1.6±8.5	0.57	0.46	0.001-118	205	87%	0.18	0.6	1.1	2.5
1,2,3-Trimethylbenzene	6.5±8.9	2.9	3.3	0.004-57	236	100%	1.6	2.9	7.6	16
p-Diethylbenzene	1.4±2.8	0.47	0.46	0.002-20	174	74%	0.20	0.45	1.4	3.0
n-Undecane	3.6±17	1.1	1.2	0.001-255	222	94%	0.51	1.1	3.6	6.5
n-Dodecane	9.8±14	5.8	5.6	0.08-122	232	98%	3.2	5.8	10	20

Table 4.2: Summary statistics of data at METU station

Compounds	Ave + Std	Median	Geo. Mean	Range	N	Occurrence	25th	50th	75th	90th
Ethane	3.4±3.0	2.6	2.4	0.032-19	327	100%	1.6	2.6	4.1	6.7
Ethylene	6.2±7.3	3.5	3.6	0.142-51	326	99%	1.7	3.5	7.6	15
Propane	1.8±2.3	0.97	1.1	0.077-22	328	100%	0.50	0.97	2.0	4.1
Propylene	3.7±4.2	2.2	2.4	0.135-37	328	100%	1.4	2.2	4.1	8.3
Isobutane	9.3±11	5.8	6.0	0.298-96	328	100%	3.2	5.8	11	21
Acethylene	1.2±1.9	0.48	0.53	0.013-16	316	96%	0.25	0.48	1.3	3.0
Trans - 2 - Butene	0.31±0.26	0.24	0.20	0.001-1.4	311	95%	0.11	0.24	0.40	0.70
1 - Butene	0.31±0.32	0.20	0.22	0.025-2.84	328	100%	0.12	0.20	0.38	0.66
Cis-2-Butene	5.2±7.1	3.4	3.0	0.002-84	318	97%	1.8	3.4	6.4	10
Cyclopentane	0.18±0.15	0.15	0.14	0.010-1.3	324	99%	0.08	0.15	0.24	0.36
Isopentane	3.4±3.4	2.4	2.4	0.023-29	327	100%	1.4	2.4	4.1	6.8
n - Pentane	0.87±2.8	0.49	0.51	0.026-50	327	100%	0.28	0.49	0.87	1.5
Trans - 2 - Pentene	0.08±0.17	0.05	0.04	0.0002-2.2	218	66%	0.02	0.05	0.08	0.15
1 - Pentene	0.15±0.25	0.10	0.09	0.001-3.8	301	92%	0.05	0.10	0.18	0.29
Cis-2- Pentene	0.06±0.12	0.03	0.02	0.0002-0.90	72	21%	0.01	0.03	0.06	0.12
2,2-Dimethylbutane	0.45±0.45	0.31	0.29	0.006-3.4	311	95%	0.16	0.31	0.62	0.98
2,3-Dimethylbutane	0.34±0.34	0.23	0.21	0.003-3.2	324	99%	0.11	0.23	0.46	0.70

Table 4.2 cont'd: Summary statistics of data at METU station

Compounds	Ave + Std	Median	Geo. Mean	Range	N	Occurrence	25th	50th	75th	90th
2-Methylpentane	1.1±1.3	0.72	0.71	0.015-17	324	99%	0.42	0.72	1.3	2.2
3-Methylpentane	0.57±0.58	0.39	0.38	0.007-4.7	324	99%	0.22	0.39	0.71	1.3
Isoprene	0.53±1.5	0.32	0.31	0.011-26	323	98%	0.16	0.32	0.59	1.0
n-Hexane	3.0±5.0	1.5	1.4	0.004-54.9	301	92%	0.65	1.5	3.6	7.0
2,4-Dimethylpentane	0.16±0.24	0.10	0.10	0.003-2.7	319	97%	0.05	0.10	0.18	0.33
Benzene	1.4±1.8	0.64	0.78	0.008-13	327	100%	0.34	0.64	1.8	3.8
Cyclohexane	0.21±0.84	0.09	0.08	0.001-14	291	89%	0.04	0.09	0.19	0.38
2-Methylhexane	0.26±0.29	0.15	0.13	0.0002-1.6	312	95%	0.06	0.15	0.37	0.71
2,3-Dimethylpentane	0.26±0.49	0.15	0.12	0.001-5.4	234	71%	0.06	0.15	0.30	0.53
3-Methylhexane	0.98±0.86	0.80	0.69	0.015-8.0	301	92%	0.46	0.81	1.3	2.0
2,2,4-Trimethylpentane	0.63±0.63	0.44	0.33	0.001-3.4	151	45%	0.16	0.46	0.88	1.5
n-Heptane	0.40±0.85	0.22	0.23	0.003-13	318	97%	0.13	0.22	0.41	0.77
Methylcyclohexane	0.14±0.28	0.07	0.07	0.0004-2.7	268	81%	0.03	0.07	0.14	0.31
2,3,4-Trimethylpentane	0.37±1.1	0.04	0.06	0.002-8.3	77	22%	0.01	0.04	0.14	1.1
Toluene	10±16	5.2	5.67	0.259-161	326	99%	2.9	5.3	11	20
2-Methylheptane	0.46±0.60	0.28	0.26	0.002-5.1	294	89%	0.13	0.28	0.53	1.1
3-Methylheptane	0.14±0.21	0.07	0.06	0.0002-2.0	290	88%	0.03	0.07	0.14	0.35

Table 4.2 cont'd: Summary statistics of data at METU station

Compounds	Ave + Std	Median	Geo. Mean	Range	N	Occurrence	25th	50th	75th	90th
n-Octane	0.22±0.29	0.13	0.13	0.002-3.4	323	98%	0.07	0.13	0.25	0.48
Ethylbenzene	0.80±1.1	0.47	0.45	0.007-11	328	100%	0.25	0.47	0.90	1.8
p-Xylene	1.3±1.7	0.73	0.77	0.072-16	327	100%	0.39	0.73	1.6	2.8
Styrene	1.1±1.9	0.43	0.44	0.006-15	277	84%	0.18	0.43	1.2	2.3
o-Xylene	1.0±1.3	0.62	0.58	0.004-13	327	100%	0.31	0.63	1.3	2.3
Nonane	0.32±0.46	0.21	0.17	0.0001-5.9	325	99%	0.08	0.21	0.40	0.74
Isopropylbenzene	0.18±0.47	0.09	0.09	0.001-6.0	229	69%	0.05	0.09	0.16	0.31
n-Propylbenzene	0.27±0.67	0.12	0.12	0.002-9.3	258	78%	0.05	0.12	0.28	0.59
m-Ethyltoluene	0.35±0.43	0.21	0.19	0.003-2.8	229	69%	0.10	0.21	0.43	0.81
1,3,5-Trimethylbenzene	0.73±0.71	0.52	0.45	0.010-4.5	314	96%	0.21	0.52	0.95	1.7
o-Ethyltoluene	0.60±1.3	0.22	0.20	0.001-12	276	84%	0.07	0.22	0.58	1.3
1,2,4-Trimethylbenzene	1.2±1.4	0.63	0.62	0.002-6.6	127	38%	0.26	0.64	1.7	3.0
n-Decane	0.84±1.	0.37	0.35	0.002-12	249	76%	0.13	0.38	0.87	2.3
1,2,3-Trimethylbenzene	3.1±2.7	2.3	2.04	0.045-16	323	98%	1.2	2.3	4.3	6.5
p-Diethylbenzene	1.3±2.8	0.59	0.53	0.008-28	223	67%	0.22	0.59	1.3	2.8
n-Undecane	2.7±5.6	1.2	0.98	0.010-55	297	90%	0.33	1.2	2.7	5.4
n-Dodecane	7.5±10	5.1	3.50	0.002-117	285	87%	2.1	5.1	9.2	15

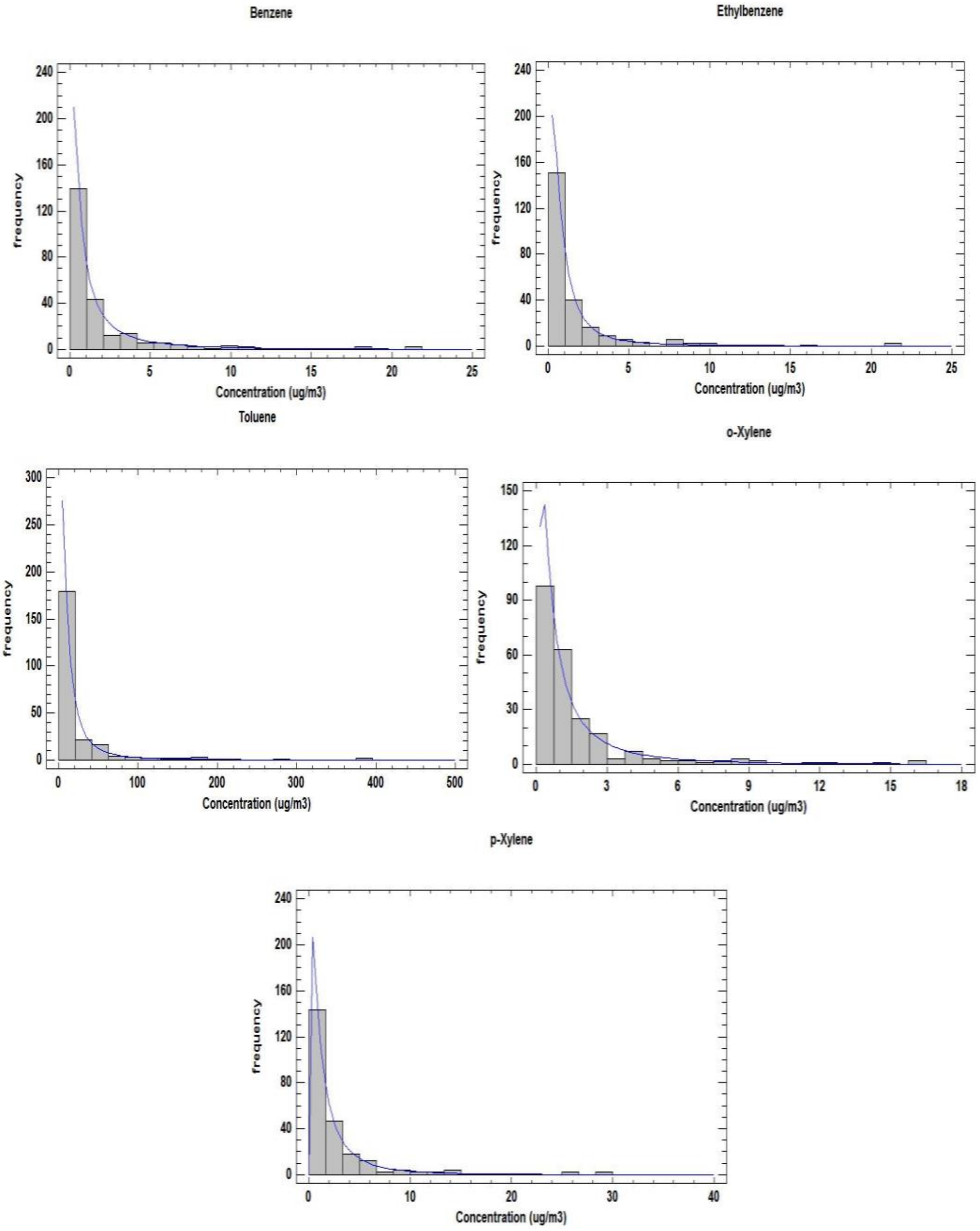


Figure 4.1 Frequency distributions of BTEX at AU

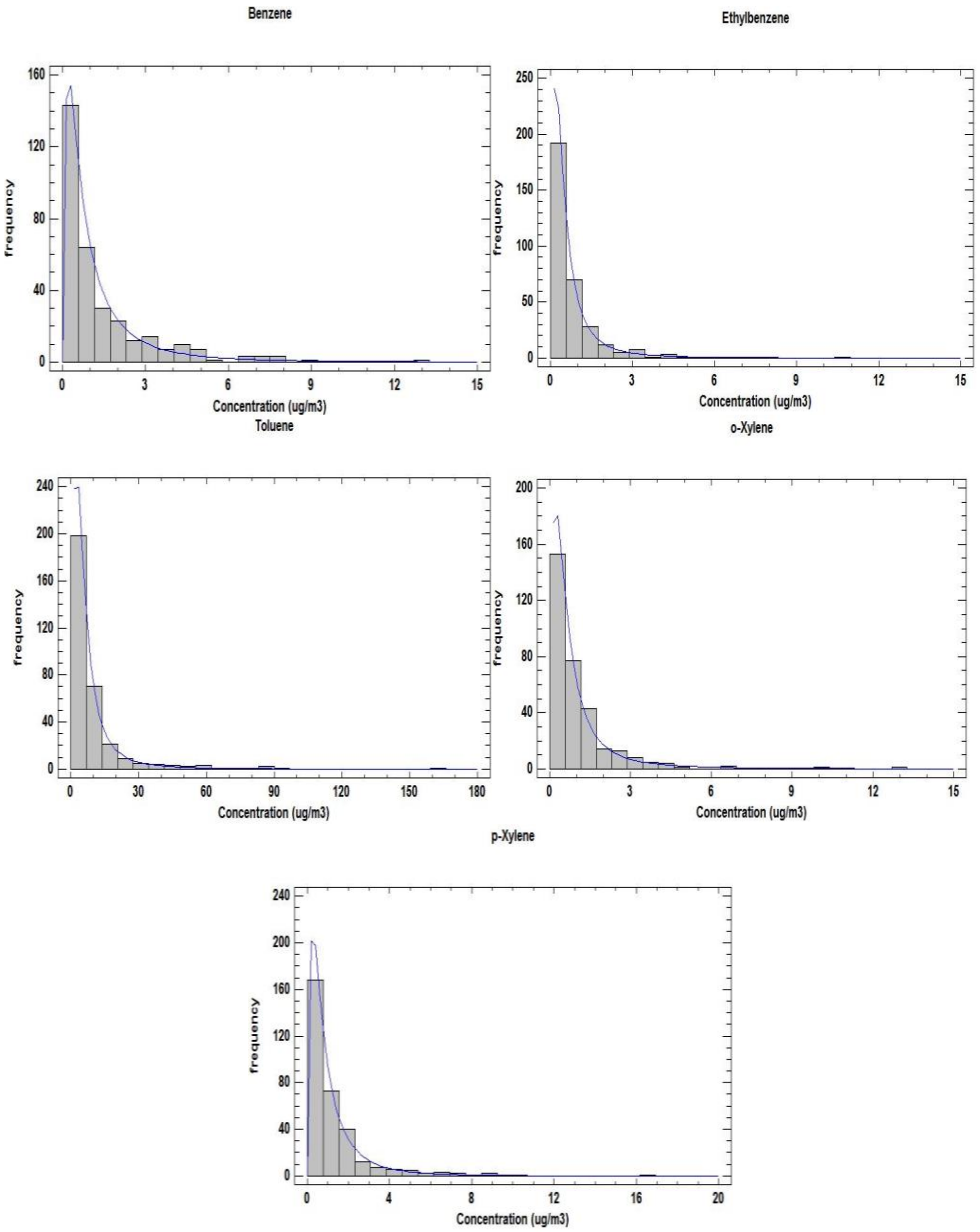


Figure 4.2 : Frequency distributions of BTEX at METU

4.2 Comparison with Literature

Comparisons of measured data with results of other studies performed in other locations or in other times can be very useful to put measured levels of pollutants into perspective. Such comparison can also generate information on sources that are active in that area. In this study, the concentrations of VOCs measured in two stations, one of which can be defined as an urban and the other one as suburban in Ankara, were firstly compared with the results obtained from the studies conducted in other cities and industrial regions of Turkey. Then, VOC concentrations were compared with the concentration values obtained in the other regions of the world.

Although comparison of data with other data from literature can be useful to get preliminary information on air quality and sources that are effective in that area, too much emphasis should not be put on such comparison, because concentration of VOCs measured at any location is highly dependent on how far sampling point is from the source.

4.2.1 Comparison of Data in This Study and Other Cities in Turkey

The VOC concentrations measured in this study were compared with the results of other VOC measurements conducted in other Turkish cities. Results are given in Table 4.3 and Figure 4.3. Since other studies in Ankara was also performed by our group in the past, using similar analytical methods similar VOCs were measured in all Ankara studies. However, different VOCs were measured in studies performed in different cities of Turkey by different groups. In order to remove such inhomogeneity comparison was limited to BTEX compounds, which were measured in all studies. As can be seen in Figure 4.3, BTEX concentrations measured at Kocaeli are higher than the concentrations measured in other cities for all BTEX compounds, except for benzene. Average benzene level at Kocaeli is 2.5 µg m^{-3} which is lower than benzene concentrations reported for some of the other cities. For all other BTEX compounds, the concentrations measured in Kocaeli are high. High VOC concentrations measured at Kocaeli is not surprising, because it is a heavily industrialized city and is affected from emissions at Dilovası, which is the most polluted industrial area in Turkey (Yolcubal et al., 2016; Bingöl et al., 2013). Even if there were no other source, only the polluters transported from Dilovası would be sufficient to increase concentrations of VOCs and other conventional pollutants to the levels we observe in this and previous studies at Kocaeli. The reason for relatively low level of benzene in same city may be that the main source of benzene in urban atmosphere is traffic and not industrial activities. There is no reason for Kocaeli to be at the forefront in terms of traffic-related pollutants. Kocaeli is followed by Bursa and İzmir provinces in terms of BTEX concentrations. The reason for relatively high BTEX concentrations should be that the cities have intense industrial activities as well as their traffic emissions are high.

Concentrations of BTEX measured in urban and suburban areas in this study are not very different from other cities. Only the toluene concentration at Ankara station is among the highest values. Toluene is given into atmosphere due to use of solvents in addition to the traffic. Since the concentrations of traffic markers, such as benzene, are not particularly high at Ankara, it would be fair to say that higher toluene levels can be due to solvent use in the city.

Another remarkable point in Figure 4.3 is that all of the BTEX concentrations measured at urban station are higher than corresponding concentrations measured at suburban station, probably due to availability of strong VOC sources, such as busy roads close to Ankara University site. Since METU is relatively far from roads and other VOC sources, measured VOC levels are expected to be lower at METU. The VOC concentrations in the two stations will be compared more thoroughly in the later sections of the manuscript.

As discussed previously, one should not overemphasized the comparison of VOC levels measured in different cities, by different groups, because data is very sensitive to distances between sampling locations and major VOC sources, such as roads. Keeping that in mind, data enabled us to determine ranges and median values of BTEX concentrations in Turkish cities. This information is given in Figure 4.3.

Concentration of benzene in Turkish cities varies between 0.85 µg m^{-3} and 10.4 µg m^{-3} with a median value of 2.0 µg m^{-3}. Toluene concentration, on the other hand varies between 3.9 µg m^{-3} measured at Aliağa urban site and 35 µg m^{-3} at Kocaeli. The lowest and highest ethylbenzene concentrations were 0.26 µg m^{-3} measured at Eskisehir and 9.7 µg m^{-3} measured at Kocaeli. m,p-xylene concentrations were between 0.5 µg m^{-3} and 37 µg m^{-3} at Kocaeli, with a median value of 2.1 µg m^{-3}. Finally, o-xylene concentrations in Turkish cities varies between 0.2 µg m^{-3} measured at Aliağa and 12 µg m^{-3} measured at Kocaeli. The median o-xylene concentration in Turkish cities is 1.1 µg m^{-3}.

It should be noted that the only VOC that is regulated in Turkey is benzene. Benzene long-term standard in Turkish air quality regulation is 5.0 µg m^{-3}. Among cities where data were used in comparison average benzene concentration in three studies exceeded the long-term standard. These are İzmir where average concentration is 10 µg m^{-3}, Bursa where average concentration was reported as 5.2 µg m^{-3} and Aliağa industrial site where average concentration was 5.0 µg m^{-3}. Average benzene concentrations in other cities comply with existing long-term benzene standard.

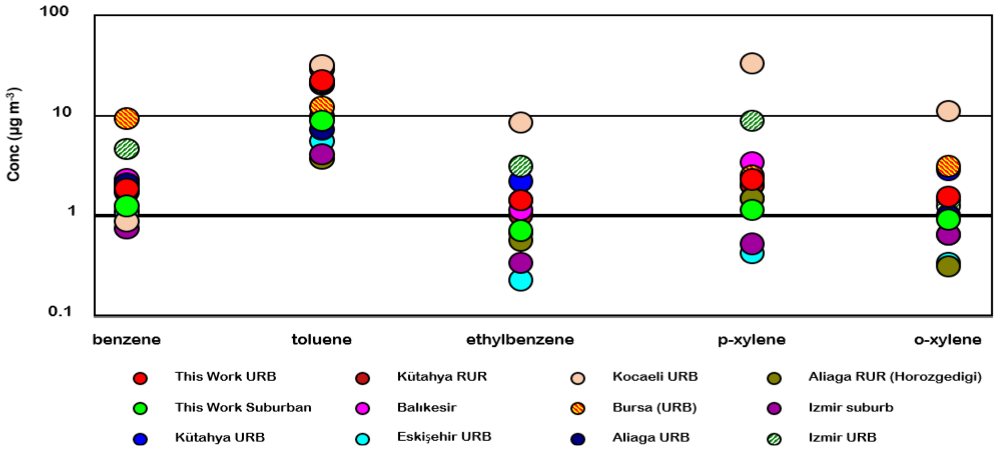


Figure 4.3: Comparison of BTEX concentrations in this study with other cities in Turkey

Table 4.3: BTEX Mean concentrations ($\mu g\ /m^3$) in this work and corresponding concentrations reported in other cities in Tukey

Location	Charac. of Site	Sampling Time	Benzene	Toluene	Ethylbenzene	p-Xylene	o-Xylene
Ankara (AU)	Urban	2015[9]	2,10	24,76	1,62	2,61	1,75
Ankara (METU)	Rural	2015	1,41	10,09	0,80	1,30	1,03
Kütahya[1]	Urban	2015	1,88	22,90	2,49	2,32	3,19
Kütahya[1]	Rural	2015	0,98	33,10	1,15	2,29	1,63
Balıkesir[2]	Urban	2010	2,63	10,90	1,29	3,80	0,73
Eskişehir[3]	Urban	2009	1,23	6,11	0,26	0,47	0,38
Kocaeli[4]	Urban	2006	2,26	35,51	9,72	36,87	12,46
Bursa[5]	Urban	2007	5,20	24,30	3,50	9,90	1,40
Aliağa[6]	Rural	2007	1,90	3,90	0,66	0,77	0,20
Aliağa[6]	Industrial	2007	4,70	3,90	0,99	2,00	0,76
Aliağa[7]	Urban	2006	2,39	7,95	0,75	1,65	1,13
İzmir[8]	Rural	2004	0,85	4,65	0,38	0,59	0,74
İzmir[8]	Urban	2004	10,40	13,50	1,60	2,87	3,58

1: (Bek, 2015), 2: (Yalçın, 2013), 3: (Demirel et al. 2014), 4: (Pekey et al. 2011), 5: (Civan, 2010), 6: (Civan et al., 2015), 7: (Doğan, 2013), 8: (Elbir et al., 2006), 9: years indicate the end of sampling period in each study

4.2.2 Comparison of Data in This Study and Other Cities around the World

Concentrations of BTEX measured in this study and corresponding data generated in other countries of the world are shown in Table 4.4. As mentioned earlier, the slight variations in the locations of sampling points used in studies can cause significant variations in VOC concentrations. Therefore, as pointed before comparison of data generated in this study with results of other measurements around the world can provide only crude information and can be used to put the measured values in this study into a perspective and nothing more.

The BTEX concentrations were generally low in cities in Europe and the US and high in Asian countries such as China and India. For example, benzene concentration vary between 46 and 87 µg m^{-3} in an urban areas in Egypt. Similarly, relatively high benzene levels, which can reach to 30 µg m^{-3}, 48 µg m^{-3} and 97 µg m^{-3} were reported for different parts of India. However, benzene levels are between 1.2 µg m^{-3} and 6 µg m^{-3} in U.K., 1.1 µg m^{-3} in Hamburg, 1.9 µg m^{-3} at Finland and 1.2 µg m^{-3} in France. Similarly, consistently high BTEX concentrations at Asian cities were also noted by Uzunpınar (2015).

The situation is not very different for other BTEX compounds. In this study, the values measured in the urban and suburban stations are closer to the VOC levels measured in the European cities. High concentrations similar to those observed in Asian and African cities were not seen in our urban and suburban data sets. It has been observed in earlier studies that VOC concentrations measured in Turkey were even lower than those reported in most European and North American countries. This was explained by smaller number of vehicles in traffic in Turkey. (Uzunpinar, 2015; Kuntasal, 2005). Vehicle counts performed at Kızılay in one of the earlier studies in Ankara demonstrated that cars passing through Kızılay was approximately quarter of the data from corresponding traffic counts performed at Ottawa, Canada. For that reason, although the emissions in Turkey are not as regulated as in developed European and North American countries, the concentrations of VOCs are low.

Table 4.4: BTEX concentrations (mean) measured in this study and corresponding concentrations reported for other cities around world

	Benzene ($\mu g/m^3$)	**Toluene ($\mu g/m^3$)**	**Ethylbenzene ($\mu g/m^3$)**	**p-xylene ($\mu g/m^3$)**	**o-xylene ($\mu g/m^3$)**
Ankara urban (AU, 2015) (this work)	2.10	24.76	1.62	2.61	1.75
Ankara rural (METU, 2015) (this work)	1.41	10.09	0.80	1.30	1.03
Helsinki, Finland urban (Hellen, 2002)	2.1	6.6	1.3	4.1	1.6
Helsinki, Finland rural (Hellen, 2002)	1.9	6.02	1.43	4.6	1.73
Dunkerque, France urban (Roukos et al. 2009)	1.19	2.52	1.08	1.07	0.55
Dunkerque, France rural (Roukos et al. 2009)	0.97	1.06	0.94	0.74	0.49
Zhejiang, China (Guo et al., 2004)	3.22	6.83	0.93	0.65	0.65
Pamplona, Spain (Parra et al. 2009)	2.84	13.26	2.15	3.38	2.63
Hamburg, Germany (Schneider et al., 2001)	1.13	4.46	–	1.2	–
Delhi, India urban (Hoque, 2008)	97	180	21	83	40
Delhi, India rural (Hoque, 2008)	48	85	7	30	15
Dehradun, India urban (Bauri et al., 2015)	29.76	83.54	9.93	25.7	17.08
United Kingdom (Derwent et al. 2000)	1.23–6.23	2.30–13.8	0.71–3.84	1.68–11.8	0.88–5.73
Ramsis and Haram, Egypt urban (Khoder, 2007)	87.2-46.2	213.8-111.8	43.3-22.77	140.8-74.62	73.77-36.23
Kafr El-Akram, Egypt rural (Khoder, 2007)	5.81	7.48	2.51	4.11	2.4

4.3 Temporal Variations in VOC Concentrations

Temporal variations in concentrations of pollutants can occur either as short- or long-term variations. Episodes and episodic changes, diurnal variations, weekday weekend differences are short-time changes. Long-term changes include seasonal changes and trend over years. This naming convention holds not only for VOCs but is also valid for all pollutants in the atmosphere.

Episodic changes, weekday – weekend changes and seasonal changes were examined in this study. Since we have only 18 months of data, it was not possible to examine the changes over many years. Also, it is not possible to examine the differences between day and night since samples were collected for 24 hours. In an earlier study, VOC concentrations were measured hourly between October and November 2013 and August 2014 using "online GC" at the METU station and changes in VOC during the day were discussed (Uzunpınar, 2015).

4.3.1 Episodic Variations in VOC Concentrations at AU and METU Stations

Episodes or episodic changes is a relative term. In a study where pollutant concentrations were measured (or samples were collected) in one minute intervals, episode or episodic change refer to variation in pollutant concentrations that occur within a few-minute time-frame. However, in studies where measurements (or sampling) is daily, episodes refer to variation in pollutant concentrations within a time-frame of few days. In either the case, these episodic variations in pollutant concentration can provide information on factors affecting pollutant concentrations in atmosphere. Episodic changes in pollutant concentrations are observed both in urban atmosphere where temporal variations of pollutants are controlled by local sources and local meteorology and in regional scale where variations in concentrations are controlled by regional sources and regional meteorology. In this study, only episodic changes in VOC concentrations due to variability in local emissions and local meteorology is discussed. Episodes, in this study, refer to variation in concentration of VOCs in the time frame of few days, due to our sampling strategy (24-hr intervals).

The reason for observed episodes in urban and industrial atmosphere can be short-term variations in local meteorology parameters, like washing the atmosphere with rain and /or sudden changes in pollutant emissions. Pollutant concentrations also show episodic changes in settlement areas as well as in remote areas to settlement areas and the pollutant emissions. While such episodic changes in rural areas remote from pollutant sources are the replacement of the trajectories of air masses during the transport, the reason of episodes in urban and industrial area can be the changes in meteorological parameters, washing the atmosphere with rain and /or sudden changes in pollutant emissions.

Episodic variations of selected VOCs at the AU and METU stations are shown in Figure 4.4. As can be seen from figure, in all VOCs, there are many episodes in both stations, particularly in winter months. This is the case for all VOCs, not just the VOCs shown in the figure. Short-term episodic changes are very typical for atmospheric data and observed in every data set and for all pollutants. Since episodic changes in pollutant concentrations can be informative about the reasons for such changes, assessment of how much each VOC varies may be useful in understanding whether meteorological factors or variability in emission are more effective in formation of episodes.

Relative variability of VOCs measured at stations had been studied in two ways. First, the coefficient of variation (CV) values for VOCs at two stations were calculated. CV, which is also known as "relative standard deviation", is a parameter given by $CV = \sigma/X$, where $\underline{\sigma}$ is the standard deviation of the measurements and $\underline{X}$ indicates the average value. Statistically, relative standard deviation is a parameter that indicates the repeatability of a large number of measurements made in succession. In addition, in environmental measurements relative standard deviation shows the variability in the data. It is expected that $CV < 0.05$ ($<5\%$) in analytical precision tests. However, in environmental studies CV or relative standard deviation indicates variability in data set and has nothing to do with repeatability of measurements.

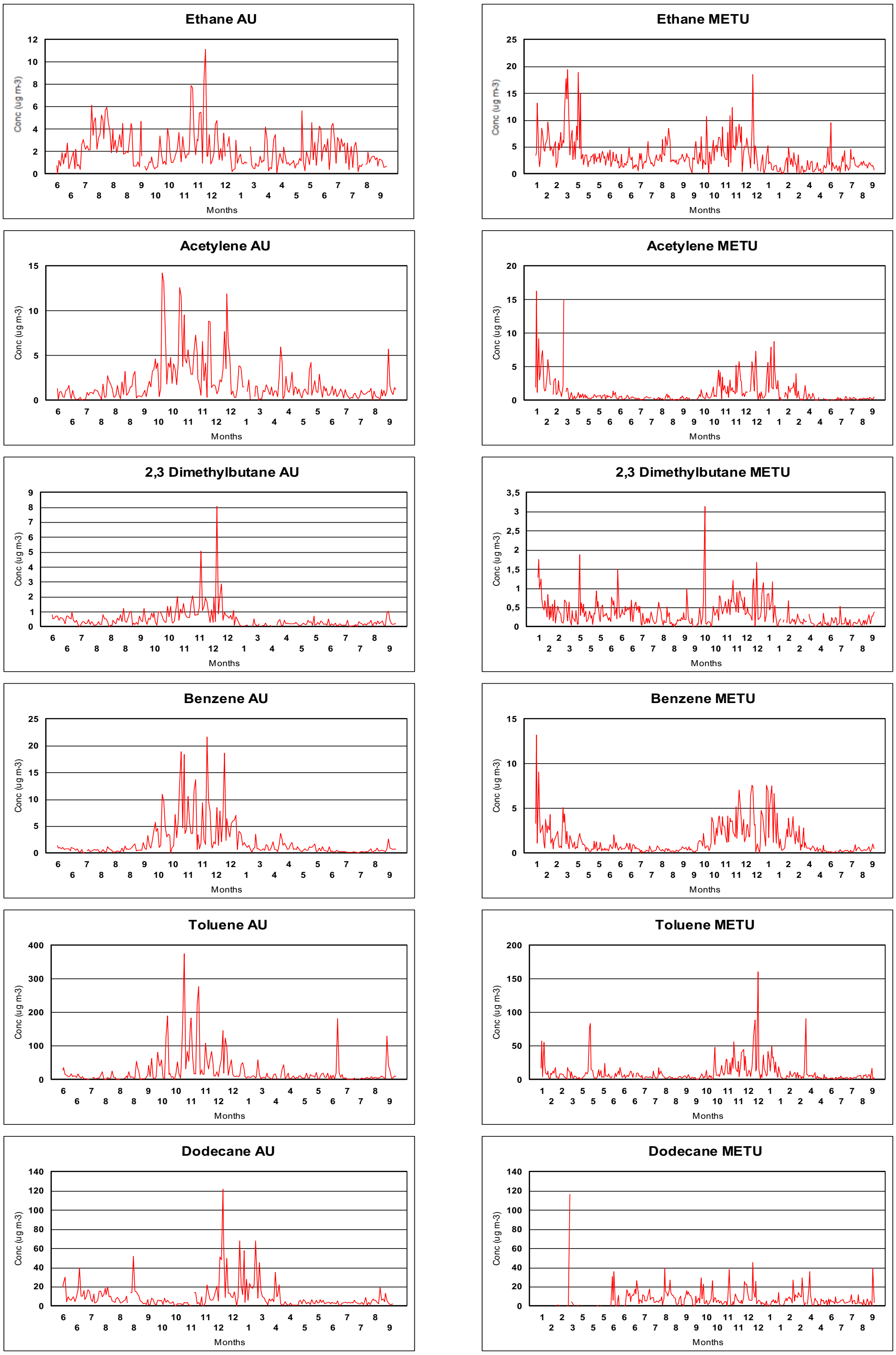


Figure 4.4: Episodic variations in concentrations of selected VOCs at both stations

In this study, CV was used as an indicator of episodic nature of data. VOC concentrations that show highly episodic behavior is expected to have high CV, conversely VOCs that does not show highly episodic behavior are expected to have small CV. With this approach, it becomes possible to assess differences in episodic behaviors of VOCs in the same station and if episodes of VOC concentrations measured at different stations are comparable.

The CV values of VOCs measured at AU and METU stations are given in Figure 4.5. Coefficient of variations vary between 0.85 for cyclopentane at urban station and 7 for n-pentane at suburban station. Most of the VOCs measured in both stations have CVs between 1.0 and 2.0. CVs between 1 and 2 implies that standard deviations of VOC concentrations are higher than their average concentrations and indicates the importance of episodes, which are shown in Figure 4.4, on temporal variability in VOC concentrations.

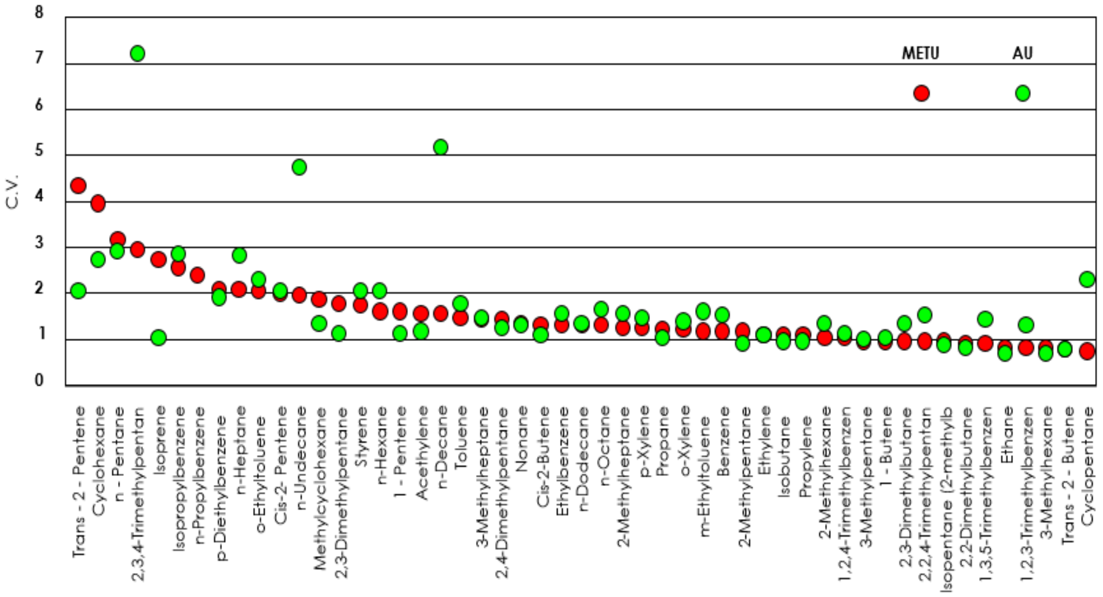


Figure 4.5: Coefficient of variation (relative standard deviation) of measured VOCs at two stations

However, there are exceptions to this general pattern. Some VOCs, like n-propylbenzene, isopropylbenzene, isoprene, 2,3,4-trimethylpentane, n-pentane cyclohexane and trans-2-pentane have higher average CVs than others, indicating that short-term variability in their data are higher than episodic variations in concentrations of other VOCs. On the contrary, CVs of few VOCs, including ethane, 1,2,3-trimethylbenzene, 3-methylhexane, trans-2-butane and cyclopentane have CVs smaller than the others, indicating that they are not as episodic as other VOCs measured in this study.

An important piece of information that comes out of CV calculations is that, for most of the VOCs measured in one station and for same VOCs measured at urban and suburban station CV values are highly similar (varies only between one and two), which indicates that an independent common factor is effective in the formation of episodes in VOC concentrations. This common and determinant factor is meteorology. Wind direction (WD) is the most important meteorological parameter in formation of episodes (Uzunpınar, 2015). When the wind flow to the station from direction of strong VOC sources (e.g. a road around the station), high VOC concentrations are measured. The measured concentrations will suddenly decrease when the wind changes its direction and comes from a sector where there is no strong VOC source. This sudden change in WD leads to formation of an episode.

Another meteorological factor that can play an important role in formation of episodes in pollutant concentrations is rain. When the station is under the influence of pollutant sources, the measured high concentrations will suddenly fall and create an episode with the beginning of the rain, which washes VOCs from atmosphere. However, rain is not as effective in formation of VOC episodes as it is in formation of episodes in concentrations of conventional pollutants, such as SO_2, because henry's low constant of most VOCs are low, which means that they are not highly soluble in water. As a result, it can be said that WD is the most important meteorological parameter in generating VOC episodes. The CV values measured at both stations were not different for most VOCs. This confirms the role of meteorological factors in episode formation.

Comparison of average-to-baseline concentration ratios of each VOCs is the second approach used to obtain information on contribution of episodes on observed mean concentrations of VOCs. Theoretically baseline concentration of VOCs is the average concentration of that VOC (or any pollutant) found after each episode in its concentration is deleted one by one. However, “most frequently observed value” is used as baseline level of each VOC (Sather et al., 2008), as it is difficult to remove all episodes one by one from data for 100 VOCs (50 VOCs were measured in each of the two stations). Previous work on our group has shown that these two values are very close to each other (Gullu et al., 1998).

The similarity of the two methods for calculating average-to-baseline to concentration (a. by using the most frequently observed concentration value and b. using average concentrations, after stripping all episodes, as the baseline concentrations of VOCs) is also tested. First, "most frequently observed concentrations” were calculated for ethane, acetylene, 2,3-dimethylbutane, benzene, toluene and n-dodecane measured at our urban station. Also, average concentrations of same compounds were calculated after all episodes are stripped from their concentrations.

Baseline concentrations calculated using these two methods are given in Table 4.5. As it can be seen in the table, there is no significant difference between baseline concentrations calculated by both methods. Systematic deletion of episodes for each VOC is a subjective method. Accordingly, the small differences between the baseline concentrations calculated by the two methods in the table is due to subjective nature of deleting episodes in the second approach. This is one of the reasons why most frequently observed value approach is adopted for baseline calculations in this study (the second reason was the difficulty in deleting every episode in data for approximately 100 VOCs).

Since both calculation of CV and average-to-base line concentration ratio are measures of variability in data, ordering of VOCs based on CV and average-to-baseline ratios should not be very different from each other. Compared to Figure 4.5

and Figure 4.6, it looks like they are similar but not identical. That is why while the CV is a variable that shows frequency of episodes, average to baseline ratio is a measure of how much episodes form annual mean concentration of VOCs.

The average and baseline concentrations of VOCs in AU and METU stations and contribution of episodes on average VOC concentrations are given in Table 4.6 and Figure 4.6, respectively. It can be seen from both table and figure that the contribution of episodes to the annual mean concentrations of VOCs varied between 11% (n-propylbenzene) and 94% (trimethylpentane) at the AU station and between 14% (cyclohexane) and 92% (styrene) at the METU station. Figure 4.6 also demonstrate that there is no one-to-one relationship in percent contribution of episodes on VOC concentrations at urban and suburban stations. For example, the lowest episode contribution in the AU station is 11% for n-propylbenzene. Contribution of episodes on average n-propylbenzene concentration at our suburban station is 25%. The highest episode contribution in the AU station is 94% for 2,2,4-trimethylpentane. The episodic contribution to 2,2,4-trimethylpentane concentration at METU station is 88%.

A point that attracts attention in Figure 4.6 is that episodic contribution for 36 of the 51 measured hydrocarbons in urban station are higher than corresponding episode contributions to their concentrations at the suburban station. Although differences are not large, this consistent pattern shows that the hydrocarbon concentrations measured at AU station are generally more episodic than those at METU station are. Approximately 60% of the average VOC concentrations measured at urban stations and 54% at METU stations are accounted for by episodes.

For 36 out of 51 VOCs (including 2,2,4-trimethylpentane, 1,2,4-trimethylbenzene, o-ethyltoluene, m,p-xylene, 2,3-dimethylpentane, 2 methylheptane, cis-2-butane, styrene, 3-methylheptane, benzene, 2,2-dimethylbutane, 1,2,3-trimethylbenzene, cis-2-pentane, ethylene, acetylene, trans-2-pentane, trans-2-butane, ethylbenzene, 2,3,4-trimethylpentane, propylene, isopentane, 3-methylpentane, p-diethylbenzene, 3-methylhexane, 2,3-dimethylbutane, propane, 1-butane, o-xylene, ethane, n-dodecane, n-pentane, isopropylbenzene, cyclopentane, n-undecane, cyclohexane, n-propylbenzene), calculated episode contributions at both stations are close to each other.

There are two notable points in this group. First one is that for the traffic markers (benzene, acetylene etc.), there is no significant difference in episodic contributions on their average concentrations at both stations. In other words, traffic derived VOCs show same degree of episodic variability at urban and suburban stations. Similar episodic contribution to traffic markers in both stations is not surprising, because traffic is a source that affects both stations and meteorological conditions affecting both stations are the same.

One point to note in this discussion is that the similarity of percentage contributions to the annual average concentrations of episodes does not mean that measured concentrations in both stations are equal. As traffic density is higher around the AU station, the VOC concentrations measured at this station are higher than those measured at the METU station. However, the percentage contributions of these episodes to these average concentrations are not different. Although contributions of episodes on average VOC concentrations are similar at urban and suburban stations, episode contribution are very different for some VOCs. It is observed that episode contributions to average concentrations of 9 VOCs (1,3,5-trimethylbenzene, methylcyclohexane, m-ethyltoluene, nonane 1-pentane, isoprene, n-hexane, 2-methylpentane, toluene) are significantly higher in the AU station. On the other hand, for 6 VOCs (2-methylhexane, 2,4-dimethylpentane, isobutane, n-octane, n-decane, n-heptane), the episodic contribution in METU is significantly higher than corresponding episode contribution at the urban station.

For some VOCs (nine VOCs named above), contribution of episodes to the measured VOC concentrations at the METU station may be due to the fact that at least a portion of the VOCs are transported from the city and that part of the episodes are smoothed during transport. Consequently, it can be concluded that VOCs, which have similar episode contributions in both stations, are the VOCs that are released from similar sources near stations. It should also be noted that the nine VOCs that have significantly higher episode contribution at urban station are compounds emitted from solvents. Some of them also have sources other than solvents like traffic, but all of them are used in solvents and are known to be emitted from solvent use, which implies that solvent emissions are more episodic than traffic emissions.

Table 4.5: Baseline concentration values of VOCs calculated using different definitions

	AU Most freq. observed value (µg m^{-3})	**AU Avg. after stripping peaks (µg m^{-3})**
Ethane	1.19	1
Acethylene	0.67	0.5
2,3-Dimethylbutane	0.23	0.2
Benzene	0.6	0.7
Toluene	11.25	10
n-Dodecane	5.63	4.5

Table 4.6: Average and baseline concentrations (µg/m^3) of VOCs at AU and METU stations

	AU Avg.	**AU Baseline**	**METU Avg.**	**METU Baseline**	**AU Avg. / METU Avg.**
Ethane	2.1	1.19	3.4	2.23	0,62
Ethylene	6.53	2.25	6.22	2.77	1,05
Propane	4.65	2.17	1.77	0.88	2,62
Propylene	8.67	3.25	3.66	0.88	2,37
Isobutane	23.58	11.88	9.29	1.54	2,54
Acethylene	1.93	0.67	1.15	0.2	1,67
Trans - 2 - Butene	0.42	0.15	0.31	0.06	1,37
1 - Butene	0.67	0.32	0.31	0.18	2,12
Cis-2-Butene	9.32	2.25	5.17	1	1,80
Cyclopentane	0.38	0.25	0.18	0.1	2,09
Isopentane	5.59	2.17	3.4	1.85	1,64
n - Pentane	1.43	0.89	0.87	0.46	1,64
Trans - 2 - Pentene	0.17	0.06	0.08	0.06	2,23
1 - Pentene	0.25	0.05	0.15	0.1	1,65
Cis-2- Pentene	0.09	0.03	0.06	0.03	1,63

Table 4.6 cont'd: Average and baseline concentrations (µg/m^3) of VOCs at AU and METU stations

	AU Avg.	AU Baseline	METU Avg.	METU Baseline	AU Avg. / METU Avg.
2,2-Dimethylbutane	0.75	0.22	0.45	0.2	1,65
2,3-Dimethylbutane	0.53	0.23	0.34	0.18	1,55
3-Methylpentane	0.84	0.33	0.57	0.28	1,46
o-Xylene	1.75	0.88	1.03	0.44	1,70
Nonane	0.53	0.1	0.32	0.16	1,63
Isopropylbenzene	0.23	0.15	0.18	0.12	1,30
n-Propylbenzene	0.56	0.5	0.27	0.2	2,05
m-Ethyltoluene	0.54	0.1	0.35	0.22	1,56
1,3,5-Trimethylbenzene	1.27	0.13	0.73	0.3	1,73
o-Ethyltoluene	0.74	0.13	0.6	0.2	1,23
1,2,4-Trimethylbenzene	2.11	0.33	1.24	0.17	1,70
n-Decane	1.62	1.05	0.84	0.25	1,92
1,2,3-Trimethylbenzene	6.54	2	3.1	1.42	2,11
p-Diethylbenzene	1.39	0.57	1.31	0.5	1,06
n-Undecane	3.6	2.5	2.72	1.8	1,32
n-Dodecane	9.82	5.63	7.5	5	1,31
Isoprene	0.78	0.2	0.53	0.28	1,47
n-Hexane	3.7	1	2.97	1.8	1,24
2,4-Dimethylpentane	0.22	0.11	0.16	0.04	1,32
Benzene	2.1	0.6	1.41	0.44	1,48
Cyclohexane	0.28	0.25	0.21	0.18	1,35
2-Methylhexane	0.45	0.22	0.26	0.02	1,71
2,3-Dimethylpentane	0.3	0.06	0.26	0.08	1,12
3-Methylhexane	1.39	0.58	0.98	0.6	1,43
2,2,4-Trimethylpentane	1.3	0.07	0.63	0.07	2,05
n-Heptane	0.6	0.5	0.4	0.2	1,50
Methylcyclohexane	0.15	0.02	0.14	0.1	1,01
2,3,4-Trimethylpentane	1.18	0.44	0.37	0.29	3,17
Toluene	24.76	11.25	10.09	7.31	2,45
2-Methylheptane	0.49	0.1	0.46	0.06	1,07
3-Methylheptane	0.19	0.05	0.14	0.04	1,38
n-Octane	0.31	0.2	0.22	0.03	1,41
Ethylbenzene	1.62	0.6	0.8	0.44	2,03
p-Xylene	2.61	0.5	1.3	0.15	2,00
Styrene	1.95	0.5	1.07	0.08	1,83

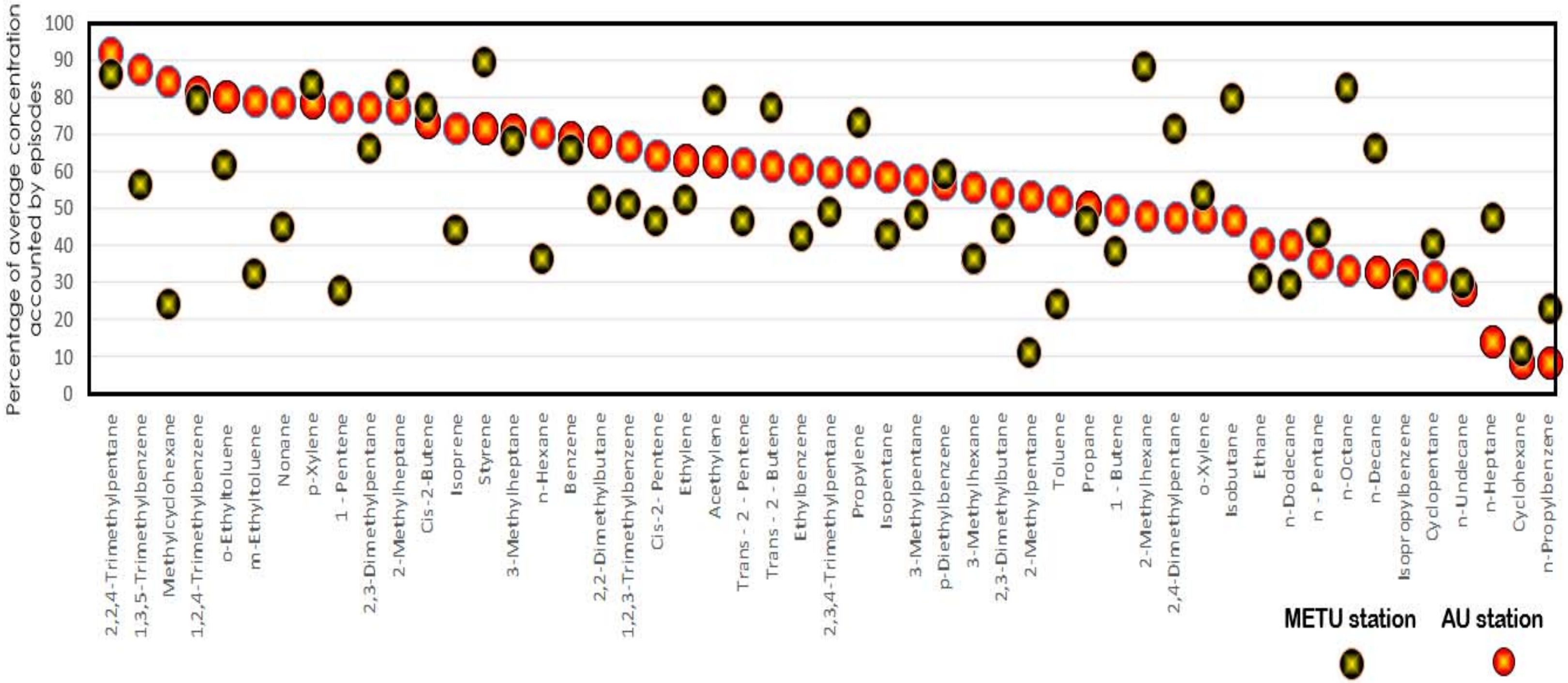


Figure 4.6: Percent contribution of episodes on average concentrations of VOCs at AU and METU stations

4.3.2 Weekday – Weekend Variations in VOC concentrations at AU and METU Stations

Weekday, weekend concentrations and WD-to-WE concentration ratios of VOCs measured at AU and METU stations are given in Figure 4.7.

Since the most important source of VOC concentrations is traffic and traffic is more intense during the weekdays than at the weekend, unless there are very specific sources of VOC concentrations, the concentrations measured during the weekdays are expected to be higher than average concentrations of most VOCs measured at weekend.

In this study, the weekday VOC concentrations measured at the AU station and at the METU station are higher than the weekend concentrations. This difference is shown in Figure 4.7a and Figure 4.7b for AU and METU stations, respectively. It is seen that weekday concentrations are systematically higher than weekend concentrations, as prepared using both station data. This is not a surprising observation as explained above. The WD/WE ratios at both stations are shown in Figure 4.7c. This figure allows comparison of WD/WE ratios measured in two stations and some interesting points stand out.

Except for two of the measured VOCs (2,2,4-trimethylpentane and 1,2,4-trimethylbenzene), the ratio of WD/WE ratio is higher than unity. The fact that most of the VOCs are traffic-derived and the traffic is more intense during the weekdays makes almost all of the VOC concentrations are higher in weekdays. This is a situation that is seen in many works (Yurdakul, 2013; Kuntasal, 2005).

For most VOCs, the WD/WE ratios measured at the AU station are generally higher than the WD/WE ratios measured at the METU station. At the AU station, the average of the WD/WE ratios of VOCs is 1.43 ± 0.28. Corresponding average value at suburban station is 1.28 ± 0.29. Although the difference is not large, it is systematically seen in most of the VOCs and can be attributed to higher traffic density around the AU station during weekdays, which makes the reduction in the weekends more pronounced.

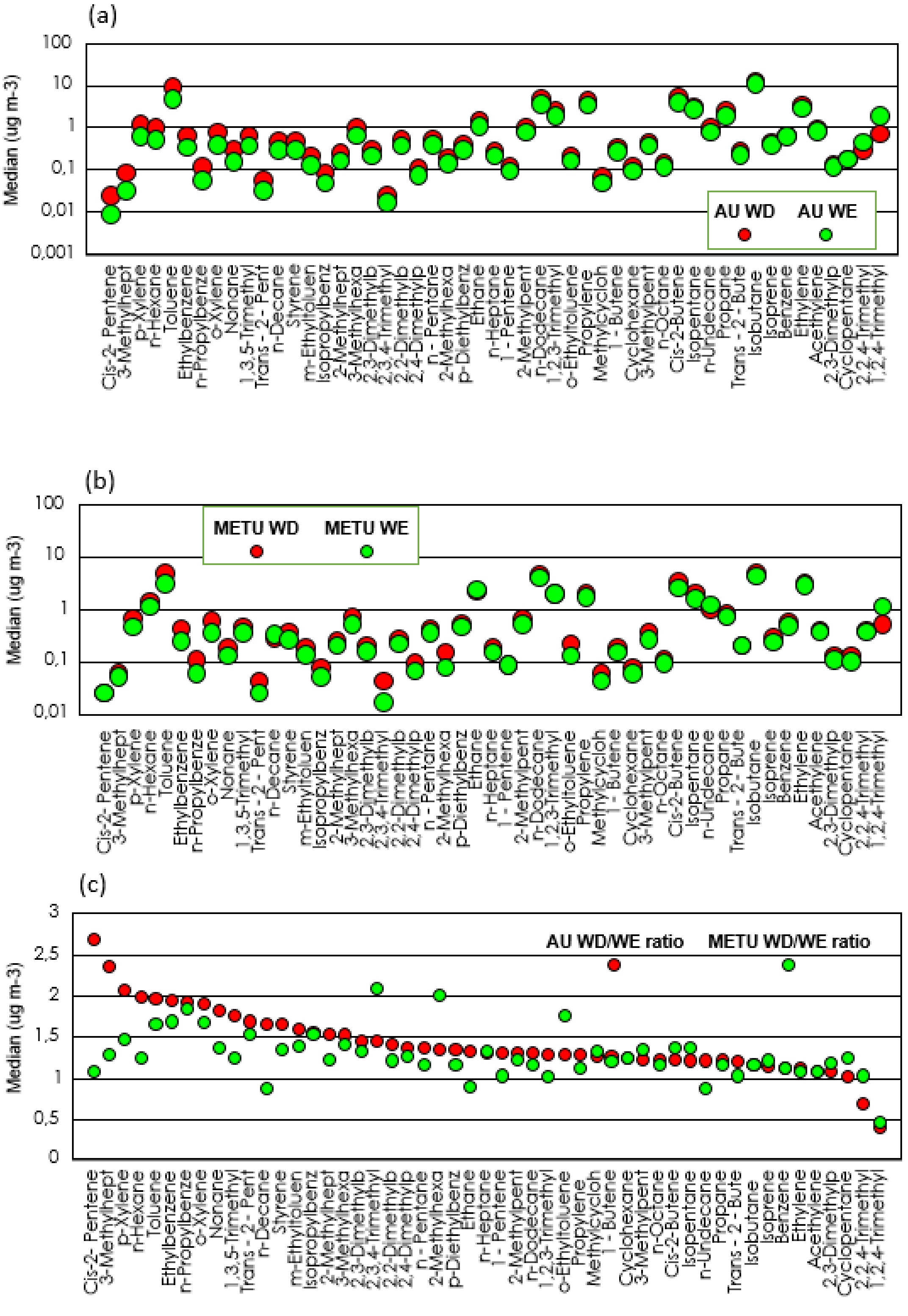


Figure 4.7: Weekday, weekend concentrations and WD-to-WE concentration ratios of VOCs at AU and METU stations

In Figure 4.7c, the WD/WE ratio of the first seven VOCs in the urban area is the highest, and the WD/WE ratios calculated for the AU are significantly higher from those calculated at the METU station (AU higher). Since the ratios of WD/WE concentration of traffic based VOCs are around 1.5, there must be other source other than traffic that runs during weekdays but stops at weekends. Also, these sources should not be active at the METU station. These sources are likely to be solvents used in photocopying and printing houses in the city. Among these VOCs, there are BTEX compounds that support this result such as m, p-xylene, ethylbenzene and toluene. The main source of BTEX compounds is traffic, but the compounds other than benzene are also used as solvents. The fact that these compounds are also in the group mentioned shows that the sources of these 6-7 VOCs are traffic and solvent at the AU station. On the other hand, there is no solvent source that much affects VOC concentrations around the METU station. That is why in METU these VOCs are dominated by traffic sources. As a result, the WD/WE ratio for VOCs in METU is not as high as seen in the AU station.

4.3.3 Long – term (seasonal) Variations in VOC Concentrations at AU and METU Stations

Seasonal variations in VOC concentrations can be due to seasonal variation in meteorology, like seasonal differences in rainfall, wind speed, temperature etc. or seasonal variations in emissions; like seasonal variations in emissions from heating sources or seasonal differences in temperature-dependent solvent emissions or evaporative gasoline emissions. These points also means that seasonal variations in concentrations of VOCs can also provide qualitative information on their sources, which can be used as supplementary information to assign sources to factors in quantitative source apportionment exercise, which will be discussed in coming sections of the manuscript.

Summer and winter concentrations of all VOCs measured in this work are given in Table 4.7. Same information is visually shown in Figure 4.8. As discussed in different parts of the manuscript, both figures and tables are used in the manuscript, because it is easier to highlight important points about seasonal variations in VOC concentrations in figures.

In both stations, with few exceptions, winter concentrations of VOCs are higher than their summer concentrations. However, winter-summer difference is not the same for all VOCs. Winter-to-summer concentration ratios range between 5.8 (for styrene at urban station) and 0.23 (for 1,2,4-trimethylbenzene at suburban station). Styrene has the highest winter-to-summer concentration ratio in both stations.

Table 4.7: Summer and Winter Concentrations ($\mu g/m^3$) of Measured VOCs at AU Station

	Summer Median	Summer Mean	Winter Median	Winter Mean
Ethane	1.91	2.05	1.57	2.16
Ethylene	4.19	4.40	7.94	10.18
Propane	2.02	2.23	7.96	8.77
Propylene	4.39	4.66	13.43	15.45
Isobutane	12.01	13.38	31.52	40.86
Acethylene	0.89	1.06	2.32	3.47
Trans - 2 - Butene	0.39	0.40	0.36	0.46
1 - Butene	0.30	0.33	1.02	1.25
Cis-2-Butene	5.25	5.55	12.99	15.92
Cyclopentane	0.21	0.22	0.41	0.66
Isopentane	3.34	3.75	6.66	8.71
n - Pentane	0.51	0.56	1.40	2.90
Trans - 2 - Pentene	0.04	0.09	0.15	0.27
1 - Pentene	0.11	0.13	0.30	0.42
Cis-2- Pentene	0.01	0.07	0.03	0.13
2,2-Dimethylbutane	0.52	0.53	1.00	1.15
2,3-Dimethylbutane	0.30	0.32	0.67	0.90
2-Methylpentane	0.99	1.11	2.11	2.67
3-Methylpentane	0.49	0.66	0.70	1.14
Isoprene	0.58	0.68	0.64	0.96

Table 4.7 cont'd: Summer and Winter Concentrations (µg/m^3) of Measured VOCs at AU Station

	Summer Median	Summer Mean	Winter Median	Winter Mean
n-Hexane	0.81	1.35	3.48	7.25
2,4-Dimethylpentane	0.10	0.11	0.24	0.40
Benzene	0.73	0.72	3.10	4.43
Cyclohexane	0.14	0.16	0.26	0.54
2-Methylhexane	0.21	0.37	0.39	0.59
2,3-Dimethylpentane	0.14	0.24	0.32	0.42
3-Methylhexane	1.13	1.34	1.21	1.48
2,2,4-Trimethylpentane	0.33	1.40	0.68	1.15
n-Heptane	0.27	0.27	0.65	1.16
Methylcyclohexane	0.07	0.08	0.20	0.26
2,3,4-Trimethylpentane	0.02	0.05	0.11	5.17
Toluene	6.74	11.55	17.03	46.67
2-Methylheptane	0.26	0.43	0.30	0.59
3-Methylheptane	0.05	0.12	0.21	0.31
n-Octane	0.14	0.15	0.37	0.57
Ethylbenzene	0.52	0.70	2.03	3.17
p-Xylene	0.83	1.13	3.03	5.12
Styrene	0.27	0.78	1.56	3.68
o-Xylene	0.69	0.77	1.94	3.38
Nonane	0.24	0.41	0.53	0.73
Isopropylbenzene	0.08	0.14	0.15	0.37
n-Propylbenzene	0.09	0.22	0.25	1.22
m-Ethyltoluene	0.17	0.25	0.54	0.96
1,3,5-Trimethylbenzene	0.46	0.99	1.22	1.76
O-Ethyltoluene	0.21	0.52	0.46	1.15
1,2,4-Trimethylbenzene	1.68	2.24	0.85	1.51
n-Decane	0.54	0.81	0.78	3.37
1,2,3-Trimethylbenzene	2.74	5.09	5.71	9.06
p-Diethylbenzene	0.55	1.23	0.64	1.72
n-Undecane	1.56	3.98	1.36	2.93
n-Dodecane	6.01	7.32	6.83	14.08

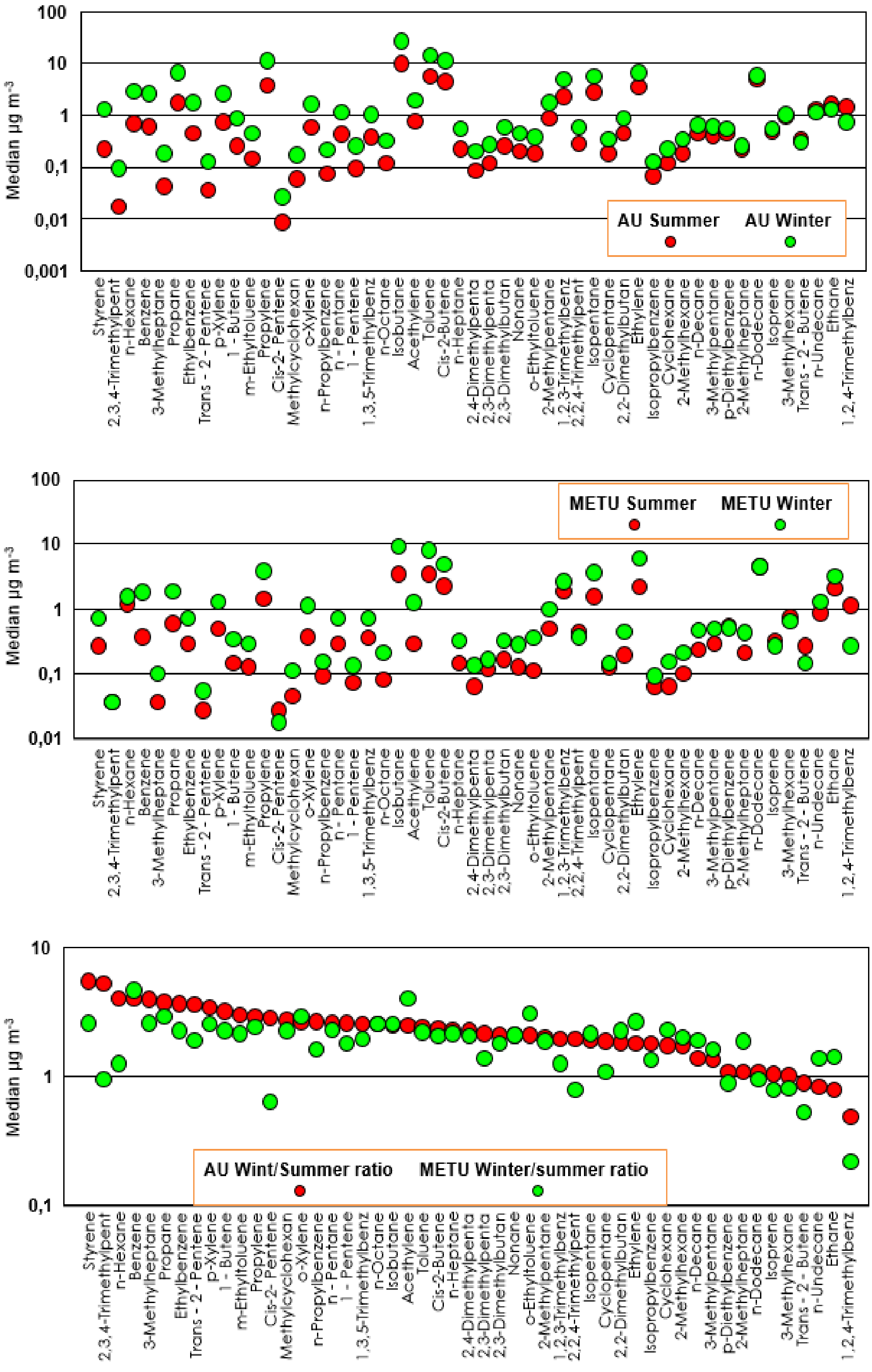


Figure 4.8: Winter-to-summer concentration ratios of VOCs at AU and METU stations

There is no VOC with a winter-to-summer ratio < 1, except for t-2-butene, n-undecane, ethane and trimethylbenzene. One important reason for higher winter concentrations for most of VOCs is the seasonal differences in meteorology, particularly seasonal differences in mixing height. Pollutants whose summer and winter emissions are close to each other are expected to have lower concentrations in summer, because mixing height is approximately a factor of two or three times higher during summer season. This means that emitted pollutants are dispersed in a larger volume in summer season, resulting in lower concentrations during summer, provided that emissions are not dramatically higher in summer months.

Nevertheless, meteorology is not the only reason (if it is, winter-to-summer concentration ratios of all VOCs would be the same). This reasoning also indicates that t-2-butene, n-undecane, ethane and trimethylbenzene have significantly higher emissions in summer. The most important summer source for VOCs is evaporative emissions, which increases with temperature.

Another reason for lower VOC concentrations during summer can be faster photochemical degradation of reactive VOCs with higher solar flux in summer (Lee et al., 2002). Please note that dominant VOC source in an urban atmosphere is traffic emissions. Since traffic emissions do not change substantially between summer and winter, one would expect to see higher concentrations of traffic-related VOCs in winter. Please also note that if traffic and mixing height were the only source of seasonal variability in measured VOC concentrations, all VOCs should have the same S/W concentration ratio. Since this is not the case, some VOC have S/W ratios close to unity, whereas others have S/W ratios, which are much larger than one, then there should be sources other than traffic affecting their summer and winter concentrations.

VOCs that have W/S concentration ratios close to unity are expected to have strong contribution from solvent use and gasoline evaporation due to enhanced evaporation during warm summer season (Kuntasal et al., 2005; Yurdakul et al., 2017). These compounds include cyclopentane, n-decane, 2,2 – dimethylbutane, isopropylbenzene, cyclohexane, 2-methylhexane, 3-methylpentnane, p-diethylbenzene. All of them are well documented components in various solvents (Watson et al., 2001). Studies conducted up to this point in our group, have shown that winter season concentrations of VOCs are generally high. Since traffic is a very unchanging source in summer and winter, the concentration of winter pollutants of traffic pollutants is high due to the effect of meteorology.

Monthly average concentrations for some of VOCs were calculated and shown in Figure 4.9 and Figure 4.10 that show well-defined seasonal pattern and those that do not show a pattern, respectively. The VOCs shown in Figure 4.9 are examples for hydrocarbons that show a well-defined seasonal variation. It is clear from the figure that winter concentrations of these groups of VOCs are high and the summer concentrations are low in both stations. Reasons that gives this pattern is discussed in previous paragraphs. Forty-seven out of 51 VOCs, measured in this study showed this pattern, indicating that traffic is dominating source for majority of hydrocarbons measured in this study. Very few VOCs showed the pattern seen in Figure 4.10.

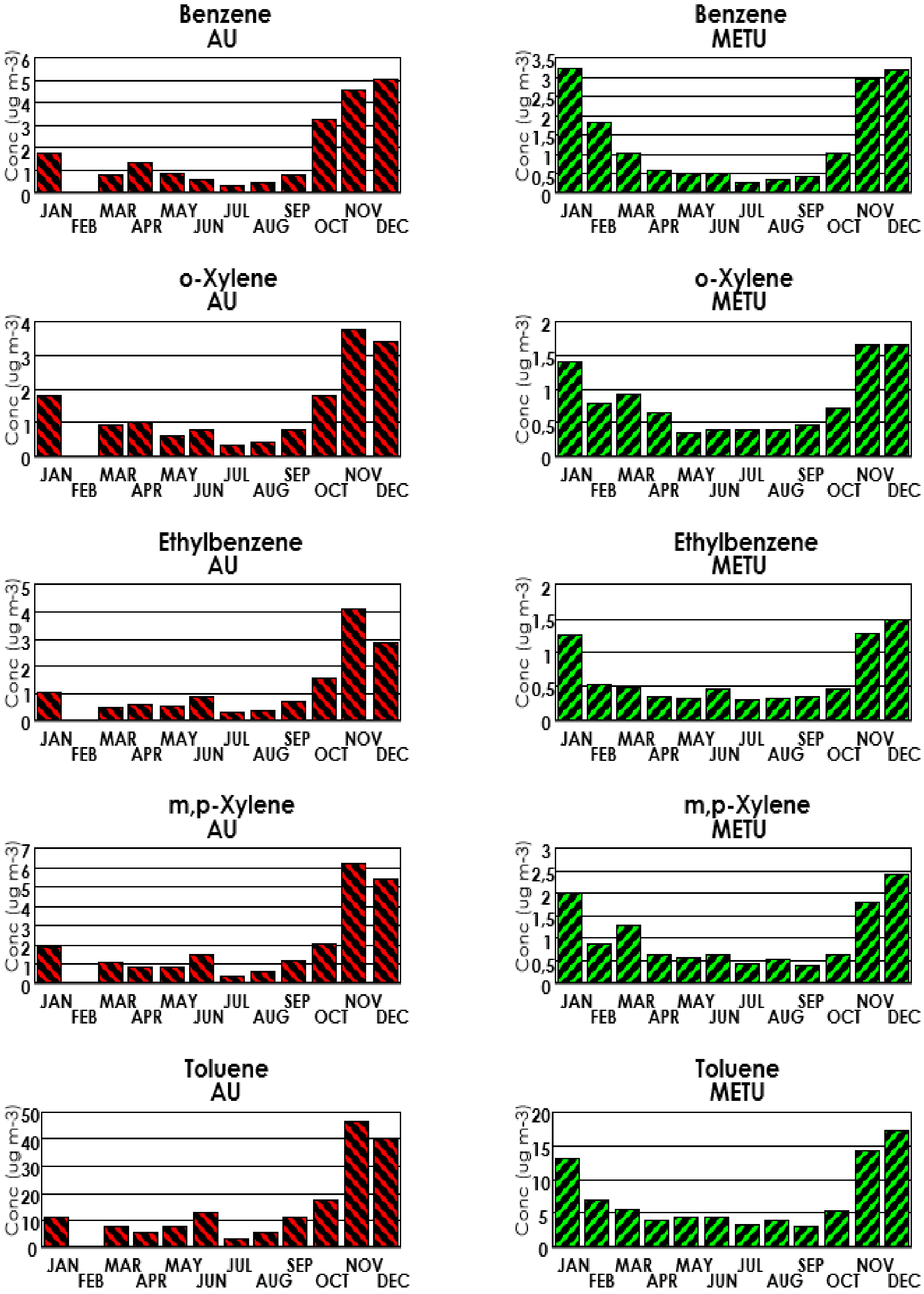


Figure 4.9: VOCs, which show well-defined seasonal patterns at AU and METU stations

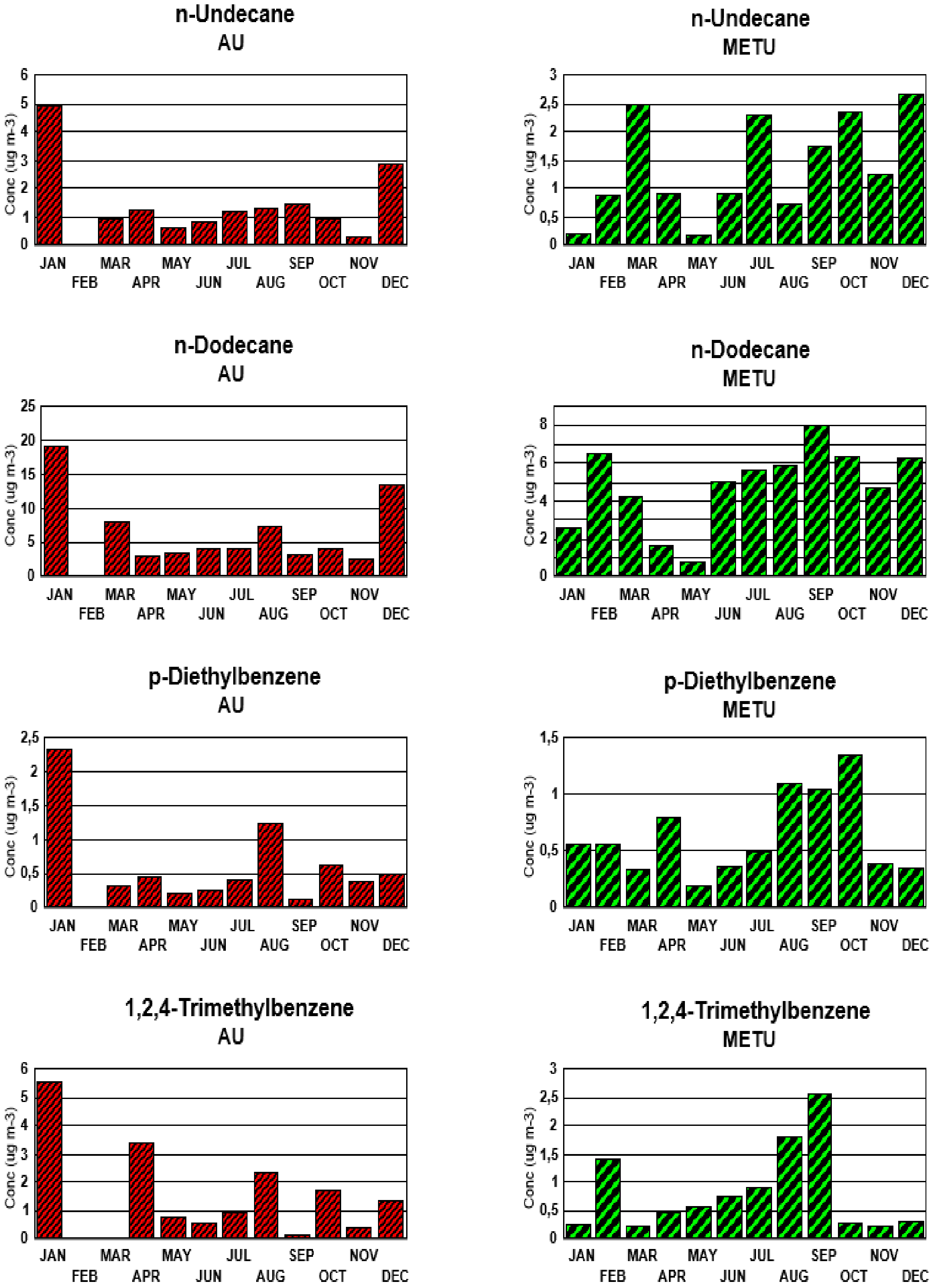


Figure 4.10: VOCs, which do not show well-defined seasonal patterns at AU and METU stations

4.3.4 Year – to – Year Variations in VOC Concentration at AU and METU Station

There are four VOC studies performed at Ankara atmosphere, before this work. The first of these is the work done in 2003 (Kuntasal et al., 2013). This was one of the first VOC studies in Turkey. Other VOC measurements were performed 2008 (Yurdakul et al., 2013) and in 2011 (Yurdakul et al., 2016). In all these studies VOCs were sampled in the METU Environmental Engineering department (Although there were more than one sampling location in some of these studies, data generated at METU station were selected for comparison). In all these studies, VOCs were sampled onto tenax sorbents and subsequently analyzed by GC-FID system equipped with a thermal desorber. Since solid sorbents like tenax are not efficient in collecting VOCs with carbon number < C4, all VOCs measured in this work (where VOCs were collected in evacuated canisters) were not measured in previous studies. However, approximately 30 VOCs measured by cartridge sampling is enough to compare with data generated in this study.

VOC concentrations measured in 2003, 2008, 2011 and 2015 are given in Table 4.8 and Figure 4.11. Although the figure and table show the same data we prefer to keep both of them because it is easier to see the changes in the figure and the table can be very useful if someone needs data in the future. BTEX compounds are highlighted in the figure. There is no consistent variation in VOC concentrations between 2003 and 2015. VOC concentrations measured in 2011 are the highest for all measured species and those measured in 2008 are generally the lowest for most of the measured VOCs. VOC concentrations measured in 2003 and 2015 are generally between the two. Data measured in this study are low for compounds like 3-methylpentane, 2,4-dimethylpentane, benzene and cyclobenzene. On the other hand, concentrations measured in 2015 are higher than corresponding concentrations measured in other years for compounds like n-dodecane, 1,2,3,-trimethylbenzene, 1,2,4-trimethylbenzene, and o-ethylbenzene. We expected to see the lowest concentrations in 2003 due to smaller traffic density in those years. However, VOC concentrations in 2003 are the lowest for VOCs like 2,2-dimethylbutane, 2,3 dimethylbutane, but high for VOCs like benzene, 2-methylhexane etc. Obviously, 2003 concentrations are not the lowest for most of the VOCs as we expected.

The lack of consistent pattern, which we expected to see in the beginning, signifies the difficulty in comparing VOC levels, due to high sensitivity of measured concentrations to distance from sources. In 2003, samples were collected at the back of the Metallurgical Engineering department and at third floor of the building. In 2008, samples were collected at the entrance of the Environmental Engineering department (ENVE) canteen. In 2011, samples were collected around the ENVE building using passive samplers. Finally, samples were collected behind the ENVE building in 2015. Results demonstrated that differences in sampling locations is more important than time variation in concentrations and samples has to be collected at exactly same point to detect long-term variations in VOC concentrations.

One of the outcomes of this comparison, which is one of the reasons why we did not observe a consistent pattern in all VOCs is that concentrations of VOCs did not change significantly in last 12 years. VOC concentration measured in 2011 are consistently high for most of the measured VOCs, which is probably due to close proximity of sampling points to traffic emissions. In 2011 sampling campaigns, some of the passive samplers were on the sidewalk. When data from 2011 sampling is not taken into account, VOC concentrations cover a narrow range. This is interesting, because number of vehicles registered in Ankara increased from 879672 in 2003 to 1678731 in 2015 (Turkish Statistical Institute, 2017). However, concentrations of VOCs are decreasing in recent years due to both traffic restrictions and improvements in engine technology (Huang et al., 2017; Martens, 2017). The decrease is not new. It had been observed for some time now (Stemmler et al., 2005). Drops in VOC concentrations as high as factor 7 was observed (Ehlers et al., 2016). Apparently, the increase in traffic intensity between 2003 and 2015 at Ankara did not affect emissions significantly, indicating that increase in emissions due to increased number of vehicles in traffic is compensated by decrease in VOC emissions per km traveled due to improvements in engine technology.

Table 4.8: Variation of VOC median concentrations (µg/m^3) between 2003 and 2015 in Ankara

	This Study AU	**This Study METU**	**2011[1]**	**2008[2]**	**2003[3]**
n - Pentane	0.59	0.49			0.49
2,2-Dimethylbutane	0.53	0.31			0.24
2,3-Dimethylbutane	0.32	0.23			0.19
2-Methylpentane	1.06	0.72			0.74
3-Methylpentane	0.54	0.39			0.64
n-Hexane	1.14	1.48	0.59		0.59
2,4-Dimethylpentane	0.12	0.10	0.44		
Benzene	0.84	0.64	1.67		1.66
Cyclohexane	0.12	0.09	0.38	1.2	
2-Methylhexane	0.22	0.15	0.35	0.17	0.34
3-Methylhexane	1.14	0.80	0.8	0.03	0.26
Methylcyclohexane	0.08	0.07	0.15	0.05	
Toluene	9.12	5.23	16	3.6	3.28
2-Methylheptane	0.28	0.28	0.39	0.14	
n-Octane	0.16	0.13	1.5	0.09	
Ethylbenzene	0.70	0.47	1.1	0.45	0.43
m,p-Xylene	1.20	0.73	5	1.13	1.49
Styrene	0.56	0.43	0.92	0.14	
o-Xylene	0.86	0.62	0.8	0.21	0.53
Nonane	0.30	0.21	1.2	0.09	
Isopropylbenzene	0.09	0.09	0.12	0.02	
n-Propylbenzene	0.13	0.12	2.7		
m-Ethyltoluene	0.23	0.21		0.12	0.28
o-Ethyltoluene	0.25	0.22		0.06	
1,3,5-Trimethylbenzene	0.62	0.52	0.68		
1,2,4-Trimethylbenzene	1.16	0.63	0.3		0.45
n-Decane	0.57	0.37	0.54	0.11	
1,2,3-Trimethylbenzene	2.97	2.32	0.73		
n-Dodecane	5.80	5.06	1.4		

[1]: Yurdakul et al., 2016, [2]: Yurdakul et al., 2013, [3]: Kuntasal, 2013

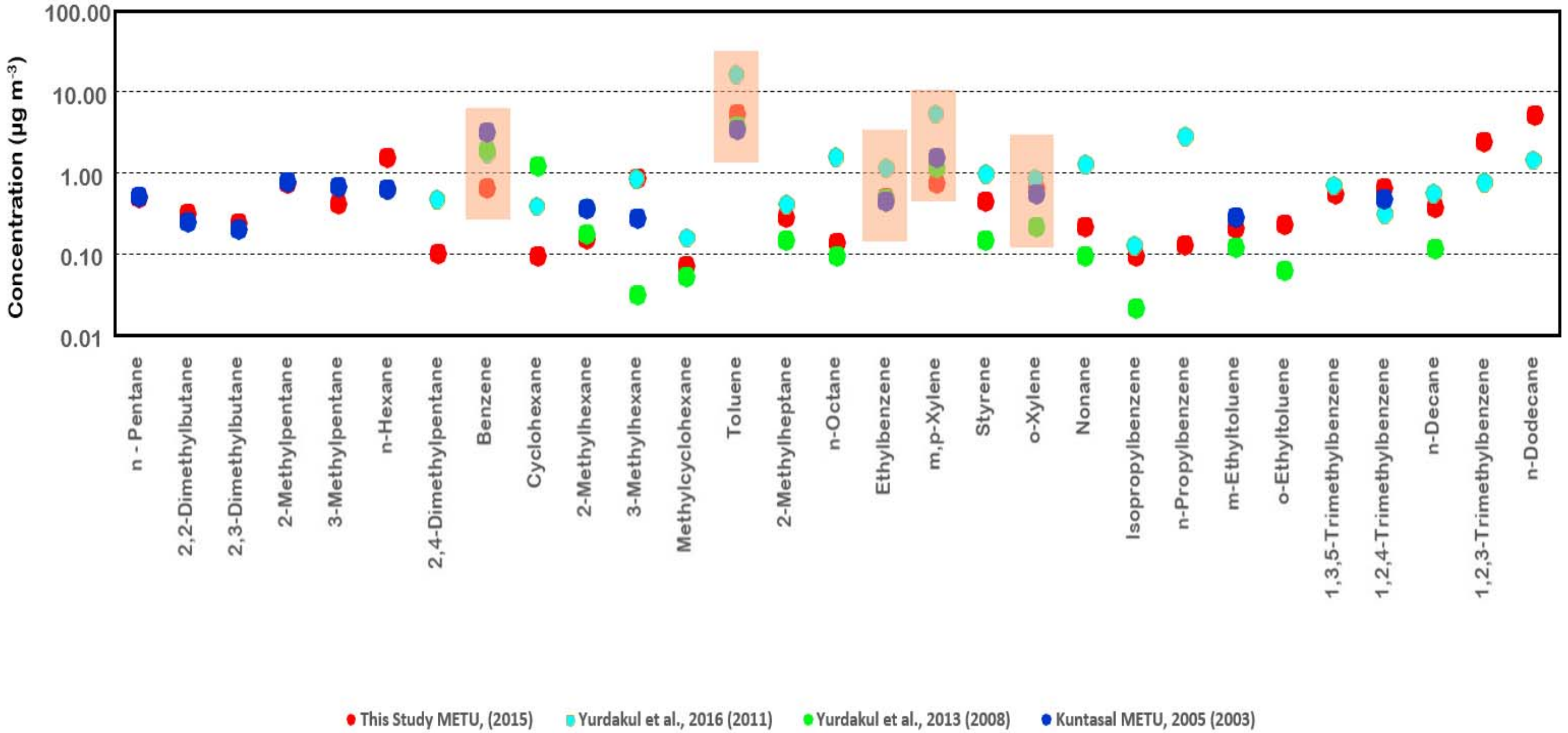


Figure 4.11: Long-term changes in concentrations of VOCs in Ankara atmosphere

4.4 Dependence of Measured Concentrations of VOCs on Local Meteorology

Meteorological conditions dominated during the sampling period and their relationship with measured concentration is very important for understanding the nature of the results. For instance, temperature, wind speed and mixing height are the meteorological parameters, which have profound effects on pollution concentrations (Penrod et al., 2014; Ramsey et al., 2014). Analysis of these meteorological parameters will be advantageous to determine whether the measured concentrations are cause of pollution episodes or not (Kuntasal, 2005). Therefore, relationship between meteorological parameters and the measured concentrations will be discussed in this part of the thesis.

4.4.1 Effect of Temperature

Meteorology is an important factor for temporal variation in concentrations of atmospheric pollutants of all types. It indirectly affects temporal variation of elemental and ionic air pollutants. For example, SO_2 generally decrease with increasing temperature, because SO_2, which is a good marker for coal combustion for space heating, is emitted more in winter. Since temperature in winter is low, it appears as if SO_2 concentration decrease with increasing temperature. Similarly, Al concentration and concentrations of other crustal elements increase with increasing temperature, because resuspension of soil particles is easier during dry summer season and limited in winter. This gives the impression that concentrations of crustal elements increase with increasing temperature. Both of these cases are examples of indirect effect of temperature. However, temperature affect temporal variation of organic compounds in a more direct way, because their chemistry in atmosphere depends on temperature. For example, reactions that destroys VOC proceeds faster at high temperature and thus VOC concentrations are expected to decrease with increasing temperature. On the other hand, we also expect to see an increase in concentrations with temperature, because formation of VOCs also becomes faster at high temperatures. When this is coupled with seasonal variation in VOC emissions (for example VOC's emitted from coal or natural gas combustion are expected to be higher in winter, whereas VOC associated with solvent evaporation is expected to be higher in summer) the result is more complex dependence of VOC concentrations on temperature.

Variation of BTEX concentrations with temperature is depicted in Figure 4.12 in both stations. More than half of the measured VOC have temperature dependences which are similar to temperature dependences shown for BTEX compounds (benzene, toluene, m,p-xylene, ethylbenzene and o-xylene) in the figure. For this group of compounds concentrations are high at low temperatures and gradually levels off. Main sources of BTEX compounds is traffic, which does not change significantly in summer and winter. Concentrations of species that have the same emissions in summer and winter is expected to have higher concentrations in winter, because mixing height is lower and ventilation is limited in winter, which leads to higher concentrations in winter. Only the VOCs (and other pollutants) that have significantly higher emissions, or enhance formation in summer can have higher concentrations in summer season.

Based on this argument, most of the VOCs that have temperature dependences like BTEX compounds are either from traffic or have a source, which is stronger in winter. Some selected examples of VOCs that have non-traffic sources are given in Figure 4.13. Butane and isopentane in the figure are known tracers of evaporative emissions from gasoline (Watson et al., 2001; McCarty et al., 2013). Octane and 1-pentane, on the other hand are used as solvents (Yu et al., 2014). Both gasoline evaporation and solvent emissions are expected to increase with temperature. Variation in concentrations of these compounds with temperature resembles the variations observed in BTEX concentrations at low temperature side, but their concentrations show a tendency to increase at temperatures > 15 – 20 ^{0}C. This pattern indicates that at low temperatures in winter atmospheric abundances of these compounds are determined by traffic emissions, because at low temperatures (around zero ^{0}C) evaporative emissions is at minimum. However, unlike in BTEX compounds, traffic is not the dominating source of this group of VOCs in summer.

Their summer concentrations are determined by evaporative emissions and solvent evaporation. Because of that their concentrations they show an increasing trend with temperature when T > 20 ^{0}C.

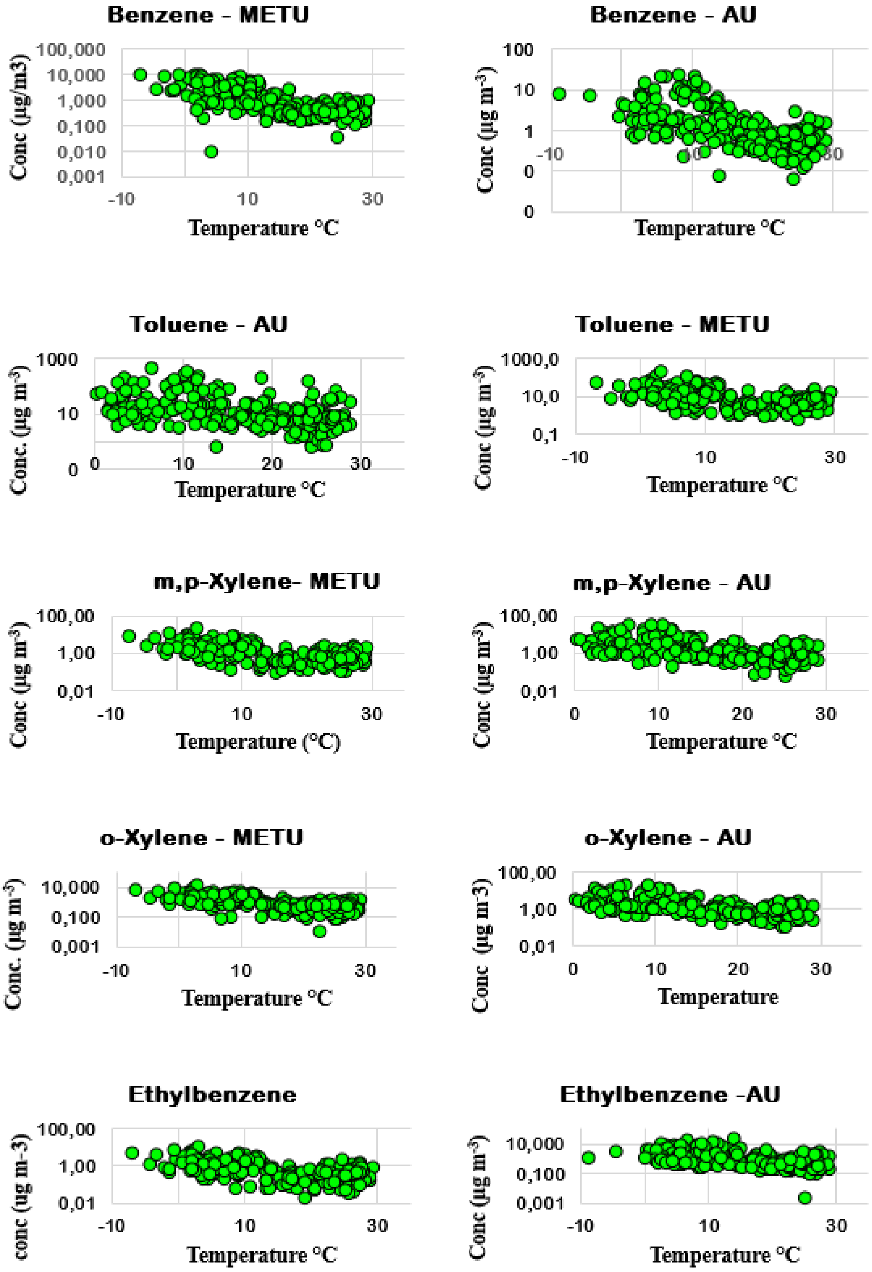


Figure 4.12: Variation of BTEX compounds with temperature at urban and suburban stations

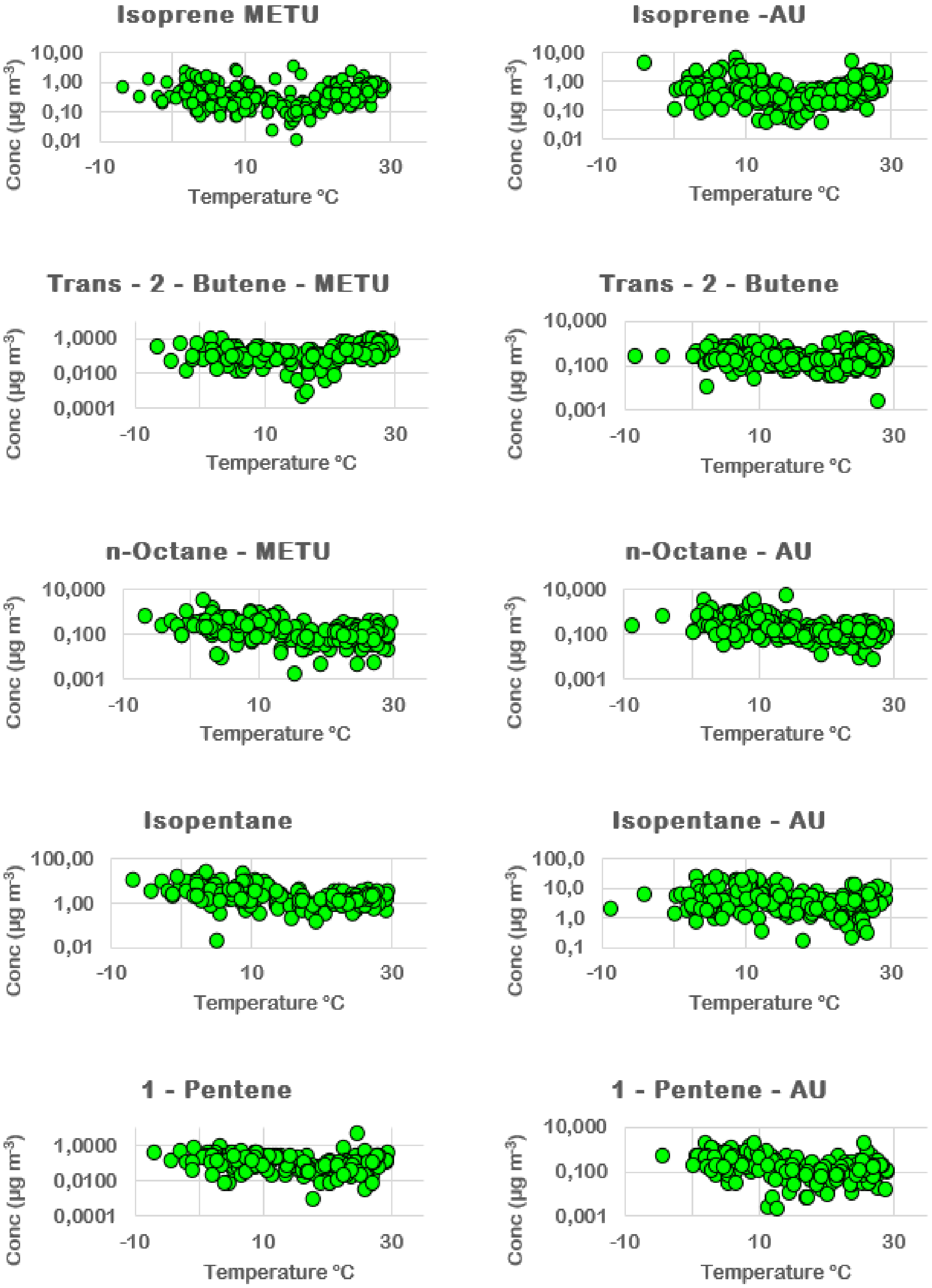


Figure 4.13: Elements that shows increasing concentrations at high temperatures in both stations

4.4.2 Effect of Wind Speed

Wind is an important meteorological parameter, because it is a measure of effectiveness of horizontal ventilation mechanism in urban atmosphere. Concentrations of VOC’s are expected to decrease with increasing wind speed (WS). This is not a specific expectation for VOCs. Concentrations of most of the pollutants, organic or inorganic, are expected to decrease with increasing wind speed due to better dilution at stronger winds. Variation in concentrations of acetylene, propylene and toluene with wind speed both at urban and suburban stations are given in Figure 4.14. The decrease in concentrations of these VOCs with wind speed is clear. These are arbitrarily selected examples; similar decreases of concentration with increasing wind speed is observed for all VOCs measured in this study, without any exception in both stations.

A point that should be noted is that wind speed is very low in Ankara. Wind frequency distribution is depicted in Figure 4.15. WS < 1.0 m s^{-1} is considered as calm in meteorology. As can be seen from the figure most frequent winds is between 1.5 m s^{-1} and 2.0 m s^{-1}, which is very close to calm condition (average WS during sampling was 2.3 m s^{-1}). Such low wind speeds indicates that horizontal ventilation over Ankara is not an effective mechanism to cleanse the city. Such low wind speed is one of the reasons of severe air pollution episodes experienced in Ankara in 70s and 80s. Because of low average wind speed, pollutants are quite homogeneously distributed over the city (Yatın et al., 2000).

4.4.3 Effect of Mixing Height

Mixing height (MH) can be roughly defined as the volume in which emitted pollutants are confined to, because atmosphere is well mixed under mixing height and transport of pollutants from boundary layer to free troposphere is limited. That is why most pollutants have short lifetimes (residence times - τ) in the mixed layer. For non-reactive species τ is approximately 10 days and is determined by the frequency of rain events. One pollutants escape from boundary layer to free troposphere their residence times can be as long as two months. Owing to these factors, mixing height is considered as the volume in which emitted pollutant are confined. This means that measured pollutant concentrations are expected to decrease as mixing height increases. Mixing height shows well-defined diurnal and seasonal variations. It is high during noontime and low at night. It is also high in summer and low in winter. Diurnal and seasonal variation of mixing height in Ankara was calculated by Genc et al. (2010). It changes from 400 m at night to 750 m at noon during winter and changes between approximately 500 m at night and 2500 m at noon during summer.

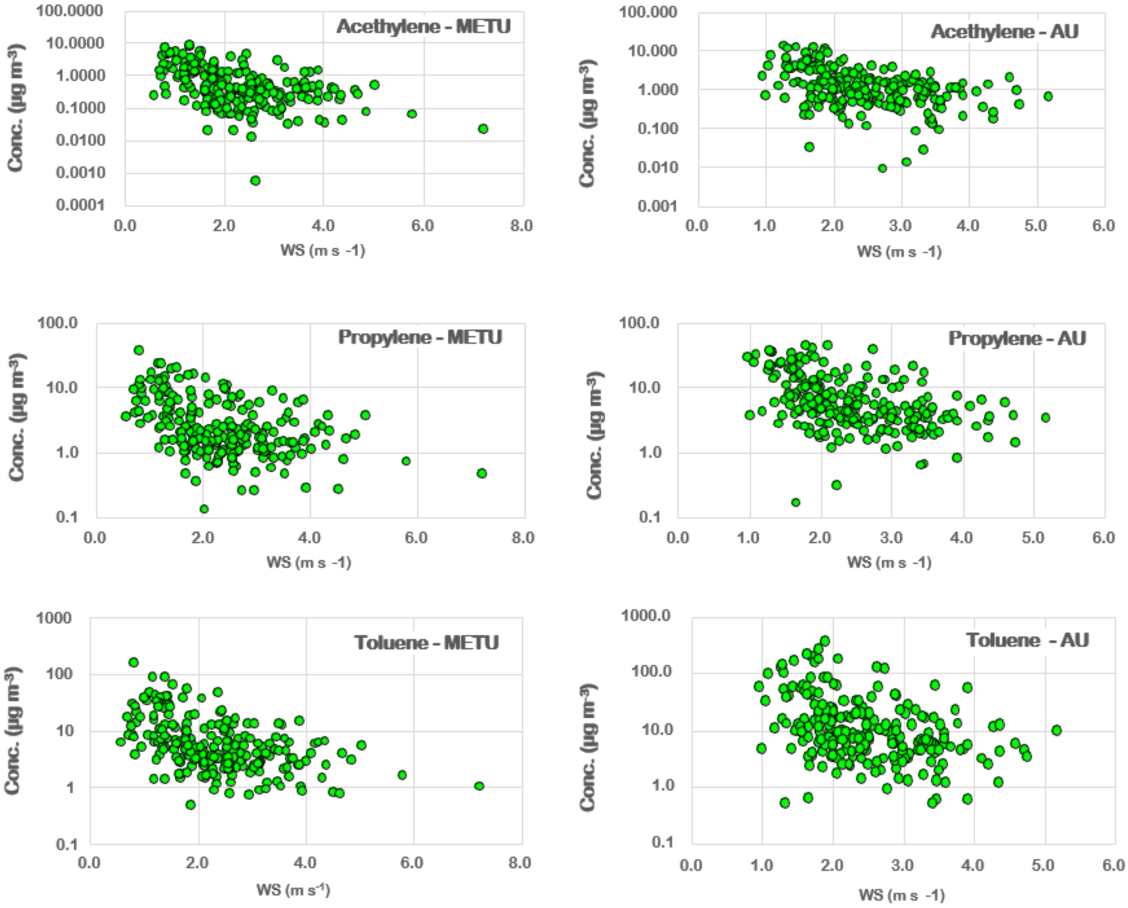


Figure 4.14: Dependence of VOC concentrations at urban and suburban stations on wind speed

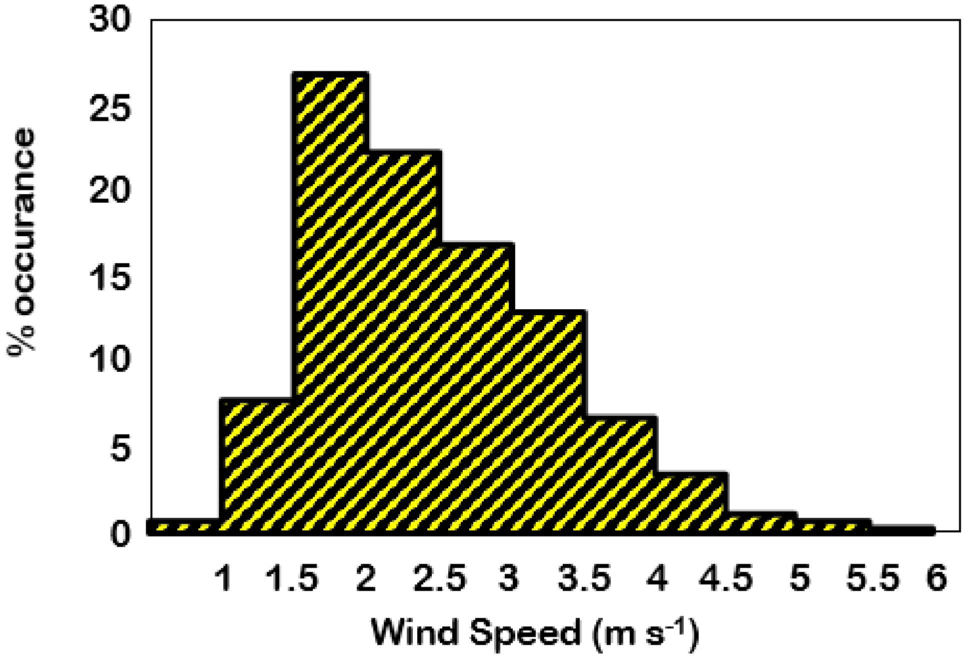


Figure 4.15: Wind frequency distribution during sampling campaigns

Concentrations of VOCs depicted different variations with mixing height at both stations. Concentrations of most, but not all, VOCs decreased with increasing mixing height as expected. Examples of this pattern is depicted in Figure 4.16 for benzene and acetylene at urban and suburban stations. VOCs in behaved in the same way in both stations. Please note that MH is low in winter and high in summer. When the concentration of a particular VOC decrease with increasing MH, this means it concentration is high in winter and decrease towards summer when MH is high. This pattern is followed by VOCs that has equal emissions in winter and summer or by VOCs that has stronger source in winter.

Traffic is one such source. Traffic emissions do not change much between summer and winter seasons. However, since MH is lower in winter, concentrations of VOCs that has traffic source is higher in winter. Consequently, traffic is a likely source of VOCs that shows inverse relation with MH.

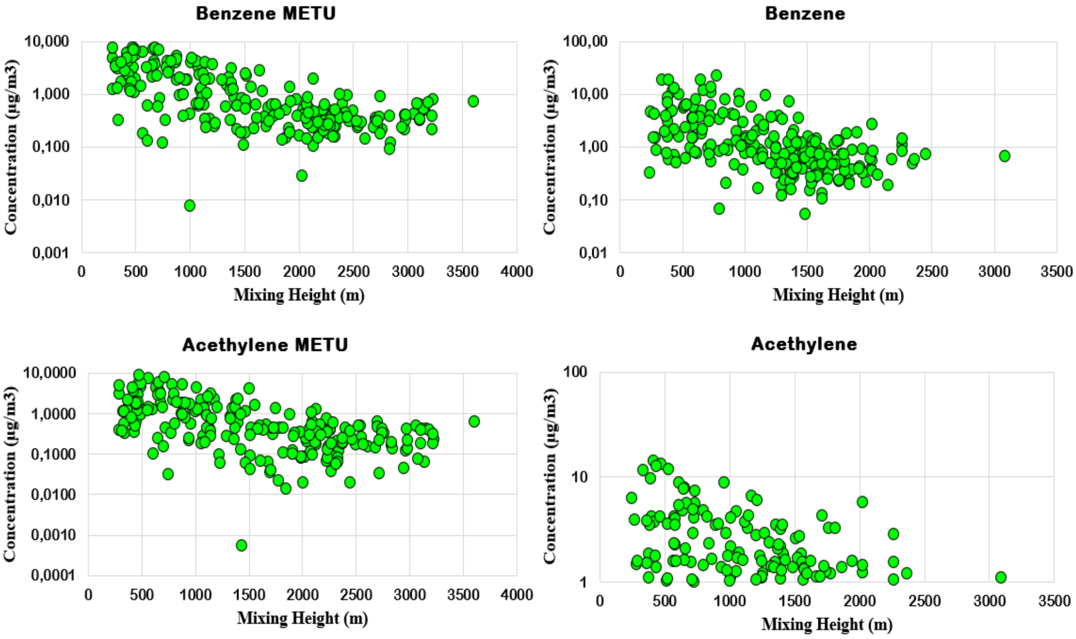


Figure 4.16: Variation of VOC concentrations with mixing height: VOC that decrease with mixing height

Concentrations of the second VOC group did not change with mixing height. Examples of this pattern is shown in Figure 4.17 for trans-2-butane and isoprene. This pattern indicates that there are sources of these VOCs when MH is high. Since mixing height is high in summer then these compounds have stronger source strength in summer. Traffic is not dominating source for these compounds. This also means that dependence of VOC concentrations on MH is not much different from their dependence on temperature. VOCs that are in this group includes isoprene, n-dodecane, trans-2-butane, cyclohexane, 3-methylhexane in urban station and isoprene, ethane, n-hexane, trans-2-butane, cyclohexane, 2-methylhexane, isopropyl benzene, cyclopentane, 3-methylhexane, trans-2-pentane, 1-pentane, n-decane at suburban station. VOCs in this group, which are not dominated by traffic is higher at suburban station. This is probably due to stronger traffic source at urban station. As discussed previously, urban station is surrounded by roads with heavy traffic, which means that traffic is a stronger source at urban station than it is in suburban one.

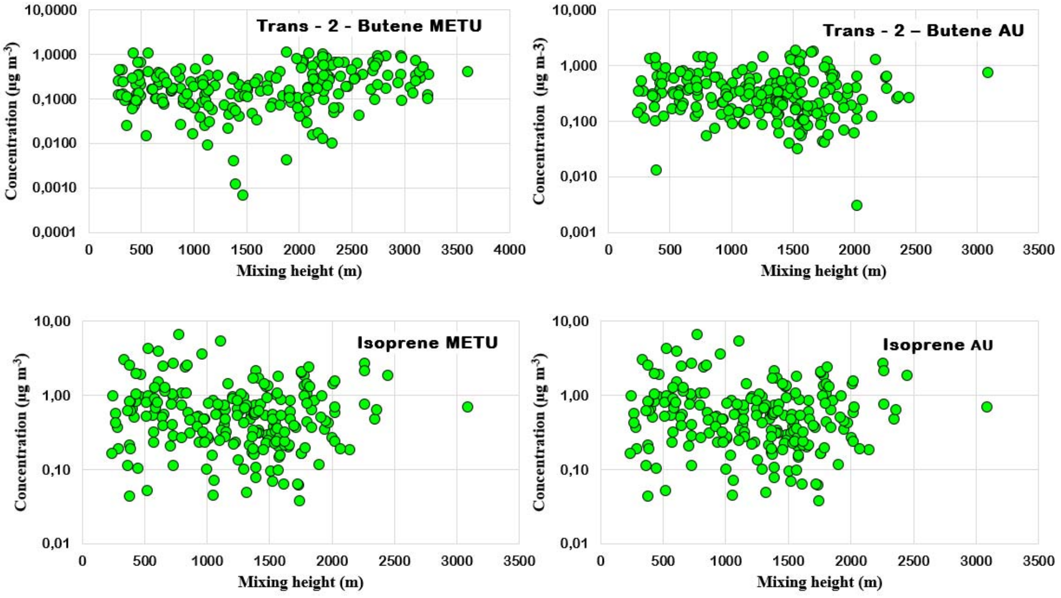


Figure 4.17: Variation of VOC concentrations with mixing height: VOC that does not vary with mixing height

Behaviors of some VOCs is between these two extremes. Concentrations of VOCs like benzene in Figure 4.16, decrease with increasing MH in the beginning and levels off and becomes independent of MH at high MHs. Main source of these compounds is traffic in winter that is why their concentrations increase at low MH values (in winter). However, later in summer (at high MH values) non-traffic sources, such as solvents, gasoline evaporation becomes more important than traffic and concentration becomes independent of MH. Most of the VOCs measured in this study, both in urban and suburban stations are in this group.

4.4.4 Effect of Ventilation Coefficient

In urban atmosphere, wind speed is an indication of the effectiveness of horizontal ventilation process. Similarly, mixing height indicates the effectiveness of vertical ventilation. Thus, overall ventilation efficiency of the city can be assessed by the product of WS and MH.

This product is called "ventilation coefficient" (VC) and considered as the assimilative capacity of the atmosphere. We calculated daily VC values by multiplying daily average WS and daily average MH. Since WS is very low in Ankara, the influence of mixing height on VC is more important than the influence of WS. Like in MH, ventilation coefficient is higher in summer and in noontime. It is lower in winter and at night.

The relation between VC and VOC concentrations is also very similar to the relation between VOC concentrations and mixing height. Three groups that are found to have different relationship with mixing height also have different relation with VC. Variation of benzene and acetylene concentrations at urban station and toluene and n-pentane concentration at suburban station are plotted in Figure 4.18 as examples of VOCs, which's concentrations decrease with VC. Both benzene and particularly acetylene are very good markers for light duty vehicle exhaust. Concentrations of these compounds decrease with increasing VC and they don't show any sign of leveling at high VCs. Concentrations of toluene and n-pentane also decrease with increasing VC, but their concentrations level-off when VC > 4000 m^2 s^{-1}. Both toluene and n-pentane have traffic source; however, their solvent source is also well documented. In winter traffic is the main source VOC's in this group, however in summer with increasing temperature solvent evaporation becomes a significant source for them. Most of the VOCs emitted from traffic behaves like toluene and n-pentane indicating that traffic is an important, but not the only source of many VOCs.

Some examples of VOCs for which non-traffic sources dominate throughout the year are given in Figure 4.19. In this group, VOC concentrations are independent of ventilation coefficient. Compounds in this group includes ethane, 2,2-dimethyl butane, 2-methyl heptane, 2,3-dimethylpentane, isoprene, 3-methyl hexane, trans-2-butane at urban station and ethane, 1,2,3-trimethylbenzene, 2,3-dimethylbutane, p-diethylbenzene, n-undecane, n-octane, Isoprene, n-dodecane, n-hexane, styrene, cyclohexane, nonane, cis-2-butane, 2-methylhexane, isopropylbenzene, cylopentane, 2,3-dimethylpentane, n-propylbenzene, 3-methylhexane, trans-2-pentane, n-decane at the suburban station. As in the case of mixing height, number of VOCs, which does not show any trend with VC, is much larger in suburban station. This is due to very strong influence of traffic on measured VOC concentrations at urban station.

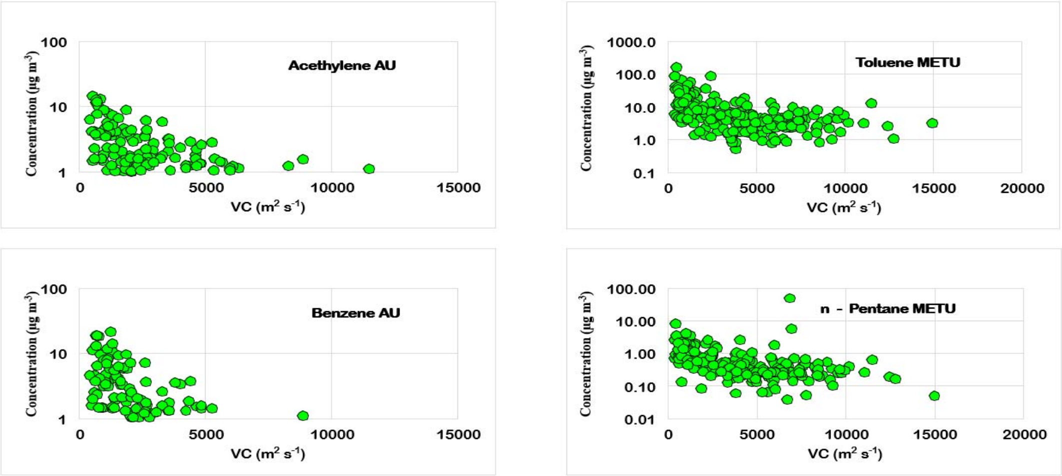


Figure 4.18: Variation of VOC concentration with VC: VOCs with concentrations decreasing with VC

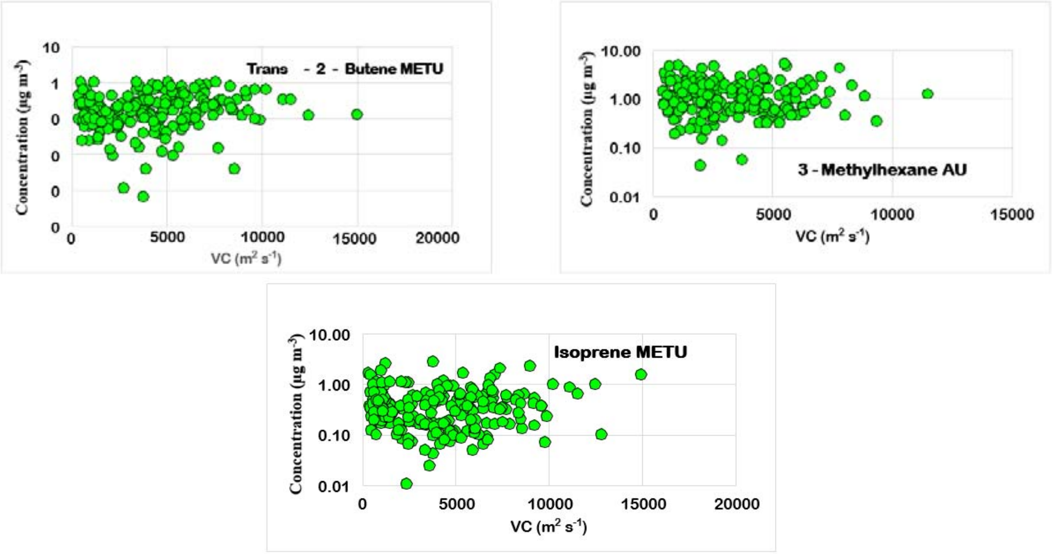


Figure 4.19: Variation of VOC concentration with VC: VOCs with concentrations independent of VC

It is difficult to find VOCs without traffic source in this station. However, since traffic source at our suburban station is not as strong as it is in urban site, non-traffic sources or evaporative sources becomes visible.

4.5 Sources contributing to VOC compositions

4.5.1 PMF Results at METU Station

Application of PMF to VOC data generated at our suburban station revealed six factors. Sources represented by these six factors and how factors were related to those sources are discussed in this section. Factor loading values for each factor at METU station are presented in Table 4.9.

Table 4.9: Factor loadings at METU station (µg/m^3)

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Ethane	1,032	1,788	0	0,170	0	0
Ethylene	2,206	1,299	0,113	0,001	1,756	0
Propane	0,039	0,194	0,066	0,016	1,134	0,207
Propylene	0,546	0,480	0,055	0,045	1,990	0,435
Isobutane	1,171	1,273	0,144	0,058	5,572	1,048
Acethylene	0,018	0,264	0	0	0,438	0,027
Trans - 2 - Butene	0,019	0,042	0,164	0,008	0,006	0
1 - Butene	0,022	0,028	0,029	0,005	0,155	0,055
Cis-2-Butene	0,213	0,292	1,681	0,096	1,865	0
Cyclopentane	0,015	0,021	0,062	0,007	0,033	0,020
Isopentane	0,449	0,563	0,416	0,021	1,524	0,263
n - Pentane	0,135	0,118	0,043	0,013	0,242	0,081
2,2-Dimethylbutane	0,067	0,075	0,070	0	0,169	0,020
2,3-Dimethylbutane	0,076	0,058	0,063	0	0,075	0,010
2-Methylpentane	0,252	0,225	0,101	0	0,257	0,076
3-Methylpentane	0,127	0,169	0,069	0	0,063	0,015

Table 4.9 cont'd: Factor loadings at METU station (µg/m^3)

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Isoprene	0,052	0,008	0,152	0,040	0,050	0,049
n-Hexane	1,429	0	0,046	0	0	0,489
2,4-Dimethylpentane	0,026	0,028	0,015	0	0,054	0,009
Benzene	0,080	0,242	0,000	0	0,778	0,128
Cyclohexane	0,007	0,038	0,028	0	0,021	0,009
2-Methylhexane	0,018	0	0,068	0,004	0,066	0,053
3-Methylhexane	0,102	0	0,234	0,064	0	0,357
2,2,4-Trimethylpentane	0,024	0	0,164	0,061	0,034	0
n-Heptane	0,023	0,022	0,042	0,023	0,114	0,053
Toluene	0	0,739	0,871	0	5,500	1,184
2-Methylheptane	0,077	0,080	0,000	0	0,092	0,062
3-Methylheptane	0,008	0,009	0,015	0,004	0,046	0,016
n-Octane	0,037	0,008	0,018	0,010	0,059	0,045
Ethylbenzene	0,030	0,006	0,071	0,023	0,472	0,135
p-Xylene	0,058	0,012	0,121	0,021	0,777	0,229
Styrene	0,032	0	0,000	0,008	0,124	0,225
o-Xylene	0,072	0	0,044	0,036	0,528	0,238
Nonane	0,021	0	0,031	0,012	0,103	0,079
Isopropylbenzene	0	0,004	0,017	0,031	0,015	0,020
n-Propylbenzene	0,001	0	0,021	0,012	0,042	0,033
m-Ethyltoluene	0,008	0	0,033	0	0,122	0,055
1,3,5-Trimethylbenzene	0,112	0,003	0,071	0	0,264	0,138
1,2,4-Trimethylbenzene	0,014	0,048	0,025	0,067	0,103	0,045
n-Decane	0,347	0	0,091	0,618	0,277	0,929
1,2,3-Trimethylbenzene	0,000	0,059	0,152	0,136	0,001	0,084
p-Diethylbenzene	0,105	0,041	0,060	1,208	0	0
n-Undecane	0	0,103	0	4,823	0,048	0,482
n-Dodecane	0	5,549	1,952	0,285	0,374	0,368
SO2	0	12,97	0	0,057	6,12	8,800
NO	0	23,65	3,365	2,572	1,747	17,10
NO2	19,32	5,67	1,868	1,262	20,05	0

Factor 1 loadings, percentages of VOC concentrations explained by Factor 1 and monthly median concentrations of G-scores are given in Figure 4.20. Although factor loadings are important to calculate contribution of each factor to total VOC concentration, fractions of VOC concentrations explained by each factor is more useful to relate factors to sources. We used percentages of VOC concentrations explained by each factor, rather than factor loadings to identify factors.

Factor 1 explains fairly large percentages of concentrations of light hydrocarbons. It explains 70% of n-hexane concentration and approximately 30% of the concentrations of 2-methyl pentane, 3-methylpentane, n-pentane,2-methyl heptane, 3-methyl heptane. These VOCs, particularly n-hexane are good markers for industrial evaporation (McCarty et al., 2013; Ho et al., 2009; Watson et al., 2001). The factor has higher scores in summer months, which supports evaporative source for Factor 1. Thus, Factor 1 is identified as industrial evaporative emissions.

Same diagnostic figures for Factor 2 is depicted in Figure 4.21. Factor 2 is also loaded with light VOCs. It explains 20% - 30% of the concentrations of trans-2-butane, isopentane, 2,2-dimethylbutane, 2,3-dimethyl butane, 2-methylbutane, 3-methylbutane, cyclohexane, 2-methylpentane. Some of these are the VOCs which were also loaded in factor one. Both Factor 1 and Factor 2 represent evaporative emissions, but there are two important differences between compositions of these two factors. Factor 2 explains 27% of the isobutane concentration. Isobutane is primarily emitted from gasoline vehicles, but it is also a good marker for evaporative emissions from cars (Watson et al., 2001; McCarthy et al., 2013). However, Factor 1 does not contribute to measured isobutane concentration. The second clue that suggest evaporative emissions from cars is the source of Factor 2 is mixing of gasoline exhaust markers into Factor 2. Factor 2 explains approximately 60% of ethane and 35% of the acetylene concentrations. These two VOCs are combustion products and cannot occur in evaporative emissions of unburned gasoline. Their presence together with evaporative emission markers in a factor indicates a mixing of evaporative emissions with exhaust emissions. It is not surprising as both emissions are generated in the same engine. Presence of isobutane and mixing with exhaust markers suggest that Factor 2 represent evaporative emissions from gasoline vehicles. Monthly median values of G-scores for Factor 2 does not show a clear seasonal pattern, as in Factor 1. This also is not surprising for evaporative emissions from light duty vehicles, because evaporative emissions depend on engine temperature and not ambient temperature. Engine temperature in cars do not change with season.

Factor 3 loadings, fractions of VOC concentrations accounted for by Factor 3 and monthly median Factor 3 scores are given in Figure 4.22. Factor 3 explains 70% of the trans-2-butane concentration. It also accounts for >30% of cis-2-butane, cyclopentane, isoprene, 2-methylhexane, 3-methylhexane, 2,2,4-timethylpentane, 1,2,3-trimethylbenzene concentrations. Most of these VOCs are associated with solvent use (Seila et al., 2001; Watson et al., 2001).bMonthly median G-scores are higher in summer, which supports solvent assignment for Factor 3, as higher emissions from solvent evaporation is expected during warm summer season. Consequently, Factor 3 is assigned as a general solvent factor.

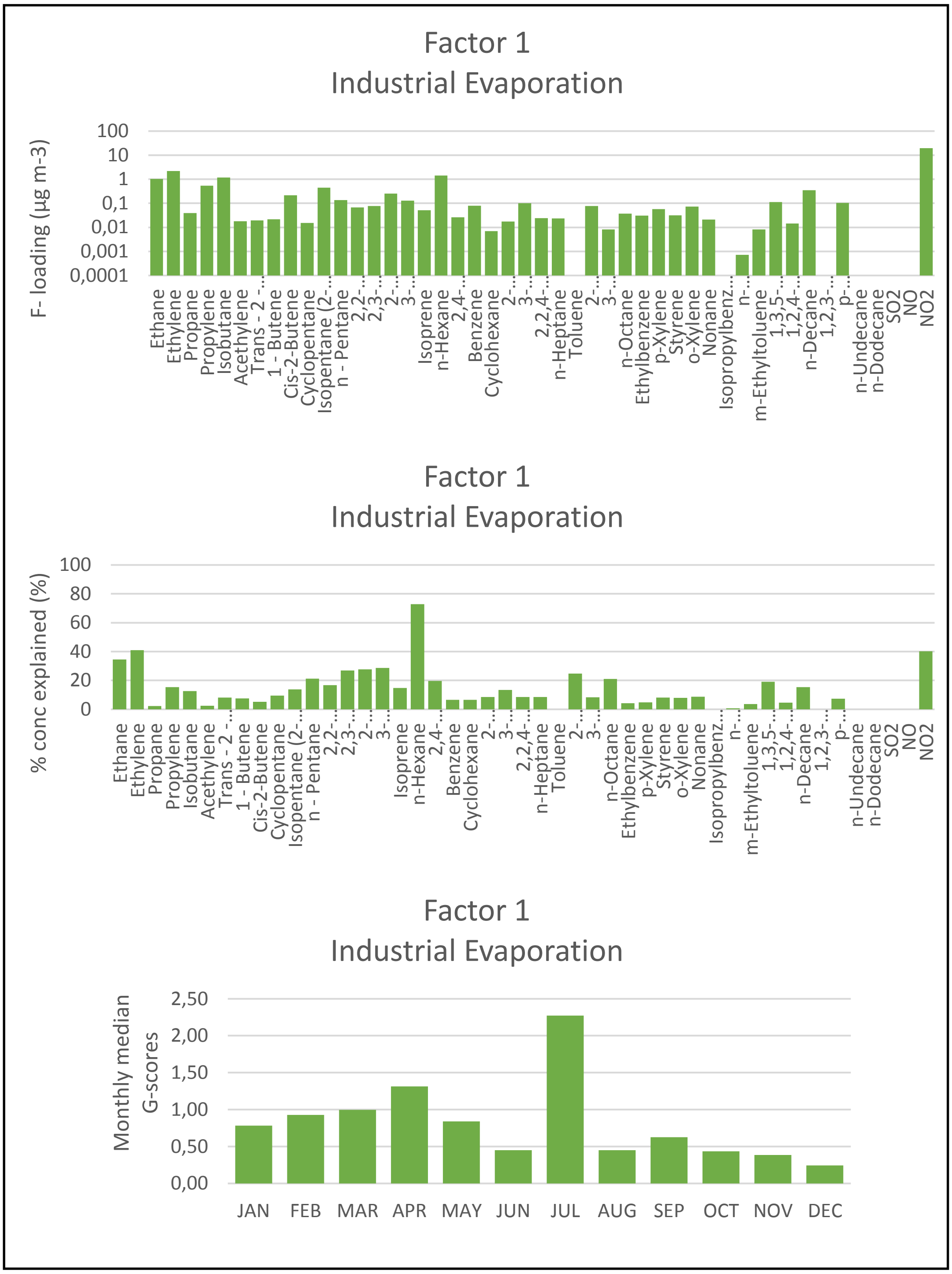
Diagnostic figures for Factor 4 is depicted in Figure 4.23. Factor 4 is loaded with heavy hydrocarbons. It explains >40% of the concentrations of isopropylbenzene, p-diethylbenzene, n-undecane and n-dodecane. These are well-known markers of diesel emissions (Watson et al., 2001; Shaoa et al., 2008; McCarthy et al., 2013; Schauer et al., 1999; Ho et al., 2009). Strong association of SO_2 with Factor 4 also supports that Factor 4 is a diesel emission factor. SO_2 was associated with coal combustion in Ankara when city was heated by coal burning in the past. However, Ankara is now heated by natural gas and SO_2 concentration measured in national monitoring network decreased significantly. In a recent study, Genç et al. (2010) showed that SO_2 in national network stations in the city depicts a diurnal pattern, which is clearly traffic with to maxima during morning and afternoon rush hours.

This observed pattern suggests that traffic became the dominating source of SO_2 in Ankara after SO_2 from combustion is phased out. Diesel traffic is the main source of

SO_2, because diesel fuel contains 10 ppm S in it. Ten ppm is not a high value. It is standard in Europe. However, it means that there is S in diesel fuel and since SO_2 emissions from coal combustion decreased significantly in the city, SO_2 emitted from diesel vehicles became apparent. G-scores are higher during winter season. Diesel emissions do not differ significantly between summer and winter. However, concentrations are higher in winter due to lower mixing height in winter season.

Factor 5 loadings, fractions of VOC concentrations accounted for by Factor 5 and monthly median Factor 5 scores are given in Figure 4.24. Factor 5 is a gasoline exhaust factor. It explains >50% of the concentrations of most well-documented traffic markers, including BTEX. Factor 5 explains approximately 50% of ethylene and 60% of acetylene concentrations. These two are combustion products. They do not exist in fuel, but formed in the engine, when fuel is burned. Because of this, ethylene and acetylene are conclusive evidence to relate a factor to exhaust emissions of light-duty vehicles (Watson et al., 2001). Another supporting evidence for association of factor 5 with light-duty vehicle exhaust is high loading of NO in this factor. Factor 5 explains approximately 50% of NO concentration. NO is formed by oxidation of atmospheric N_2 in high temperatures in engine and thus, together with CO, considered as best inorganic marker for gasoline exhaust emissions. As in diesel factor, Factor 5 scores are high in winter. Exhaust emissions of gasoline powered engine do not change significantly between summer and winter seasons, consequently higher concentrations of Factor 5 scores in winter is due to seasonal variations in meteorology, particularly the mixing height.

Factor 6 loadings, fractions of VOC concentrations accounted for by Factor 6 and monthly median Factor 6 scores are given in Figure 4.25. Factor 6 is another solvent factor. It explains significant fractions of concentrations of known solvent markers, including hexane, 3-methyl hexane, n-decane. Factor 6 scores are higher in summer, supporting solvent source for Factor 6.



Factor 1
Industrial Evaporation

Factor 1
Industrial Evaporation

Factor 1
Industrial Evaporation

Figure 4.20: Factor 1 diagnostic figures at METU station

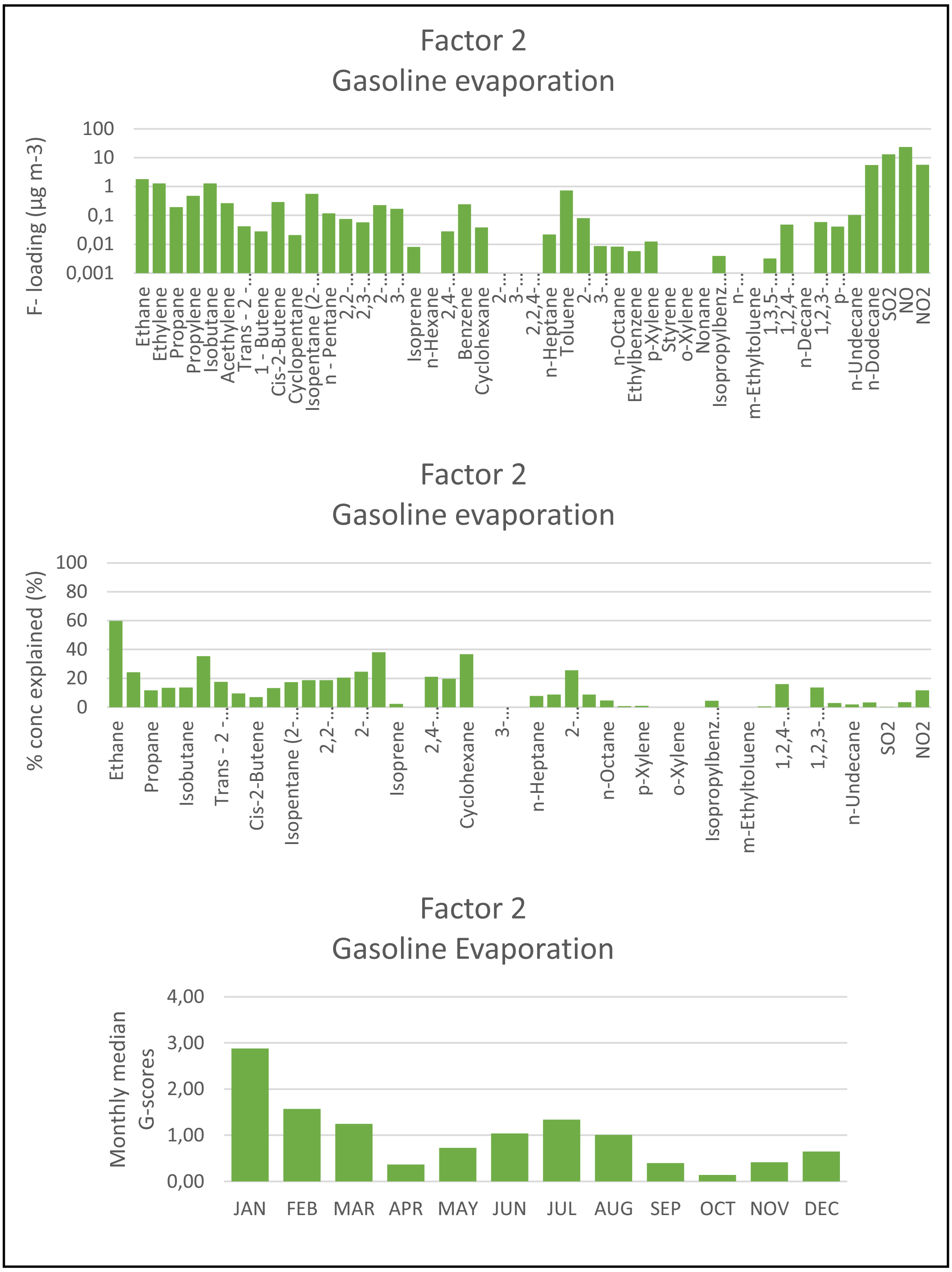


Figure 4.21: Factor 2 diagnostic figures at METU station

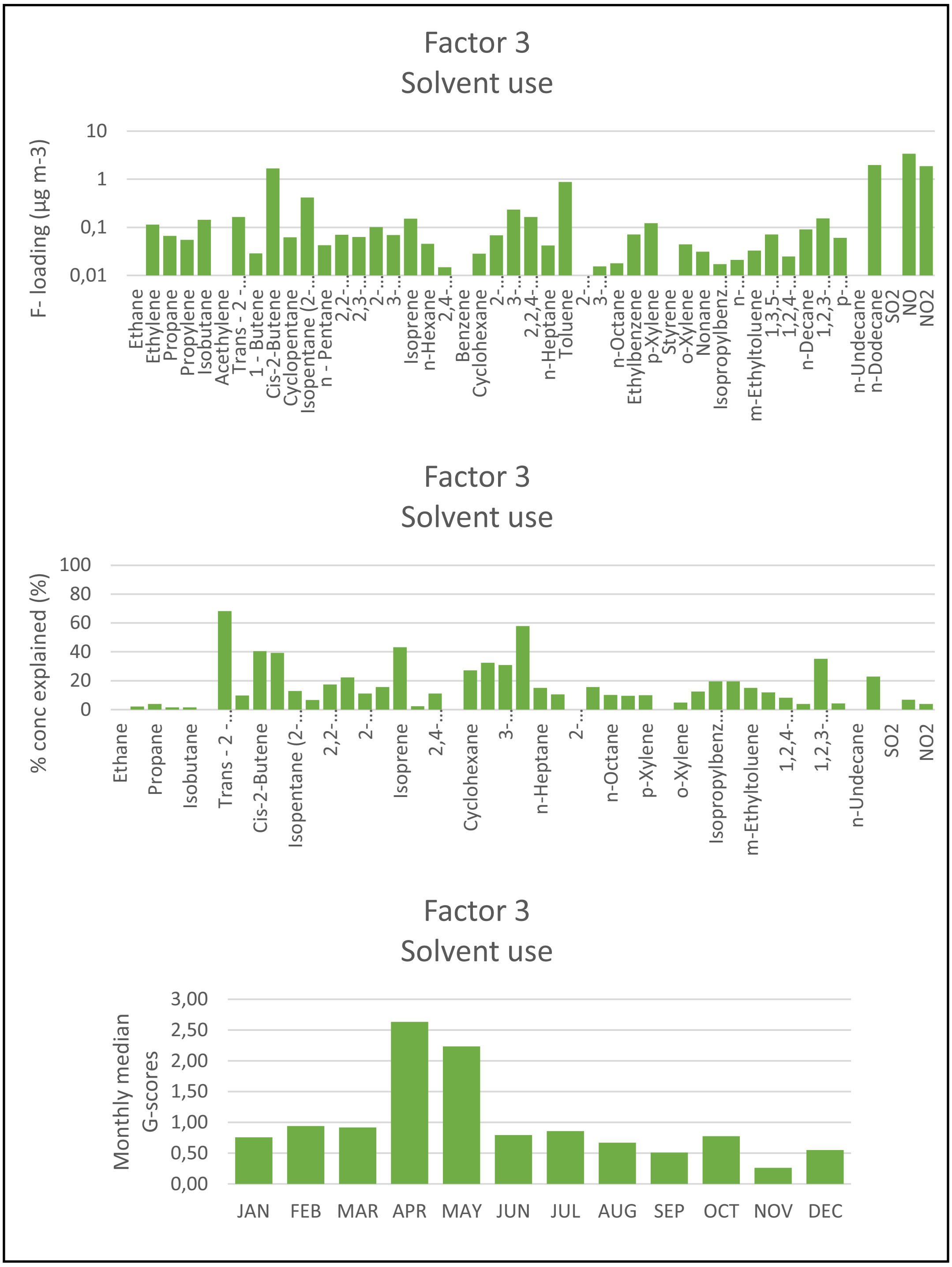


Figure 4.22: Factor 3 diagnostic figures at METU station

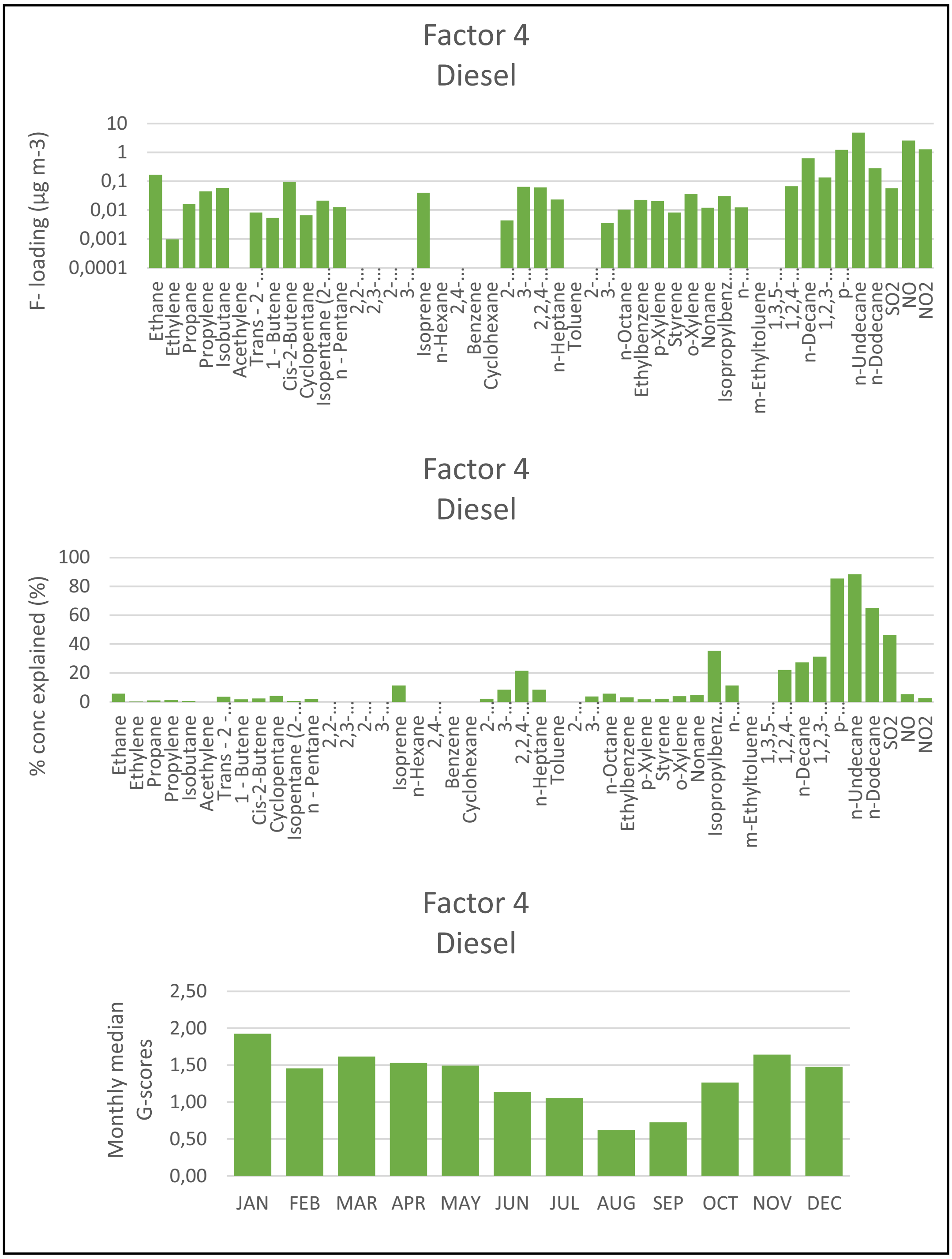


Figure 4.23: Factor 4 diagnostic figures at METU station

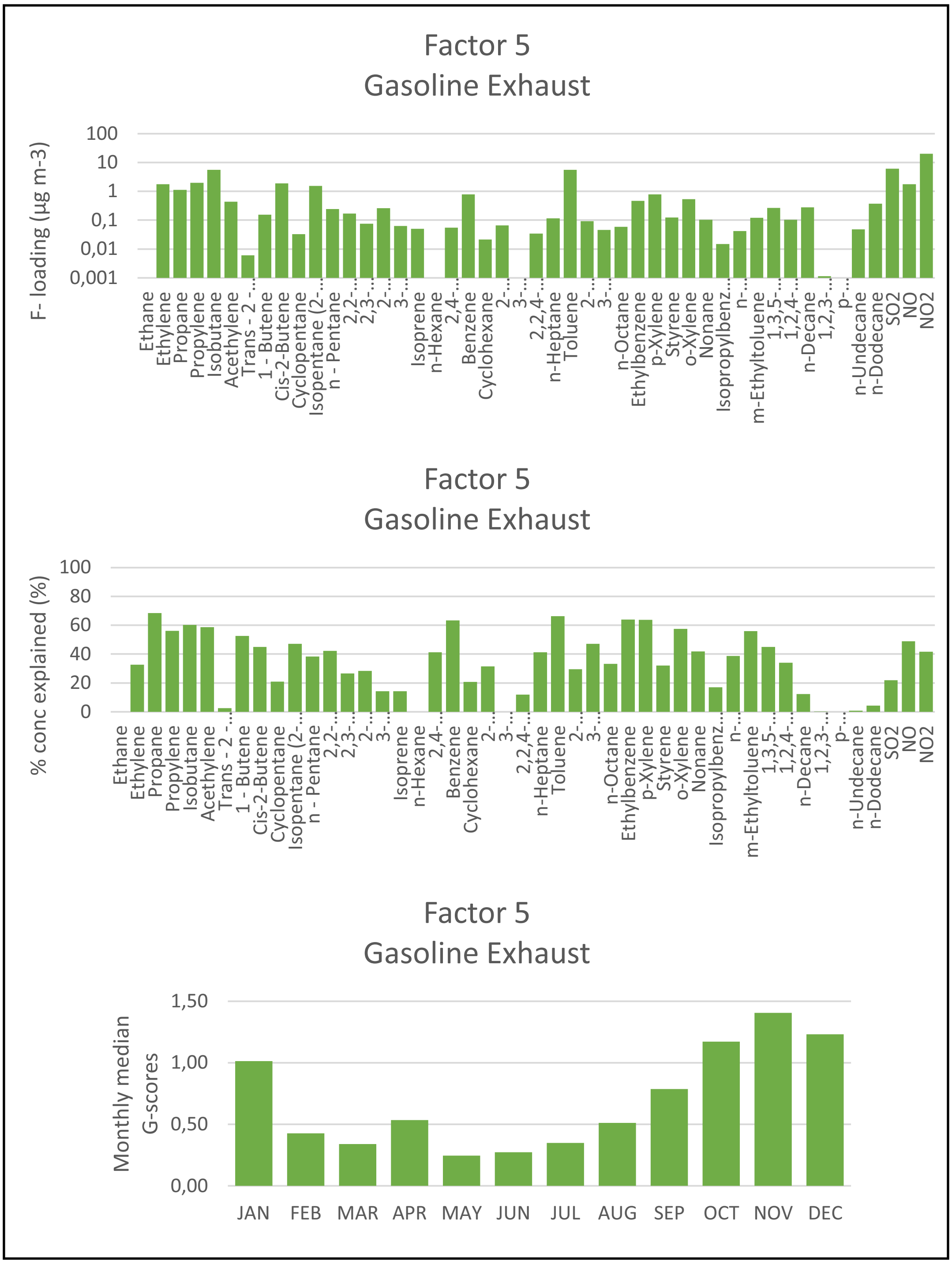


Figure 4.24: Factor 5 diagnostic figures at METU station

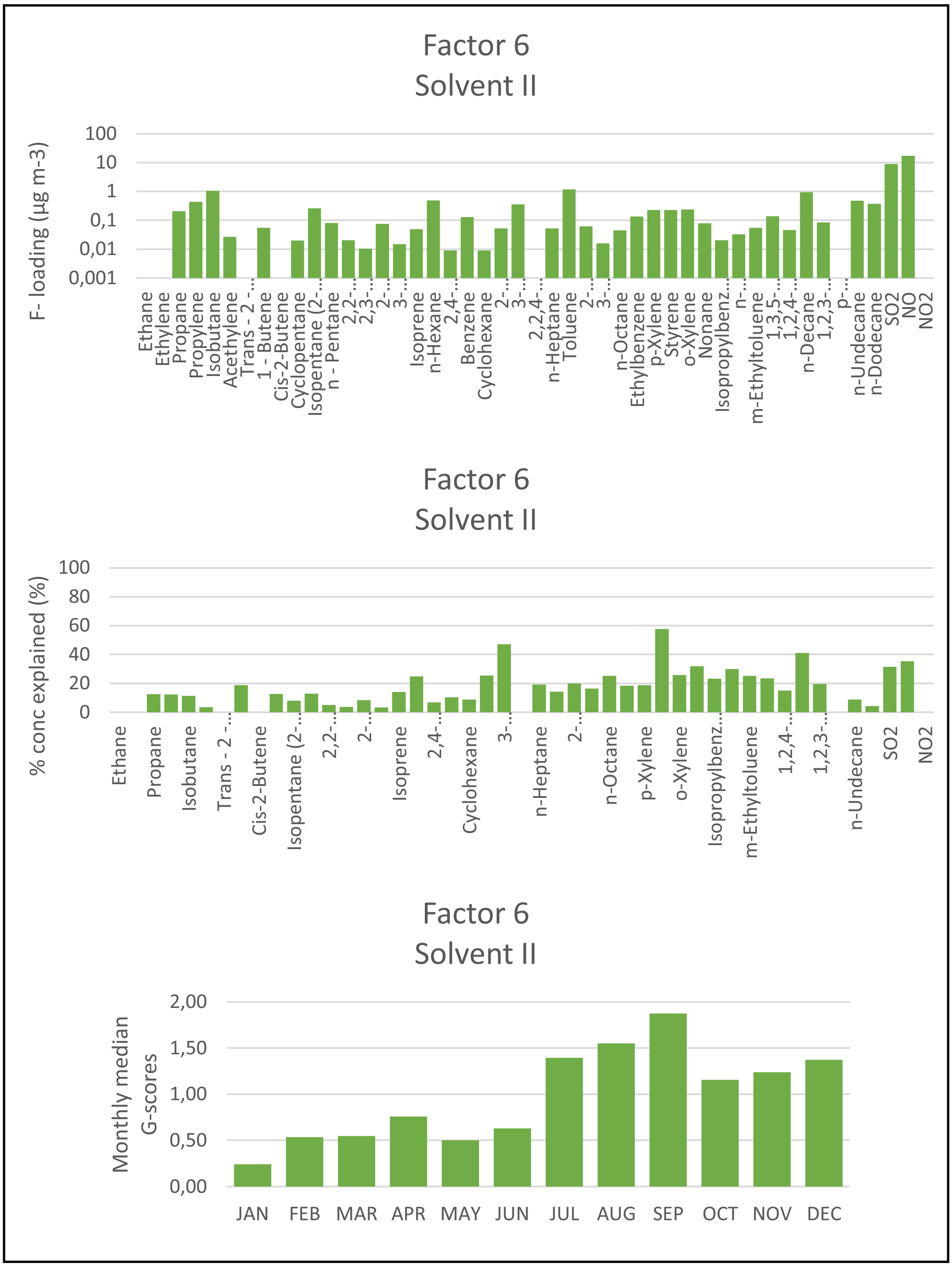


Figure 4.25: Factor 6 diagnostic figures at METU station

4.5.2 PMF Results at AU Station

Factor loading values for each factor at AU station are presented in Table 4.10.

Table 4.10: Factor loadings at AU station (µg/m^3)

	Factor 1	**Factor 2**	**Factor 3**	**Factor 4**	**Factor 5**	**Factor 6**
Ethane	0,084	0,029	0,046	1,162	0	0,364
Ethylene	0,808	0	0,194	0,478	0,302	3,786
Propane	1,444	0,932	0,001	0,125	0,125	1,724
Propylene	2,586	1,584	0	0,427	0,050	3,792
Isobutane	6,658	3,538	0	1,307	0,043	11,286
Acethylene	1,221	0,059	0	0,156	0,012	0,210
Trans - 2 - Butene	0,019	0,040	0,068	0,088	0,013	0,116
1 - Butene	0,164	0,166	0,011	0,017	0,045	0,208
Cis-2-Butene	0,000	1,674	0,465	0,000	0,729	5,038
Cyclopentane	0,039	0,051	0,036	0,033	0,025	0,089
Isopentane	0,854	0,857	0,060	0,495	0,035	3,150
n - Pentane	0,174	0,198	0,004	0,032	0,009	0,497
1 - Pentene	0,023	0,062	0,024	0,010	0,035	0,046
2,2-Dimethylbutane	0,091	0,072	0,012	0,077	0	0,424
2,3-Dimethylbutane	0,059	0,048	0,028	0,037	0	0,258
2-Methylpentane	0,440	0,006	0,061	0,143	0,001	0,884
3-Methylpentane	0,166	0	0,042	0,138	0	0,296
Isoprene	0,003	0,057	0,052	0,175	0,046	0,275
n-Hexane	0	0,775	0,016	0,000	0,203	0,367
2,4-Dimethylpentane	0,064	0,037	0	0,012	0	0,073
Benzene	0,876	0,423	0,024	0,019	0,069	0,097
Cyclohexane	0,053	0	0,002	0,034	0,006	0,071
2-Methylhexane	0,014	0,105	0,140	0,003	0	0,086
3-Methylhexane	0	0,213	0,263	0,217	0,158	0,213
2,2,4-Trimethylpentane	0	0	0,466	0	0,040	0,071
n-Heptane	0,029	0,174	0,010	0,029	0,052	0,147

Table 4.10 cont'd: Factor loadings at AU station (µg/m^3)

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
Toluene	5,596	6,045	0,100	0	0,010	3,829
2-Methylheptane	0,045	0,077	0,014	0,083	0,020	0,016
3-Methylheptane	0,029	0,023	0,012	0,016	0,009	0,033
n-Octane	0,014	0,114	0,011	0,010	0,042	0,049
Ethylbenzene	0,363	0,584	0,043	0	0,009	0,330
p-Xylene	0,624	1,071	0	0	0,043	0,544
Styrene	0,157	0,651	0	0,029	0,023	0
o-Xylene	0,442	0,753	0,024	0,014	0,078	0,239
Nonane	0,047	0,224	0,018	0,045	0,040	0,047
Isopropylbenzene	0,001	0,035	0,018	0,032	0,019	0,007
n-Propylbenzene	0,000	0,097	0,020	0,023	0,011	0,011
m-Ethyltoluene	0,024	0,229	0,009	0	0,021	0,075
1,3,5-Trimethylbenzene	0,127	0,405	0,080	0,016	0,000	0,227
o-Ethyltoluene	0,000	0,286	0,002	0,089	0,130	0
n-Decane	0,016	0,219	0	0,098	0,069	0,076
1,2,3-Trimethylbenzene	0,205	0,953	4,098	0,469	0	0
p-Diethylbenzene	0	0,158	0,017	0,263	0,022	0
n-Undecane	0	0	0,022	0,073	1,458	0,079
n-Dodecane	0	0,447	0	0,803	6,769	0
SO_2	1,749	0	0,696	2,016	1,134	0
NO	18,03	4,283	0,166	3,535	2,744	0
NO_2	14,65	2,257	1,001	17,20	6,605	0,693

Factor 1 loadings, percentages of VOC concentrations accounted for by factor 1 and monthly median G-scores are given in Figure 4.26. Factor 1 is enriched with light hydrocarbons, which also includes marker species for gasoline exhaust, such as acetylene and BTEX compounds. This factor is gasoline evaporation factor.

The reasons for assigning Factor 1 as gasoline evaporation was previously discussed in the manuscript. The scatterplot graph between the two gasoline evaporation factors (AU and METU) are given in Figure 4.28. The R^2 is 0.80 and $P[r,n] <0.05$

indicates that these two profiles are related with each other with statistical significance > 95%.

Diagnostic figures for Factor 2 is given in Figure 4.27. Factor 2 accounts for >40% of the concentrations of heavy hydrocarbons. Although this gives the impression that diesel emissions is the major source of this factor, there is two points, which do not support this argument. (1) The factor does not include dodecane, which is a well-known diesel marker and SO_2, which is association with diesel emissions in Ankara was shown in a previous study (Genc et al., 2010) and discussed earlier in the manuscript. (2) Factor 2 profile does not correlate well with Factor 4 (diesel factor) loadings found in METU PMF. Because of these points Factor 2 was not assigned as diesel factor. Another possible source where heavy hydrocarbons are enriched is asphalting activities. Emissions from paved asphalt is known to be enriched by heavy hydrocarbons (Watson et al., 2001).

In a previous study at Bursa, vigorous asphalting activities were performed during our sampling at roads that are very close to station. This generated a very clear asphalt factor in PMF. In that study timing of asphalt pavement activities were monitored and related with increase and decrease in VOC concentrations and factor scores. The asphalt factor loadings found at Bursa Study is regressed against Factor 2 loadings in this work at urban station. Results of regression is shown in Figure 4.29. R^2 value is 0.77, which indicates that asphalt factor in Bursa correlates strongly with Factor 2 profiles in urban station in this work.

Factor 2 scores have fairly high values in March April and May, but do not show a specific pattern in remainder of the year. Please note that March, April and May are the months when roads are repaired after harsh winter season. Consequently, Factor 2 is identified as Asphalt pavement activities.

Diagnostic figures for Factor 3 are given in Figure 4.30. Factor 3 accounts for a significant fraction of the concentrations of 3-methylhexane, 2,2,4-trimethylpentane, n-heptane and p-diethylbenzene. These are marker species for solvent use (Watson et al., 2001; McCarthy et al., 2013). Higher values of Factor 3 scores in summer season also supports a solvent source for this factor.

Factor 3 qualitatively resembles Factor 3 found in METU PMF exercise, which is also enriched by these marker species. However, solvent factors found in both suburban and urban stations do not show a statistically significant correlation (R^2 = 0.07 and P[r,n] > 0.05). There may be two reasons for that; (1) our suburban and urban stations may be affected from different type of solvents used in their proximities and (2) VOCs measured at suburban station have sources in the city and transported to METU area. During this transport some reactive VOCs may degrade and disappear changing the solvent profile intercepted at METU station. In any case, Factor 3 found in urban station is identified as solvent factor, representing emissions from solvents used both in the city and in the proximity of the station.

Diagnostic figures for Factor 4 are presented in Figure 4.31. Factor 4 explains >30% of the concentrations of Ethane, t-2-butene, hexane, 3-methylheptane, n-propylbenzene and undecane. Composition of this factor is fairly similar to the composition of industrial evaporation factor found in PMF exercise at our suburban station (Factor 1). Linear regression between METU and AU industrial evaporation factors are depicted in Figure 4.33. The R^2 is 0.8 and P[r,n) < 0.05, suggesting that these two factor profiles are correlated with a statistical significance > 95%. Higher scores during summer season is also similar to monthly variation of Factor 1 scores in METU PMF. Thus, Factor 4 was identified as industrial evaporation factor.

Factor loadings, fractions of VOC concentrations explained by Factor 5 and monthly median G-scores for Factor 5 are given in Figure 4.32. Factor 5 explains 85% and 90% of the concentrations of SO_2 and dodecane, respectively. It also accounts for > 40% of the concentrations of p-diethyl benzene and n-undecane. These species are good indicators of diesel emissions. Composition of Factor 5 is similar to the composition of diesel factor found in suburban station. This is shown in Figure 4.34

where diesel factor loadings found at urban and suburban stations are regressed against each other. R^2 value is 0.87. It should be noted that two data far from the rest of the data (for undecane and SO_2) have dominating influence on R^2. However, P[r,n] <0.05 indicating that probability of chance correlation is less than 5% and these two profiles are correlated with 95% confidence. Thus, Factor 5 was identified as Diesel factor.

Factor loadings, percentages of VOC concentrations accounted for by Factor 6 and monthly median Factor 6 scores are given in Figure 4.35. Factor 6 is enriched with large number of hydrocarbons, including traffic markers such as ethylene, acetylene and BTEX compounds. This is atypical gasoline exhaust profile. Approximately 50% of NO is accounted for by this factor alone, which supports traffic source for Factor 6.

The regression between gasoline exhaust factors found in urban and suburban stations are given in Figure 4.36. Relatively high R2 0.82 and P[r,n] < 0.05 shows that the two exhaust factors are related with >95% statistical significance.

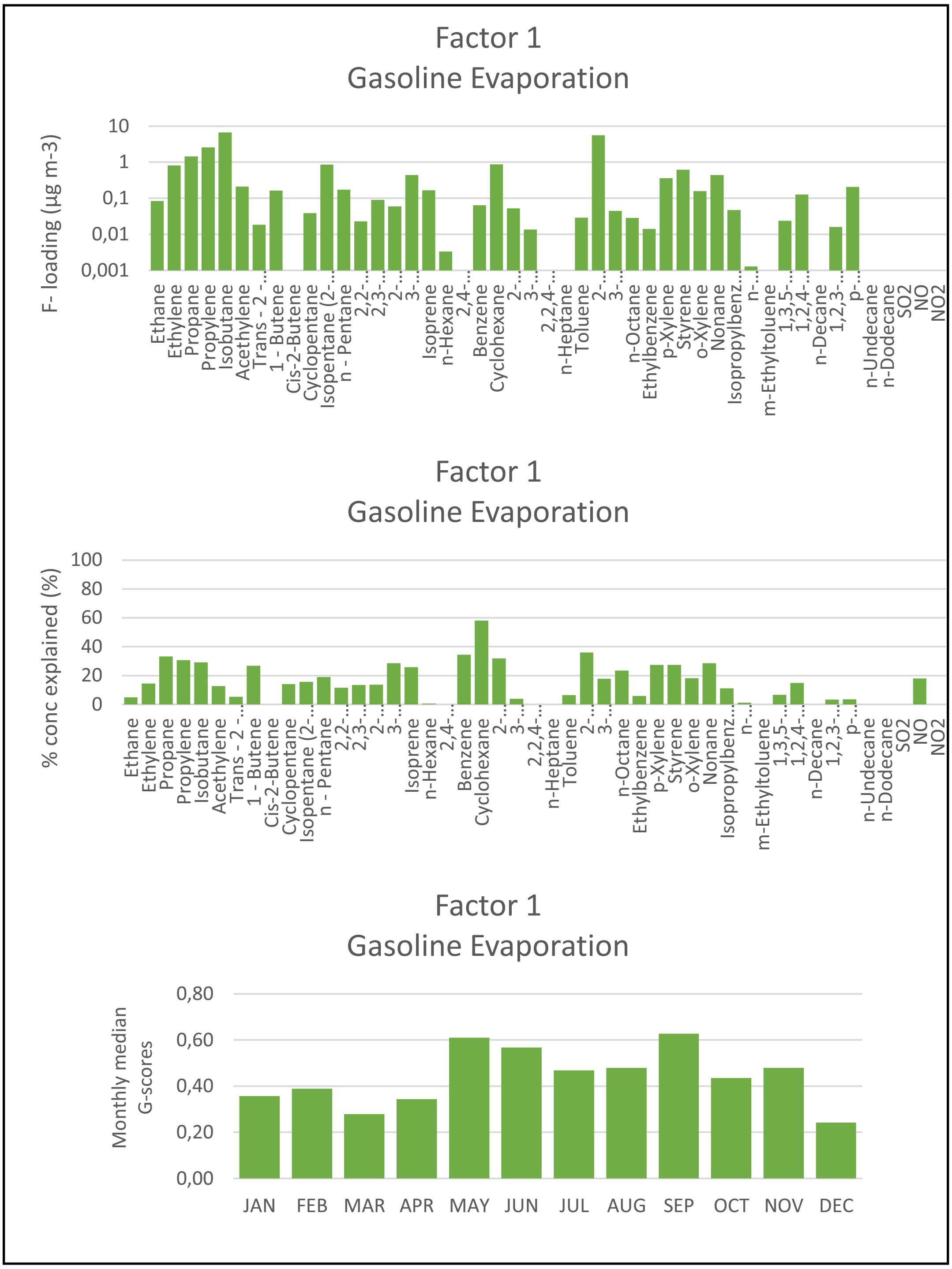


Figure 4.26: Factor 1 diagnostic figures at AU station

Factor 2
Asphalt Pavement

Factor 2
Asphalt Pavement

Factor 2
Asphalt Pavement

Figure 4.27: Factor 2 diagnostic figures at AU station

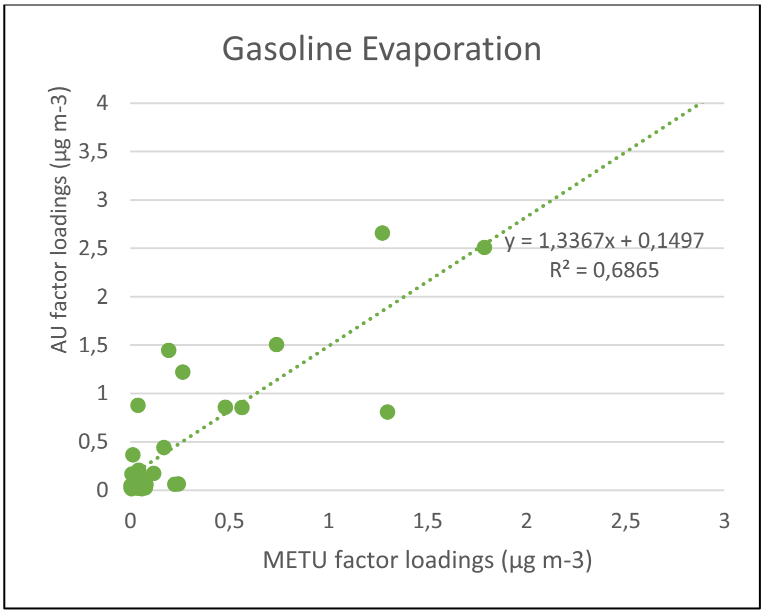


Figure 4.28: Comparison of compositions of gasoline evaporation factors generated at urban and suburban stations

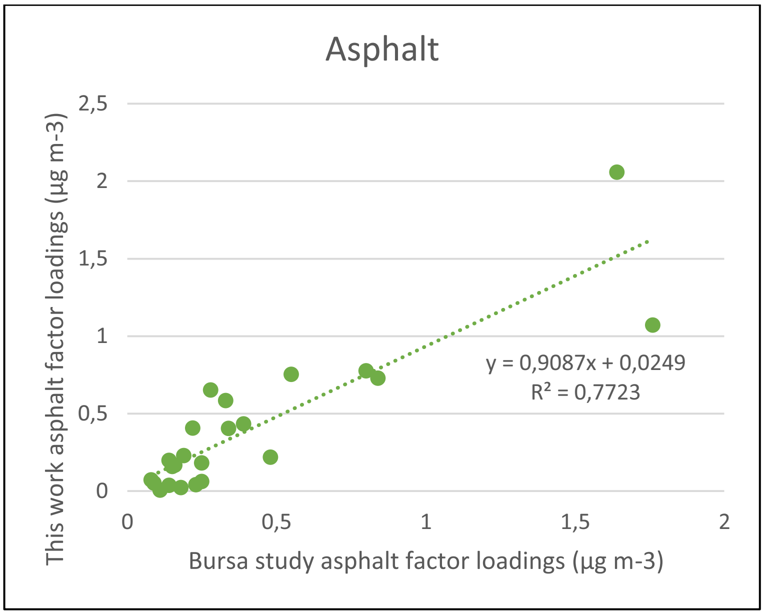


Figure 4.29: Comparison of compositions of asphalt profile generated in this work with asphalt profile found in Bursa study

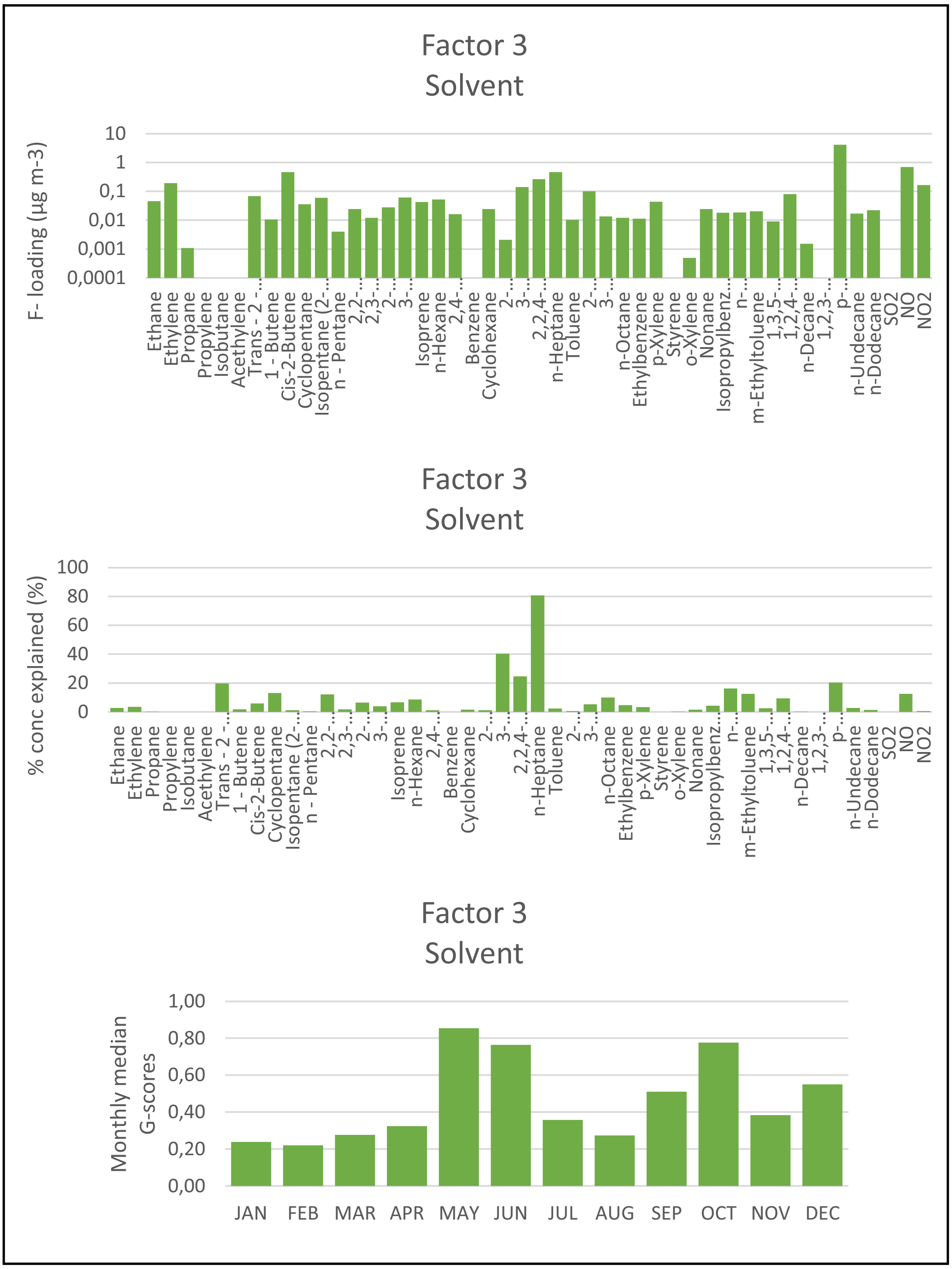


Figure 4.30: Factor 3 diagnostic figures at AU station

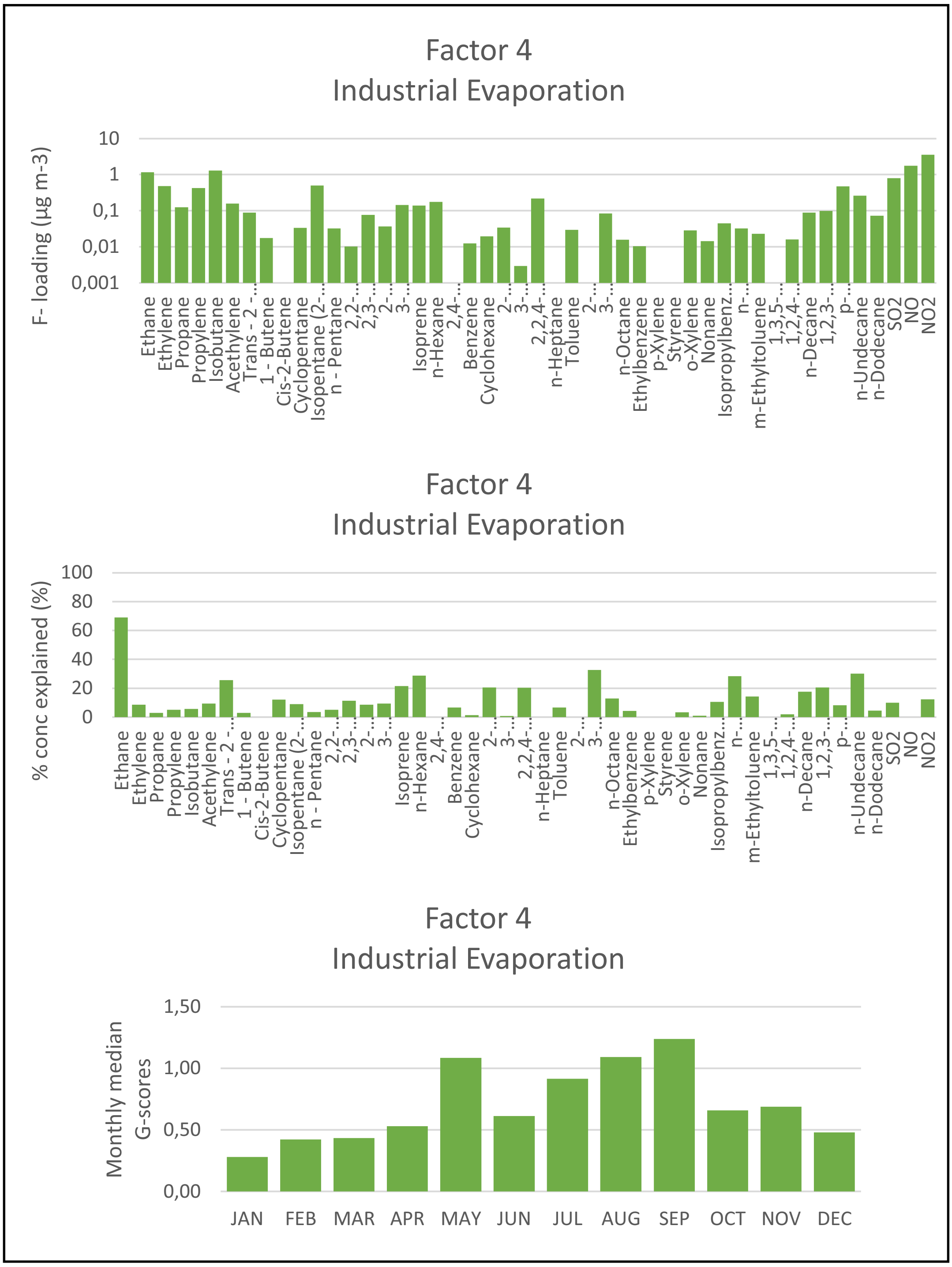


Figure 4.31: Factor 4 diagnostic figures at AU station

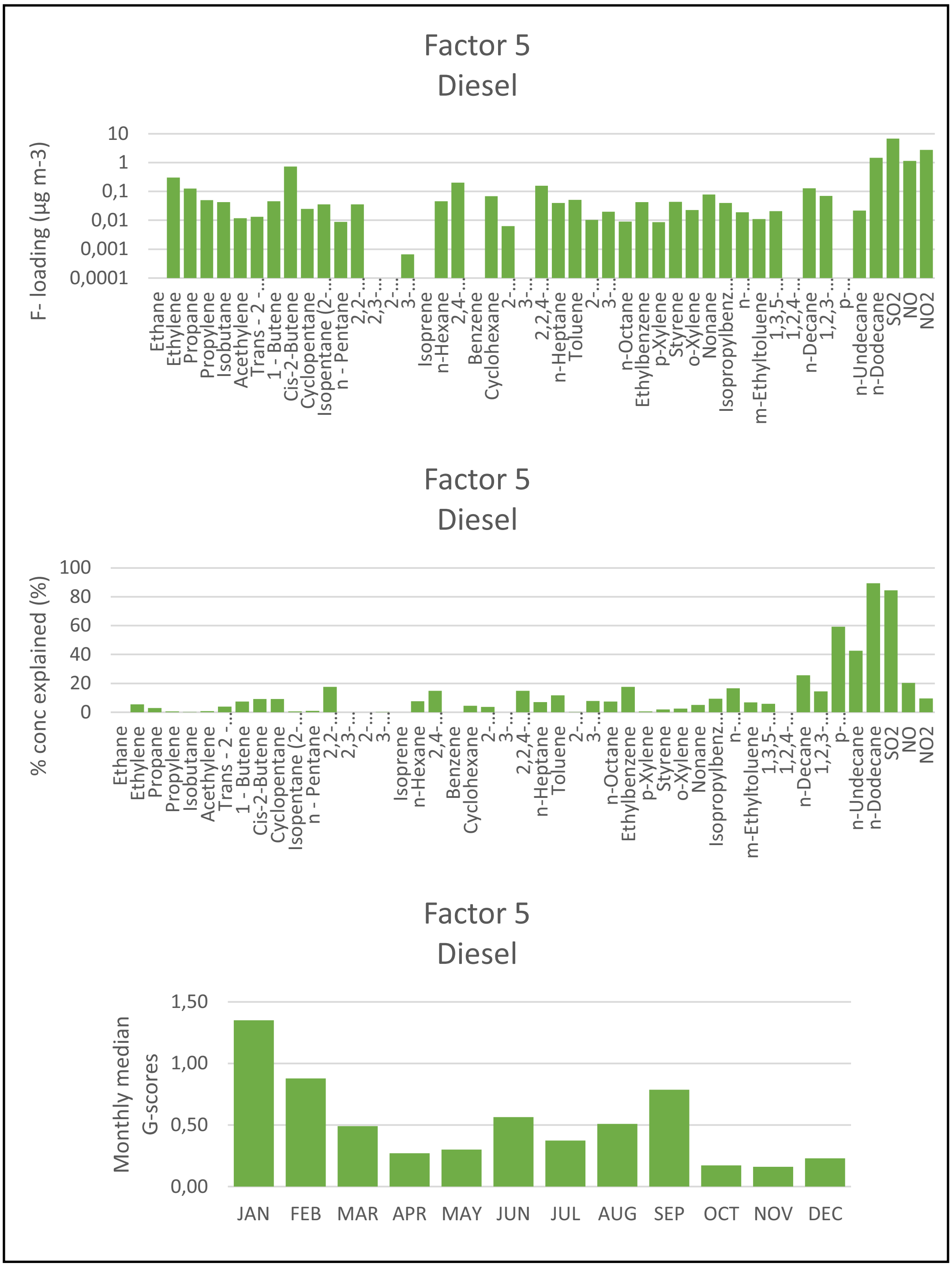


Figure 4.32: Factor 5 diagnostic figures at AU station

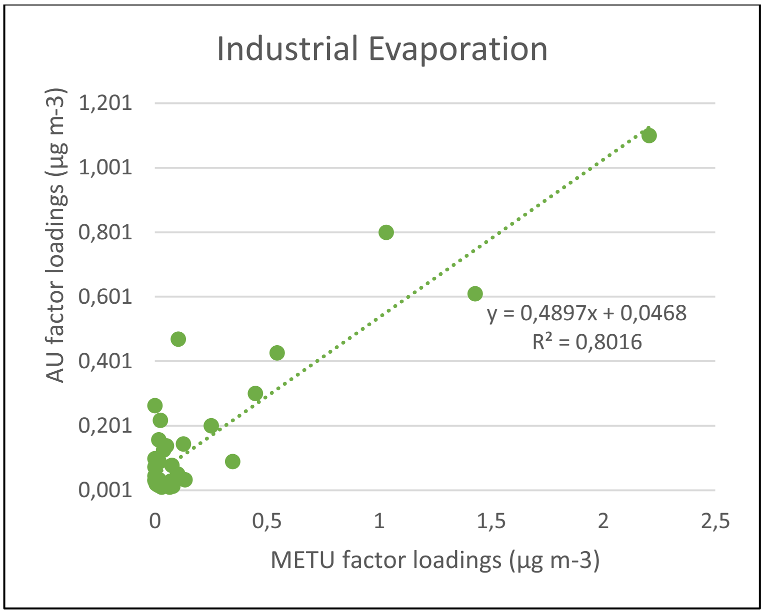


Figure 4.33: Comparison of compositions of industrial evaporation factors generated at urban and suburban stations

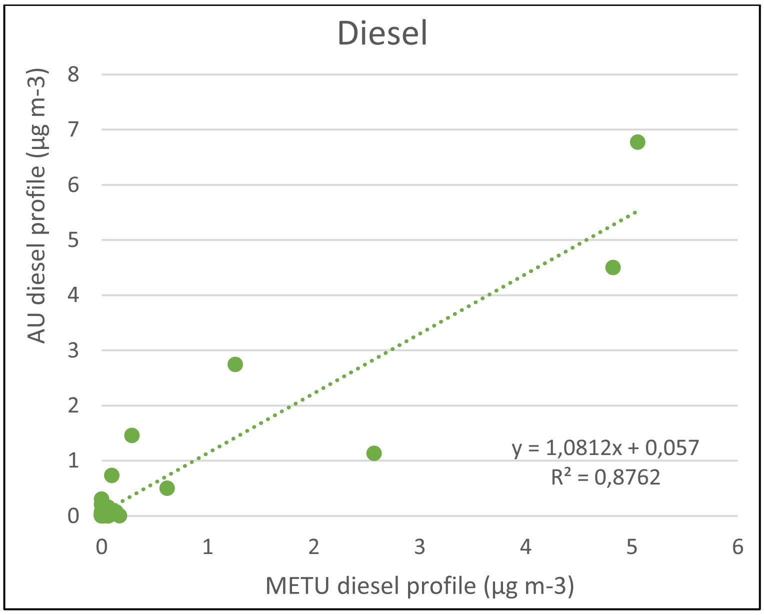


Figure 4.34: Comparison of compositions of diesel profiles generated at urban and suburban stations


Factor 6
Gasoline Exhaust

Factor 6
Gasoline Exhaust

Factor 6
Gasoline Exhaust

Figure 4.35: Factor 6 diagnostic figures at AU station

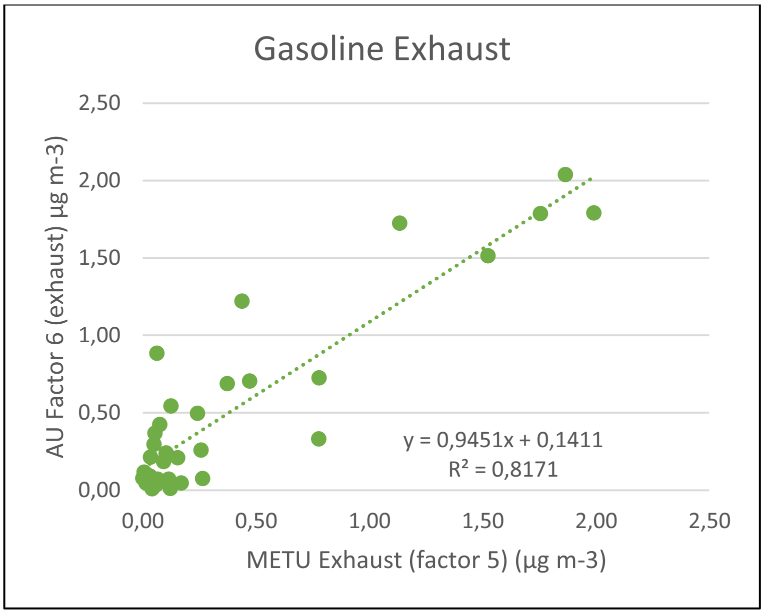


Figure 4.36: Comparison of compositions of gasoline exhaust profiles generated at urban and suburban stations

Results of the PMF runs at urban and suburban stations revealed few interesting points:

Total VOC mass, in both stations consists of 6 components. Five of these components, namely gasoline exhaust, diesel exhaust, industrial evaporation, solvent and gasoline evaporation are observed in both stations. Each station had one component, which is not observed in the other one. This component, which is unique for urban station is asphalt factor and the component that is unique for suburban station is a second solvent factor. Another important point that came out of this work is the similarities of factors. Except for solvent factor, common factors in both stations have similar composition. They all are related with > 95% statistical significance. For many years now, we keep on seeing the same phenomena; Particle and gas composition in Ankara atmosphere is not significantly different at city center and at suburbs of the city. This is attributed to slow wind speed and inefficient horizontal and vertical ventilation of Ankara. Inefficient ventilation results in longer residence time of particles and gases over the city, which in turn, results in relatively homogeneous distribution of all pollutants. Similarity of factor profiles found in the city center and at a suburban area in this work is the confirmation of earlier observation of homogeneous distribution of pollutants.

Contribution of factors to to total VOC mass in both stations is depicted in Figure 4.37.

Gasoline exhaust factor have the highest contribution to total VOC mass in both stations (38% at each station). Contributions of gasoline evaporation and asphalt pavement activities contribute approximately 23% each at urban station. Contribution of remaining factors (solvent, industrial evaporation, Diesel) is <10% at urban site. Gasoline evaporation factor is the second highest contributor to total VOC mass at suburban station (19%), which is followed by industrial evaporation (13%), diesel (11%) and solvent (10%) factors.

Obviously, traffic is the most important source of VOCs in Ankara atmosphere. Gasoline exhaust, diesel emissions and gasoline evaporation, totally accounts for 68% of measured total VOC concentration at suburban station and 65% at urban station.

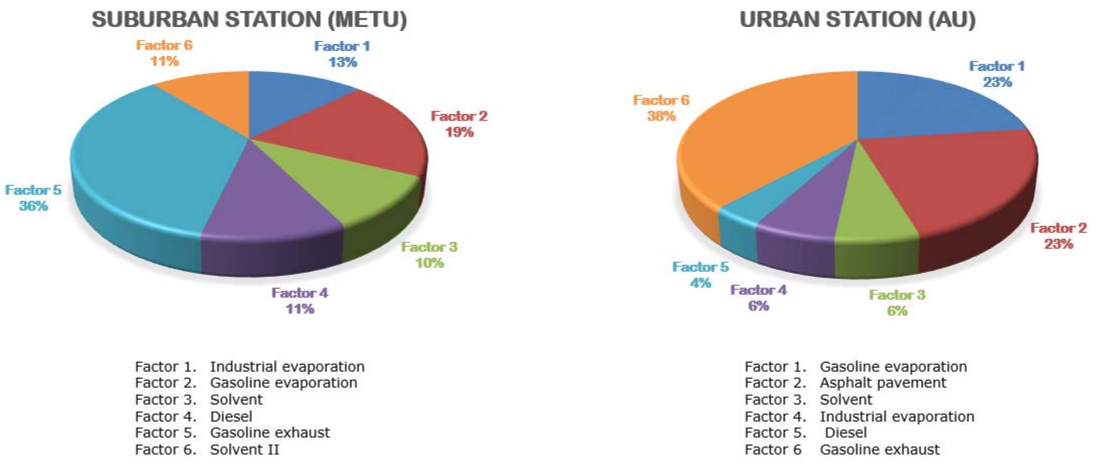


Figure 4.37: Contribution of factors to total VOC concentrations at urban and suburban stations

CHAPTER 5

CONCLUSION AND FUTURE WORK

In the scope of this thesis study, two sampling stations were examined in Ankara, one located in AU (urban), the other located in METU (suburban) in order to measure 51 VOCs. 569 VOC samples were collected daily in total by means of 6L canisters between January, 2014 and September, 2015 and analyzed by GC/FID system. The conclusions of the study presented in this thesis are summarized as follows:

- Mean concentrations of VOCs were observed in the range of 0.09 µg m^{-3} (cis-2-pentene) and 24.76 µg m^{-3} (toluene) at AU station, and in the range of 0.06 µg m^{-3} (cis-2-pentene) and 10.09 µg m^{-3} (toluene) at METU station. During sampling period, the annual limit of 5 µg m^{-3} for benzene was exceeded twenty five times at AU station and fifteen times at METU station.
- Two different comparison studies applied to measured concentrations with: other cities in Turkey and other cities around the world. Comparisons show that: (i) VOC concentrations measured in different years did not show a consistent increasing or decreasing pattern in Ankara, (ii) concentrations of BTEX measured in urban and suburban areas in this study are not very different from other cities. Only the toluene concentration at AU station was among the highest values, (iii) the BTEX concentrations are generally low in cities in Europe and the US and high in Asian countries such as China and India and the values measured in this study are closer to the VOC levels measured in the European cities and (iv) the comparison of VOC

concentrations does not seem to make much sense since concentrations are highly dependent on the proximity of the station to the road.

- In order to make comprehensive explanation, temporal variations in VOC concentrations were studied.
- For 36 out of 51 VOCs, calculated episode contributions at both stations are close to each other. There were many episodes in both stations, particularly in winter months. In order to understand whether meteorological factors or variability in emissions is more effective in formation of episodes, relative variability of VOCs had been studied. According to results, independent common factor, which is effective in the formation of episodes in VOC concentration, was meteorology.
- The weekday VOC concentrations measured at both stations were higher than the weekend concentrations. This is due to the fact that the most important source of VOC concentrations is traffic and traffic is more intense during the weekdays than in the weekend. The ratio of WD/WE was lower than 1 for only two of the measured VOCs: 2,2,4-trimethylpentane and 1,2,4-trimethylbenzene. The reason behind this result is the main source of those two VOCs are not the traffic.
- In both stations, with a few exceptions, winter concentrations of VOCs were higher than their summer concentrations due to the seasonal differences in meteorology, particularly in mixing height and faster photochemical degradation of reactive VOCs with higher solar flux in summer. On the other hand, evaporative emissions, which increase with temperature, might be the reason for the compounds which show inverse relationship.
- The relationship between meteorological parameters: (i) temperature, (ii) wind speed, (iii) mixing height, (iv) ventilation coefficient and the measured concentrations was discussed.
- Most of the VOCs showed decreasing concentrations with the temperature. BTEX are among these compounds. Some of the compounds, such as isoprene, isopentane, tans-2-butene, n-octane and 1-pentene, had increasing

concentrations with increasing temperature since their concentrations were determined by evaporative emissions and solvent evaporation.

- Increasing wind speed caused a decrease in the concentration for all VOCs measured in this study, without any exception in both stations.
- Concentrations of VOCs showed different variations with mixing height at both stations. Concentrations of most VOCs decreased with increasing mixing height. Concentrations of the second VOC group did not change with mixing height. VOCs in this pattern indicates that there are sources of these VOCs when MH is high.
- The relation between ventilation coefficient and VOC concentrations was also very similar to the relation between VOC concentrations and mixing height. Some of VOCs decreased with increasing mixing height while some of them are independent of VC.
- Application of PMF revealed six factors for both stations. In suburban station main sources were industrial evaporation (factor 1 : 13%), gasoline evaporation (factor 2: 19%), solvent (factor 3: 10%), diesel (factor 4: 11%), gasoline exhaust (factor 5: 36%), solvent II (factor 6: 11%). While in urban station, main gasoline evaporation (factor 1: 23%), asphalt pavement (factor 2: 23%), solvent (factor 3: 6%), industrial evaporation (factor 4: 6%), diesel (factor 5: 4%), and gasoline exhaust (factor 6: 38%).

The future works that may add values to the findings reported in this study are listed below:

- For environmental studies, contamination is a serious problem, which affects the whole study. Therefore, cleaning procedure of canisters should be carried out meticulously. Moreover, in order to protect canisters from dust, canisters should be placed in a shelter. This shelter also prevents the canisters from meteorological events such as rain and snow. These are the parameters affecting the efficiency of the sampling.
- Further studies related to collected and processed data could not have been conducted in the period of this thesis study. Cancer and non-cancer related

health risks due to VOCs in Ankara atmosphere can be calculated since VOCs have significant effects on human health. Also, in the scope of environmental effects of VOCs, whether VOCs or NO_2s are significant for the O_3 production in Ankara can be identified as a future work.

- In this thesis study, eight canisters and two sampling kits were used totally for two stations to collect air samples. There were some problems due to malfunctioning of the sampling kit faced in the sampling periods. The sampling was repeated a few times due to this issue, which was time-consuming. In order to prevent such problems, having backup equipment or using different sampling methods might be considered.
- During study, decrease in the measured concentrations was observed due to storing samples in the canisters for long time. Although, canisters are suitable for storing the samples for long time, it should be avoided if it is possible.

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