SOURCES OF VOLATILE ORGANIC COMPOUNDS AT URBAN AND RURAL KÜTAHYA ATMOSPHERE

THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

TUĞÇE BEK

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
ENVIRONMENTAL ENGINEERING

DECEMBER 2015

Approval of the Thesis:

SOURCES OF VOLATILE ORGANIC COMPOUNDS AT URBAN AND RURAL KÜTAHYA ATMOSPHERE

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ABSTRACT

SOURCES OF VOLATILE ORGANIC COMPOUNDS AT URBAN AND RURAL KÜTAHYA ATMOSPHERE

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December 2015, 181 pages

This study is a part of a fairly extensive study to investigate contributions of the two thermal power plants, Tunçbilek and Seyitömer, on air quality at Kütahya atmosphere. VOCs were measured at two sampling stations, one was established in the down-town of Kütahya and the other one in the Northeast of the Kütahya. Samples were collected using canisters and they were analyzed using GC-FID system.

Average concentrations of VOCs varied between 0.12 $\mu g/m^3$ and 23 $\mu g/m^3$ at urban station and 0.06 $\mu g/m^3$ and 33 $\mu g/m^3$ at rural station. VOC concentrations measured in this study were comparable to corresponding concentrations measured in other cities in Turkey, but lower than VOC data reported for other cities around the world.

The effect of wind direction was very important, as such dependence may reveal the effectiveness of thermal power plants on measured VOC concentrations. Concentrations of some of the VOCs were high in wind sectors that includes Seyitömer and Tunçbilek power plants, but the evidence was not strong enough to be conclusive.

Finally, source apportionment study was conducted using PMF and eight different factors were identified in both stations. These factors were grouped under the following 4 components: (1) traffic related sources (31.3% of the ∑VOC), (2) Kütahya urban plume (15.3% of the ∑VOC), (3) solvent usage (38% of the ∑VOC and (4) Tavşanlı-urban plume (15.4% of the ∑VOC). While in urban station factors were grouped under the following 3 components : (1) traffic related sources (58.6% of the ∑VOC), (2) solvent use (37.6% of the ∑VOC), and asphalt operations (3.8% of the ∑VOC).

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

ÖZ

KÜTAHYA MERKEZİ VE KIRSALINDAKİ UÇUCU ORGANİK BİLEŞİK KAYNAKLARI

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Tez Yöneticisi: Prof. Dr. Gürdal Tuncel

Aralık 2015, 181 sayfa

Bu çalışma Kütahyada bulunan Tunçbilek ve Seyitömer termik santrallerinin hava kalitesine olan katkılarının araştırıldığı oldukça geniş çaplı bir çalışmanın bir parçasıdır. Uçucu organic bileşik (UOB) konsantrasyonları biri Kütahyanın merkezinde diğeri Kütahyanın kuzeydoğusunda kurulmuş olan iki istasyonda ölçülmüştür. Örnekler kanister kullanılarak toplanmış ve GC-FID sisteminde analiz edilmiştir.

Ortalama UOB konsantrasyonları kent istasyonunda 0.12 $\mu g/m^3$ ile 23 $\mu g/m^3$ arasında, kırsal istasyonda ise 0.06 $\mu g/m^3$ ile 33 $\mu g/m^3$ arasında değişmektedir. Bu çalışmada ölçülen UOB konsantrasyonları Türkiyede ölçülen UOB konsantrasyonlarıyla karşılaştırılabilir bulunmuştur, ancak dünya genelinde rapor edilen konsantrasyonlardan düşüktür.

Rüzgar yönü, termik santrallerin UOB konsantrasyonlarına olan etkisini ortaya çıkarabilmek için çok önemlidir. Bazı UOB konsantrasyonları Seyitömer ve Tunçbilek termik santrallerinin bulunduğu yönlerden esen rüzgar yönlerinde yüksek ölçülmüştür, ancak bu termik santrallerin UOB konsantrasyonlarına olan katkılarını açıklamak için yeterince güçlü bir kanıt değildir.

Son olarak, PMF kullanılarak bir kaynak paylaştırma çalışması yütürülmüş ve her iki istayonda da 8 farklı faktör tanımlanmıştır. Bu faktörler kırsal istasyonda 4 başlık altında şöyle gruplandırılmıştır: (1) trafik (toplam UOB konsantrasyonunun %31.3’ü), (2) Kütahya kent etkisi (toplam UOB konsantrasyonunun %15.3), (3) solvent kullanımı (toplam UOB konsantrasyonunun %38’i), ve (4) Tavşanlı kent etkisi. Kentsel istasyonda ise faktörler 3 başlık altında: (1) trafik (toplam UOB konsantrasyonunun %58.6’sı), (2) solvent kullanımı (toplam UOB konsantrasyonunun 37.6%’sı), ve (3) asfalt işlemleri (3.8%) şeklinde gruplandırılmıştır.

Anahtar Kelimeler : Kütahya, UOB, reseptör modellemesi, PMF

ACKNOWLEDGEMENTS

First of all, I would like to express my gratefulness to my thesis supervisor Prof.Dr.Gürdal Tuncel for his guidance and recommendations in the course of this research.

I would like to thank to examining committee members Prof. Dr. İpek İmamoğlu, Assoc. Prof. Dr. Tuba Hande Ergüder Bayramoğlu, Assoc. Prof. Dr.Eftade Gaga and Assist.Prof. Dr. Barış Kaymak for their valuable contributions.

I also would like to special thank to Dr. Sema Yurdakul for her guidance throughout the study and unlimited support whenever I need to her experiences, and I would like to thank to Dr. Güray Doğan for his unconditional support during source apportionment studies.

I would like to thank to current members of Air Pollution and Quality Research Group Ebru Koçak, İlker Balcılar, Tayebeh Goli and Ömer Ateş for their cooparetiveness.

This study was supported by The Scientific and Technological Research Council of Turkey (TUBITAK) through project no : 112Y305. And, I would like to thank to all members of this project, Prof. Dr. Tuncay Döğeroğlu, Prof. Dr. Mustafa Odabaşı, Prof. Dr. Tolga Elbir, Prof. Dr. Sema Burgaz, Assoc. Prof. Dr. Gonca Demircigil, Assist. Prof. Dr. Hicran Altuğ, Assist. Prof. Dr. Ozan Devrim Yay, Dr.Yetkin Dumanoğlu, Dr.Özlem Özden Üzmez, Akif Arı, Gizem Tuna, Narin Polat, Emre Can, İbrahim Hacığolu, Gülzade Küçükaçıl and all unmentioned contributors who work for this large scaled scientific project.

I would like to thank my dear friends Gül Ayaklı Özkılıç, Zeynep Malkaz, İlke Çelik, Cansu Karakaş, Ezgi Sert, Burcu Koçer Oruç, Ruken Dilara Zaf, Zeynep Özcan, Hale Demirtepe, Gülçin Kaltalı, Didem Erdemli, and Halil Delibaş for their sincere supports, and I would like particularly thank to Sena Uzunpınar for her genuine and unconditional support every time. Also, I would like to thank to Kemal Akat for his support to gain time during one of the most critical period.

I appreciate to Veli Dalkılıç, and employees in Kütahya Meteorology Directorate, Hasan Basri Keçeci, Ramazan Cafer Polat, and Zihni Kale for their important supports throughout the sampling period.

Additionally, I would like to appreciate to the department staff Mrs.Güldane Kalkan, Mrs.Gülçin Şahin, Mr.Cemalletin Akın, Mr.Kutlay Öztürk, and Mrs.Döndü Çakır for their motivation and helpfullness.

And, I would like to express my innermost gratitudes to Barış Munzur for his endless supports not only temporarily, but also throughout my life.

Finally, I would like to express my deeply gratitutes to my family, especially to my father, my mother, Hüseyin Güngör and my dear aunt Yeter Güngör for their unconditional confidence, belief, love and support for all my initiatives throughout my life.

To memory of my brother. . .

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LIST OF ABBREVIATIONS

AQAMR: Air Quality Assessment and Monitoring Regulation

AU : Anadolu University

BTEX: Benzene, Toluene, Ethylbenzene, Xylenes

BVOC: Biogenic Volatile Organic Compounds

CEN: European Commission for Standards

CFCs: Chlorofluorocarbons

CMB: Chemical Mass Balance

CPF: Conditional Probability Function

DEU: Dokuz Eylül University

E.C.: European Commission

EU: European Union

EVAP. : Evaporative

FA: Factor Analysis

GC/FID: Gas Chromatography/Flame Ionization Detector

GC/MS: Gas Chromatography/Mass Spectrometry

HPLC: High-performance Liquid Chromatography

LPG: Liquefied Petroleum Gas

MDL: Method Detection Limit

METU: Middle East Technical University

MH: Mixing Height

NMHC: Non-methane Hydrocarbons

NMOC: Non-methane Organic Compounds

PAMS : Photochemical Assessment Monitoring Stations

PCA : Principal Component Analysis

PM : Particulate Matter

PMF : Positive Matrix Factorization

QA/QC : Quality Assurance/Quality Control

RH : Relative Humadity

S/W : Summer-to-Winter Ratio

T : Temperature

TPP : Thermal Power Plant

USEPA : United States Environmental Protection Agency

VC : Ventilation Coefficient

VOCs : Volatile Organic Compounds

WD : Wind Direction

WS : Wind Speed

WKDAY : Weekday

WKEND : Weekend

WHO : Worl Health Organization

∑VOC : Total Volatile Organic Compounds

CHAPTER 1

INTRODUCTION

Air pollution is in the agenda of the world over the course of many years due to its important adverse effects on both environment and human health. Furthermore, there has been an increasing trend in this important pollution by virtue of increasing population, industrialization, increasing density of traffic, and space heating etc (Coskun et al., 2010). It is possible to encounter various air pollutants which emits from different sources. Volatile organic compounds (VOCs) are one of the most important one. They are defined as organic chemical compounds which can evaporate easily under normal conditions of temperature and pressure. According to USEPA, VOCs were defined as any carbon containing compounds whose vapor pressure is greater than 10^{-1} torr under normal conditions, excepted carbon monoxide (CO), carbon dioxide(CO_2), carbonic acid (CH_2O_3) , metallic carbides or carbonates, which participates in atmospheric photochemical reactions .

VOCs are emitted to the atmosphere from both anthropogenic and natural sources. The most dominant anthropogenic emission sources are organic solvent usage, oil and chemical industries, combustion processes, and motor vehicle exhausts. (Passant, 1995). Natural sources are another important emission source category which contribute VOCs emissions. Trees, a variety of plants, animals, natural forest fires and biological processes in bogs or marshes are typical examples of this category(Derwent,1995).

This study is a part of a large-scaled scientific project which was funded by TUBITAK (112Y305). The main aim of the project was, in addition to regular sources, such as traffic and space heating, the influence of two high emitting power plants, namely Tunçbilek and Seyitömer Power Plants in Kütahya, on the ambient air quality of the province. Within the scope of the project, concentrations of VOCs in the ambient air was measured and sources of them was determined using Positive Matrix Factorization (PMF) modelling tool. In accordance with this aim two different sampling locations were designated in both rural and urban regions of the Kütahya and two sampling stations were established in these locations respectively.

Air samples were collected using stainless steel 6L canisters and analyzed with GC-FID system. After specified sampling period, obtained results were interpreted using meteorological data and necessary tools.

In the later parts of the study, general characteristics, sources and effects of VOCs were explained in detail, and another essential information were given. Furthermore, VOCs emission legislations in Turkey, European Union Directives concerning VOCs, and harmonization of Turkish legislation in the accession process of Turkey were mentioned briefly. Then, monitoring experimental and analytical methods were introduced in detail. Meteorological parameters were included in the whole data interpretation and results were examined statistically. In Chapter 5, source apportionment studies were conducted using PMF and in addition to regular sources of VOCs in Kütahya, possible contributions of thermal power plants on the concentrations that were measurued in urban and rural stations were investigated. Finally, all study were clarified and concluded properly.

CHAPTER 2

LITERATURE REVİEW

2.1 Volatile Organic Compounds (VOCs)

Atmospheric pollution has been an important phenomenon since the time immemorial, and it has increased day by day because of many different factors such as industrilization, increasing migration rate from rural to urban areas, rapid expansion in population growing etc (Coskun et al., 2010). And, there are so many different pollutants in the atmosphere which emit from different sources, and volatile organic compounds, or VOCs, have received much attention for decades due to their adverse health and environmental effects. Mostly, they have been observed at ground level atmosphere of both rural and urban areas. In a multitude of expressions could be used to identify VOCs. Basically, the term make a reference to organic compounds which appear in the atmosphere as gases, however , they could be found in solid and liquid phases (Derwent, 1995).

In scientific literature, VOCs are defined as organic chemical compounds which can evaporate easily under normal conditions of temperature and pressure. According to EPA 1997a, VOCs were defined as having vapor pressure greater than 10^{-1} torr under normal conditions (at 25 °C and 760 mmHg). Besides, in some cases boiling point temperature is used to defined and classified VOCs. For instance, European Union uses this physical characteristic of compounds, and they identify VOCs as any organic compound having an initial boiling point less than or equal to 250 ^{o}C at the standard atmospheric pressure, 101.3 kPa (USEPA, Technology Transfer Network Emission Measurement Center, 2015).

According to their chemical and physical properties, VOCs could be varied different classes. Pure hydrocarbons contain only carbon and hydrogen such as alkanes, alkenes, alkynes and aromatics. Besides, VOCs which contain oxygen, chlorine, or any other halogens in addition to carbon and hydrogen is other important groups of them. Aldehyhes, ketones, alcohols, chlorinated alkans/alkens, or chloroflorocarbons could be given as an example the latter class.

VOCs was added to hazardous air pollutant (HAP) list into Clean Air Act with an amendment in 1990 (TO-15). And, it is known that 50000 to100000 chemical compound being produced and each year, 1000 more added to this huge amount. Furthermore, organic chemicals constitute most of them besides pesticides and biocides. Prominent amount of them have environmental and health concerns due to their presence in detectable amounts in various components of the environment , toxicity, tendency to bioacumulate, persistance, dissociation and also transport talent to long distances.

2.2 Sources of VOCs in The Atmosphere

Organic compounds are emitted to the atmosphere from both anthropogenic and biogenic sources. The most dominant anthropogenic emission sources are organic solvents, oil and chemical industries, combustion processes, traffic. (Passant, 1995). In the past time, especially in the industrialised countries, researchers dwelled on mostly high level of smoke and sulphur dioxide formation which was resulted from combustion processes. But, in the recent years they have mostly focused on traffic emissions and fossil fuel usage due to huge amount of air pollutants formation with increasing urbanization. The most prominent pollutants have been carbon monoxide (CO), nitrogen oxides (NO_x), and as a matter of course VOCs (Gee & Sollars, 1998).

VOCs comprise a wide variety of species and emit from several sources. Because of this, the amount and variety of relevant source categories responsible for anthropogenic emisssions. Combustion processes, fossil fuel usage and its mining, treatment, storage and distribution, organic solvents and their containing products, various industrial processes, and biological processes are the most common anthropogenic sources of VOCs (Friedrich & Obermeier, 1995) while emissions of vegetation is the main natural sources of them (Ling, 2011).

Especially fossil fuel combustions are the most prominent VOCs emission sources. Combustion processes can be divided into two main categories which are exhaust gas emissions from internal combustion engines and flue gas emissions prior to combustion (Passant, 1995). Theoretically, when a complete combustion of fossil

fuels occurs, major products are carbon monoxide and water. But, practically complete combustion can not be occured, it is more or less incomplete. Because of this, combustion processes lead to VOC emissions (Friedrich & Obermeier, 1995).

Another important source is chemical solvents which have a wide spread utilization fields such as industrial coating materials, industrial processes, in the formulation of chemical products, cleaning of metal or plastic materials, dry cleaning of textiles etc. Chemical solvents can evaporate easily and this case is a fundamental aspect of their function after their usage. During their utilization, some part of emissions can be controlled with handling or storage of materials, washing of equipments, and spillages, and this is called fugitive emission. However, especially in the open areas control of solvents emissions cannot be possible.

Major emissions from fossil fuels occur due to their production, processing, storage and distribution. In addition, huge amount of VOCs emit from refineries and chemical plants. Emissions occur from storage of volatile materials, venting and flaring of gases and fugitive emissions from valves and pumps. Also, distribution of fuel is another important source of VOCs; emissions occurring during loading of road tankers, filling station storage facilities and during vehicle refueling (Passant, 1995).

Natural and biogenic sourcess are another critical emission source category which contribute VOCs emissions and trees, a variety of plants, animals, natural forest fires and biological processes in bogs or marshes are typical examples of this category(Derwent,1995).

2.3 Effects of VOCs on Human Health and Environment

There are so many differrent organic compounds in the atmosphere which match up to VOCs definition, and due to their omnipresent existence in the atmosphere and significant impacts on the environment and human health, they are considered as critical parameters for evaluation of air quality in both indoor and outdoor environments (Ramírez, 2012). And depending on their a characteristics, concerns about VOCs are divided into two main categories as adverse effects on human health and the environment.

Among the health effects of VOCs, the most common issue is their toxic and carcinogenic health effects at varying exposure levels. VOCs have an important chemical diversification, therefore they are classified as incompliance with unknown health effects to extremely toxic or carcinogenic effects (Ramírez, 2012). Some VOCs have an impact on human senses via their odour, some others exert a narcotic effect, and specific types can cause to chronic health problems (Derwent R. G., 1995). Generally, chronic health effects of them can be sorted as either carcinogenic or non-carcinogenic. Non-carcinogenic effects are defined as irritative, sensorial impacts, destruction into the liver, kidney and nervous system, asthma and other critical respiratory effects. When the point in question is their carcinogenic effects, importance of VOCs is become most prominent due to increasing cancer incidences in the recent years. According to World Health Organization (WHO), leading carcinogenic effects of them arise mostly in lung, blood, liver, kidney, respiratory system and biliary tract. With respect to these carcinogenic effects, consultants classify VOCs. For instance, according to International Agency for Research Cancer (IARC), benzene is classified as one of the most important human carcinogen. (Ramírez, 2012). According to EPA’s reports, incomplete combustion products and chemical solvent usage are the main curators of carcinogenic VOCs emissions (EPA, 1990). The most prominent organic compounds which thoroughly dispersed in the atmosphere and added into carcinogens include; benzene, 1,3-butadiene, as potential leukaemia, formaldehyde as potential nasal carcinogen, polynuclear aromatic hydrocarbons as potential lung cancer inducing agents, polychloricated hydrocarbons (PCBs), dioxins and furans (Derwent R. G., 1995).

As for main environmental concerns about VOCs, the below environmenral problems have been noticed ;

- Stratospheric ozone depletion
- Ground level photochemical ozone formation

- Increasing efffects on the climate change
- Accumulation and persistence in the environment

These important effects of VOCs on the environment will be discussed briefly the following subsections.

2.3.1 Stratospheric ozone depletion

Stratospheric ozone depletion is an important phenomenon, because it cause to more UV radiation entering the troposphere. Also, this situation affects photodissociation rates through tropospheric reactions (Ma & Michiel, 2000). Typical stratosopheric ozone measurements was started in 1924 with a spectrograph to measure total ozone column which was suited for outdoor air usage (Müller, 2012). The stratospheric ozone layer show an alternation in time, and both natural effects and anthropogenic activities are responsible for this change (Dameris & Baldwin, 2012). Also, VOCs have an indirect but important role in stratospheric ozone depletion. Most of organic compounds have a steady stade in the atmosphere and they can participate in tropospheric removal reactions and reach to the stratosphere. Especially, some organic compounds , such as containing bromine or chlorine group, eradicate ozone layer via stratospheric photolysis and hydroxyl radical destruction reactions. Commonly, chlorinated and bromine containing chemical solvent usage have been classified as stratospheric ozone layer depleting compounds (Derwent R. G., 1995).

2.3.2 Tropospheric (ground-level) photochemical ozone formation

According to many scientific studies, VOCs have an important role in increasing levels of tropospheric ozone and decreasing levels of stratospheric ozone layer. Due to this fact, it has an importance with regard to human health, forest ecosystems and agricultural crops (Wang & Austin, 2006). Wide range of organic compounds are discharged into the troposphere as a result of human activities and natural sources and they stimulate ozone formation (Singh & Zimmerman, 1992). Ground level ozone formation originates from photochemical reaction of nitrogen oxides (NO_x) and VOCs. The most common NO_x precursors are fossil fuels, chemical solvents and various industrial processes. NO_x levels have a critical impact on ozone production (CASA, 2015).

VOCs can be removed from the atmosphere by various physical processes such as wet and dry deposition. However, chemical photolysis reactions with hydroxyl radicals (-OH), nitrate (-NO_3) radicals and O_3 attract more notice. Because, different decomposition products have been formed as a result of this chemical reactions (Atkinson, 2000) and these products cause to many significant adverse environmental and health effects. Also, ozone is an important greenhouse gas and it stimulates global warming. Furthermore, it is a source of -OH radicals in troposophere (Reynolds, 1993).

Ozone formation potential of every VOCs are variable and in order to evaluate obtained VOC values contribution to grpond level ozone formation, this potential is an important parameter. In 1994, phtochemical reactivity potentials were estimated and six VOCs sensitive conditions were determined about their impacts on ozone concentrations by Carter. With reagrd to these conditions, ozone producing potency of VOCs is named the Maximum Incremental Reactivity (MIR). To estimate ozone producing potency of a compound, concentration of it is multiplied by MIR value. For instance, if MIR value of *trans*-2-butene and *cis*-2-butene is greater than 10, it means more than 10 g of ozone can be generated from 1 gram of related compound (Carter, 1994).

2.3.3 Increasing effects on the climate change

VOCs from both mobile and stationary sources are defined as ozone precursor (Pitts & Pitts, 2012) and they effect climate change indirectly. Most of the VOCs can be easily oxidized in the atmosphere, nevertheles, some of them accumulate in the troposphere during specific meteorological events. These accumulative or long-lived compounds are catagorized as radiative active gases, and they absorb solar radiation, also they stimulate ozone formation,which is an important greenhouse gas, in free troposphere. Furthermore, their Global Warming Potentials (GWP) can be expressed carbon dioxide, so they promote greenhouse effect curicially (Derwent R. G., 1995).

Climate change is not affected only by anthropogenic sources, but also by biological processes that change associated with climate. Especially, VOCs emissions from biogenic sources very susceptible to climate change, and they have more important function in climate forcing due to their impacts on oxidative balance, increasing in greenhouse gas concentrations and formation of aerosols in the atmosphere (Constable et al., 1999).

2.3.4 Accumulation and persistence in the environment

While some VOCs easily evaporate, others, especially having high molecular weight compounds, are able to persist to survive longer in the environment. They can be transported throughout long distances before undergo physical or chemical removal processes (Ling, 2011). Semi-volatile organic compounds are in tendency to adsorb onto any particulate matter which suspends in the air due to their complexity and molecular size. In this condition, they can be transported from long distances to their arising point by wind, rain or any other meteorological event. Firstly, they are deposited in the rain water and after a certain time period, re-evaporate back to the atmosphere and start another cycle. This situation can be cause to biological accumulation and these types of VOCs are able to highly toxic for both humans and animals (Derwent R. G., 1995).

2.4 VOC Emission Legislations

As it was stated in the previous sections, air pollution is an important phenomenon and it has several important impacts on the environment and human health. For this reason, air pollutant emissions must be under control in specific national and international levels. VOCs are one of the most important air pollutant groups and scientific autorities have paid attention to control of their emissions. For this aim, various legal, technical, scientific and institutive studies are being carried on by almost all developing and developed countries, like Turkey. Especially, within the European Union (EU) harmonization period, Turkish legislation studies on air pollution has been accelerated in last 10 years. Therefore, in accordance with this study, recent legislations about VOCs will be summerized in the below sub-sections.

2.4.1 VOCs Emission Legislations in Turkey

Regulations on controlling organic vapour pollutants in air have been issued world-wide (Khan & Ghoshal, 2000). Similar to other countries, air pollution is an important problem in Turkey. In Turkish environmental legislation, air quality standarts have been enhanced with respect to EU directives due to harmonization procedure of the Turkish legislation within EU admission process (Coşkun et al., 2010). Turkey is not only a candidate country of EU, but also a member of the Organizaton of Economic Co-operation and Development (OECD). And according to them, economical development of Turkey has been accelerated immediately, hence, industial activities and also energy consumption has increased. As a result of these situations, amount of air pollutant emissions, especially result from industries, and regulations to control of them gain much importance in the recent years (Alyüz and Alp, 2014).

VOCs were defined and listed in Air Quality Assessment and Management Regulation (AQAMR). In 2008, it was amended and within this amendment, thirty NMVOCs, including BTEX compounds, namely benzene, toluene, ethlybenzene and o-xylene, are listed under the measurement of ozone precursor section of the regulation, in the appendix II. However, only benzene was directly taken into considiration with the new aspect of the regulation, and annual average exposure limit was determined as 5 µg/ m^3 in the ambient air (T.C. Resmi Gazete, 2008).

Emissions from petrochemical industries, petroleum refineries and storage and transportation of petroleum was regulated with Industrial Air pollution Control Regulation that was published in the Official Gazette No : 27277 on 03.07.2009. In this regulation, both long and short term air quality limit values was determined for benzene, toluene, ethylbenzene, xylenes, olefins, isopropylbenzene, and trimethylbenzene which are important parameters to interpret VOCs contributions of air quality assessment in the ambient air (MoE&U, Industrial air pollution control regulation, 2009). Additionally, in the Exhaust Gas Emissions Control and Gasoline and Diesel Quality Regulation that was published in the Official Gazette No: 28837 on 30.11.2013, maximum concentration limits of aromatic compounds, olefins and benzene was determined for gasoline fuel usage (MoE&U, 2013).

2.4.2 European Union Directives on VOCs Emissions and Harmonization of the Turkish Legislation in the Accession Process of Turkey

Initially, EU developed environmental protection policies to provide a specific competition in the internal market in 1970s, yet for the purpose of mitigating global environmantal problems, they have launched and lead many initiatives both within their bordens and also in the international area.

EU environmental legislation is made up of over 300 regulations, hence in a country begins consultations, like Turkey, there must be a sufficient time period to adapt related regulations. For this aim, all requirements of EU policies has been brought into confirmity with Turkish legislation system within the EU accession process. The most prominent point to be considered in this process is EU directives and EU comission decisions that have constituted the vast majority of their legislation (REC Turkey, 2010). This situation means that, Turkey can designate its own efforts on the harmonization period with the leadership of these EU directives and decisions. Within the scope of these directives, air pollution is one of the most critical issue. Furthermore, VOCs emissions are examinated in specific EU directives. The most prominent EU directives about VOCs emissions can be introduced as follow;

- 94/63/EC : Council directive on control of VOC emissions resulting from the storage of petrol and its distribution from terminals to service stations.
- 1999/13/EC : Council directive on the limitation of emissions of VOCs due to the use of organic solvents in certain activities and installations
- 86/277/EEC: Council Decision of 12 June 1986 on the conclusion of the Protocol to the 1979 Convention on long-range transboundary air pollution on long-term financing of the cooperative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe (EMEP)
- 2000/541/EC : Commission decision of 6 September 2000 on criteria for assessing national plans according to Article 6 of Council Directive 1999/13/EC
- 2001/81/EC : Council on national emission ceilings for certain atmospheric pollutants
- 2004/42/EC : Council directive on the limitation of emissions of VOCs due to organic solvent usage in certain paints and varnishes and vehicle refinishing products
- 2003/17/EC : Council directive on the Quality of petrol and diesel fuels sets maximum concentrations of olefins, aromatics and benzene for gasoline fuel
- 2000/69/EC : Council directive on limit values for Benzene and Carbon Monoxide in ambient air

All of the above EU directives' main aim is human health and environmental protection and also implementation the most effective pollution reduction measures at local, national and community level. Consequently, EU directives gain importance to reach appropriate objectives for ambient air quality, especially taking into harmonization of the Turkish legislation in the relevant accession process.

2.5 Source Apportionment Techniques

In order to identify emission sources of each pollutant and determine contribution of relevant sources to the measured concentration of a particular pollutant in the collected air sample, source apportionment, or receptor modelling, studies have been carried out for many years. In the literature, it is possible to encounter with several studies that different source apportionment techniques used for particulate matter (PM) (Oanh et al., 2009), VOCs (Watson, Chow & Fujita, 2001; Song et all, 2008), polycyclic aromatic hydrocarbons (PAHs) (Jang et al., 2013), and polychlorinated biphenyls (PCBs) (Çetin et al., 2007).

To prevent air pollution and improve air quality, source identification is an important part of scientific studies. For this aim, various modelling tools and approaches can be used throughout source apportionment studies. The most prominent approaches are divided into two main categories as receptor-oriented models and source-oriented models. And there are different types of aforementioned models which are namely Principle Component Analysis (PCA), Unmix, Positive Matrix Factorization (PMF) and Chemical Mass Balance (CMB). For both approaches, the principal rule is establishing an accurate mass balance and mass conservation to identify and apportionment of sources in the atmosphere (Hopke, 2009). Both mentioned types of source apportionment models will be presented the below. In this study, in order to determine VOCs sources in the rural and urban Kütahya atmosphere, a receptor orientel model , which is namely PMF, was applied to obtained data set.

As it can be estimated from the name of the model, source profiles should be known to use source oriented models. Chemical Mass Balance (CMB) is a well known source oriented model that is considerably applied in many source apportionment studies to control ambient air pollutants, such as VOCs, or to evaluate the precision of relevant pollutant’s emission inventories (Srivastava A. , 2004). For using this model, emission source profiles should be specified and probable sources are traced (Hopke, 2009). Also, specified source profiles are importantly different from each other. CMB needs to particular cognition of emission source type, in contrast to other types of receptor models. Additionally, CMB is performed individually to each examination, rather than performing all collected data (Watson et al., 2001).

As for receptor oriented models, it can be said if there is not any available information about source profiles, in order to identify ambient air pollution sources and evaluate their contribution to air pollutant concentrations, receptor oriented models have widely been used (Guo H. W., 2004). PMF, UNMIX, and PCA are the most common multivariate receptor oriented models types which are able to resolve a series of examination at the same time in order to specify the number of sources, chemical composition, and contributions to each analysis (Miller,2002). Additionally, preliminary knowledge about pollutant tracers is important part of source identification studies. In some instances, supplemental methods can be used, for example benefiting from pollution roses or potential contribution function (Doğan, 2013). In this study, PMF was applied to collected sample data set and some auxiliaries was used to complete source apportionment study. PMF was developed by Paatero and Tapper (Xie and Berkowitz, 2006). It is one of the advanced receptor modeling algorithm which can solve factor analyzing problems using least square method without any source profile requirement (Paatero and Tapper, 1994). This receptor model can be used for not only VOCs data set but also a number of different data sets such as 24-h PM $_{2.5}$ data , different types of toxic air compounds data , accumulation data and aerosol data (Brown et al, 2007). PMF can be easily applied to relevant data set and the main advantage of this model in comparison with other source apportionment models is that absent data and below detection limit data can be managed much more efficiently using higher approximative error data (Doğan, 2013).

2.5.1 Positive Matrix Factorization (PMF)

PMF is the most frequently used source apportionment technique in the literature. It uses least square method to find number of sources without any information about related factors which concludes specific sources (Paatero, et al., 2002). PMF does not show a negative result and also supply a minimised solution using an "objective function", which is represented by Q. This fuction is identifies as follow equation;

$$Q = \sum_{i=1}^{I} \sum_{j=1}^{J} \left| \frac{x_{ij} - \sum_{n=1}^{N} g_{in} f_{nj}}{s_{ij}} \right|^2 \qquad \text{Equation(1)}$$

"x_{ij} represents a measured variable j in sample i, g_{in} represents the contribution of source n to sample i, f_{nj} represents the contribution of variable j to source profile n and S_{ij} is an estimate of the uncertainties in variable j in sample i " (Hopke, 2009; Pekey and Doğan, 2013).

There are two input files in PMF model. One of them is concentration file and the otherone is uncertainity file. To be able to obtain an accurate result, estimation of uncertainity is very critical step. The model does not accept any blank cell, so all missing data cells should be substituted with a proper value. For this aim an approach should be used which was suggested by Polissar, et al. (1998). According to this suggestion, measured VOCs concentration values are used directly, and uncertainty values of them are supposed to total value of a selected percentage of measured concentration and minimum detection limit value of related compound. And, missing values in concentration files are replaced with geometric mean values, and uncertainty value of related specie are substituded by 4 times of geometric mean of the compound. As for concentrations that are below minimum detection limit value,

they should be substituted with half of minimum detection limit and uncertainity of them should be set 5/6 of minimum detection limit value of related compound. As it can be seen in the Chapter 5, this methodology was used in this study while input files were preparing.

At the end of the PMF runs, three significant outputs are obtained, namely factor profiles (F-loading), factor contribution matrix (G-Score) and error matrix. F-Loading represent the apportionment of each compounds to factors. Also, G-score represents variation of the temporal proportion of each sources to the samples. So, high G-score in a factor means that contribution of the sample is high to related factor. Finally, all these outputs are evaluated and source characterization can be completed by the user. For this aim, all markers of possible factor should be identified.

There are so many different studies which is related to ambient air quality in the literature that is used PMF as a source apportionment technique (Polissar et al., 2001; Kim et al., 2003; Wei, et al., 2014). Generally, air samples are collected using different samplers such as tedlar bag, canisters, online analyzers, or passive tubes, and then collected air samples, except collected using online analyzers, are analyzed using a GC system in all of those studies. After all of relevant studies, in order to realize sources of VOCs, source apportionment tools have been used for many years. Some examples were submitted in this part of the study.

Brown, et al.,(2007) studied on PMF and CMB techniques in 2 different urban site. In that study, 5 and 6 factor contribution were determined, and main sources of VOCs were defined as evaporative emissions, traffic related sources, liquid gasoline usage, coating, natural gas usage and biogenic emissions.

Borbon et al. (2003) tried to identify essential sources of NMHCs in Lille, Nothern France, using a receptor-oriented model by taking into consideration temporal and spatial variations of them. It took about 4 years, and about 40 (C_2-C_9) ambient NMHCs were measured hourly in two urban sites of Lille. They developed 3 supplementary approaches in order to identify possible sources around sampling site. For this aim, univariate, bivariate statistics and original NMHCs-to-acethylene ratio analysis were completed, and using principal component analysis (PCA) method the following four main source catagory were determined; motor vehicle exhaust, fossil fuel combustion, evapotrative emissions and biogenic emissions.

Elbir, et al., (2007), collected air samples during two years in an urban and a sub-urban sites of İzmir, and different types of VOCs were measured. After all necessary processes, a source apportionment study were conduceted and PMF was selected as a source apportionment model. In urban area 6 factors were determined, and they included traffic related sources, exhaused and residental heating, solvent usage, dry cleaning and an undefined source, while in sub-urban area 3 factors were determined (gasoline and diesel vehicle emission and seolvent usage).

Yurdakul, (2014) conducted a source apportionment study with 148 VOCs samples that were collected from Bursa, which is one of the most industrialized city of Turkey, in two campaigns as an hour time intervals using an online GC system. And, PMF were executed to generated data set. 8 factors were designated in both sampling campaigns and most abundant sources were determined as vehichle exhaust emission, paint and solvent usage, evaporation of gasoline, asphalting operations and some different industrial processes.

Doğan, (2013) collected ambient air samples in two different sampling station, one of them is in Aliağa and other one is in Horozgediği village , during summer and winter between 2005 and 2005 in İzmir. Sampling stations were established in near to some industrial facilities and between two high VOCs emitted company Petkim and Tüpraş. Concentration of more than 50 VOCs were measured in both stations and using PMF model a source apportionment study were conducted. Toluene was measured as the most abundant specie that contribute concentration of VOCs in both stations. Using PMF, 10 possible VOCs sources were estimated, which are namely motor-vehicle exhaust emissions, natural gas, evaporative and indurstrial emissions, solvent usage, and mixed emissions that originated from Petkim and ship demolition plants. And also, in this study PMF was used to be conducted a receptor modelling study. All deteail were given in the Chapter 5.

2.6 VOCs Markers

Markers of any pollutants may show an alteration according to each source in different studies due to measurements and evaluations may be different in each study (Watson, et al, 2001). Yet, the below part of the study some compounds which are known commonly as the markers of relevant sources in the literature were summerized.

Traffic is the most productive source of VOCs. Ethane, ethylene, propane, 1-butene, isobutane/n-butane, n-pentane, hexane, BTEX, 1,2,4-trimethylbenzene originate from motor-vehichles commonly (Kuntasal Ö. , 2005). Yet, according to type of vehicle these compounds may show an alteration. For example, diesel motor-vehicles emit heavy VOCs mostly, such as n-decane, and n-undecane (Watson, et al., 2001).

The another high VOCs emission source is solvent usage and different industries. Styrene, n-decane, and some other heavy hydrocarbons emits to atmosphere due to solvent usage. Also, toluene, styrene, nonane, 1,2,4-trimethylbenzne are the most common VOCs that emit due to solvent usage (Watson, et al., 2001; Wadden, 1995).

Another possible VOCs source is coal-fired thermal power plants. According to literature, BTEX are emitted from there mostly. (Garcia, et al., 1992) Coal combustion emissions from residental areas depends on type of used coal, and they are mainly sources of acethylene, ethylene, propylene, ethane, propane, benzene and toluene (Liu, et al., 2008).

Up to now, athropogenic sources of VOCs were summarised, but biogenic emissions are another important sources of VOCs. They are mostly characterized by isoprene. However, biogenic sources may show an alteration depends on type of vegetation, and meteorological conditions. For this reason, it is difficult to classify biogenic sources of VOCs (Doğan, 2013).

Table 2.1 Emission sources of VOCs

	Emission Sources					
Ethane	vehicle exhaust^{1,2,3,4}	evap. emissions^{1,2}	natural gas leakage^{2}	coal combustion^{2}	biomass burning^{2,3}	LPG^{2,4}
Ethylene	vehicle exhaust^{1}	incomplete gasoline combustion^{1,4}	coal combustion^{2,4}			
Propane	vehicle exhaust^{1}	natural gas^{1,3}	coal combustion^{2}	biomass burning^{2}	diesel^{1,2,3,4,6}	LPG^{4}
Propylene	coal combustion^{1}	biomass burning^{1}	incomplete gasoline combustion^{2}	liquefied gasoline evaporation^{1,2}		
Isobutane	vehicle exhaust$^{1.2}$	gasoline evap.$^{1.2}$				
Acethylene	vehicle exhaust$^{1.2}$	evap. emissions$^{1.2}$	coal combustion^{4}	biomass burning^{2,4}		
Trans-2-butene	gasoline evap.^{1,2}					
1-Butene	vehicle exhaust^{1,2,6}	natural gas^{6}	LPG^{1,2,3}			
Cyclopentane	gasoline evap.$^{1.2}$	solvent usage$^{1.2.3}$				
Isopentane	solvent usage^{1,2}	natural gas^{4}	LPG$^{1.2.3}$			
n – pentane	vehicle exhaust^{8}	gasoline evap.^{8}	refinery products^{1}			
Trans-2-pentene	gasoline evap.^{8}	natural gas^{7}	LPG^{2}			
Cis-2- pentene	natural gas^{1,2}	LPG^{2}	industrial processes^{2}			
2,2-dimethylbutane	gasoline evap.^{8}	liquefied gasoline^{1}	diesel exhaust^{2}			
2-methylpentane	natural gas	refinery products^{1}	solvent usage^{2}	gasoline evaporation^{2}	vehicle exhaust^{10}	
3-methylpentane	gasoline evap.^{8}	refinery products^{1}				
Isoprene	biogenic^{1,8,9}	vehicle exhaust^{6}				
n-hexane	vehicle exhaust^{10}	solvent usage^{1,2,3}	cigarette smoke^{5}	refinery products^{1}	gasoline^{2}	
2,4-dimethylpent.	refinery products^{1}	solvent usage^{1}				
Benzene	vehicle exhaust^{1,2}	industrial processes^{4}	solvent usage^{1,2,3,7}	gasoline evap.^{1,2,8}	coal combustion^{1}	coating^{2}
Cyclohexane	vehicle exhaust^{1,2}	refinery products^{1}	gasoline evap.^{8}			
2-methyhexane	vehicle exhaust^{2}	refinery products^{1}	gasoline evap.^{8}			
2,3-dimethylpent.	vehicle exhaust^{2}	refinery products^{1}	gasoline evap.^{8}			
3-methylhexane	vehicle exhaust$^{1.2.6}$	refinery products^{1}	gasoline evap.^{3}			

Table 2.1 (Continued)

	Emission Sources					
2,2,4-trimethylpnt.	evap.emission[9]	industrial processes[1,11]	petroleum products[11]	gasoline[11]	vehicle exhaust[11]	
n-heptane	painting[2]	gasoline evap.[2,8]				
methylcyclohexane	refinery products[1]	industrial processes[9]				
2,3,4-trimethylp.	evap.emission[1,8]	solvent usage[2]	diesel exhaust[9]			
toluene	vehicle exhaust[2,10]	industrial processes[6]	solvent usage[1,2,3,8]	painting[1,2]	coal combustion[1,2]	coating[1]
2-methylheptane	solvent usage[2,3]	evaporative emission[3]				
3-methylheptane	solvent usage[2,3]	refinery products[1]				
n-octane	refinery products[1,8]	solvent usage[2,3]	painting[7]	coating[4]		
ethylbenzene	vehicle exhaust[2,10]	solvent usage[2]	painting[7]	coating[4]		
m-Xylene	vehicle exhaust[10]	coating[2,4]				
styrene	vehicle exhaust[5]	industrial processes[5]	solvent usage[5]	polymer combustion[5]	cigarette smoke[5]	coating[5]
o-Xylene	vehicle exhaust[10]	painting[2,7]	coating[4]			
nonane	vehicle exhaust[10]	industrial processes[8]	solvent usage[2,9]	evaporation[2,7]	asphalt operations[2]	
isopropylbenzene	industrial processes[1]	unleaded gasoline[3]				
m-ethyltoluene	solvent usage[1,3]	gasoline[8]	evap.emission[2]			
1,3,5-trimethylb.	unleaded gasoline[3]	industrial processes[1.8]	refinery products[1]			
o-ethyltoluene	unleaded gasoline[3]	industrial processes[8]				
1,2,4-trimethylb.	vehicle exhaust[10]	solvent usage[2.3]	unleaded gasoline[3]			
n-decane	diesel exhaust[4]	asphalt operations[2]				
1,2,3-trimethylb.	diesel exhaust[4]	asphalt operations[2]				
n-undecane	vehicle exhaust[1,10]	asphalt operations[2]				
n-dodecane	asphalt operations[2]					

[1]Doğan, 2013; [2]Yurdakul, 2104;[3]Kuntasal Ö.,2005; [4]Barletta, et al., 2005; [5]WHO, 2000; [6]Buzcu & Fraser, 2006; [7]Civan, et al., 2015;[8]Lau, et al, 2010; [9]Watson, et al., 2001; [10]Elbir, et al., 2007; [11]USEPA, 1993

CHAPTER 3

MATERIALS AND METHODS

3.1 Sampling Locations

Kütahya is located inner Western Anatolia portion of Aegean Region which is a transition area between Central Anatolia and along the costland areas of Aegean Region. It is between $38^{o}70^{''}$ and $39^{o}80^{''}$ north latitude via $29^{o}00^{''}$ and $30^{o}30^{''}$ east longitude. Additionally, it covers about 1.5% of all Turkey territory with 11.875 km^{2} surface area. According to population registration system (addres based) data in 2013, 572.059 citizen live in the Kütahya.

Although, it is located in the Aegean Region, due to distance from sea and altitude, climate is different from Aegean costline. It has a transition climate between Aegean, Marmara, and Central Anatolia Region. In the province, summer is hot and dry, and winter is cold and wet. The hottest months are July and August while the coldest months are January and February. The highest measured temperature is 38.6 ^{o}C, and the lowest temperature is -28.1 ^{o}C. So, based on these values, it can be said that there is an important temperature difference annualy (Dinç, et al, 2011).

As it was mentioned previously, this study is a part of a larger project which was supported by TUBITAK. The main aim of the project is, in addition to regular sources, such as traffic and space heating, the influence of two high emitting power plants in Kütahya on ambient air quality, namely Tunçbilek and Seyitömer Power Plants. In accordance with this aim two different sampling locations were designated both rural and urban region of the Kütahya and two sampling stations were established in these locations respectively. In an attempt to specify sampling locations, safety, electric availability, stuff support, and smooth accessibility factors were taken into consideration. In addition to these physical factors, pollution maps of the region, which were created using AERMOD modelling tool of United States Environment Protection Agency (USEPA) by the project team members of Dokuz

Eylül University (DEU), was a good indicator for sampling location selection. Also, multi-criteria decision making method was used for certain decision(Hacıoğlu et al., 2015). By means of relevant polluiton maps, 7 possible locations were evaluated and Göbel Thermal Spring Plant that was suggested by Municipality of Tavşanlı was selected as rural sampling location. It was 15-20 km distance from Tunçbilek Power Plant as crow flies and according to wind direction this site might be exposed to air pollution due to the plant. Selected location is not very near to residental areas except Göbel county and Göbel Thermal Spring Plant where is located in eastern side of the rural station. Coal and wood are used for space heating in winter instead of natural gas in Göbel. Also, people frequently have gone to the thermal spring plant and sometimes some activities have been organized by them, such as having barbecue or picnic, around rural station. Additionally, Tavşanlı-Simav road and Tavşanlı-Kütahya road is near to this station. All these factors were taken into consideration when observed results were evaluated extensively.

Subsequently, similar site selection studies were done for urban sampling location and 5 different point were visited. After all assessments, Kütahya Directorate of Meteorology garden was determined as urban sampling station considering suggestions of The Kütahya Directorate of Environment and Urban Planning. This place is located in downtown of Kütahya.

In addition to VOCs samplers, there have been automatically analyzers to measure nitrogen oxide (NO), nitrogen dioxide (NO_2), sulphur dioxide (SO_2) and ozone (O_3) concentrations continously in both stations. Additionally, coarse (PM_{10}) and fine ($PM_{2.5}$) particles were collected to identify chemical composition of airborne particles in the project scope.

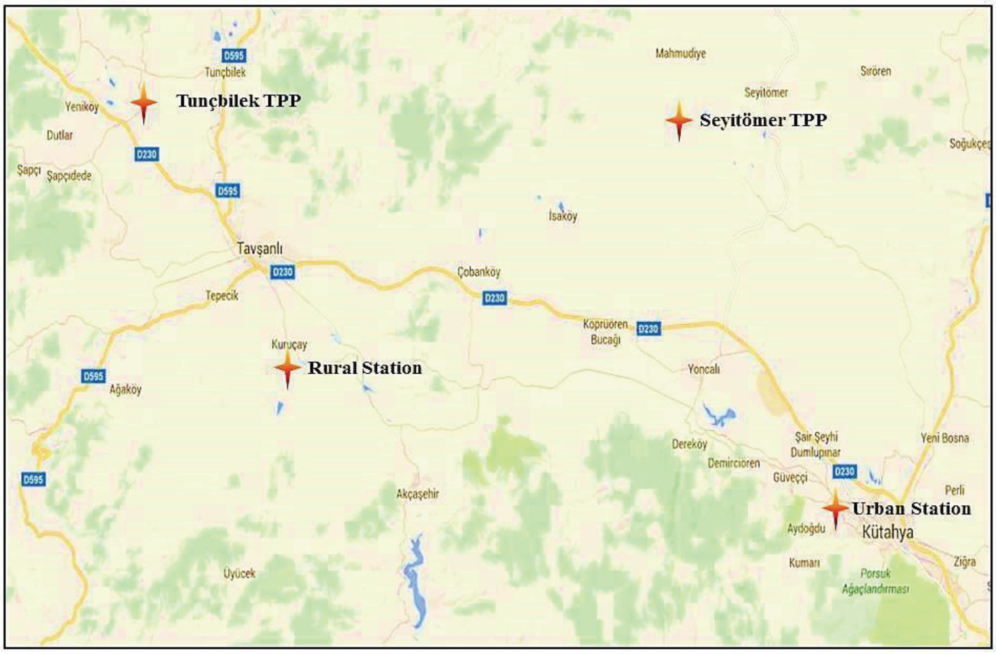


Figure 3.1 Locations of sampling stations

3.2 Sampling Campaigns

At the beginning of the study, sampling period was determined as two campaigns as summer and winter, but due to some challenges in sampling sites summer and winter campaigns were combined and months between summer and winter were added to sampling period. Thus, amount of collected sample was increased and better interpretation of statistical studies obtainment was aimed.

In both stations, 24-hour sampling was conducted three times in a week. In urban station, sampling period was between 27th June, 2014 and 13th March, 2015, while in rural station this period was started 7th July, 2014 and maintained until 27th March, 2015. Throughout sampling period, 93 and 75 samples were collected from both sampling stations respectively.

3.3 Sampling Methodology

For VOCs sampling 6L electropolished stainless steel vessel designed RESTEK TO-CAN canisters and the same brand integrated passive air sampling kits were used. They were figured in figure 3.2. In the literature, it is possible to encounter different

VOCs samplers such as sorbent tubes, tedlar bags. But, depending on whether active or passive sampling, where they are used, or sampling period, different advantages might be occur relative to each other. Passivated canisters are frequently used to detect VOCs in whole air sampling and they are used in several air monitoring programmes (Kelly & Holdren, 1995). Canister methodology is practicable a great deal of polar and non-polar VOCs in the ambient air from ppbv to ppmv grade (Wang & Austin, 2006).

The size of canisters can be diversified from 400 ml to 15 L, according to analyte concentration in the sample, sampling period, collected air flowrate and volume. For higher concentrated samples, smaller size canisters are selected. 6L canisters are used to up to 24-hour ambient air sampling mostly. Stainless steel canisters have prevented sample leakage along the vessel wall and degradation during elapsed time to analysis. Additionally, in attempt to decrease possible interactions with analyte in the sample, interior surface of all canisters are designed with inert material, so

sample stability can be provided (RESTEK, 2014). In addition to above advantages, collected sample in the canister can be analyzed more than once, and cleaning procedure is easily.

In this study, to realize 24-hour sampling, an integrated passive sampling kit was used and air flowrate was adjusted using flow controller on the sampling kit which provide precise sampling without the useage of any pump. With reference to RESTEK documents, to determine essential flowrate, sampling period must be considered. According to related documents, to collect air in the vacuumed canister during 24-hour, air flowrate should be in the 2.8-3.5 ml/min range. So, sample flows into the canisters by means of difference between inner and outside presseure.

Figure 3.2 Canister and integrated sampling kit

During sampling period, some challenges were experienced about sampling kits. After about 2 weeks, filter of sampling kit was fouled by dust around the sampling stations and they must be cleaned with methanol in the labaratory. So, for the necessary cleaning period, sampling must be ceased. Furthermore, cleaning process of sampling kit had taken a long time and after cleaning, there was a waiting period during a week at least, and after this period to check whether it is clean or not, a 24 hour sampling trial should be done. And, generally cleaning repetition was necessary. Although, it was cause to decleration in sampling period initially, fortunately, two more sampling kit were purchased in reserve and fixed the problem.

For the whole sampling period 12 canisters were used which half of them were used at urban and rest of them were used at rural station. Before sampling, all canisters were cleaned properly, and at the end of the cleaning process, to be sure the cleaning of the canisters, they were presurized with high purity dry nitrogen and analyzed with GC-FID. According to EPA TO-14A and TO-15 methods, if target VOCs' concentrations are less than 0.2 ppbv (USEPA, 1999a&1999b) or less than 10% percent of the background air concentration (Sweet & Vermette, 1992) the canister can be certified as cleaned. After this procedure, clean canisters were vacuumed and send to stations by cargo. Every week, 3 canisters were sent to each stations and after sampling they were returned to labaratory. Before analyze using GC-FID system, they were presurized with high purity nitrogen.

3.3.1 Preperation of collected samples for analysis

Before sampling, three preperation stages were followed as cleaning which was sourced by USEPA TO-14A and 15 methods, cleaning checking, and vacuuming of canisters. For the first step, canisters were cleaned using the canister cleaning system which is shown in the Figure 3.3.

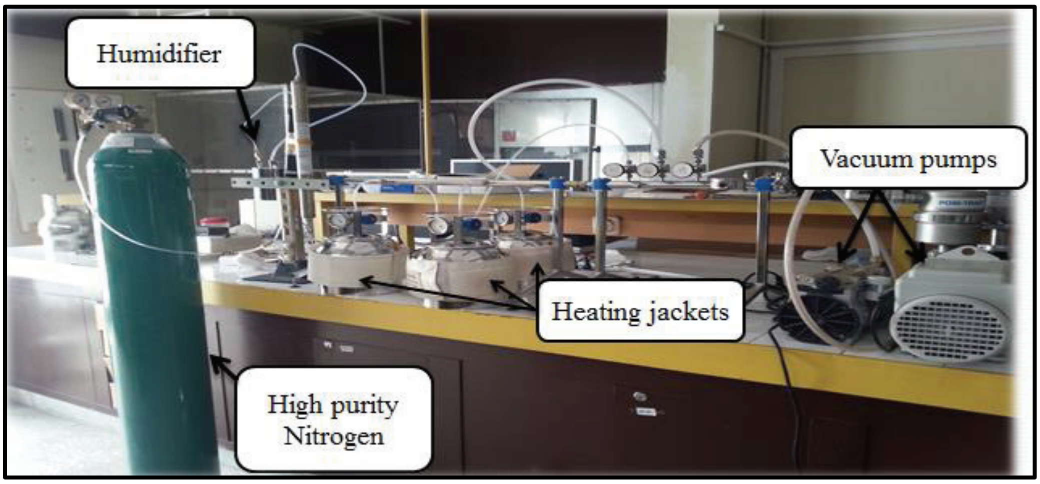


Figure 3.3. Canister cleaning system

Firstly, canisters were coated with heating jackets and discharged air inside the canisters using vacuum pumps. After vacuuming, canisters were pressurized with humidified high purity nitrogen up to 10 inHg and after sufficient waiting period, for about 30 minutes, they were vacuumed until the pressure reach to -27 inHg and again waited for 30 minutes in vacuum. This circuit was repeated 3 times when heating was continue.While 3rd vacuuming heating was ceased and this final vacuum was proceeded about 1 hour and final canister pressure reach to -27 inHg and it means that canisters were ready to collect sample. However, to check the cleaning of them, from time to time after cleaning process, canisters were pressurized with dry nitrogen up to 14.7 psi and analyzed with GC-FID. As it was mentioned in the previous

section if concentrations of target VOCs are less than 0.2 ppbv (USEPA,1999a,1999b) or less than 10% percent of the background air concentration(Sweet & Vermette,1992), the canister can be assumed as cleaned. Finally, cleaned canisters were vacuumed and sent to the stations.

Following the 24-hour sampling, samples returned to labaratory for analysis. Yet, canisters were still in vacuum pressure, videlicet inlet pressure was still lower than atmospheric pressure, i.e -7 psi. Because of this, samples were pressurizzed with high purity dry nitrogen up to atmospheric pressure, both to increase in amount of sample in case analysis repetition is necessary and to be able to inject sample to the GC-FID system. Also, collected sample concentration is diluted by this way and any contamination is prevented with the analysis equipments. Thus, each collected samples were pressurized up to atmospheric pressure, 14.7 psi, before analysis. And, to be able to obtain homogenous sample distribution in the canister, samples were waited about 1 hour and then analyze.

3.4 Analytical Methodology

3.4.1 Target VOCs

Non-methane hydrocarbons (NMHCs) are substantial markers of ozone and .other photo-oxidants(Qin et al., 2007). In 1994, US EPA necessitated installed Photochemical Assessment Monitoring Stations (PAMS) in US on the purpose of following increasing in the concentrations of NOx and VOCs in time and NMHCs were started to observed in PAM stations. In the scope of this study, 51 PAMS NMHCs, which contain from 2 to 12 carbons (C2-C12) ,were evaluated successfully in both sampling stations. Target VOCs and detection detection frequency of them in both stations were listed Table 3.1. Throughout sampling period, 93 and 75 samples were collected from urban and rural sampling stations respectively. And all of them can be detected with quite high frequencies in both stations**.**

Table 3.1 Detection frequency of VOCs in both stations

Compound	**Retention Time (min)**	**Detection Freq.in Urban Station (%)**	**Detection Freq.in Rural Station (%)**
Ethane	8.500	100	100
Ethylene	9.460	100	100
Propane	11.62	100	100
Propylene	12.94	100	100
Isobutane / n-butane	13.65	100	100
Acetylene	14.55	100	100
Trans – 2 – Butene	16.69	100	100
1 – Butene	16.99	100	100
Cis-2-Butene	17.59	100	100
Cyclopentane	18.18	100	100
Isopentane	19.10	100	100
n – Pentane	19.89	100	100
Trans – 2 – Pentene	22.51	100	100
1 – Pentene	23.32	100	100
Cis-2- Pentene	23.96	100	100
2,2-Dimethylbutane	24.65	100	99
2,3-Dimethylbutane	25.36	100	99
2-Methylpentane	25.53	100	99
3-Methylpentane	25.70	100	99
Isoprene	27.26	100	99
n-Hexane	13.84	100	99
2,4-Dimethylpentane	15.33	100	99
Benzene	16.58	100	99
Cyclohexane	17.06	100	99
2-Methylhexane	17.23	100	99
2,3-Dimethylpentane	17.41	100	99
3-Methylhexane	17.71	100	99
2,2,4-Trimethylpentane	18.48	100	99
n-Heptane	18.91	100	99
Methylcyclohexane	20.33	100	99
2,3,4-Trimethylpentane	21.70	100	99
Toluene	22.08	100	99
2-Methylheptane	22.33	95	99
3-Methylheptane	22.74	99	99
n-Octane	24.00	100	99
Ethylbenzene	26.82	100	99
m,p-Xylene	27.23	100	99
Styrene	28.12	100	99
o-Xylene	28.35	100	99
Nonane	28.73	100	99

Table 3.1 (Continued)

Compound	**Retention Time (min)**	**Detection Freq.in Urban Station (%)**	**Detection Freq.in Rural Station (%)**
Isopropylbenzene	29.78	100	99
n-Propylbenzene	31.14	100	97
m,p-Ethyltoluene	31.40	100	97
1,3,5-Trimethylbenzene	31.52	100	97
o-Ethyltoluene	31.71	100	97
1,2,4-Trimethylbenzene	32.28	100	97
n-Decane	33.07	100	97
1,2,3-Trimethylbenzene	34.19	100	97
p-Diethylbenzene	35.40	100	97
n-Undecane	37.13	100	99
n-Dodecane	41.56	100	99

3.4.2 Analysis of collected samples

Agilent 6890 Gas Chromatography which is equipped with two flame ionization detectors were used for analysis. For desorption of VOCs, Markes Unity Thermal Desorber unit, and for sampling from canisters Markes Air Server were used with the assistance of sample pump. Sample presented using Air Server was accumulated on cold trap and desorbed with Unity Thermal Desorber. The analytic system is shown in the Figure 3.4

Figure 3.4 Analytical system

There are two phases in gas chromatography, including mobile and stationary phases. Mobile phase is identified as sample which is carried by an inert carrier gas such as nitrogen, helium or argon. And, stationary phase is composed of a packing material or a support which behave as stationary phase, or it may be covered by the liquid stationary phase. The main principle of GC is “distribution equilibrium” between mobile and stationary phases (Badjagbo, et al., 2007).

Polarity is an important factor for seperation of species in a gas mixture. If a compound have only consisted of carbon and hydrogen atoms and have only carbon-carbon single bond, such as alkanes, that compound is identified as non-polar compound and it can be seperated by “non-polar capilary columns”. However, if a compound include one or more double or triple carbon-carbon bonds in addition to carbon and hydrogen atoms, such as aromatic hydrocarbons and aklenes, that compound is identified as polarizible, and it can be seperated by “high polar capilary columns” effectively (Sigma-Aldrich,2015). In this study, two capillary columns are used in the GC-FID system. 1st column is Agilent 19091PS15 HR-Al/S Al_2O_3 deactivated alumina plot column which is attahed to FID1 detector, and 2nd one is “Agilent 122-1063 which is attached to FID2 detector. Through FID1 detector non-polar VOCs are detected, whereas through FID2 detector polarizible VOCs are detected.

Furthermore, to analyze the samples some auxilary gases were used. To carry samples into the columns high purity nitrogen was used as carrier gas, and to provide ignition of FIDs high purity hydrogen and dry air were used. All of the auxilary gases were provided from the Linde Group.

A sample analysis takes 46 minutes. During analysis, a peak occurs for each compound according to their retention time. When analysis is completed, a chromatogram is obtained for each sample. To be illustrated, one each sample chromatograms getting from urban an rural stations were shown in the figure 3.5 . Also, retention time values of all compounds were given in the table 3.1. As it can be figured out from the Figure 3.5, all peaks are much more prominent in urban station than rural station. All related explanations are presented in the Chapter 4, but generally VOCs concentrations are higher in urban areas than rural areas. So, this is an expected situation.

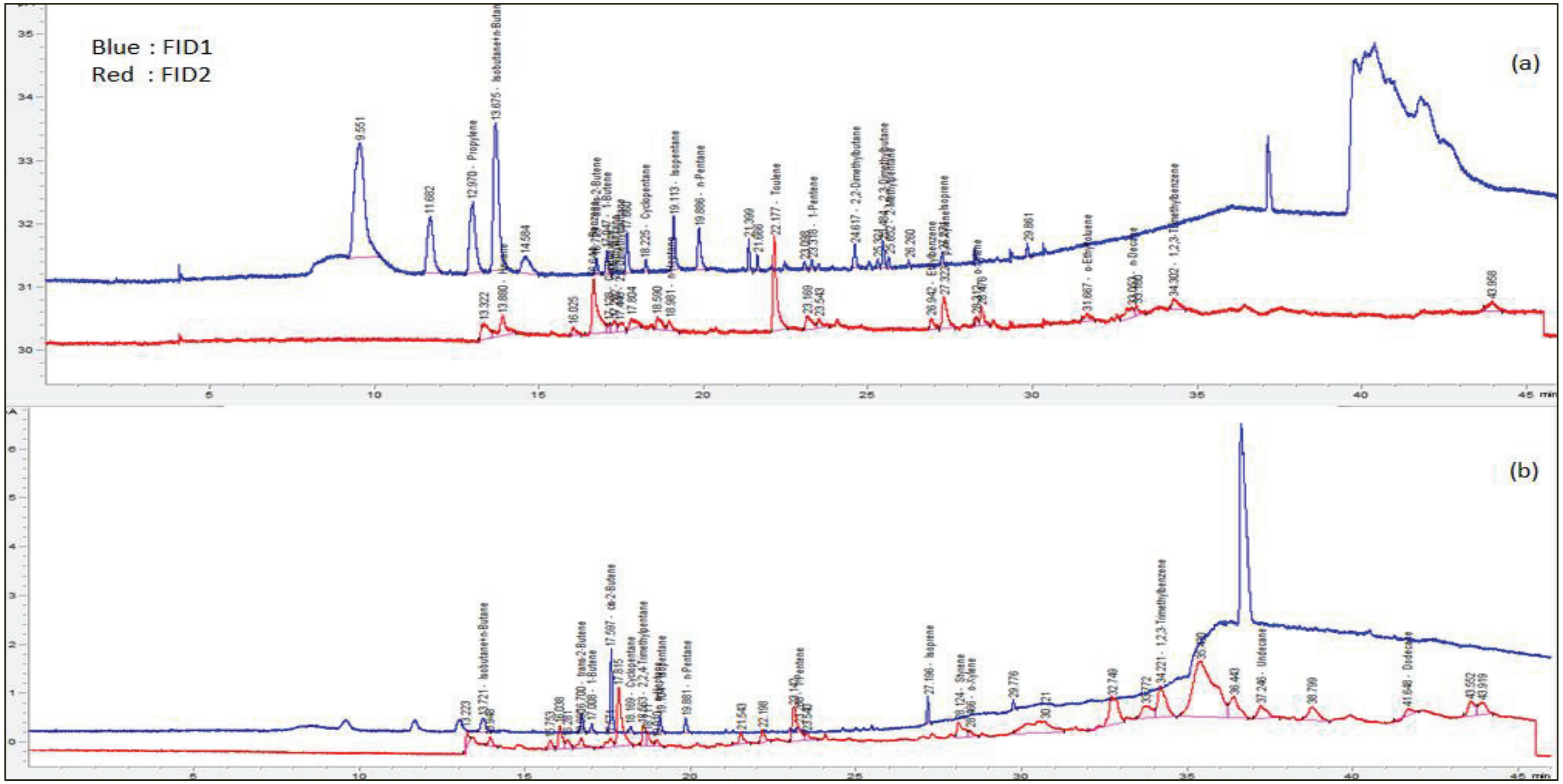


Figure 3.5 Sample Chromatograms (a) from urban station, (b) from rural station

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

QA/QC studies are an important part of this study to be interpret outputs of all analysis properly. 54 compunds were evaluated in 170 chromatograms for urban and rural stations totally. To prevent potential errors during sampling and analysis procedure, the below QA/QC protocols were implemented in experimental and data interpretation period.

3.5.1 Experimental QA/QC studies

3.5.1.1 Quantification and calibration

To quantify VOCs, GC-FID system was calibrated using 100 ppbv PAMS standard gas solution. This high concentrated solution was diluted before injection to the analytical system to prevent any possible contamination using RESTEK directions. For this aim, a canister was cleaned according to previously mentioned cleaning procedure sufficiently and pressurized up to -10 psi with high purity dry nitrogen. Subsequently, 240 ml of 100 ppbv standart gas solution was injected to the pressurized canister and in conclusion to reach necessary pressure for analysis, the canister was pressuized to 14.7 psi. After all these processes were finished, canister was kept for at least 24-hour to provide a homogenous gas distribution in the canister and also provide stabilization of gas mixture. Furthermore, final concentration of the standart gas solution was decreased from 100 ppbv to 2.1 ppbv using the below calculation steps;

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

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

$$= 3.78 \text{ L}$$

After 240 ml of standard solution injection to the canister;

0.24 L / 3.78 L = 0.0635 (standard ratio in 1L volume)

0.0635 * 100 ppb = 6.35 ppbv (concentration of the standard)

$$\text{Dilution factor} = \frac{\text{P(after dilution)} - \text{P(lab pressure)}}{\text{P(lab pressure)} - \text{P(before dilution)}} = \frac{14.7 + 14.7}{14.7 - 10 \times 0.491} = 3.0$$

Final concentration of standard solution: 6.3 ppb/ 3.00 = 2.1 ppbv

Diluted standard gas solution was injected to the analytical system six times from 100 ml to 600 ml to get six point calibration curves for each VOC and some of obtained calibration curves shown in the Figure 3.6.

Obtained chromatograms were analyzed using ChemStation software program which is developed for GC-FID system. Each peak areas were measured with manual integration using this program and slope of calibration curves of each compounds were divided by measured area, thereby mass amounts of each compounds were measured as nanogram with reference to standard gas volume. Chromatogram of 600 ml standard gas solution was given in the Figure 3.7

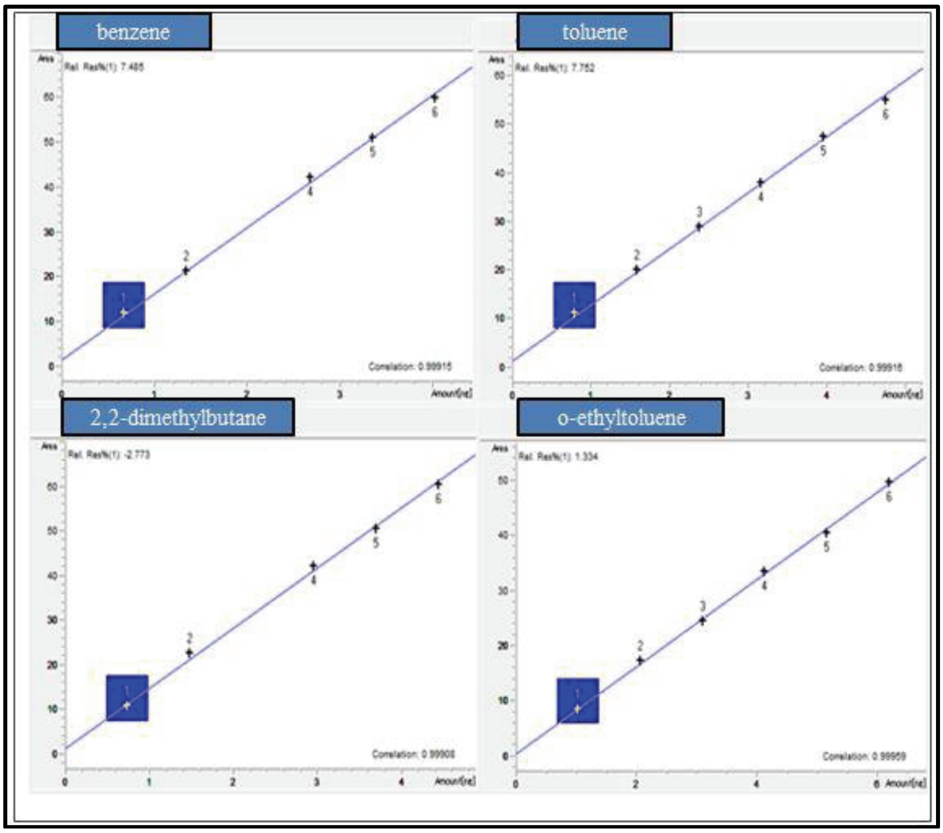


Figure3.6 Calibration curves for some VOCs

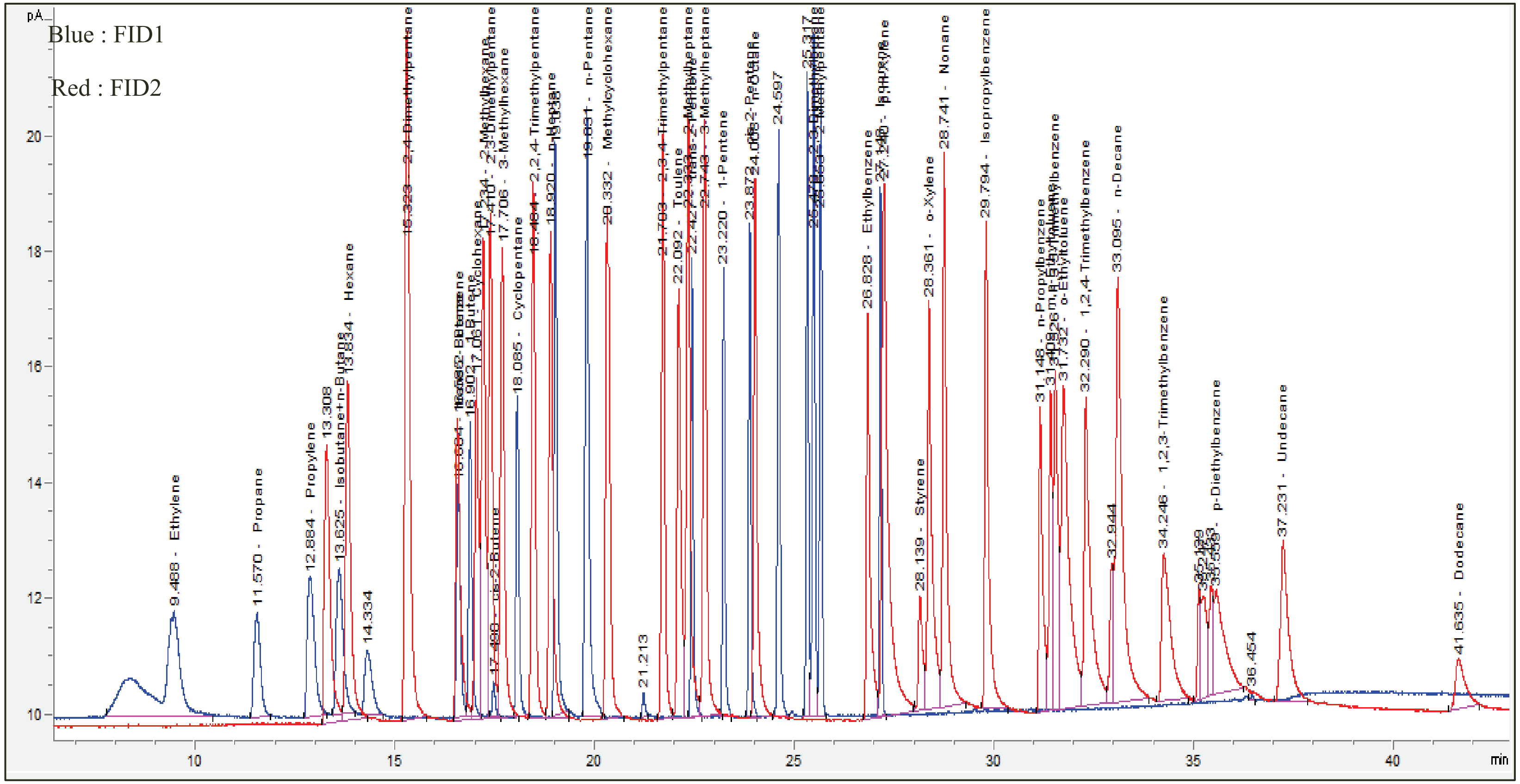


Figure 3.7 Chromatogram of 600 ml standard gas solution

3.5.1.2 Method detection limits of VOCs (MDL) and Blank Subtraction

According to USEPA TO-15 method directions, to determine method detection limits of all target VOCs, 100 ml standard gas solution, which was prepared like through calibration studies, injected to the system 7 times consecutively and standard deviation values of each VOCs were calculated. USEPA TO-15 method introduces a constant which is student's t value as 3.14. And according to the method's directions, to calculate MDL values of each compound, obtained standard deviation values from seven replicated injection should be multiplied with the constant value. Consequently, MDL values of compounds change between 0.016 (for cis-3-butene) and 0.073 (for 1,3,5-trimethylbenzene).

A software program, which is namely ChemStation Software, was used throughout the GC processes. In order to quantify obtained peaks for each compound, their areas were determined with manual integration by Chemstation. However, it causes some problems to obtain straight quantification of small peaks. If area of a peak is less than a certain value, which was specified by the software program that peak cannot be integrated (Doğan, 2013; Yurdakul, 2104). So, calculated MDL values were taken into consideration and the value which was specified by the program was adjusted to 0.1. In this way, small peaks did not eliminated from the whole chromatogram. The measured concentrations of corresponding areas were included in average concentrations, but in the PMF study a certain approach was used to eliminate any mistakes in source apportionment, and detailed explanation about the applied approach was made in the Chapter 5.

And also, a clean canister were sent to the station in different days and waited without collected sample until it was sent back to laboratory. And blank concentrations were measured for all VOCs. This process was repeated 5 times during sampling period in both stations, and blank subtraction study was conducted. Although, almost all of blank concentrations were lower than measured concentrations, some concentrations were less than blank concentration, so only these values were removed and recorded as missing data. In the Table 3.2, blank concentrations of species, and amount of below blank concentration values were provided with calculated MDL concentrations, and percentage amount of below MDL.

Table 3.2 MDL, blank concentrations and frequency detection of VOCs

Compound	MDL (μg/m^3)	Blank C. (μg/m^3)	Urban Station			Rural Station		
			S/B	% amount of below MDL c.	% amount of below blank c.	% amount of below MDL c.	S/B	% amount of below blank c.
Ethane	0,019	0.07	39.14	0	2	0	9.84	4
Ethylene	0,046	0.048	87.08	0	1	0	38.44	1
Propane	0,082	0.038	76.47	0	1	1	38.08	0
Propylene	0,050	0.026	113.02	0	0	0	33.84	0
Isobutane	0,097	0.04	104.60	0	1	0	28.05	1
Acethylene	0,049	0.036	25.46	0	1	4	9.40	1
Trans – 2 – Butene	0,074	0.052	11.59	3	1	20	5.27	6
1-Butene	0,064	0.034	15.23	2	0	0	8.22	1
Cis-2-Butene	0,016	0.3	55.08	0	1	4	29.74	1
Cyclopentane	0,105	0.038	8.92	13	1	6	4.17	2
Isopentane	0,170	0.058	45.60	1	1	8	20.82	1
n – Pentane	0,115	0.018	67.14	4	0	66	34.06	1
Trans – 2 – Pentene	0,111	0.032	4.84	35	2	32	2.85	4
1-Pentene	0,123	0.034	6.02	23	2	86	4.85	2
Cis-2- Pentene	0,146	0.03	1.63	19	8	0	1.06	1
2,2-Dimethylbutane	0,146	0.03	28.58	7	0	54	6.43	0
2,3- Dimethylbutane	0,143	0.032	6.99	33	1	26	2.93	1
2-Methylpentane	0,145	0.052	11.46	13	2	40	5.42	12
3-Methylpentane	0,161	0.036	8.22	29	10	37	4.77	6
Isoprene	0,157	0.032	13.14	13	0	5	5.80	0
n-Hexane	0,138	0.078	10.49	3	3	48	12.38	2
2,4-Dimethylpentane	0,094	0.014	12.65	23	1	0	10.28	1
Benzene	0,093	0.032	35.96	3	0	26	21.51	0
Cyclohexane	0,069	0.036	10.49	7	0	21	5.82	1
2-Methyhexane	0,109	0.028	10.85	26	1	14	8.77	1
2,3-Dimethylpentane	0,212	0.034	12.68	37	1	6	9.28	5
3-Methylhexane	0,089	0.026	51.66	3	0	1	39.94	0

Table 3.2 (Continued)

Compound	**MDL ($\mu g/m^3$)**	**Blank C. ($\mu g/m^3$)**	**Urban Station**			**Rural Station**		
			S/B	% amount of below MDL c.	% amount of below blank c.	% amount of below MDL c.	S/B	% amount of below blank c.
2,2,4-Trimethylpentane	0,099	0.026	30.25	6	0	6	22.48	0
n-Heptane	0,073	0.03	12.53	5	0	24	12.17	0
Methylcyclohexane	0,120	0.026	6.49	31	0	58	5.47	0
2,3,4-Trimethylpentane	0,047	0.032	3.71	19	1	0	3.14	2
Toluene	0,088	0.392	12.23	0	4	22	12.00	20
2-Methylheptane	0,133	0.042	8.13	24	3	46	4.50	10
3-Methylheptane	0,098	0.028	10.61	19	0	17	5.56	1
n-Octane	0,117	0.034	8.22	23	1	10	7.95	0
Ethylbenzene	0,089	0.038	17.86	6	0	6	10.04	0
m-Xylene	0,122	0.024	8.53	47	2	20	24.61	1
Styrene	0.051[*]	0.068	11.52	9	0	0	9.04	0
o-Xylene	0,102	0.034	28.28	2	0	17	17.54	1
Nonane	0,091	0.034	8.13	11	0	28	7.31	0
Isopropylbenzene	0,074	0.036	4.49	0	2	0	4.92	4
n-Propylbenzene	0.029[*]	0.046	4.93	0	1	0	3.92	1
m-Ethyltoluene	0.073[*]	0.044	4.10	0	41	1	3.49	55
1,3,5-Trimethylbenzene	0.073[*]	0.042	12.84	0	2	0	8.45	0
1,2,4-Trimethylbenzene	0,094	0.042	12.33	0	1	4	11.12	1
n-Decane	0,137	0.04	16.09	3	2	20	10.26	0
1,2,3-Trimethylbenzene	0,089	0.07	40.45	2	0	0	17.31	0
m-Diethylbenzene	0,115	0.068	14.36	0	1	4	5.90	2
n-Undecane	0,110	0.054	33.79	13	0	6	12.95	0
n-Dodecane	0,106	0.126	55.17	1	0	8	19.51	0

* (Yurdakul, 2014)

3.5.1.3 Leak Test

In order to collect specified amount of sample, there must not be any leakage from the canisters. According to USEPA TO-15 method, if there is a change between initial and final pressure which less than 2 psig, canisters are leak free. Before the begining of sampling period, to determine the whether there is any leakage from the canisters or not, presurized canisters were controlled 24, 48 and 72 time intervals, and after the proper time no change was observed in pressure, so it was concluded that there is no leakage from canisters.

3.5.1.4 Reproducibility of samples

After collected samples, to determine wherther there is a change in concentrations of compounds in time, sample was collected in METU, Environmental Engineering Department and analyzed just after the sampling and after 24, 48 ,72 and 96 hour intervals. Figure 3.8 shows the results of analysis for BTEX compounds. As it can be seen from the figure, there is a progressive decreasing in concentrations. There might be various reason for this situation. Firstly, it was thought that there should be leakage from canisters, however leakage test already were carried on. So this option was eleminated. Secondly, absoption might be occurs on the inner wall of canister. Furthermore, with the increasing number of analysis, the amount of sample decreases, additionally concentration of sample is not very high. So, this may cause to decreasing analyte concentration. Finally, homogenous distribution increases with in time, so for the first analysis it can be said that compounds with.trace.concentrations.might.not.be .homogeneously.distributed.in the canisters. As a conclusion, due to obtained results, after essential time for stabilization, collected samples should be analyze directly.

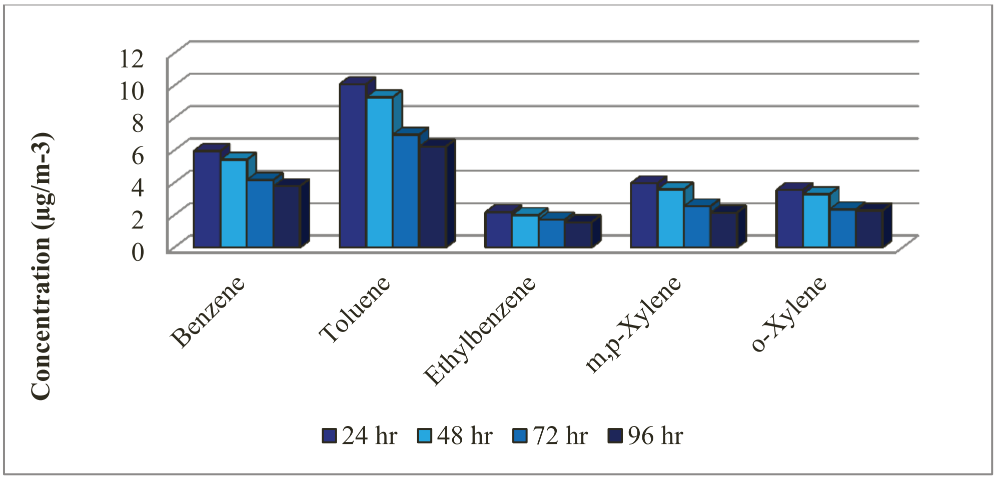


Figure 3.8 Reproducibility of BTEX with in time

3.5.1 Data quality control

Possibility of making a mistake is high in the experimental studies and chromatographic analysis, for this reason inspection of obtained data set is a critical step. In other words, applying a quality control study to obtained data set is an obligatory to be able to ensure accuracy of it.

There may be some irregularity in obtained data set due to several reasons, such as sudden changes around the sampling location or meteorological parameters, various analytical problems during analysis, or failure in manual integration of chromatograms etc. And these situations cause to important inaccuracy in interpretation of data set. Furthermore, it is crucial to determine whether the main reason of inaccuracy. Problem may result from a single data point, or there may be a systematic mistake. To designate this, obtained data set was controlled following the below three-step quality control procedure, containing time series plots, scatter plot matrices, and fingerprint plots (Kuntasal,2005 & Yurdakul, 2104). Thereby, possible mistakes and outliers in data set was controlled.

3.5.2.1 Time series plots

Time series plots were figured for each compounds throughout sampling period for both stations and controlled whether there is any abnormal alteration in concentrations or not. In the Figure 3.9 time series plots of BTEX compounds were provided as an illustration. As it can be seen from the figure, there are sudden increases and decreases in some days. Actually, this kind of sudden episodic changes are typical for environmental data sets. Transport pattern, changes in emission amounts, and sudden changes in meteorological conditions may cause such episodic variations in pollutant concentrations (Doğan, 2013). But yet, in order to determine whether those values are outliers or not, all relevant chromatograms and calculations were examined once again in order to check the accuracy of integration of those days. But, any of them do not designated as an outlier.

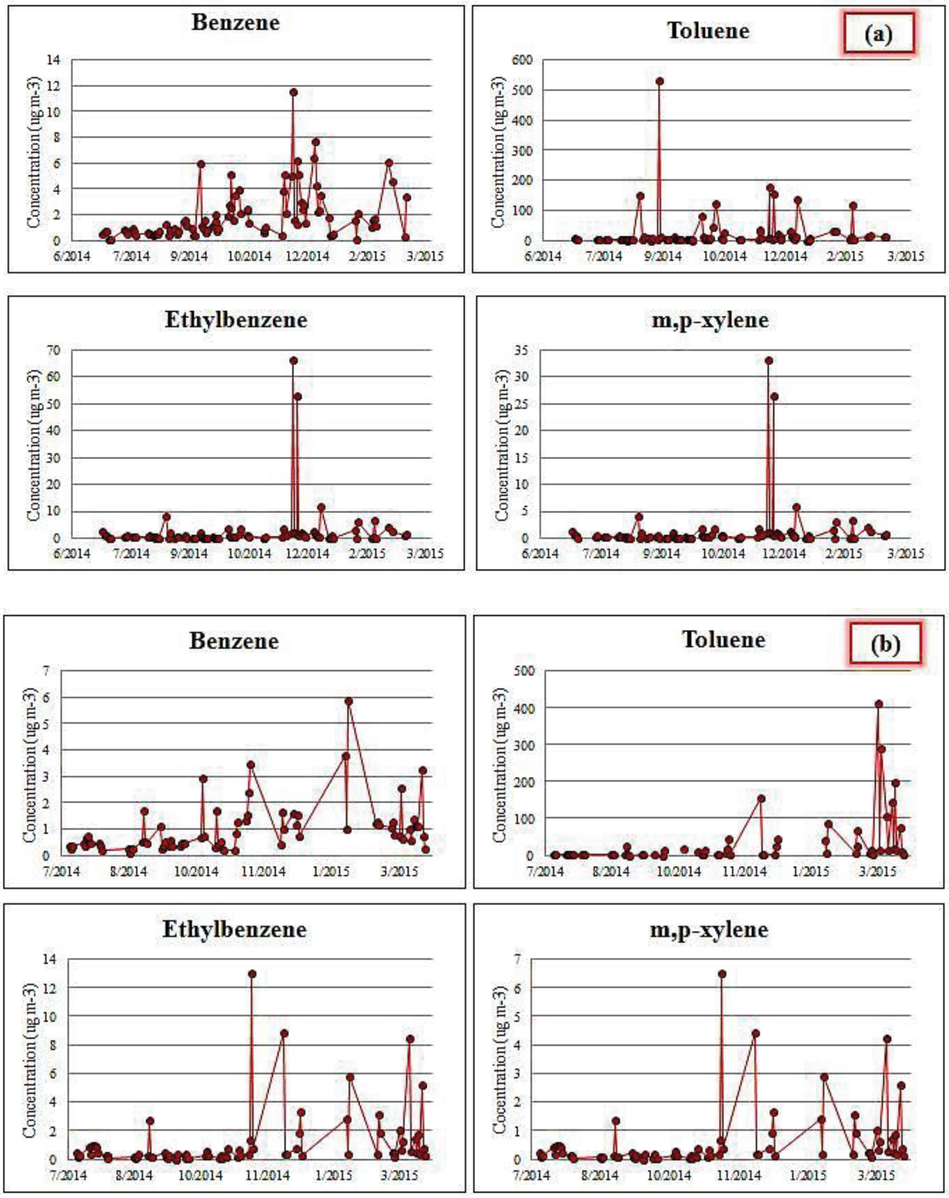


Figure 3.9 Time series plots of BTEX compounds obtained (a) from urban station, (b) from rural station

3.5.2.2 Scatter plot matrices

As the second step of the data quality control study, scatter plot matrices were figured in order to possible abnormalies between structurally similar compounds. In the Figure 3.10, scatter plot matrices of BTEX compounds were provided as an example. These species can seperate together, and all of them are traffic related compounds. (Majumdar et al., 2011). As in time series plots, possible outlier points were investigated using scatter plot matrices, and all of them re-examined properly. But, any outliers were identified in whole data set.

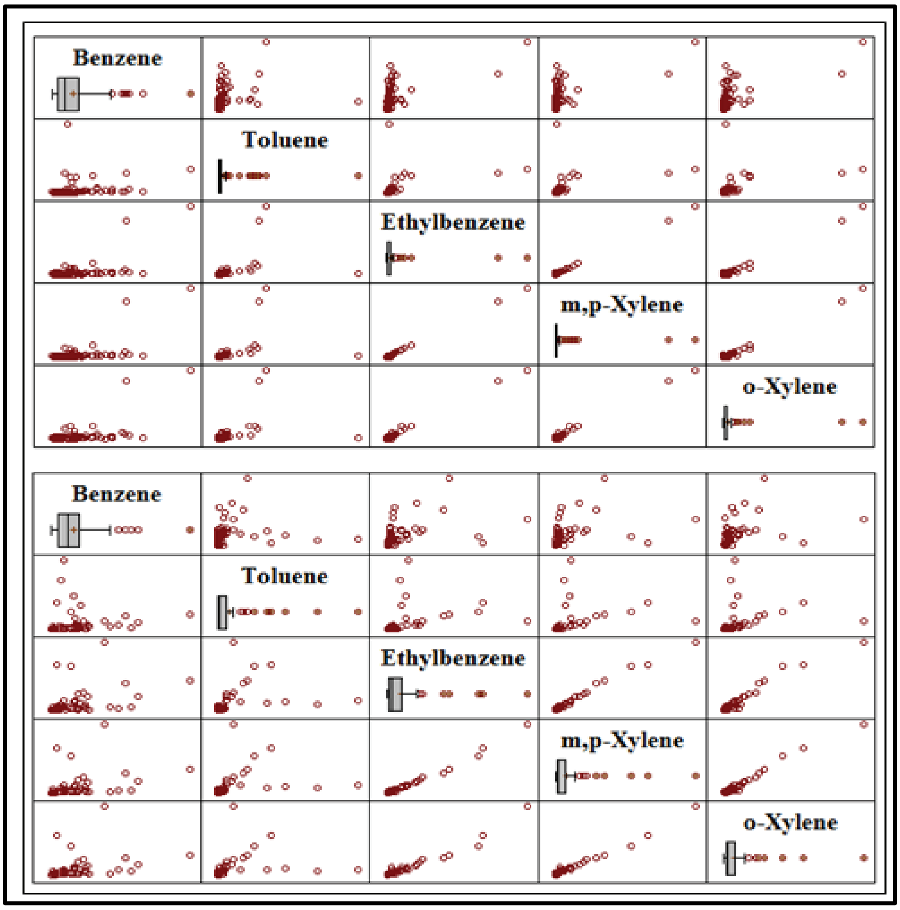


Figure 3.10 Scatter matrices plots of BTEX compounds obtained (a) from urban station, (b) from rural station

3.5.2.3 Fingerprint Plots

As the final step of the data quality control study, fingerprint plots were figured for each individual sampling day comprising all target VOCs, because they can give suggestive information about daily changes (Kuntasal Ö. , 2005) and they can be a good indicator to identify sample compositions. (Yurdakul, 2104). To decide characteristics of concentration distributions, and also to check abnormality in general concentration pattern fingerprint plots were drawn for all sequential days as shown in the Figure 3.11. Thus, possible outliers were checked as in previous steps, but any outliers were not identified in whole data set.

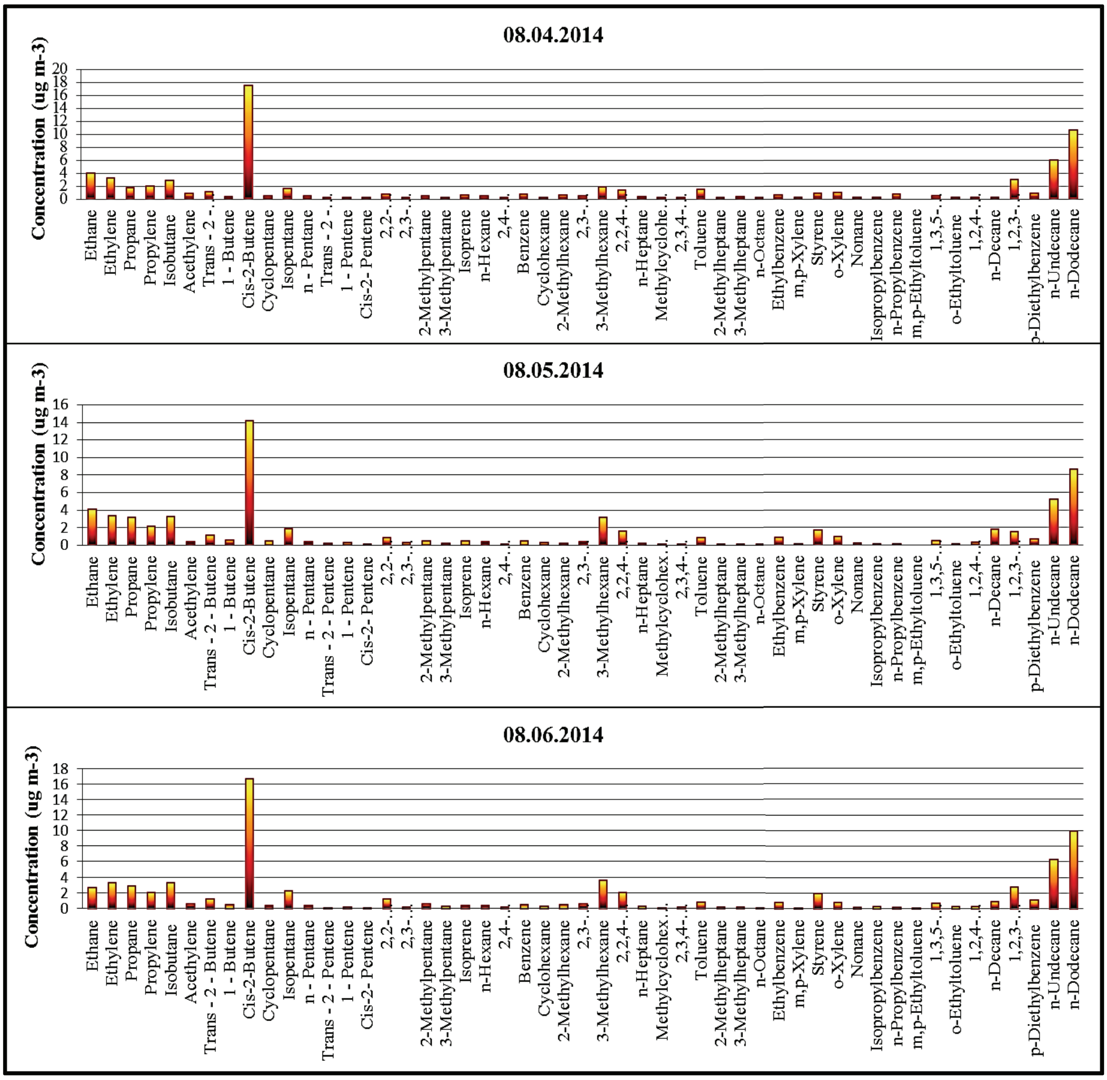


Figure 3.11 A sample for fingerprint plot sequential days

3.6 Positive Matrix Factorization (PMF)

As mentioned in section 2.5, there are various source apportionment studies in the literature, and PMF, which is created by Paatero (1997), is one of the most frequently using tool for the purpose of determination of possible source contributions of any pollutants in the atmosphere. And, in this study, in order to determine possible source contributions to VOCs concentrations that were measured in urban and rural stations a PMF study was conducted. For this aim EPA PMF 5.0 program was used.

There are two types of input file to be able to run the program which include concentrations of target compounds and uncertainity values of them. The program does not accept any blank cells in input files. And also, in order to obtain a successful result, uncertainty estimation is very important part of PMF studies as well as not to be any blank cell in input files (Pekey & Doğan, 2013). Due to this fact, the below three setps methodology were used which was developed by Pollisar et al. (1998) ;

i. measured VOCs concentration values were used directly, and uncertainty values of them were supposed to sum of 5 percentages of measured concentration and minimum detection limit value of the compound
ii. missing values of a compound in concentration files were replaced with geometric mean value of related compound, and accompanying uncertainty value was substituded by four times of geometric mean of the compound
iii. concentrations that were below minimum detection limit value were substituted with half of minimum detection limit of the each compounds and uncertainity of them were set 5/6 of minimum detection limit value

After preperation of input files, an approach should be developed to obtain successive results from PMF. In this step, determination of factor number is very critical. In order to determine using factor number differences between “goodness-of-fit” parameter (Q values) is the major factor. After a run that is based on a specified number of factors, PMF supply two different Q value as Q_{true} and Q_{robust}. These pararmeters are calculated by the programme. Q_{true} represents calculated all points while Q_{robust} "excludes points cannot fit by the model which represents uncertainity to scaled residual ratio is greated than 4". And also, another Q value is $Q_{theoretical}$, and it is calculated by the user using the following equation.

$$Q_{\ theoretical} = nm - p(n + m) \qquad \text{Equation (2)}$$

m, n and p represent the amount of collected samples during sampling period, the number of target VOCs, the number of factors respectively. According to EPA, the ratio of Q_{true} to Q_{robust} should be lower than 1.5, on the contrary the obtained results affected disproportionally. Also, calculated $Q_{theoretical}$ value should not be very different from Q_{robust} value (Gupta, et al., 2011).

Q values are one of the most important parameters to be able to check the performance of the model. At least 20 runs at different seeds (beginning points) were performed and minimum Q values were selected at the first step of the PMF trials. Some other quality control studies were done after obtained Q results of each run. First of all, amount of missing data for each specie was determined and, if the amount of missing data is high for a compound, it should be eliminated. For this reason 3 of VOCs in 51, which are 3-methylpentane, 2-methylheptane and m,p-ethyltoluene, were removed from the input files.

Additionally, signal-to-noise (S/N) ratio of each species is another important parameter to obtain an accurate soultion. If the ratio is between 0.2 and 2, related compound is designated as "weak specie", and if the ratio is lower than 0.2, it is designated as "bad specie" and removed from the model input. Thus, weak and bad species were determined and in order to prevent any mistake in factor profiles, bad species removed from the PMF input. However, it can not be sufficient to decide whether a specie is weak or bad for the model just using S/N raito. Correspondingly, the next steps are practiced by using r^2 values which are obtained from predicted concentrations to observed concentration graph and by checking scaled residual analysis histograms for each data. In order to make a decision in relation to this, two approaches were specified. If r^2 value of a specie is very low, in other words if distribution of a specie is highly poor, and amount of replacement is high, that compound designates as "bad". However, if a specie distributes poorly, but amount of replacement is low, it is designates as “weak”. By this means, contribution of disproportionate species to model fit could be reduced and more accurate results can be obtained (Brown, et al., 2007).

Three outputs are obtained end of the PMF runs. Theses are factor profiles (F-Loadings), factor contributions (G-Score) and error profiles. Factor profiles represent the apportion of each compounds to factors. The variance of each compounds is defined as explained percentage. In order to describe sources, factor profiles and explained percentage are used. Also, G-score represents variation of the daily proportion of each sources to the samples. Thus, high G-score in a factor means that contribution of the sample is high to related factor.

After the all above steps, F-PEAK run is executed to check rotation and to estimate Q value. For this aim 5 different run were applied with different F-PEAK values. They change between -1 and 1.5. When the minimum variation of Q value (dQ) is obtained, the corresponding F-PEAK value was selected. In all results of PMF runs, when F-PEAK is equal to -0.5, it can be reached to minimum dQ value.

Error estimation is another important part of the PMF to be ensure accuracy of the model. In the 5.0 version of PMF two different error estimation method can be used. First one is “Base Model Displacement Method (BS-DISP)” and the second one “Base Model Bootstrap Method (BS)”.

BS-DISP is used to designate rotational ambiguity in obtained results by detection of the higher source profile range without a significant increasing in Q values. After the BD-DISP run, the programme give some error codes to be able to consider whether the obtained results are acceptable or not. For example, if the code is zero, it means that there is no error, but if the code is 6 or 9 it means that the run shoul be cancelled. Also, every displacement in all factors were determined, and four different dQ_{max} value, 4,8,15 and 25, were calculated by the programme. In any displacement happen for dQ_{max} is equal to 4, it shows that there is an important amount of rotational ambiguity (USEPA, 2014).

At the final step, BS was applied to control stability of the analysis. It is pretty new error estimation method into the new version of PMF. It is used to decide if a small change occurs in data set, whether related factors are robust sufficiently or not. According to obtained results from the BS runs, over the 80% of all data should be mapped into the all factors to be able to make an accurate interpretation. And also it means that decided number of factors were appropriate and present uncertainities are accepttable. In this study, these two error estimation methods were applied and possible rotational ambiguity were checked.

At the beginning of the PMF study, different number of factors, from 5 to 11, were tried and all of the above steps were executed for all of them. And, finally best fit factor number were designated in both stations. Also, all factors were identified by an evaluation of the F-loading, explained percentage and G-score results. In addition to them, wind roses were prepred for each factor to determine possible contributions of TPPs in the region on VOCs concentrations. All of the obtained results were given in the Chapter 5 and discussed in detail.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Meteorology of the Study Area

Meteorology is an important atmospheric science, and it assists to designate the characteristics of the airshed. Meteorological parameters, such as wind speed, temperature, relative humadity and mixing height, have a crucial importance in air pollution studies and they should be taken into account for the interpretation of obtained results(Kuntasal, 2005). Fluctuations in the local meteorology effects the transportation, dispersion and purification of air pollutants in the atmosphere (Verma & Desai, 2008). Accordingly, this section was prepared in order to recognize the meteorological conditions of Kütahya, and also comprehend the relation between long term meteorological conditions, which prevail from 1964 to 2014, and throughout our sampling period. So, it was important to specify whether conducted study was represent merely sampling period or longer. Both during sampling period and long term meteorological parameters were obtained from General Directorate of Meteorology for and wind speed (WS), wind direction (WD),temperature (T), relative humadity (RH) and rainfall parameters were compared for the two relevant period in the Figure 4.1.

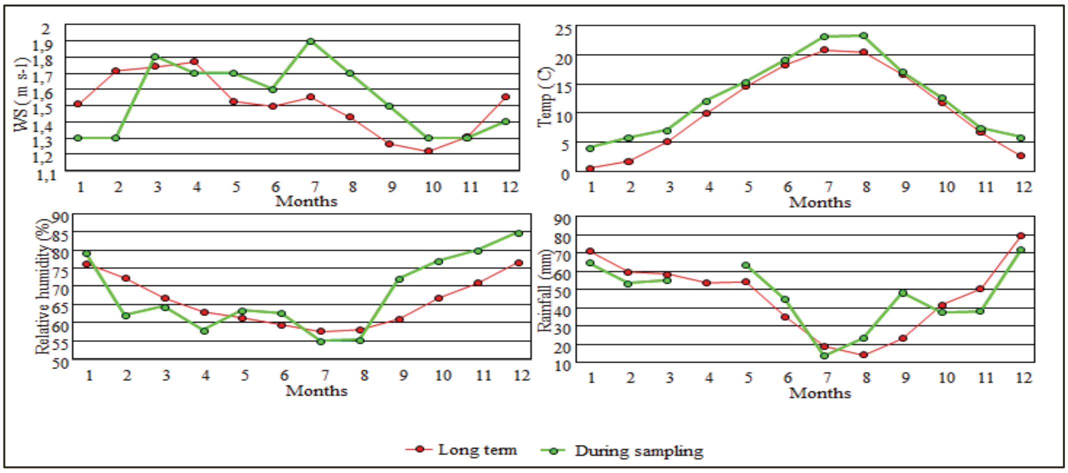


Figure 4.1 Monthly variation of T, WS, RH and rainfall at Kütahya region

Although, Kütahya is located in the Aegean Region, due to distance from sea and altitude, climate is different from Aegean costline. It has a transition climate between Aegean, Marmara, and Central Anatolia Region. In the province, summer is hot and dry, and winter is cold and wet (Dinç et all, 2011). The hottest months are July and August whereas the coldest months are January and February. While considering the obtained meteorological data, it was deduced that temperature shows a typical regionally behaviour. In the summer months, monthly average temperature has reached up to 23 ^{0}C, whereas in the winter months it has decreased to till 2-3 ^{0}C. There is not a remarkable difference between monthly average temperature measurements for long term and during sampling period. If it is considered that temperature determines the rate of photochemical reactions, due to similarity between long and short term temperature measurements, obtained data set and relevant interpretations do not only belong to sampling period, also explicitly represent a longer period.

Wind speed is another important meteorological parameter. It is quite low in the region, and changes between 1.3 m/sec and 1.8 m/sec in the winter and summer months respectively. Wind speed is a significative meteorological parameter for air pollutant distribution. Namely, when wind speed is low, pollutant accumulation potential increases. So, the measured VOC concentrations are expected to decrease with the increase in the wind speeds. Also, this template is observed in the literature by a majority. As in temperature, long term monthly average wind speed is similar to measured average wind speed values during sampling period.

When relative humadity measurements were considered, it was concluded that there is a regionally representative behaviour. It increases up to 80-85% in the winter months, while in the summer months are relatively dry, and relative humadity is decreases to 20%. As it can be seen from the figure 4.1, as in temperature and wind speed, there is not a significant difference between long and short term measurements.

As it was expected due to general climatology of the region, amount of rainfall is higher in the winter months than in the summer months. Amount of annually rainfall was calculated as 558 mm when long term meteorological values were used, however, if short term, namely during sampling period, values are used, this amount was calculated as 560mm. As it can be concluded that there is not a huge difference between two values like other parameters.

Mixing height and ventilation coefficient are very important meteorological parameters that must be taken into consideration due to their effect on the pollutant concentratios in the atmosphere. Mixing height means that the distance between layer and ground level which vertically dispersed and proper mixing of pollutant due to convection, or mechanical turbulance (Seibert, 2000). In this study, monthly alterations in mixing height and ventilation coefficient were provided in the Figure 4.2. Mixing height was below 1000 m level in winter months, while increased up to 2500-3000 m in summer months. Ventillation coefficient shows us the assimilative capacity of the atmosphere, and it was calculated with multiplication of mixing height and wind speed. As it was mentioned, both of these parameters were higher in summer months that winter. Hence, alteration in ventilation coefficient followed the mixing heights closely. The critical point to take into considiration is that this alterations will effects summer and winter concentrations of VOCs and other measured parameters in the scope of the conducted scientific project. In the further parts of the study, seasonal variations of VOCs concentrations will be discussed.

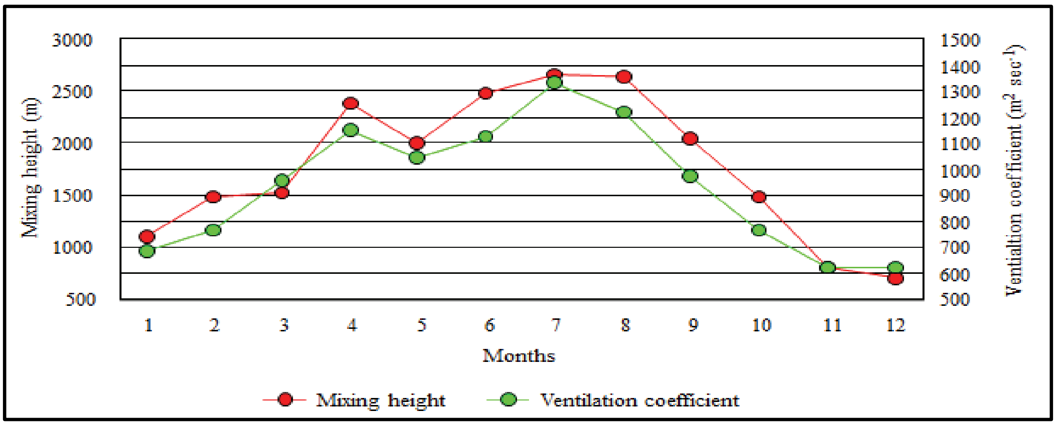


Figure 4.2 Monthly variation of Mixing Height and Ventilation Coefficient at Kütahya region during the study period

In attempt to observe prevailing and dominant wind directions of the region, wind roses was prepeared using long term (1964 – 2014) data and data collected during sampling in both stations. As it can be seen from the Figure 4.3, in rural station the wind is blowing mostly W and ESE sectors during sampling, while the wind is blowing generally between N and WNW sectors in urban station not only sampling period but also extended period of the time. Interesting side of this condition that Tunçbilek and Seyitömer Thermal Power Plants were located in dominant wind directions. Thus, it is understood that Kütahya is downwind of these power plants and air pollutants released from these plants are transported towards Kütahya.

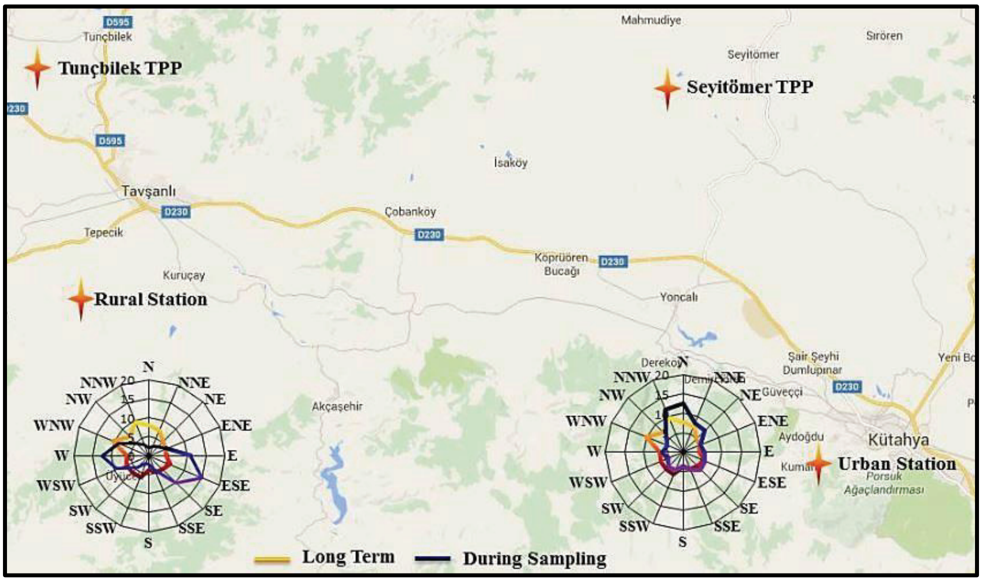


Figure 4.3 Wind roses at Kütahya prepeared using long term (1964 – 2014) data and data collected during sampling in both stations

Additionally, in rural station dominant wind sectors are different from both long term and in urban station. In rural station dominant wind sectors are W and ESE during sampling. Tavşanlı-Simav road and urban part of the Kütahya are located in those directions.So, it can be said that traffic related species may result from Tavşanlı-Simav road, and some pollutants may be transported from urban side of the Kütahya to rural station. All these possibilities were discussed in the further sections in detail, and also a source apportionment study were conducted to find major sources of VOCs in both stations.

But yet, when a preliminary consideration were made, it can be understood that wind roses which were prepared using long term data and obtained data from urban station during sampling period match each other roughly. However, there are some differences between them. In the long term wind roses, the percentage of wind blowing from WNW and NW sectors is higher than recorded amounts during sampling period. On the contrary, during sampling period the percentage of wind blowing from NNW and N sectors are higher than in long term wind rose. All of these considerations show that urban Kütahya is located downwind of Tunçbilek and Seyitömer Power Plants and it is not suprising that the air quality of the province is affected from these plants. Accordingly, for the pollutants with same emission amounts both in summer and winter seasons, winter concentrations can be expected to be higher compared to summer concentrations.

4.2 General Features of Data

4.2.1 Descriptive Statistics of the Measured VOCs Concentrations

In this study 51 VOCs were detected in both rural and urban stations and essential statistical values for appropriate interpretation, such as average concentration with plus or minus standart deviation, median, geometric mean, minimum and maximum concentration ranges, and their number of detection were provided in Table 4.1. As it can be seen from the table in urban station average concentration range is between 0.12 μg/m^3 and 23 μg/m^3 and for cis-2-pentene and toluene respectively. Correlatively, in rural station this range is changing between 0.06 μg/m^3 and 33 μg/m^3 for same compounds respectively. As it was seen above, toluene has the highest average concentration in both stations. It is possible to encounter with determination of different limitations for toluene in both indoor and outdoor air quality measurements. In the ambient air, the main source of toluene is generally automobile emissions (ATSDR, 2000). Additionally, it can release to ambient air in course of any production activities, solvent usage, or disposal of any industrial products containing toluene (USEPA, 2012).

As it was seen from the Table 4.1, in both stations, median and geometric mean values are very close to each other, whereas average concentrations of each compound were approximately two times higher than both median and geometric mean values. It can be deduced from this circumstances that whole VOCs show a right-skewed distribution prominently. Fundamentally, several frequency distribution models show right-skewed distribution. However, in order to understand which distribution is applicable, “goodness of fit test” must be performed. In this study, it was performed for the entire VOCs through chi-square test, and obtained results were discussed in the following section.

Table 4.1 Descriptive statistics of measured VOCs

	Urban Station					Rural Station				
	Mean	**Med.**	**Geo. Mean**	**Range**	**N**	**Mean**	**Med.**	**Geo. Mean**	**Range**	**N**
Ethane	3.58±3.45	2.78	2.17	0.0691-18.31	93	1.10±1.22	0.69	0.68	0.0297-7.05	72
Ethylene	9.38±11.64	3.98	5.00	0.1111-61.63	93	3.52±4.58	1.85	1.94	0.1172-28.85	74
Propane	5.11±6.26	2.87	3.23	0.3367-38.48	93	2.50±3.96	1.45	1.47	0.0546-30.44	75
Propylene	6.42±8.61	2.92	3.44	0.0857-48.84	93	2.20±3.29	0.88	1.08	0.1009-16.97	75
Isobutane	7.73±9.23	3.97	4.43	0.1083-53.83	93	3.23±6.09	1.12	1.33	0.1204-35.00	74
Acethylene	1.59±1.84	0.85	0.93	0.0850-11.16	93	0.66±0.93	0.34	0.34	0.0096-4.99	74
Trans - 2 - Butene	0.72±0.71	0.60	0.44	0.0072-4.07	93	0.38±0.45	0.27	0.21	0.0124-3.00	70
1 - Butene	0.86±1.05	0.52	0.53	0.0260-5.98	93	0.53±0.82	0.28	0.26	0.0023-4.55	74
Cis-2-Butene	17.83±14.14	16.52	13.19	0.3927-82.15	93	13.2±11.9	8.92	9.09	0.5616-68.70	74
Cyclopentane	0.54±0.82	0.34	0.29	0.0147-5.92	93	0.25±0.38	0.16	0.14	0.0098-2.86	73
Isopentane	5.57±7.64	2.62	2.94	0.1352-49.07	93	3.26±8.19	1.21	1.16	0.0339-67.36	74
n - Pentane	3.88±15.42	1.21	1.16	0.0208-147.5	93	1.71±3.71	0.61	0.72	0.0489-27.16	74
Trans - 2 - Pentene	0.30±0.43	0.15	0.16	0.0062-2.74	93	0.16±0.28	0.09	0.08	0.0041-2.24	72
1 - Pentene	0.35±0.41	0.20	0.23	0.0040-2.87	93	0.24±0.26	0.16	0.14	0.0043-1.26	73
Cis-2- Pentene	0.12±0.29	0.05	0.05	0.0034-2.58	93	0.06±0.08	0.03	0.03	0.0030-0.54	74
2,2-Dimethylbutane	1.25±1.36	0.85	0.75	0.0030-7.25	93	0.46±1.32	0.19	0.21	0.0250-11.19	74
2,3-Dimethylbutane	0.42±0.60	0.23	0.19	0.0005-4.24	93	0.24±0.67	0.09	0.08	0.0005-5.69	73
2-Methylpentane	1.26±2.79	0.60	0.55	0.0180-24.97	93	1.11±3.18	0.28	0.31	0.0055-24.20	65
3-Methylpentane	0.69±1.53	0.30	0.27	0.0036-12.87	93	0.57±1.28	0.17	0.16	0.0035-8.09	69
Isoprene	0.82±1.15	0.42	0.42	0.0011-5.95	93	0.39±0.63	0.19	0.20	0.0064-4.44	74
n-Hexane	3.85±8.64	0.82	1.15	0.0328-46.52	90	2.56±5.53	0.97	1.05	0.0511-43.11	72
2,4-Dimethylpentane	0.66±2.97	0.18	0.20	0.0036-28.53	92	0.41±0.93	0.14	0.16	0.0172-6.20	73
Benzene	1.88±1.97	1.15	1.17	0.0704-11.50	93	0.98±0.97	0.69	0.69	0.1024-5.87	74
Cyclohexane	1.12±2.15	0.38	0.43	0.0153-13.92	93	0.84±2.66	0.21	0.22	0.0020-21.94	73
2-Methylhexane	0.72±1.13	0.30	0.30	0.0114-7.65	92	0.47±0.78	0.25	0.21	0.0097-5.61	73
2,3-Dimethylpentane	0.60±0.69	0.43	0.32	0.0069-3.95	92	0.38±0.32	0.32	0.27	0.0129-2.07	70

Table 4.1 (Continued)

	Urban Station					Rural Station				
	Mean	Med.	Geo. Mean	Range	N	Mean	Med.	Geo. Mean	Range	N
3-Methylhexane	1.74±1.56	1.34	1.12	0.0458-9.30	93	1.74±1.92	1.04	1.04	0.0871-10.76	74
2,2,4-Trimethylpent.	1.02±0.81	0.79	0.65	0.0108-3.80	93	0.66±0.44	0.58	0.52	0.0287-2.20	74
n-Heptane	0.63±0.72	0.38	0.38	0.0100-4.71	93	0.56±0.74	0.37	0.35	0.0100-4.57	74
Methylcyclohexane	0.27±0.28	0.17	0.16	0.0001-1.36	93	0.25±0.36	0.14	0.11	0.0001-2.14	74
2,3,4-Trimethylpent.	0.22±0.25	0.12	0.12	0.0014-1.51	92	1.14±4.28	0.10	0.12	0.0019-25.38	72
Toluene	22.90±65.74	4.79	4.65	0.2099-532.8	89	33.1±73.3	4.70	6.00	0.0921-413.3	59
2-Methylheptane	0.80±1.94	0.34	0.27	0.0025-15.20	85	4.25±29.6	0.19	0.17	0.0032-240.0	66
3-Methylheptane	0.93±1.64	0.30	0.34	0.0084-7.90	92	0.42±0.62	0.16	0.18	0.0034-3.15	73
n-Octane	0.48±0.62	0.28	0.27	0.0118-4.66	92	0.42±0.50	0.27	0.23	0.0008-3.22	74
Ethylbenzene	2.49±8.77	0.68	0.62	0.0154-66.45	93	1.15±2.18	0.38	0.44	0.0060-12.98	74
m,p-Xylene	2.32±8.81	0.41	0.46	0.0267-65.39	91	2.29±5.07	0.59	0.69	0.0225-32.09	73
Styrene	1.27±1.72	0.78	0.58	0.0162-12.93	93	0.94±1.22	0.61	0.52	0.0279-8.25	74
o-Xylene	3.19±9.88	0.96	1.05	0.0976-72.72	93	1.63±3.20	0.60	0.72	0.1035-22.09	73
Nonane	0.59±1.00	0.28	0.30	0.0204-6.08	93	0.75±1.55	0.25	0.29	0.0204-9.00	74
Isopropylbenzene	0.35±0.47	0.16	0.18	0.0054-2.30	91	0.24±0.24	0.18	0.15	0.0034-1.37	71
n-Propylbenzene	0.51±0.79	0.23	0.19	0.0002-5.61	92	0.36±0.63	0.18	0.14	0.0002-4.15	73
m,p-Ethyltoluene	0.37±0.45	0.18	0.16	0.0043-2.25	55	0.26±0.32	0.15	0.12	0.0058-1.34	33
1,3,5-Trimethylbenz.	1.05±1.56	0.54	0.52	0.0117-8.33	91	0.76±1.33	0.35	0.32	0.0017-8.72	73
o-Ethyltoluene	0.83±1.25	0.38	0.40	0.0040-7.75	90	0.43±0.55	0.24	0.22	0.0036-2.91	69
1,2,4-Trimethylbenz.	1.08±1.63	0.52	0.52	0.0349-8.55	92	0.63±0.65	0.47	0.36	0.0009-3.50	72
n-Decane	1.60±2.57	0.64	0.61	0.0065-13.71	91	1.42±4.14	0.41	0.44	0.0045-34.25	73
1,2,3-Trimethylbenz.	4.41±5.24	2.83	2.38	0.0244-31.72	93	1.76±1.96	1.21	1.04	0.0203-10.01	73
p-Diethylbenzene	1.49±1.67	0.98	0.82	0.0256-9.14	92	0.59±0.73	0.40	0.34	0.0061-4.14	71
n-Undecane	2.76±2.53	1.82	1.69	0.0666-10.49	93	1.28±1.59	0.70	0.71	0.0908-9.45	73
n-Dodecane	8.51±7.43	6.95	5.38	0.2397-39.14	93	4.85±6.10	2.46	2.73	0.1815-34.23	73
∑Alkans	2.09±2.29	1.02	1.20	0.22-8.51	27	1.36±1.27	0.84	0.93	0.24-4.85	27
∑Alkenes	3.84±5.82	0.84	1.27	0.12-17.83	10	2.13±4.04	0.46	0.64	0.06-13.20	10
∑Aromatics	3.15±5.79	1.38	1.54	0.35-22.9	14	3.22±8.62	0.85	0.96	0.24-33.10	14

Another remarkable point of Table 4.1 is rather high data capture rates of almost all VOCs. As it was mentioned in the former sections, 24-hour sampling was conducted in both sampling stations and 93 and 75 air samples were collected from urban and rural stations respectively. Avarage data capture rates of VOCs change between 59% for m-p,ethyltoluene and 100% for most of species. Actually, when all of data capture rates were examined, a low capture rate as 59% was achieved for just one compound, m-p,ethyltoluene. Scilicet, if m-p,ethyltoluene excluded from whole VOCs, this capture rate will have changed between two higher ratio such as 90% and 100%. In urban station, 18 VOCs including propylene, 1-butene, n-pentane, 2,2-dimethlybutane, isoprene, benzene, cyclohexane, 3-methylhexane, 2,2,4-trimethylpentane, n-heptane, methlycyclohexane, ethylbenzene, styrene, o-xylene, nonane, 1,2,3-trimethylbenzene, n-undecane and n-dodecane were captured with 100% capture rate. And, other compounds excluding m,p-ethyltoluene was captured with at least 90% capture rate. This rates show us that overall average capture rate of VOCs is 97 % in urban station. Whereas, in rural station average data capture rate is between 44% for m,p-ethyltoluene and 100% for only two compounds; propane and propylene. In this station, m,p-ethyltoluene, toluene, 2-methylpentane, and 2-methylheptane have the lowest capture rates respevtively. However, remainded compounds were captured between 98% and 90% rates. Thus, overall average capture rate was calculated as 95% in this station. After all these considerations, it can be concluded that almost all of VOCs can be detected with very high capture rates in both stations and they are proper indicators to be carried out statistical tests with low uncertainties in further sections.

4.2.2 Frequency distributions of measured VOCs

Frequency distribtion studies are important to find out form of representation of obtained data set and also to show reliability of performed statistical tests (USEPA,1992 ; Limpert et al., 2011). As it was mentioned in the previous section, mean concentrations with plus and minus standard deviation values, median, and geometric mean values were given in the Table 4.1. All of these values were submitted, because, all of them have been used in the literature for interpretation of different data set.

Environmental, especially atmospheric data do not show Gaussian (normal ,or symmetrical) distribution, they generally show log-normal distribution (Limpert et al., 2011). However, statistical tools were usually designed for gaussian distribution models, accordingly, applicability of many statistical tests on environmental data have been a longstanding enigma. For this reason, if it is possible, non-parametric statistical tests are prefered. But, there are not any non-patametric statistical test to be performed all of necessery actions. So, in many cases any statistical tools which were designed for a data set that shows gaussian distibution used for environmental data (Finley & Paustenbach, 1994). Many studies on this subject show that differences between obtained results from parametric and non-parametric tests are not very high as far as alter accurate results (Jia et al., 2008).

In this study, a frequency distribution study was conducted with a 95% confidence test and best fitting models were determined for all of target VOCs using a goodness of fit test which is Chi-square test. Obtained results were summerized in the Table 4.2. In urban station 8 of 54 VOCs, ethane, propylene, isobutane/n-butane, 1-butene, 2,2-dimethylbutane, 2,3-dimethylpentane, and toluene, could not satisfy the 95% confidence criteria, while in rural station, 3 of 54 VOCs, trans-2-pentene, methylcyclohexane and 2-methylheptane, could not pass the 95% confidence test, and accordingly, it can be deduce that all of these VOCs cannot distribute log-normally with 95% confidence. All of the VOCs show a right-skewed distribution, yet it can not be concluded that all of their distribution is log-normal. The most common distribution models are log-normal and loglogistic distribution models. When look at the obtained results from chi-square test, it can be comprehended that in urban station 10 VOCs show log-normal and 20 of them show loglogistic distribution. And also, in rural station 12 VOCs show log-normal and 20 of them show loglogistic distribution. Apart from these two distribution models, different distribution models such as Weibul, Birnbaum-saunder, Gamma and Inverse Gaussian were seen.

Table 4.2 Types of distributions that fits to measured VOC distributions with better than 95% confidence

Compound	**Urban Statiom**	**Rural Station**
Ethane	gamma	lognormal
Ethylene	loglogistic	lognormal
Propane	inverse gaussian	loglogistic
Propylene	loglogistic	inverse gaussian
Isobutane/n-butane	loglogistic	inverse gaussian
Acethylene	birnbaum-saunders	loglogistic
Trans - 2 - Butene	gamma	weibull
1 - Butene	loglogistic	loglogistic
Cis-2-Butene	gamma	lognormal
Cyclopentane	loglogistic	loglogistic
Isopentane	lognormal	loglogistic
n - Pentane	loglogistic	loglogistic
Trans - 2 - Pentene	loglogistic	loglogistic
1 - Pentene	loglogistic	gamma
Cis-2- Pentene	lognormal	lognormal
2,2-Dimethylbutane	loglogistic	loglogistic
2,3-Dimethylbutane	weibull	loglogistic
2-Methylpentane	lognormal	loglogistic
3-Methylpentane	lognormal	lognormal
Isoprene	loglogistic	loglogistic
n-Hexane	inverse gaussian	lognormal
2,4-Dimethylpentane	loglogistic	inverse gaussian
Benzene	lognormal	inverse gaussian
Cyclohexane	lognormal	loglogistic
2-Methylhexane	lognormal	lognormal
2,3-Dimethylpentane	weibull	gamma
3-Methylhexane	gamma	lognormal
2,2,4-Trimethylpentane	weibull	gamma
n-Heptane	loglogistic	loglogistic
Methylcyclohexane	gamma	weibull
2,3,4-Trimethylpentane	weibull	loglogistic
Toluene	inverse gaussian	lognormal
2-Methylheptane	loglogistic	loglogistic
3-Methylheptane	lognormal	lognormal
n-Octane	lognormal	weibull
Ethylbenzene	loglogistic	loglogistic
m,p-Xylene	inverse gaussian	inverse gaussian
Styrene	weibull	lognormal
o-Xylene	loglogistic	inverse gaussian
Nonane	loglogistic	inverse gaussian
Isopropylbenzene	loglogistic	gamma
n-Propylbenzene	weibull	weibull
m,p-Ethyltoluene	birnbaum-saunder	birnbaum-saunder
1,3,5-Trimethylbenzene	loglogistic	loglogistic
o-Ethyltoluene	loglogistic	lognormal
1,2,4-Trimethylbenzene	lognormal	weibull
n-Decane	loglogistic	loglogistic
1,2,3-Trimethylbenzene	weibull	loglogistic
p-Diethylbenzene	weibull	loglogistic
n-Undecane	gamma	inverse gaussian
n-Dodecane	weibull	inverse gaussian

To illustrate their distribution, frequency distributions of isoprene, benzene and cyclopentane which show the most common distributions, log-normal and loglogistic, were provided in Figure 4.4. At first sight, there is not a huge difference between log-normal and loglogistic distributions, also both of them show a right-skewed distribution.

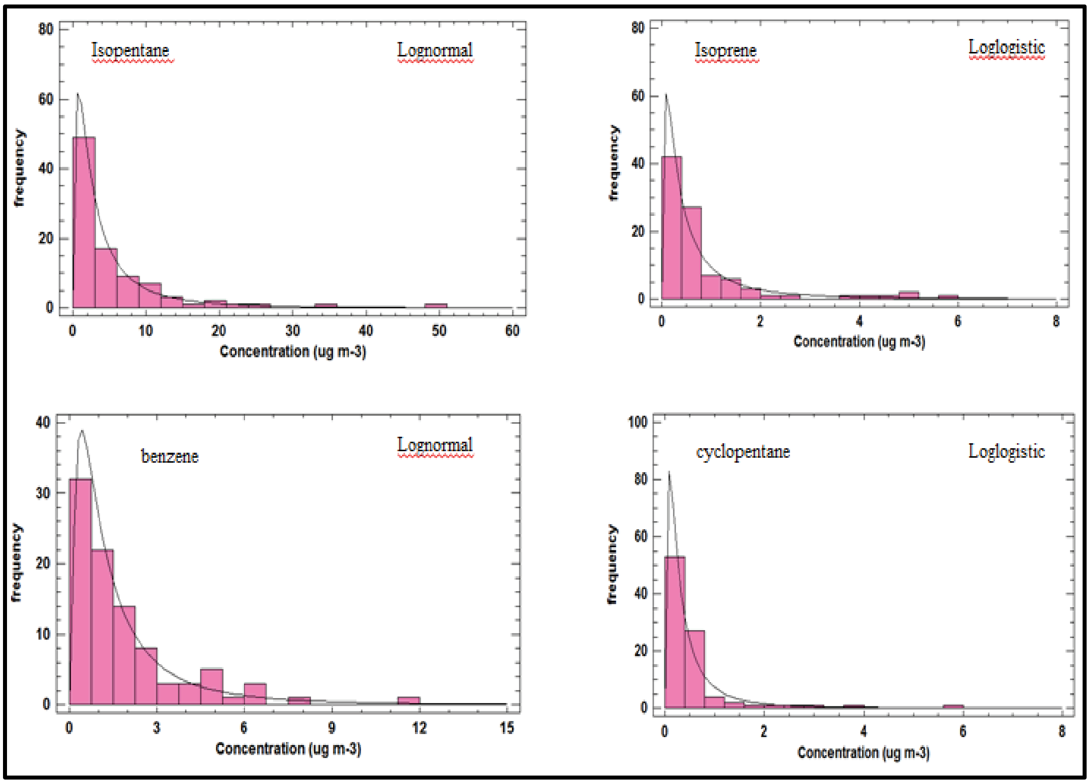


Figure 4.4 Frequency distribution of selected VOCs

Although, measured VOCs adapt different distributions, it was observed that all of them show a right-skewed distributions with different ratings. And, this is an important detail to conclude which parameter can represent obtained data set properly. As a conclusion, it was decided that mean values with standard deviation do not represent whole data set properly, on the contrary, median, geometric mean, and geometric standard deviation are suitable parameters for whole data representation.

4.3 Comparison of VOC Concentrations Measured in This Study With Similar Data from Literature

This part of the study includes 2 sub-sections to be able to make a comparison between concentrations that were measured in this study and similar studies in other cities of Turkey, and around the world respectively.

Comparison of measured concentrations in different locations with each other give information not only about differences in concentration values, but also, if it is investigated carefully, can help us to determine many important parameters on concentration alterations such as main sources of relevant VOCs, fluctuations of emissions in time, effects of meteorological parameters and many more. However, measured concentrations, especially for organic compounds, strictly depends on characteristics of the sampling site. Due to the fact that, this kind of comparisons should not be attributed a huge significance seperately. For example, traffic emissions have more or less effects on VOCs concentrations. So, some measurements that conducted near to high traffic loading roads is generally higher. Accordingly, fluctuations in VOCs concentrations from one sampling site to another, or one province to another depend on measurement points as well as emission amounts. Nevertheless, categorical differences between conducted concentration measurements in this study with other cities measurements can give some information about pollution degree of the province, Kütahya.

In this study, for comparison obtained data from urban and rural stations with literature, a two stage comparison process was conducted. Firstly, measured concentrations in this study were compared with the concentrations that were measured at different provinces of Turkey. And, at the second stage, BTEX concentrations obtained in this study from both stations were compared with the some studies that were conducted at various locations around the world.

In addtition to mentioned two stage, another important comparison study was performed between urban and rural stations where were used in this study for sample collection. But, this comparison study was submitted in one of the further sections individually, because of this it was not discussed in this section.

4.3.1 Comparison of data obtained in this study with other cities in Turkey

As it was stated earlier, especially alterations in concentrations of organic compounds strictly depend on distance between sampling location and emission sources as well as emission amounts (Yurdakul, 2104). Sampling sites may be located at different distances from traffic loadings, possible industries or any possible sources around the sampling station. Consequently, comparison of concentrations that were measured in different locations may not be sufficient indicator individually to be able to determine major sources of pollutants. However, it can give information about pollution degree of the related province.

Comparison of the average VOCs concentrations obtained in this study from both urban and rural stations with studied in some other provinces of Turkey was demonstrated in the Figure 4.5. Some of these studies which were conducted in Aliağa, Ankara, Bursa and Balıkesir were performed by the team members of our air quality research group from METU. Although, used different sampling tools, such as canisters (Uzunpınar, 2015), online GC-FID system (Doğan, 2013; Yurdakul, 2104), passive adsorption tubes (Yalcın, 2013 ;Dumanoğlu et al., 2014 ;Elbir et al.,2007 ;Demir, et al., 2011), same analytical methodology were used for all of these studies. Thus, it can be said that comparison of each data were performed in analytically homogeneous conditions. A number of point is important, and first of them is huge amount of VOCs measurements have been conducted in Turkey. Thus, it made possible to use 8 different studies around Turkey for comparison conduction only in this study. Furthermore, used 8 data set included only little part of the whole generated data in Turkey.

Another remarkable point is that measured VOCs changed between in a large range. For example, benzene was measured as 1,88 and 0.98 $\mu g/m^3$ in urban and rural stations respectively in this study, whereas in other studies this concentration value increases up to about 10 $\mu g/m^3$. Similar large ranges were observed among some other species, and as it was clarified earlier, these types of differences in concentrations result from differences in emission amounts, meteorological conditions during sampling period, as well as sampling station locations and their distances from relevant emission sources.

In this study, both in rural and urban stations almost all measured concentrations of VOCs were the least concentrations which was measured up to now in Turkey. Furthermore, not only measured concentrations of any particular VOCs were low but also whole measured concentrations of VOCs were generally low in Kütahya. For this reason, it was thought that VOCs concentrations were much more affected by emission amounts than by sampling locations. Also, VOCs concentrations measured at rural station are the lowest concentrations among almost all results, and it is not an unexpected outcome actually. Because, as it was known that many concentrations measured in an urban area generally higher than rural concentrations because of emission amounts, and all of except data were obtained from various urbanized areas. Additionally, concentrations measured in urban area is lower than the others like measured concentrations in rural stations, it was deduced that Kütahya is not under the influence of a critical VOCs emission problem. On the other hand, many studies have shown that Kütahya is one of the most troubled provinces of the Turkey due to conventional inorganic pollutants, especially in terms of PM_{10} concentrations (Zafer Development Agency, 2015). In contrast with high PM_{10} concentrations, low VOCs concentrations indicated that sources of VOCs and PM_{10} must be different from each other..

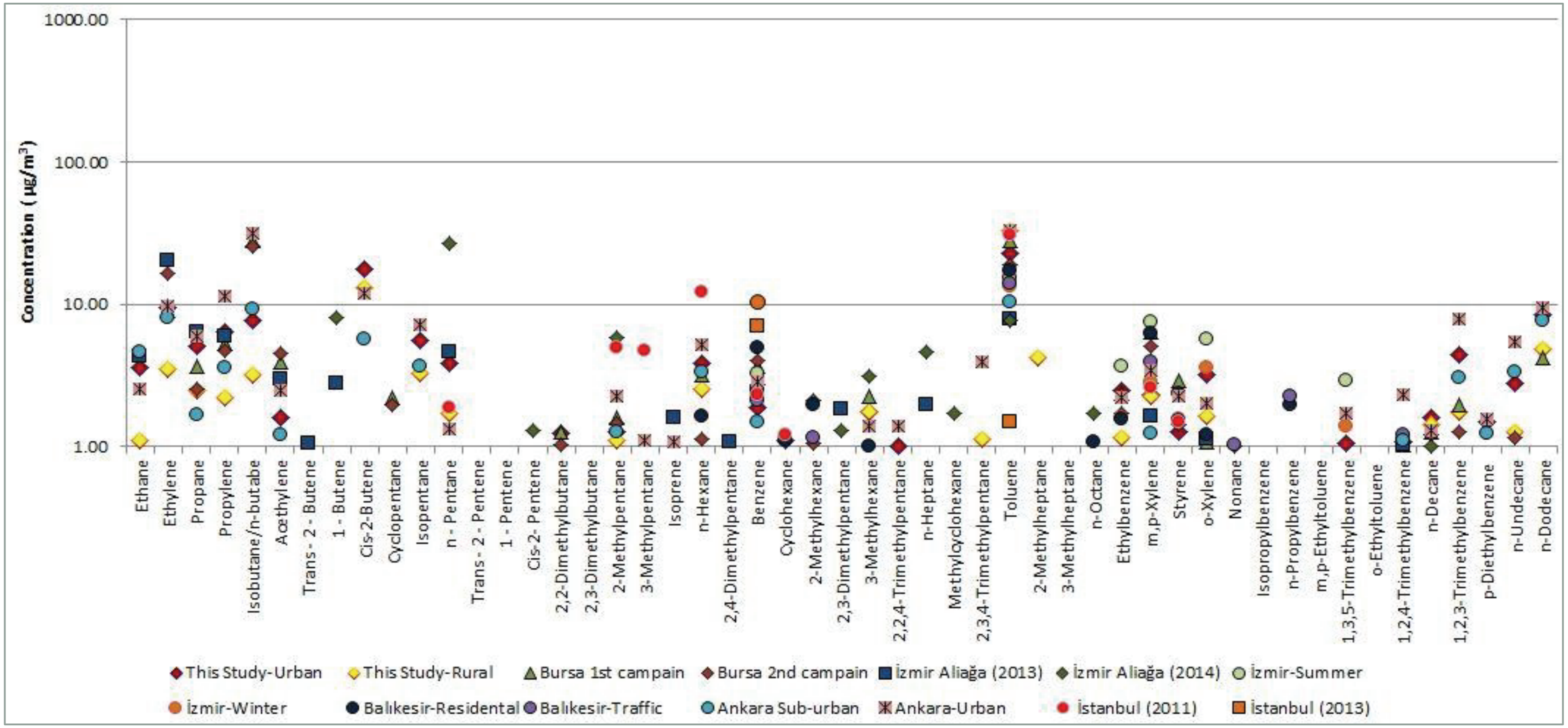


Figure 4.5 Comparison of average VOC levels measured in rural and urban stations with corresponding data from other cities in the country

4.3.2 Comparison of BTEX data obtained in this study with other cities around the world

BTEX can be defined as structurally similar VOCs which are natural including's of petroleum origin compounds and they can enter the environment due to both anthropogenic and biogenic sources. For instance, the major biogenic sources of BTEX are volcanic emissions and forest fires, besides that major anthropogenic sources includes motor vehicle and aircraft exhausts, coal combustion, and any leakage during petroleum transformation, or any solvent usage etc. (Leusch & Bartkow, 2010). If it is necessary to summarize their sources individually, it can be said that benzene is used mostly in consumer products such as plastics, nylons, paints, synthetic rubbers, and cigarettes. Toluene is commonly used as solvent for coatings, paintings, oils or resins etc. Ethylbenzene sources may be similar with benzene, and xylenes are used as solvents like toluene and printing, rubber and especially leather industries include it (MDE, 2007). Comparison of the average BTEX concentrations that were measured in this study at both urban and rural stations with different studies in some other parts of the world, and obtained results were shown in the Figure 4.7. Previous to make any comment about the comparisons between relevant data, reference studies were summarized below briefly;

- *Hong Kong, China (Guo et al., 2007);*

C_1-C_8 VOCs were measured at four urban and rural sites in Hong Kong from September, 2002 to August, 2003. To collect air samples, cleaned and vacuumed electro-polished stainless steel canisters were used and 24-h sampling was conducted once every six days in a year. Collected samples were analyzed with GC-FID and MS systems in University of California at Irene. To determine the main sources of each VOC, PCA with absolute scores modelling was used and results showed that traffic emissions were main sources of VOCs in urban and sub-urban areas of Hong Kong and other sources were petroleum evaporation, industrial emissions, and various solvent usages. Whereas in rural sites of the city, combustion sources, industrial and biogenic emissions had an important effects in VOCs concentrations. As a conclusion, it was reported that anthropogenic sources are the major VOCs sources in urban, sub-urban and rural areas of Hong Kong.

- *Beijing, China* (Song, et al., 2008)

This study was conducted in order to make a comparison between most common source apportionment techniques which are CMB, UNMIX and PMF. For this aim, ambient VOCs were collected during August, 2005 through a dual coaxial Teflon line system on the roof of a building where in the campus of Peking University which is surrounded by high density traffic roads, residential areas and some electronic materials producers. Collected samples were analyzed with GC-FID/MS system and obtained average concentration values were reported in the relevant article. Results deduced that gasoline related sources, LPG and petrochemical production were the main VOCs sources around the sampling area.

- *Tokyo, Japan (Hosh et al., 2008);*

In this study, concentrations of 52 VOCs were measured in the ambient air in two points in an urban location of Tokyo. A monthly sampling procedure was conducted from April, 2003 to March, 2005 and samples were collected with canisters and analyzed using GC/MS system. Measured average concentrations were reported in the article.

- *Shanghai, China (Cai ,et al., 2010);*

Ambient air samples were collected from the commercial center of Shanghai between 2007 and 2010. Samples were collected in a day within 3-h intervals using canisters and analyzed with GC/MS system. After interpretation of all data set, it was deduced that the most abundant VOCs were toluene and propane. And, all of measured average concentrations were reported with them.

- *Leeds, Liverpool and London, United Kingdom* (Derwent, et al., 2000)*;*

In order to measure 26 C_2-C_8 VOCs, an hourly sampling was conducted using an online GC system with thermal desorption and cryogenic trapping unit continuously during 1996. As it was reported that obtained data set was one of the largest data set in Europe in that year. Sampling was conducted in 11 sub-urban and 1 rural areas. Most important VOCs sources were found as motor vehicles, petroleum products evaporation, natural gas, and various industrial sources. All measured average concentrations were presented in the article.

- *Munich, Germany* (Rappenglück & Fabian, 1998)*;*

In order to determine BTEX concentrations at two urban locations in Munich a semi-continues measurements were done using GC-FID system. For this aim, samples were collected from near to an industrial site and near to a railway station throughout October, 1993. Samples were collected using online GC-FID system within 30 minutes time intervals.

- *Paris, France* (Ait-Helal, et al., 2014)*;*

Primary and secondary VOCs were measured in Paris and sampling was conducted in two seperate sub-urban area and sampling period was determined as summer and winter campaigns in 2009. Air samples were collected with sorbent cartridges from 4 meters above the ground level. Collected samples were analyzed with GC-FID and HPLC-UV systems. Obtained average concetration values were submitted in the article.

- *Barcelona, Spain* (Filella & Penuelas, 2006)*;*

In this study, not only potential VOCs sources, but also daily, weekly, and seasonal changes in VOCs concetrations were investigated in a sub-urban site where is near to Barcelona. Samples were colleced in four different periods in a year so as to observe changes in VOCs concetrations with respect to meteorological conditions. Samples were collected using an online PTR-MS system and obtained results were reported in the article.

- *Los Angles, New York and Washington D.C.* (Baker, et al., 2008)*;*

In order to measured and define major NMHCs in 28 United Stated cities, for 5 weeks every summer from 1999 to 2005. Samples were collected with canisters and adequetly ventilated urban sites were selected for sampling, so as to prevent any point-source effect. Collected samples were analyzed with three different gas chramotgography system such as GC-FID, GC-MS and GC-ECD.

- *New Orleans, USA (Chung, et al., 2009);*

This study was conducted in a very large metropolitan area with various petroleum industries, which name is Lousiana where is near New Orleans, and in 2005 Hurricane Katrina accordingly landfall happened in there. And, in order to determine effects of the hurricane on the air qulity of the region air samples were collected with canisters and organic vapor monitors (OVMs) from 18 different zones where were away from local pollutants between October,2005 and February,2006. And, collected samples were analyzed with GC-MS system.

As it was stated earlier part of this section, this type of comparison studies can not be literally expressive for interpretation of obtained data set, yet it may help us so as to understand pollution degree of relevant provinces. When studies evaluated in this manner, according to Figure 4.6 it can be deduced that BTEX concetration ranges bewteen Kütahya and other studies around the world generally was large like other cities in Turkey. Only toluene concentration was relatively higher than other parts of the world, but toluene emissions commonly result from any solvent usage, as it was seen from the Figure 4.6, toluene concentration is higher at the rural station than at the urban station. After sampling period was started, a treatment plant was consturcted near to rural station, so it was thought that related construction workings may cause to this high toluene concentration in this station. And concentrations of other compounds were lower than measured concetrations in compared studies. BTEX concentrations generally depends on amount of automobiles, when it is compared with other parts of Turkey and world, there have not been so much automobiles around Kütahya. Accordingly, sampling locations and emission amounts cause differences in BTEX concetrations.

Same data set were shown in the Figure 4.6 (b) in a different way, and some categorical differences were determined. In this figure, same data set was used, but provinces which are in same continents were coded with same colors only. As it can be seen, Europe, Asia and North America is encoloured with green, yellow and dark blue respectively. Interestingly, concetrations change between continents. Measured concetrations from North American studies were lower than other continents. There may be several reasons of it. One of them may be different emission control strategies of all these continents. And, main reason may be related to sampling locations, sampling time, meteorological contditions, amount of automobiles, amount of industries, extreme conditions during sampling etc. However, it can be certainly said that pollution degree of Kütahya is lower than both other provinces of Turkey and the world.

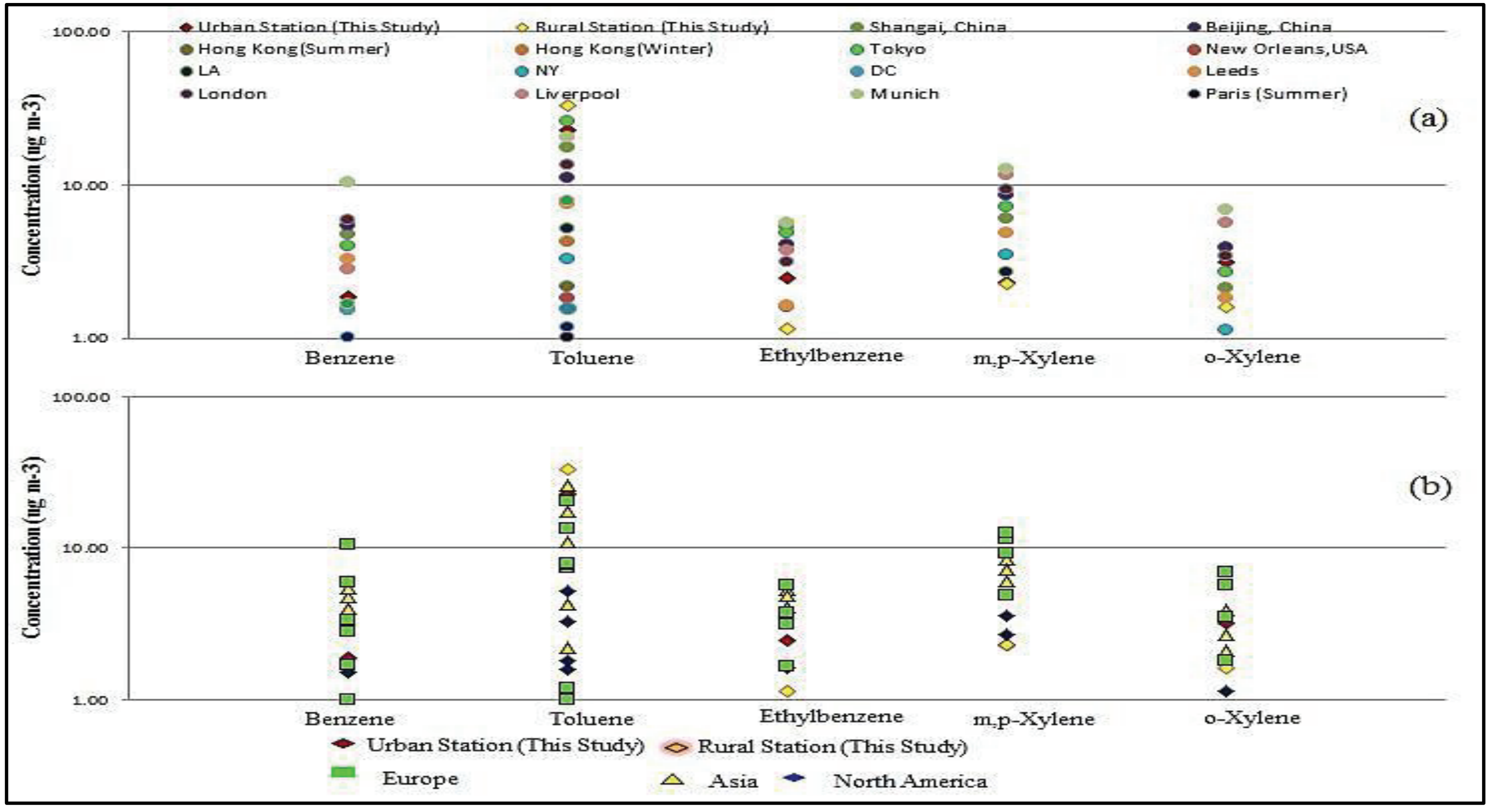


Figure 4.6 Comparison of average BTEX levels in rural and urban stations corresponding data from (a) other cities around the world and (b) relevant continents (Please note that same data set was used, only provinces which are in the same continents were coded with same colors)

4.4 Temporal Variations in Measured VOCs Concentrations

Several parameters affects VOCs concetrations and their atmospheric reactivity in the ambient air. For this reason, investigation of temporal variations of measured VOC concetration is an important step for making a comprehensive data interpretation.

VOCs concentrations may show important changes between especially summer and winter days due to several seasonal meteorological conditions, such as rainfall, high or low temperatures (Villanueva, et al., 2014). VOCs were much more effectively removed from ambient air by chemical reactions of VOCs with –OH radicals throughout summer due to higher temperature values and sunlight (Lee, et al., 2002). So, generally winter VOCs concentrations are higher than in summer.

In this study, temporal variations of VOCs concetrations were investigated in the following three sub-sections. Firstly, time-series plots were created and shot-term temporal variations were discussed. And then, weekday and weekend variations of concetrations were compared and evaluated. Finally, seasonal variations in VOCs concetrations were investigated, and also possible effects of meteorological conditions on concentrations were taken into considerations for all of the three sections.

4.4.1 Short-term variations of VOCs concentrations

In order to show episodic alterations in VOCs concentrations during sampling period, time series plots were prepared for all target compounds. Relevant figures that was prepared for selected VOCs from both urban and rural stations were provided in the Figure. 4.7.

All of time-series plots indicated apparent and sudden episodic changes in concentrations that are just as typically almost all environmental data sets. Transport patterns, increasing in emission amounts and sudden changes in meteorological conditions are main reasons of episodic variations for regional concentration measurements (Doğan, 2013). For example, due to alteration of wind direction, pollutants may be transported from their sources to sampling locations, and some measured concentrations show a sudden increase. Later on, a new clean air mass reaches from another wind sector, and the same concentrations may decrease abrubtly again. As a consequence, several episodes happens by these reasons commonly (Öztürk,et al., 2012 ; Kubilay & Saydam, 1995). In several studies in the literature, wind sector dependence was reported as main reasons of episodic variations in compounds atmospheric time-series (Xie & Berkowitz, 2006 ; Kim, et al., 2004 ; Doğan, 2013; Yurdakul, 2104). In addition to these factors, rainfall may be another reason of episodes. Rainfall can scavange gases in the atmosphere at different levels. Some gases, which are highly soluble in the water, can be scavanged effectively. Accordingly, atmospheric concentrations of soluble gases much more lower than concetrations of non-soluble gases in the atmosphere when it rains. Solubility of VOCs that was measured in this study is not very high, but it does not equal to zero at the same time. All of their solubility degree in water is different from each other. Thus, rainfall scavange all of target VOCs with different levels. Accordingly, each time series plots reflect all of these subjects.

As it was stated eralier, atmospheric pollutants showed sudden episodic changes in time series. In order to clarify main reason of these sudden changes in concetrations which can be seen in the Figure 4.7, meteorological parameters, especially variations of mixing height and ventiletion coefficient, wind direction, rainfall and temperature changes were considered. There were not any abrupt changes in temperature, rainfall amounts or wind direction. But, there were remarkable changes in mixing height and ventiletion coefficient values in the day that concentrations change suddenly comparing to former or the next day. Consequently, it was decided that changes in meteorological parameters may be the main reason of the related episodic changes in concentrations.

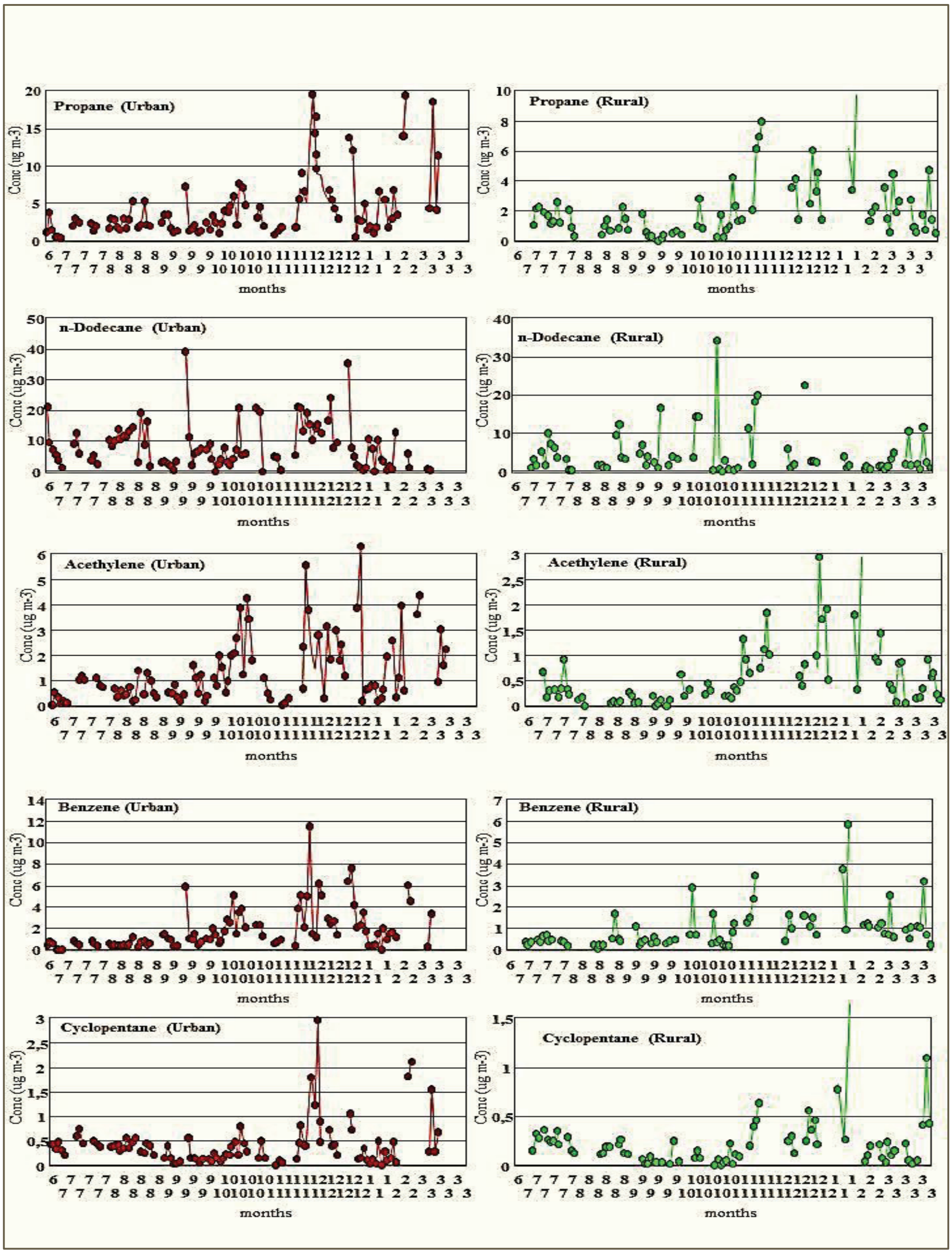


Figure 4.7 Time series plots of selected VOCs in urban and rural stations

4.4.2 Weekday/Weekend variations of VOCs concentrations

A variety of studies in the literaure have showed that VOCs concetrations are mostly higher on weekdays than at the weekends, due to increasing in amount of human activities on weekdays (Martinez G.F., et al., 2001). On weekdays, measured alkanes, alkens and aromatic hydrocarbons showed a double peak pattern due to traffic loadings in a day (Cai, et al., 2010). More precisely, concentrations of all pollutants which emit due to traffic emissions is higher in weekdays than at the weekends generally. Because, on weekdays people must use much more motor vehicles in order to go to work or their any other requirements. Accordingly, especially in urban sites weekdays must be more mobile than weekends and it means increasing in emissions, particulary traffic related emissions.

In this study, average weekday(WKDY) and weekend(WKEND) concentrations of VOCs that were measured in urban and rural stations and WKDY/WKEND ratios were shown in the Figure 4.8 and Figure 4.9. In urban station, average concentrations of all VOCs, except four of them, were higher in WKDAY than WKEND Thus, most of the WKDY/WKEND ratios are greater than 1. Only, WKEND concentrations of 1,2,3-trimethlybenzene, ethane, 1,2,4-trimethylbenzene and n-propylbenzene were higher, or very close to WKDY concentrations. Accordingly, WKDY/WKEND ratios of urban station changed betweem 0.7 and 2.3, and average value was calculated as 1.4 ±0.4. This is not an unexpected result. As it was stated earlier, traffic is an important VOCs emission source as well as solvent usage or industrial processes. For example, propane, iso-butane/n-butane, acethylene or BTEX compounds are the most common traffic related VOCs (Tsai et al., 2006), and all of them were measured higher in weekdays than at the weekends. Because of this, it was thought that due to low amount of traffic activities at the weekends, VOCs concetrations were lower at that days than weekdays. WKDY/WKEND ratio of urban station, which was calculated as 1.4 ±0.4, clarified that traffic related emissions in weekdays was 1.4 times greater than at the weekends.

When related results from rural station was examined, different outcomes were obtained. Concentrations of almost half of target VOCs (22 out of 51) were higher in weekdays than measured at the weekends and average WKDY/WKEND ratio was calculated as 1.0 ± 0.5. Concetrations of measured VOCs in rural station are determined by pollutant transportation and local activities effect them little or nothing. Meteorological conditions are much more determinative factors than changes in emission amounts around the sampling location on concentrations of transported pollutant. All of these situations showed us an expected result that were not significant differences between WKDY and WKEND concentrations in rural station. However, interestingly, only WKDY/WKEND ratio of 2,3,4-trimethylpentane is very high (5.25), comparing to others. 2,3,4-trimethylpentane emits to the atmosphere from evaporative sources and also through solvent usage. Accordingly, there must be a factor related to evaporative or solvent sources which increase concentrations of the compound in weekdays. Actually all other VOCs which emit from similar sources were controlled, but similar situation was not observed. As it was stated in previous sections, after starting sampling period, a treatment plant were established near to rural station, and workers work for construction of the plant in weekdays mostly. Accordingly, high value of WKDY/WKEND ratio of 2,3,4-trimethylpentane may be affected by related construction works around the station.

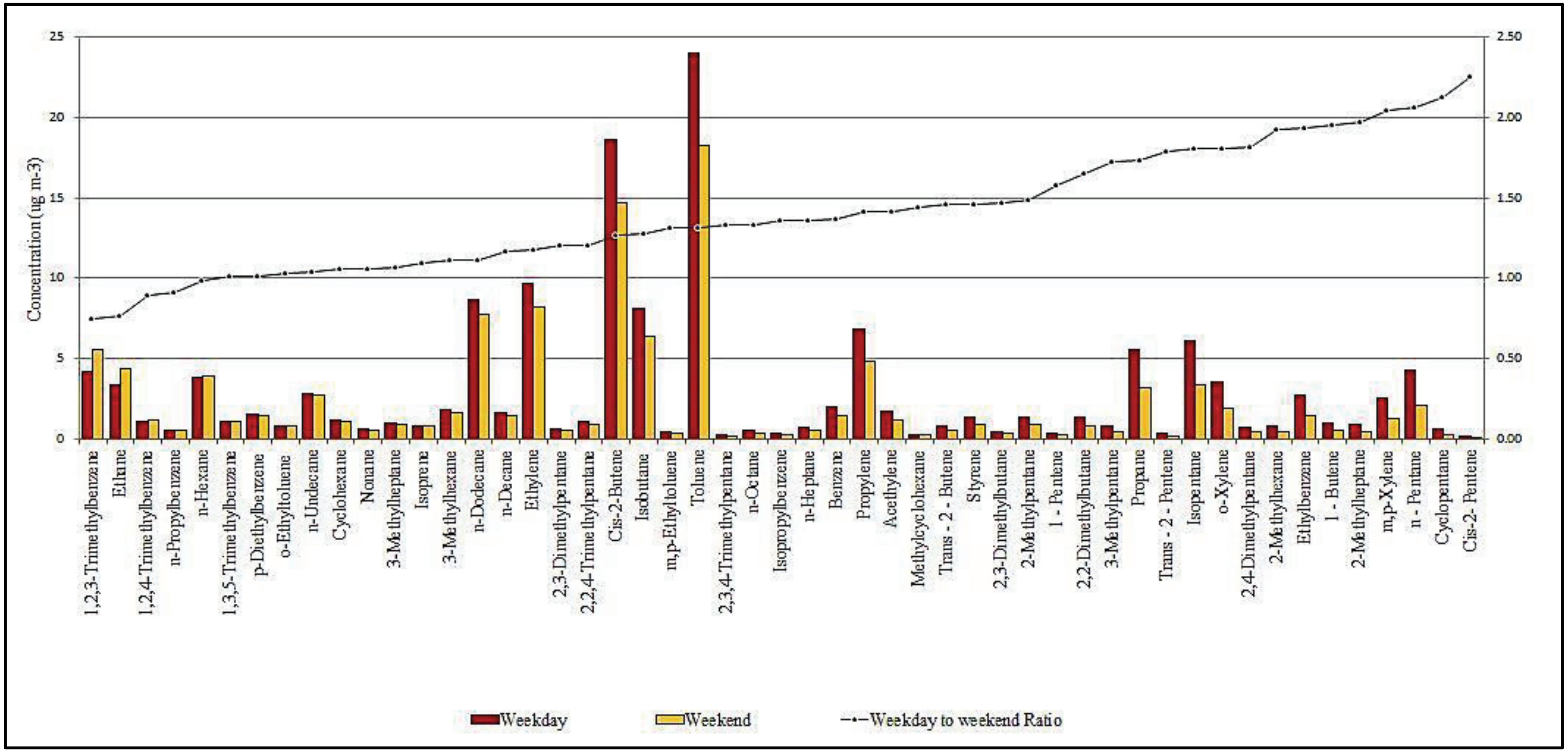


Figure 4.8 Weekday-to-weekend ratios of VOCs at urban station

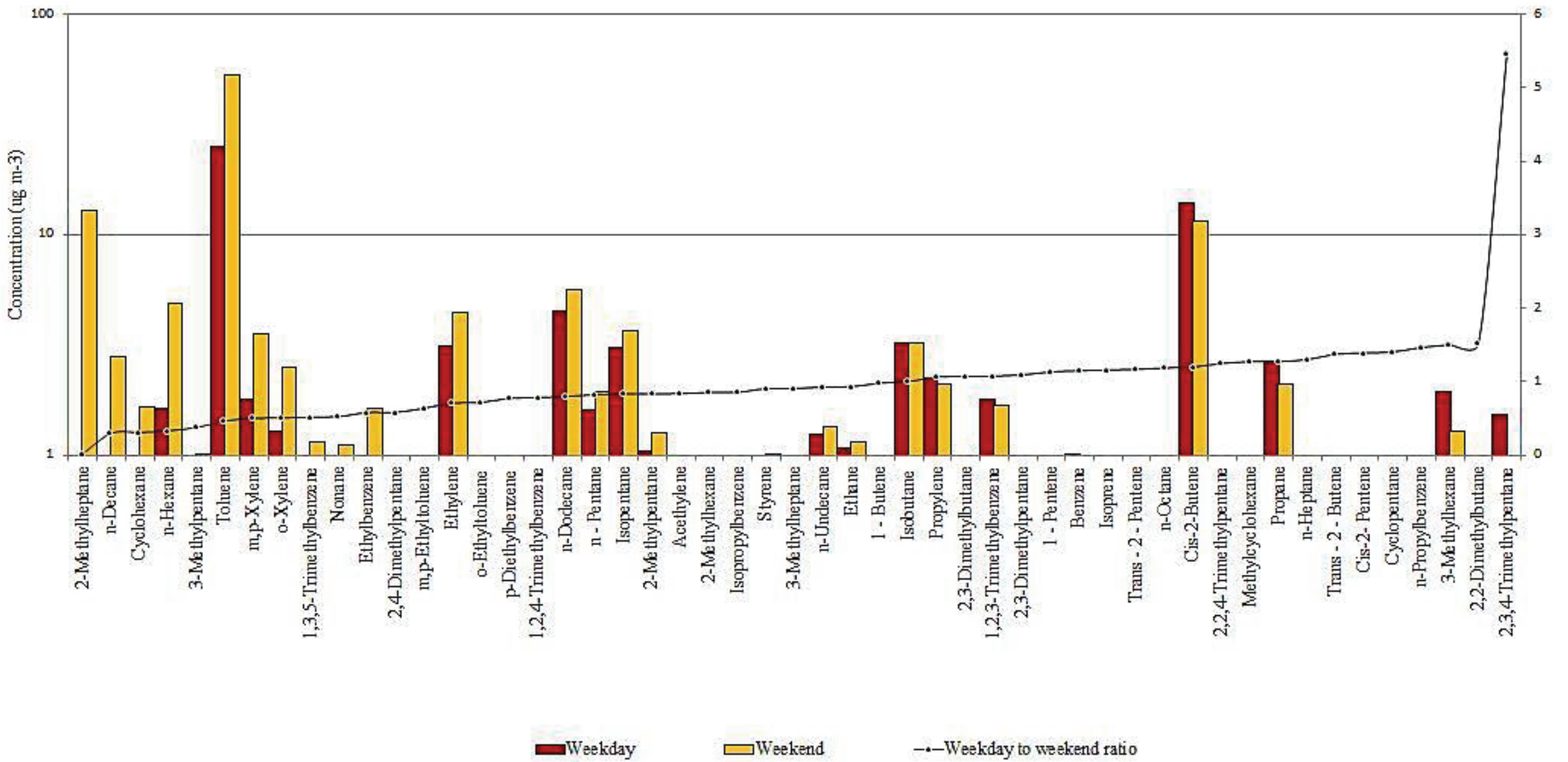


Figure 4.9 Weekday -to-weekend ratios of VOCs at rural station

4.4.3 Seasonal variations of VOCs concentrations

This part of the study was prepared in order to investigate seasonal variations of VOCs concetrations to be able to estimate their sources, transport or scavenging processes. Seasonal variations effects VOCs concetrations directly (Odat, 2009 ; Balogun, et al., 2015 ; Ho, et al., 2004). As it was stated earlier, various meteorological parameters, such as wind speed and direction, mixing height, temperature, humidity, ventilletion coefficient etc., can change concentration of VOCs and any other pollutants in the atmosphere, and traditionally all of these meteorological parameters change according to seasonal conditions (Civan, et al., 2015 ; Boissard, et al., 2001).

Sampling was conducted in summer (June, July, August, and September) and in winter (October, November, December, January, February, and March) seasons. All of measured average and median concetrations in these months were summerized under the groups of summer and winter seasons in the Table 4.4 and Table 4.5 and selected VOCs were shown in the Figure 4.10 and Figure 4.11 in order to compare montly diffrences of concetrations for urban and rural stations respectively. Accordingly, summer to winter (S/W) ratios of concetrations of all measured VOCs were submitted in the Figure 4.12.

In both stations, almost all of measured seasonal VOCs concentrations were higher in winter than in summer as expected. Actually, this result has been obtained in many different studies for many years. There may be two main reasons of this outcome ; higher emission amounts, or decreasing of mixing height and ventilation coefficient in winters. If it is necessary to summerize briefly, it can be stated that mixing height is the principal indicator of the vertical ventillation ,and also an important meteorological parameter. Another important parameter is wind speed. Furthermore, these two important parameters generate much more significative marker to explain increasing in pollutant concentrations in winter seasons, namely ventilation coefficient (Goyal & Rao, 2007 ; Rao, et al.,2003 ; Doğan, 2013). And, mixing height and ventilation coefficient are lower in winter when they compared to summer measurements, and this cause to decrease of assimilative capacity and responsively cause to increase in pollutant concetrations in the atmosphere(Genç, et al., 2010).

Additionally, due to higher temperature and effect of sunlight, reaction rates increse in summer, and VOCs were removed from atmosphere (Lee, et al., 2002). Correspondingly, it is easy to comprehend that even emissions amounts are the same in two seasons, winter concetrations of air pollutants are commonly higher than summer concetrations due to lower mixing height and reaction rates in winter.

In the Figure.4.12 summer-to-winter (S/W) ratios were provided to observe variations in concetrations between two seasons more precisely. Y-axis was arranged in logaritmic-scale, for this reason summer bars which represent measured average summer concetration appeared very small in contrast to winter bars. In urban station, just 10 of all target VOCs, including p-diethlybenzene, n-undecane, 2,2,4-trimethylpentane, n-decane, 3-methylhexane, n-dodecane, 1,2,3-trimethylbenzene, 1,2,4-trimethlybenzene, 3-methylheptane, and 2,4-dimethylpentane had S/W ratios greater than or equal to 1.0. That means, related VOCs emission amounts must be considerably high in the summer season thatn that of in winter.

As for rural station, 9 of all target VOCs had S/W ratios greater than 1.0, including p-diethylbenzene, n-undecane, 2,2,4-trimethylpentane, n-decane, 1,2,3-trimethlybenzene, 1,2,4-trimethylbenzene, styrene, and n-pentane. There are some differences between the reason of changes in S/W ratios that were calculated in urban and rural station. Emission is out of question in rural sites mostly, and due to the fact that differences in concentrations between summer and winter cannot result from emission changes in there. Seasonal variations on the side of dominant wind direction may cause more frequent transportation of pollutants, so concentrations of pollutants that are measured in summer may increase in rural station.

Trimethylbenzenes, trimethylpentanes and n-pentane are emitted from solvent usages, while styrene represents industrial emissions due to used for polystyrene, plastics and resins production mostly, and it is released to the atmosphere from various industries (Wadden,et al., 1995). Similary, n-decane and other heavy VOCs are emits from industrial sources (Watson, et al., 2001). For this reason, it is not a mistake, if it is thought that differences between pollutant concetrations of summer and winter in rural station result from air masses from residental areas and from high emitted industrial areas, although there are not any local sources. There is not an important differences in S/W ratios of some VOCs which had higher concentrations in winter season due to their high concetrations around their source locations.

Summer concetration of 6 of almost 10 VOCs in both stations, including p-diethylbenzene, n-undecane, 2,2,4-trimethylpentane, n-decane, 1,2,3-trimethylbenzene, and 1,2,4-trimetlhybenzene, was greater than winter concentrations. When look at these 6 compounds, it was understand that almost all of them used as solvent. So, measured greater summer concetrations is an expected result. Actually, this is an important outcome that attained. Due to lack of emission sources which effect concetration of VOCs directly in rural sites, observed seasonal changes represent approximately seasonal changes in regions where convection occur. Accordingly, it was decided that temporal variations in rural stations were similar to temporal variations in urban stations with little differences.

Monthly average concetrations of some selected VOCs in both urban and rural stations were provided in the Figure 10 and Figure 11. Two of the selected VOCs in urban stations, benzene and acetylene, are well known tracers of gasoline fueled motor vehicles (Watson, et al., 2001), whereas other two are heavy hydrocarbons compounds, namely 3-methylhexane and 2,2,4-trimethlypentane, and they are released from mostly diesel engine motor vehicles, but it is known that all of these VOCs used as solvent or used for solvent enrichment in various areas (Wadden, 1995).

Benzene and acethylene concetrations were low in summer months in Turkey as well as summer patterns of any other parts of the world. This pattern was dominated by meteorological conditions. It was stated in the section 4.1, mixing height reached up to 2500 m in summer months, whereas this value decreased to 1000 m in winter months in Kütahya. If it is thought that pollutants are diluted in a box which has 10 km x 10 km surface lenght and its height is equal to mixing height in Kütahya, differences between volumetric amounts of pollutants of summer and winter months will be equal to differences between the volume of boxes. In other words, pollutants are two and a half times as much diluted in summer. Accordingly, it is expected that summer concetrations are approximately two and a half times lower than winter concetrations. However, it must be note that this argument is applicable fpr only

VOCs that have same emission amounts in summer and winter. For some VOCs, due to higher emission amounts which result from solvent usage in summer, emission amounts come into prominence.

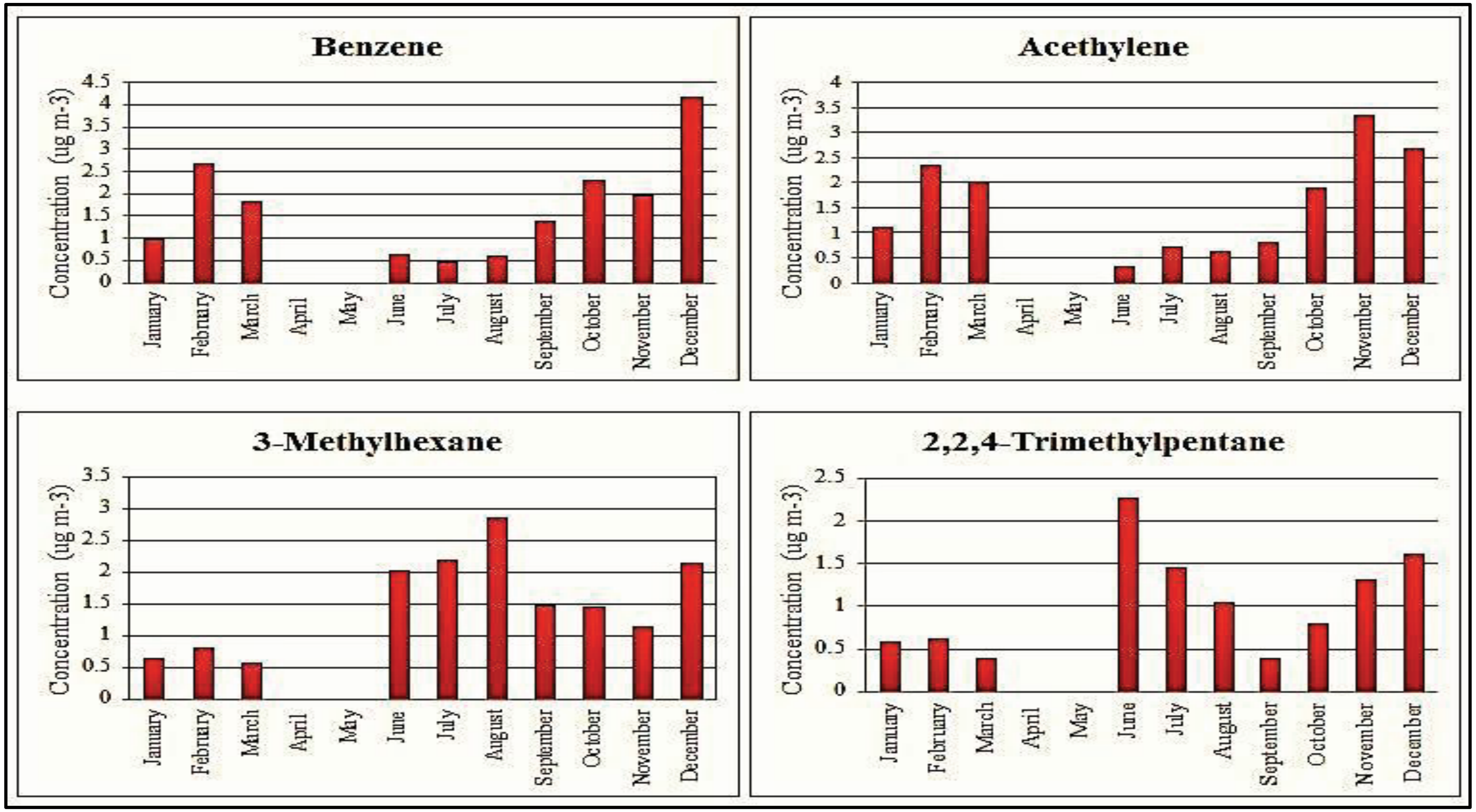


Figure 4. 10 Monthly average concentrations of selected VOCs at urban station

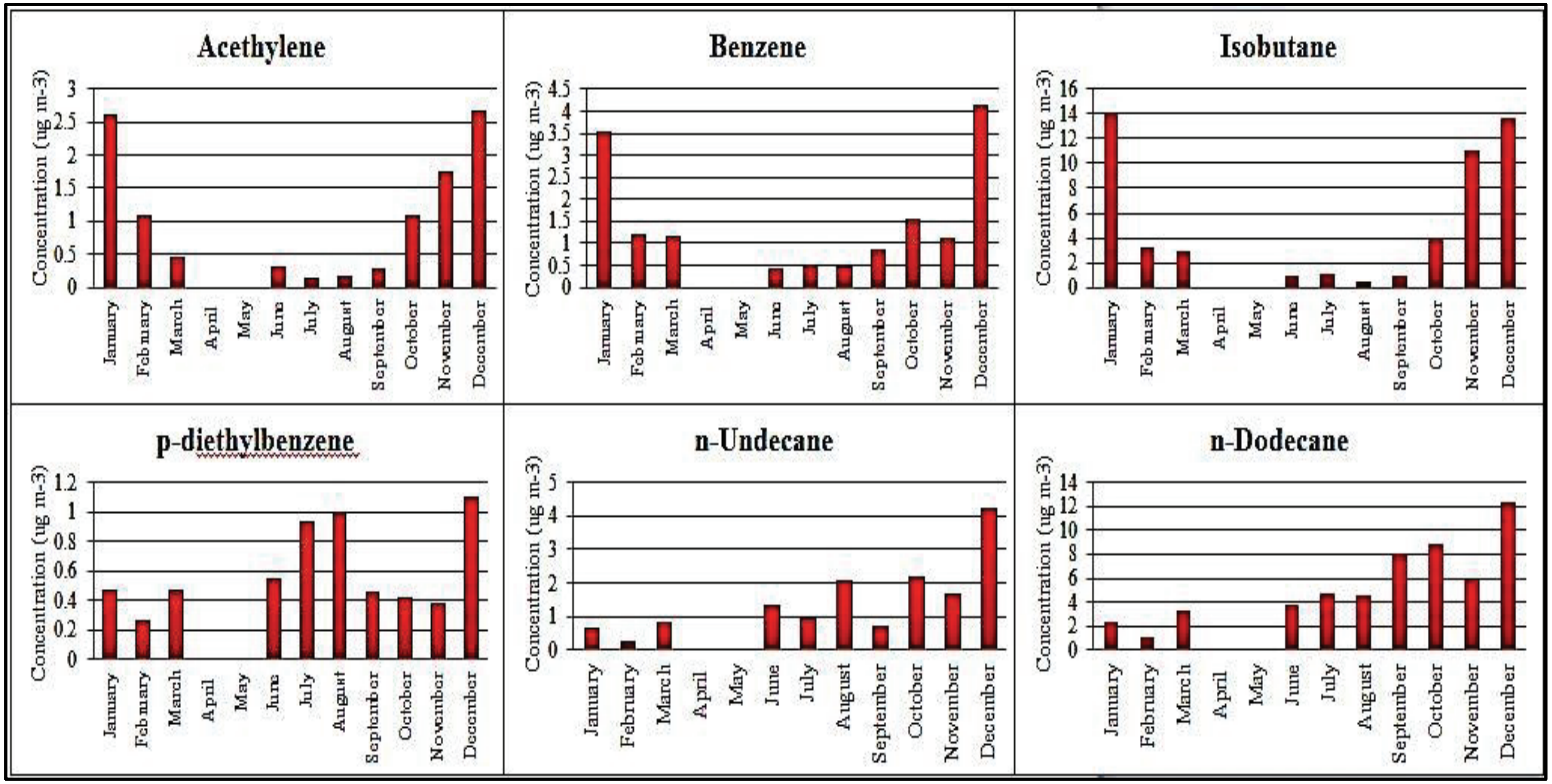


Figure 4. 11 Monthly average concentrations of selected VOCs at rural station

In addition to benzene and acthylene, two samples of diesel engine motor vehicle markers (Watson,et al.,2001) and also solvent ingredients (Wadden,et al.,1995), which are 3.-methylhexane and 2,2,4-trimethylpentane, were shown in the Figure 4.10. As it was stated previously, this study was conducted between June,2014 and March,2015. Accordingly, samples were not collected in April and May. Average monthly concetrations in summer of these two heavy hydrocarbons were equal to or even greater than average monthly concentrations in winter as any other solvent markers. This pattern shows that heavy VOCs that were measured in urban station is effected both emissions arising from traffic and solvent evaporation.

As for rural station, general patterns is not very dissimilar to case in urban station. To show this, Figure 4.11 was prepared using some selected VOCs. Acethylene, benzene and isobutane is gasoline markers (Watson,et al., 2001). All of average monthly summer concentrations were lower than winter concetrations as in urban station. Furthermore, monthly changes in measured concetrations of heavy hydrocarbons were not very different as in urban station. And this situation confims the reached conclusions about effects of seasonal changes on VOCs concetrations. Although, there were not any specific emission source of VOCs around rural station, seasonal changes were not very different from the urban part of the city. Because, observed temporal changes in rural stations represent temporal variations in the region from where transported pollutants. Due to important emission source regions were generally residental areas, it was not observed very specific changes between temporal variations in both stations. The critical point must be noted here that the similarity between temporal variations in urban and rural stations do not mean that VOCs measured in rural station were not transported from urban site of Kütahya. Because, temporal variations of VOCs in any residental area are not very different from urban station.

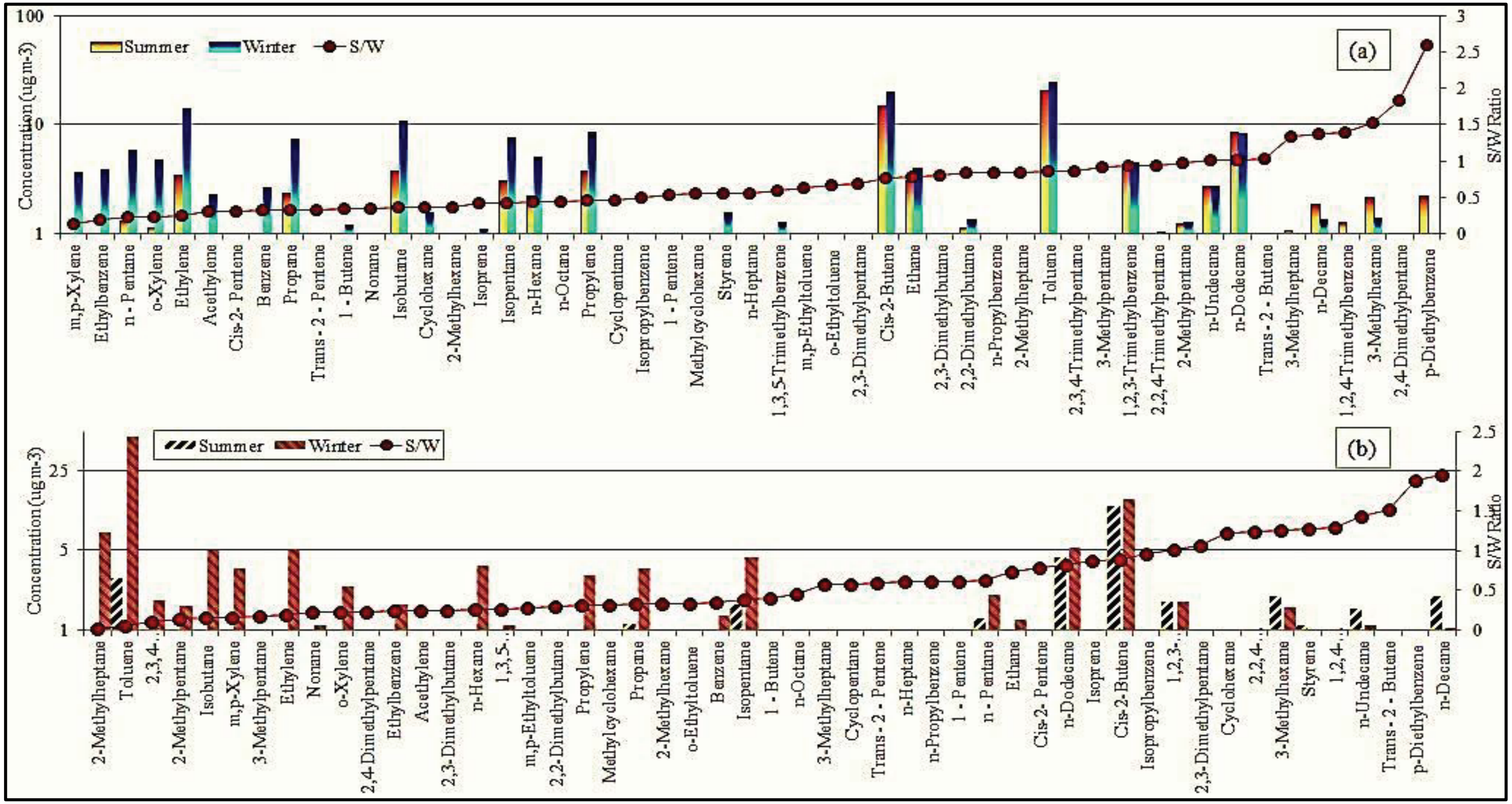


Figure 4.12 Summer, winter and summer to winter ratios of VOCs measured at (a) urban station, and (b) rural station

Table 4.3 Summer and winter season concetrations of measured VOCs at urban station

	Summer			Winter		
	Mean	**Med.**	N	**Mean**	**Med.**	N
Ethane	3.09±2.12	3.07	41	3.99±4.22	2.45	50
Ethylene	3.46±2.30	3.12	41	14.1±13.8	10.08	51
Propane	2.36±1.36	2.07	41	7.32±7.66	4.48	51
Propylene	3.83±7.48	2.15	41	8.47±8.95	6.18	52
Isobutane	3.80±2.85	3.05	40	10.7±11.1	7.75	52
Acethylene	0.70±0.44	0.56	41	2.31±2.20	1.79	51
Trans - 2 - Butene	0.73±0.44	0.80	41	0.71±0.88	0.37	51
1 - Butene	0.40±0.25	0.34	41	1.21±1.29	0.75	52
Cis-2-Butene	15.10±8.1	16.70	41	20.0±17.3	16.31	51
Cyclopentane	0.33±0.17	0.35	41	0.71±1.07	0.30	51
Isopentane	3.11±3.69	1.85	41	7.56±9.29	3.65	51
n - Pentane	1.33±2.00	0.56	41	5.9±20.40	1.60	52
Trans - 2 - Pentene	0.14±0.11	0.12	41	0.43±0.54	0.23	50
1 - Pentene	0.24±0.18	0.19	41	0.45±0.52	0.25	50
Cis-2- Pentene	0.05±0.06	0.04	37	0.17±0.37	0.08	49
2,2-Dimethylbutane	1.13±1.09	0.82	41	1.35±1.54	0.89	52
2,3-Dimethylbutane	0.37±0.66	0.21	41	0.46±0.55	0.27	51
2-Methylpentane	1.24±3.86	0.43	41	1.28±1.46	0.77	50
3-Methylpentane	0.66±1.99	0.27	41	0.72±0.90	0.36	43
Isoprene	0.45±0.32	0.41	41	1.10±1.46	0.44	52
n-Hexane	2.25±7.43	0.55	40	5.13±9.39	1.40	50
2,4-Dimethylpentane	0.88±4.49	0.12	40	0.49±0.55	0.25	52
Benzene	0.86±0.91	0.67	41	2.68±2.20	2.11	52
Cyclohexane	0.56±1.03	0.23	41	1.56±2.66	0.59	52
2-Methylhexane	0.36±0.37	0.18	40	0.99±1.42	0.46	52
2,3-Dimethylpentane	0.48±0.44	0.43	41	0.71±0.83	0.43	51
3-Methylhexane	2.15±1.77	1.86	41	1.41±1.30	1.02	52
2,2,4-Trimethylpentane	0.98±0.87	0.67	41	1.05±0.77	0.83	52
n-Heptane	0.44±0.54	0.24	41	0.79±0.80	0.58	52
Methylcyclohexane	0.19±0.20	0.15	41	0.34±0.32	0.23	52
2,3,4-Trimethylpentane	0.20±0.29	0.09	40	0.23±0.21	0.16	52
Toluene	20.78±88.69	1.81	38	24.5±42.2	8.62	51
2-Methylheptane	0.73±2.36	0.26	41	0.86±1.48	0.40	44
3-Methylheptane	1.08±2.13	0.17	41	0.81±1.10	0.37	51
n-Octane	0.28±0.35	0.13	40	0.63±0.74	0.40	52
Ethylbenzene	0.72±1.34	0.33	41	3.87±11.5	0.95	52
m,p-Xylene	0.51±1.40	0.20	39	3.67±11.4	0.74	52
Styrene	0.87±1.02	0.47	41	1.59±2.07	0.88	52
o-Xylene	1.15±1.87	0.69	41	4.8±12.94	1.30	52
Nonane	0.29±0.25	0.21	41	0.83±1.27	0.38	52
Isopropylbenzene	0.22±0.34	0.12	39	0.45±0.53	0.26	52
n-Propylbenzene	0.46±0.67	0.17	41	0.55±0.89	0.24	51
m,p-Ethyltoluene	0.27±0.39	0.07	21	0.43±0.48	0.28	34
1,3,5-Trimethylbenzene	0.75±1.12	0.43	40	1.29±1.81	0.77	51
o-Ethyltoluene	0.66±1.23	0.34	40	0.97±1.25	0.47	50
1,2,4-Trimethylbenzene	1.28±2.17	0.42	41	0.92±1.00	0.61	51
n-Decane	1.88±2.87	0.70	40	1.38±2.32	0.60	51
1,2,3-Trimethylbenzene	4.23±6.00	2.37	41	4.56±4.61	3.36	52
p-Diethylbenzene	2.26±2.12	1.33	41	0.87±0.78	0.58	51
n-Undecane	2.78±2.13	2.04	41	2.75±2.82	1.65	52
n-Dodecane	8.59±6.97	7.38	41	8.44±7.84	5.75	52

Table 4.4 Summer and winter season concetrations of measured VOCs at Rural station

	Summer			Winter		
	Mean	**Med**	**N**	**Mean**	**Med**	**N**
Ethane	0.89±0.75	0.66	27	1.22±1.42	0.75	45
Ethylene	0.98±0.62	0.87	29	5.16±5.24	3.54	45
Propane	1.13±0.72	1.02	30	3.41±4.90	1.91	45
Propylene	0.94±1.39	0.56	30	3.04±3.89	1.62	45
Isobutane	0.77±0.79	0.61	30	4.91±7.44	2.33	44
Acethylene	0.23±0.21	0.18	29	0.95±1.09	0.60	45
Trans - 2 - Butene	0.48±0.31	0.49	28	0.32±0.51	0.19	42
1 - Butene	0.28±0.21	0.19	29	0.70±1.00	0.31	45
Cis-2-Butene	12.27±9.4	7.75	30	13.8±13.5	9.44	44
Cyclopentane	0.17±0.11	0.16	29	0.30±0.48	0.18	44
Isopentane	1.65±3.42	0.65	30	4.36±10.2	1.88	44
n - Pentane	1.26±2.56	0.37	30	2.01±4.32	0.81	44
Trans - 2 - Pentene	0.11±0.11	0.09	29	0.19±0.36	0.09	43
1 - Pentene	0.17±0.14	0.14	29	0.29±0.30	0.18	44
Cis-2- Pentene	0.05±0.10	0.02	29	0.07±0.07	0.04	45
2,2-Dimethylbutane	0.19±0.18	0.15	30	0.65±1.69	0.21	44
2,3-Dimethylbutane	0.09±0.09	0.04	30	0.35±0.86	0.19	43
2-Methylpentane	0.22±0.20	0.11	24	1.63±3.92	0.52	41
3-Methylpentane	0.14±0.13	0.11	28	0.86±1.60	0.30	41
Isoprene	0.36±0.25	0.32	30	0.41±0.80	0.17	44
n-Hexane	0.92±0.82	0.64	28	3.61±6.87	1.64	44
2,4-Dimethylpentane	0.14±0.16	0.10	30	0.59±1.18	0.19	43
Benzene	0.47±0.30	0.41	30	1.33±1.11	1.09	44
Cyclohexane	0.94±4.05	0.12	29	0.77±1.08	0.38	44
2-Methylhexane	0.21±0.18	0.20	29	0.63±0.96	0.39	44
2,3-Dimethylpentane	0.40±0.26	0.37	27	0.37±0.36	0.26	43
3-Methylhexane	1.98±1.64	1.30	30	1.57±2.09	0.95	44
2,2,4-Trimethylpentane	0.75±0.48	0.75	30	0.60±0.41	0.57	44
n-Heptane	0.40±0.23	0.33	30	0.66±0.93	0.39	44
Methylcyclohexane	0.11±0.08	0.09	30	0.34±0.43	0.21	44
2,3,4-Trimethylpentane	0.19±0.31	0.11	30	1.82±5.53	0.09	42
Toluene	2.86±5.50	1.27	21	49.9±87.2	14.49	38
2-Methylheptane	0.16±0.13	0.16	27	7.09±38.5	0.22	39
3-Methylheptane	0.29±0.60	0.10	30	0.51±0.63	0.30	43
n-Octane	0.25±0.17	0.21	30	0.54±0.60	0.36	44
Ethylbenzene	0.40±0.51	0.26	30	1.66±2.69	0.54	44
m,p-Xylene	0.54±0.89	0.28	29	3.44±6.25	0.88	44
Styrene	1.08±1.60	0.63	30	0.85±0.88	0.56	44
o-Xylene	0.53±0.57	0.34	30	2.39±3.99	0.84	43
Nonane	0.24±0.20	0.18	30	1.09±1.94	0.36	44
Isopropylbenzene	0.23±0.28	0.16	28	0.24±0.22	0.19	43
n-Propylbenzene	0.26±0.74	0.09	30	0.43±0.54	0.29	43
m,p-Ethyltoluene	0.09±0.09	0.05	6	0.30±0.34	0.18	27
1,3,5-Trimethylbenzene	0.29±0.29	0.20	30	1.08±1.65	0.50	43
o-Ethyltoluene	0.20±0.20	0.12	26	0.58±0.64	0.37	43
1,2,4-Trimethylbenzene	0.73±0.67	0.51	29	0.57±0.64	0.32	43
n-Decane	2.00±6.21	0.44	30	1.02±1.51	0.34	43
1,2,3-Trimethylbenzene	1.77±2.16	1.22	30	1.76±1.84	1.20	43
p-Diethylbenzene	0.81±0.97	0.58	30	0.43±0.45	0.33	41
n-Undecane	1.56±2.09	0.76	30	1.09±1.11	0.70	43
n-Dodecane	4.31±3.81	3.44	30	5.23±7.30	2.08	43

4.5. Effect of local meteorology on measured VOC concentrations at urban and rural stations

In the previous parts of the study, effects of meteorological conditions on VOCs concetrations were stated. And, in this section effects of related parameters on concentrations were investigated and showed in prepared figures in more detail.

Local meteorology effects measured concentrations of any air pollutants significantly as well as emission amounts, especially in urban locations. On the other hand, convection of air pollutants from emission sources have an important effect on concetrations of pollutant in the atmosphere . However, this factor is more important for rural sites than urban sites due to local emissions which can completely cover the effects of remote emissions (Kindap,et al., 2006).

4.5.1 Effect of temperature on measured VOC concentrations

Temperature may affect measured VOCs concentrations in two ways. Firstly, reaction rates of oxidation reactions increase with high temperatures and VOCs removed from the atmosphere (Na & Kim, Chemical mass balance receptor model applied to ambient C2-C9 VOC concentration in Seoul, Korea: effect of chemical reaction losses, 2007). So, due to temperature dependence of oxidation reactions, VOCs show a decrease in concentrations that was measured in summer. Correspondingly, concentrations of VOCs will be higher in winter than summer, even if emission amounts are the same in two seasons.

Secondly, due to increase in evaporation rates of some VOCs in summer, which are especially solvent related compounds, concentrations of them look like increasing with high temperature. Consequently, each VOCs may show different patterns with temperature variations. In this study, selected VOCs were provided in Figure 4.13a and b in order to show their behaviours according to dependence on temperature differences. VOCs were divided into two groups. First one shows a decrease in concentrations with increasing temperature. Ethylene, propane, acethylene and m,p-xylene were examples for this group. They are known as the most common traffic related VOCs, except ethylene and propane (Yurdakul, 2104). So, the main reason of this change can not be related to changes between temperatures. This change mostly results from increases in mixing height and ventilation coefficient values in summer, at the same time when temperature is high.

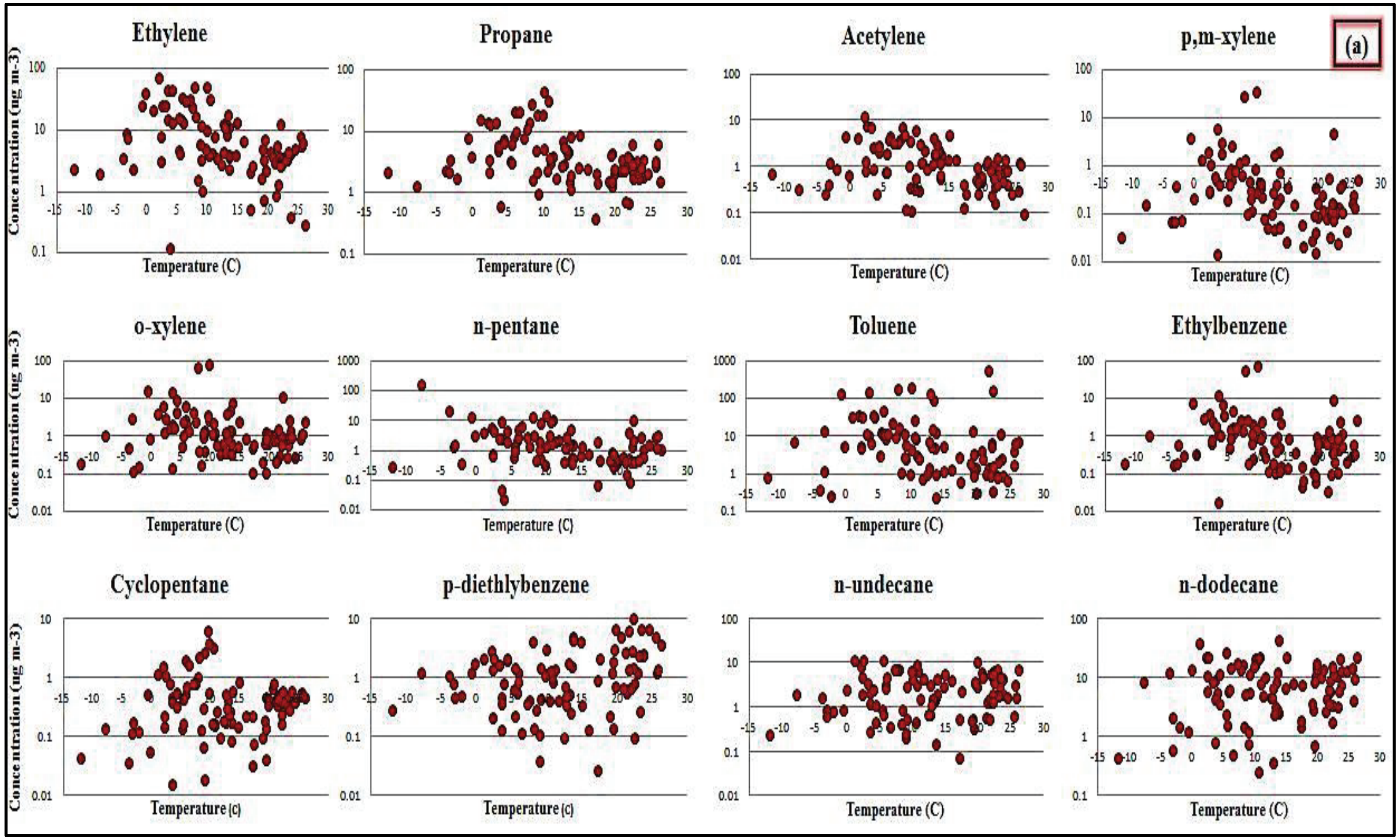


Figure 4.13 a Variation of VOC concentrations with temperature at urban station

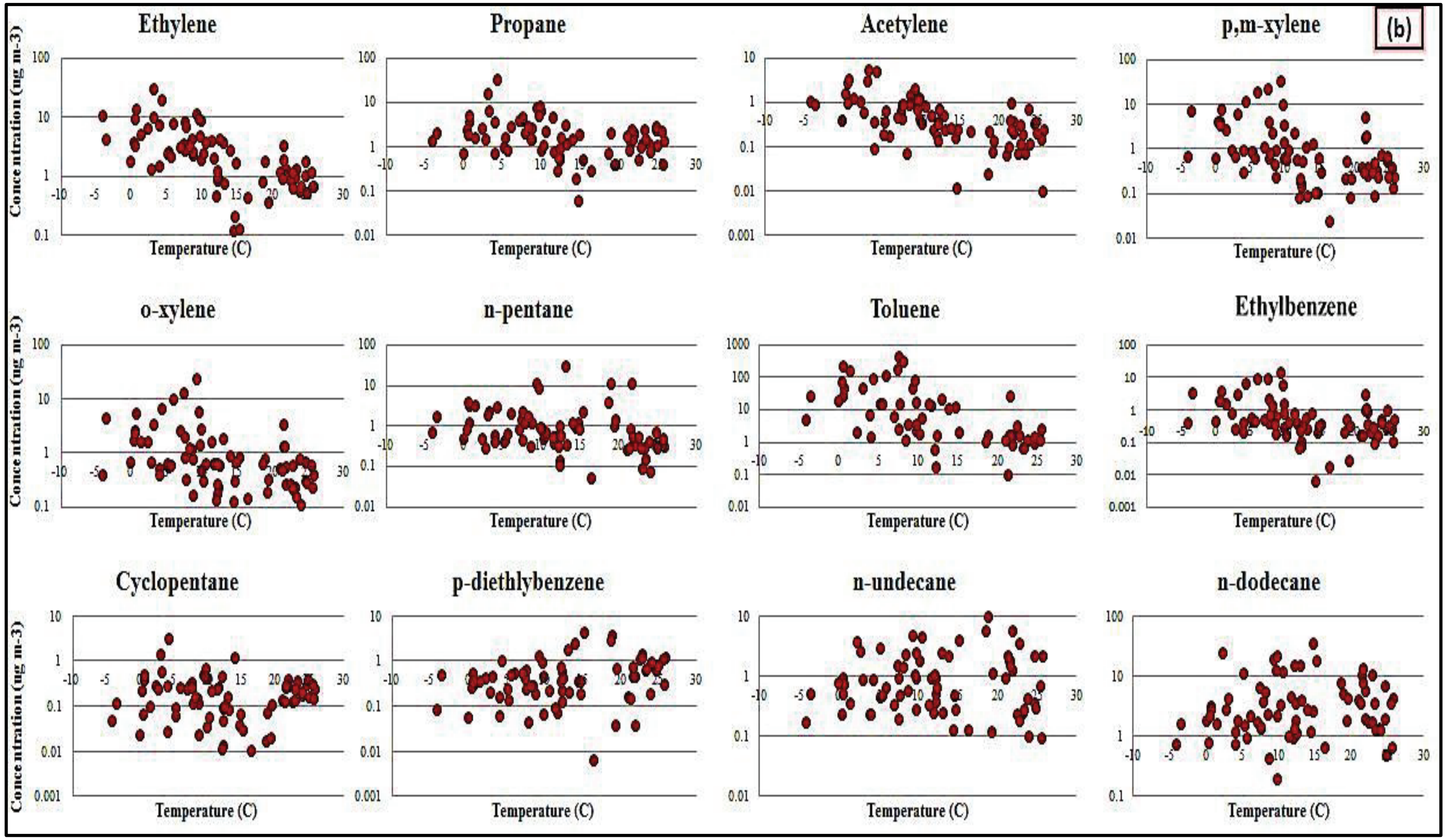


Figure 4.13 b Variation of VOC concentrations with temperature (b) at rural station

Ethylene and propane, which are in the first group, are released to atmosphere due to natural gas usage (Yurdakul, 2104). According to Environmental Status Report for Kütahya in 2014, natural gas have been used in all public buildings and 68% of residental areas of the city in recent years. Due to heating purposes, natural gas related emissions are higher in winter than summer. Although, mixing height did not change seasonally, variations of these compounds with temperature would be in this manner quite likely. This variation pattern is not acceptable only for mentioned VOCs, concentration of a majority of target compounds decrease with increasing temperature.

Concentrations of the second group of selected VOCs do not show an explicit variation with temperature. Cyclopentane, p-diethylbenzene, n-undecane and n-dodecane represent this second group in the Figure 4.16. These VOCs are used as solvent in different areas. Due to high evaporation rates in summer, emission of these solvent related compounds are expected to be higher in summer than winter. Because of this, it is decided that higher mixing height values in summer are not sufficient to decrease concetrations of these compounds.

In addition to these two groups, some compounds,such as toluene, ethylbenzene, o-xylene and n-pentane, show a combined behaviour of first and second group. These concentrations were determined by both traffic and solvent related emissions. Correspondingly, concentrations of these VOCs neither showed a distinct decreasing with temperature like traffic related compounds, nor showed a behaviour like solvent dominated VOCs. This situation is due to close contributions of traffic and solvent dominated emissions on related VOCs concentrations.

As it can be seen from the Figure 4.16 (a) and (b) that classified groups of VOCs showed same behaviours with respect to temperature variations in urban and rural stations. If concentration of VOCs decrease with increasing temprature or did not show a distinct behaviour in urban station, similar changs were observed in the rural station. Although, this result may appear interesting at first sight, it is significative for urban station. Emission changes with temperature can be anticipated in urban areas due to existence of emission sources. However, there are not any specific emission sources near rural station. Because of this, making a mention of seasonal variations of emissions and also variations of concentrations do not constitute a meaningful whole sufficiently. It is necessary to pay attention to a point that concentrations of VOCs that were measured in rural station do not generated in there. They transport to rural station from somewhere. During this transportation, air masses passing over the several small, or large settlements. And, it was thought that VOCs that measured in rural station from there. Temperature dependence of VOCs in all settlements are approximately similar to each other, so similar variations were observed in both urban and rural stations.

4.5.2 Effect of wind speed on measured VOC concentrations

As it was stated eralier a few times, two important meteorological mechanism effect pollutant concentrations in the atmosphere which are horizontal and vertical ventilation(Şen,1998). And, wind speed is an important indicator of horizontal ventillation around sampling locations (Yang, et al., 2011).

VOCs and also other atmospheric pollutants that are released into the atmosphere from urban locations, move away from there with two major mechanism. As it was stated eralier a few times, two important meteorological mechanism effect pollutant concentrations in the atmosphere which are horizontal and vertical ventilation(Sen, 1998). Vertical ventilation which means convective stability of the atmosphere, and mixing height is the main indicator of it. Another mechanism is horizontal ventillation and, wind speed the main indicator of it around sampling locations (Yang, et al., 2011). I is expected that air pollutants can be transported from urban locations with increasing wind speed. Correspondingly, this situation cause to decreasing of concentrations when wind speed increases.

In order to indicate variations of selected VOCs concentrations with wind speed Figure 4.14 was prepared. In both stations, variations of VOCs concentrations with wind speed is highly straightforward. As expected, almost all measured concentrations of VOCs showed a decreasing trend with wind speed, unlike an non-decreasing trend as in the case with temperature.This trend takes part in the literature typically (Rivett, et al., 2003 ; Harrison, et al., 2004; Kuntasal, 2005; Doğan, 2013). As it can be seen from the Figure 4.17, acethylene and benzene follow mentioned pattern.

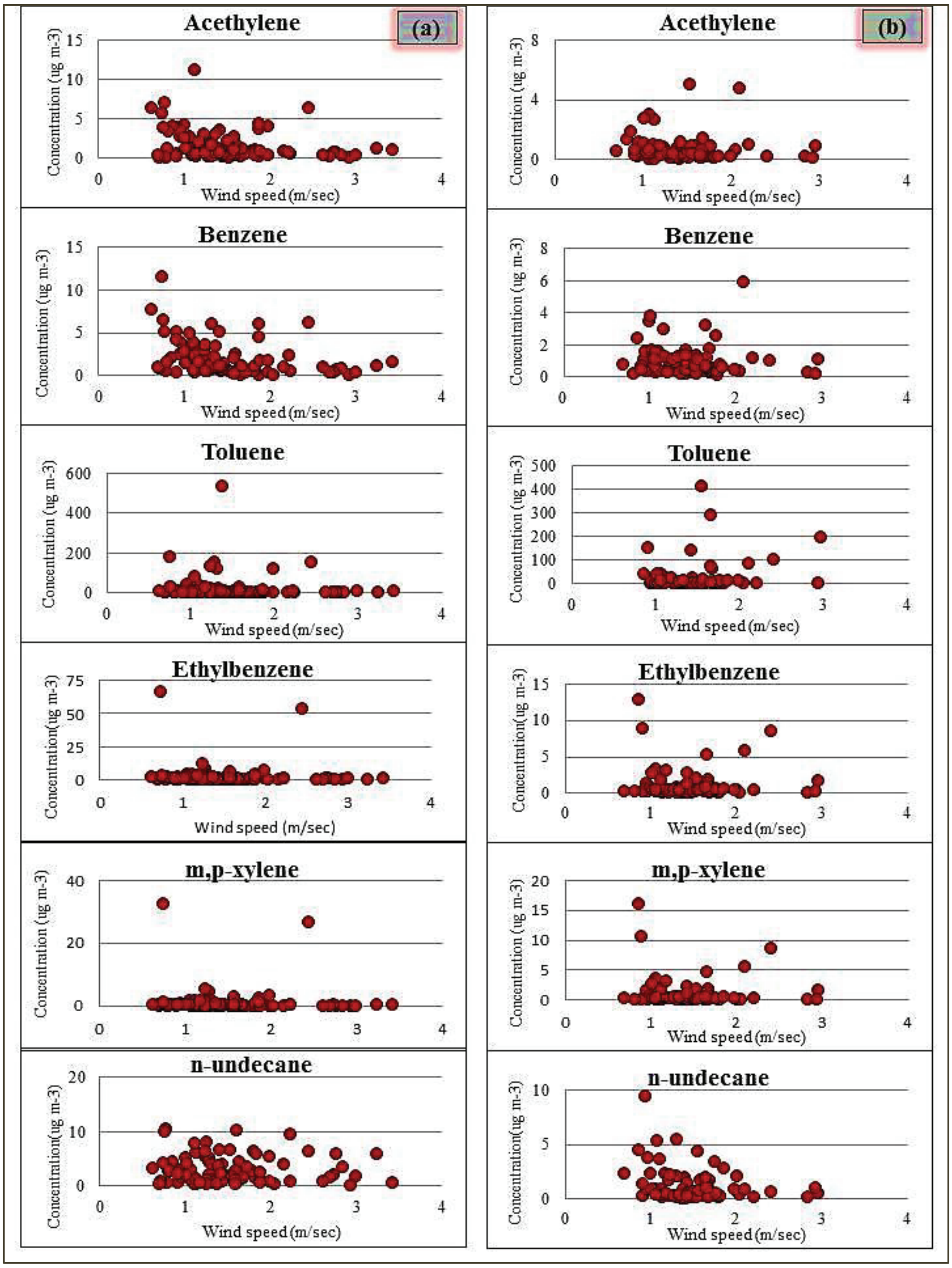


Figure 4.14 Variation of concentration with wind speed (a) urban station and (b) rural station

4.5.3 Effect of rainfall on measured VOCs concentrations

Rainfall is an important scavenging process which dissolve gaseous pollutants or wash particulate matters in the atmosphere. Continual rainfall provide better air quality (Sato, et al.,2006). In this study, obtained data set were divided into two groups as dry and rainy days and concentrations that were measured in those days were compared. All concentrations of dry days and rainy days, and their ratio were submitted in the Table 4.5.

It would be normally expected that measured VOCs concentrations in dry days were greater than measured concentrations in rainy days. However, the expected result could not be appear in the table. Measured concentrations in dry days were not greater than concentrations in rainy days. Similarly, it did not appear a meaningful statistical relation between them. This type of relations were observed systematically in many studies for gases and particles that were conducted by our Air Pollution and Quality Research Group, consequently, not to reach similar results for VOCs was surprizing. Thus, it was decided that the main reason of this distinctive behaviour may be lower solubility of VOCs in comparison with inorganic pollutants. In other words, rainfall could not wash and could not cause decreasing concentrations of VOCs in the ambient air, and it demonstrates that rainfall is not an efficient meteorological event for scavenging of VOCs from atmosphere.

Solubility of a VOC in water should not be equated with any others, because solubility differs from one to another. Different variations of concentrations of selected VOCs according to rainfall in urban and rural stations were shown in the Figure 4.15 and Figure 4.16 respectively. Measured acetylene concentrations were higher in dry period than rainy period as it was an expected trend normally. According to related figures, it can be seen that in June, July, September and October, concentrations in rainy days were higher than that in dry days. However, low amount of rainfall in summer months may cause to this situation, and it may be allaged that measurements of these months were unreliable sufficiently to compare variations of concetrations according to effect of rain. But, in winter months rainfall is enough to obtain more reliable results.

It was not observed a significant variation in benzene concentrations that was measured in dry and rainy days in Figure 4.15 and Figure 4. 16, and a huge portion of VOCs show similar behaviour with benzene. However, measured concentrations of some VOCs, such as 2,2,4-trimethylpentane, were high in rainy days in both urban and rural stations. In order to clarify this situation Henry’s Law Constant of all VOCs were examined. This value is $3.3x10^{-4}$ M/atm for 2,2,4-trimethylpentane, $2.5x10^{-3}$ M/atm for 1-pentene, $1.1x10^{-2}$M/atm for ethane, $4.2x10^{-2}$ M/atm for acetylene, and $1.8x10^{-1}$ M/atm for benzene (Sander, 1999). As it can be seen that Henry’s Law Constant of 2,2,4-trimethylpentane is the lowest one, on the other hand the related value of benzene is the higher one comparing to others. And, according to Henry’s law solubility of a compound in water is directly proportionate to Henry’s Law Constant. Accordingly, solubility of 2,2,4-trimethylpentane in water should be lower, and solubility of benzene should be higher than others. Consequently, higher concentration of some compounds, such as 2,2,4-trimethylpentane, in rainy days than that in dry days can be explained with this relation.

Table 4.5 Effect of rainfall on measured VOCs concentrations in both stations

	Urban Station							**Rural Station**						
	Rainy Days			**Dry Days**				**Rainy Days**			**Dry Days**			
	Mean	Med.	N	Mean	Med	N	D/R	Mean	Med	N	Mean	Med	N	D/R
Ethane	3.60±3.69	2.89	40	3.57±3.28	2.78	51	0.99	0.79±0.78	0.55	30	1.32±1.42	1.00	42	1.66
Ethylene	9.76±10.5	5.08	40	9.08±12.5	3.77	52	0.93	3.89±4.09	2.58	31	3.25±4.92	1.67	43	0.83
Propane	5.81±7.51	3.10	40	4.57±5.11	2.44	52	0.79	2.95±5.36	1.75	31	2.18±2.60	1.41	44	0.74
Propylene	6.52±8.99	2.95	41	6.34±8.39	2.48	52	0.97	2.26±3.28	1.15	31	2.16±3.34	0.86	44	0.96
Isobutane	8.43±11.2	4.12	41	7.18±7.37	3.82	51	0.85	3.28±5.18	1.65	31	3.20±6.73	1.04	43	0.97
Acethylene	1.56±1.33	1.12	40	1.62±2.17	0.73	52	1.04	0.67±0.94	0.34	31	0.66±0.93	0.33	43	1.00
Trans - 2 - Butene	0.65±0.83	0.32	41	0.78±0.60	0.78	51	1.22	0.32±0.55	0.18	29	0.43±0.36	0.39	41	1.34
1 - Butene	0.94±1.21	0.53	41	0.79±0.92	0.43	52	0.83	0.66±1.08	0.29	30	0.45±0.57	0.25	44	0.68
Cis-2-Butene	17.9±15.5	16.44	40	17.7±13.2	16.79	52	0.99	12.79±13.3	8.40	31	13.5±11.0	10.0	43	1.05
Cyclopentane	0.63±1.11	0.25	41	0.47±0.49	0.38	51	0.75	0.26±0.50	0.13	31	0.24±0.26	0.19	42	0.94
Isopentane	5.65±7.11	2.83	40	5.51±8.09	2.41	52	0.97	2.99±4.05	1.29	31	3.46±10.2	1.14	43	1.15
n - Pentane	6.15±22.9	1.25	41	2.09±2.73	1.06	52	0.34	2.47±5.23	0.81	31	1.16±1.91	0.52	43	0.47
Trans - 2 - Pentene	0.37±0.56	0.17	40	0.25±0.28	0.14	51	0.67	0.14±0.16	0.10	30	0.17±0.35	0.09	42	1.19
1 - Pentene	0.34±0.36	0.21	40	0.36±0.45	0.20	51	1.08	0.22±0.24	0.14	31	0.26±0.27	0.18	42	1.20
Cis-2- Pentene	0.09±0.11	0.05	38	0.14±0.37	0.05	48	1.48	0.05±0.05	0.03	31	0.07±0.10	0.03	43	1.30
2,2-Dimethylbutane	1.46±1.74	0.91	41	1.09±0.95	0.79	52	0.75	0.31±0.34	0.18	31	0.57±1.71	0.20	43	1.82
2,3-Dimethylbutane	0.43±0.54	0.27	41	0.41±0.65	0.22	51	0.97	0.15±0.15	0.09	30	0.30±0.87	0.09	43	1.97
2-Methylpentane	1.16±1.46	0.60	40	1.34±3.51	0.58	51	1.15	0.67±0.88	0.27	27	1.42±4.08	0.29	38	2.14
3-Methylpentane	0.52±0.59	0.33	35	0.81±1.93	0.28	49	1.55	0.45±0.99	0.17	28	0.66±1.45	0.17	41	1.46
Isoprene	0.86±1.30	0.40	41	0.78±1.03	0.44	52	0.90	0.36±0.78	0.17	31	0.40±0.51	0.25	43	1.11
n-Hexane	3.87±7.46	1.39	40	3.84±9.56	0.79	50	0.99	2.29±3.25	1.20	31	2.77±6.81	0.97	41	1.21
2,4-Dimethylpentane	0.39±0.46	0.18	41	0.87±3.98	0.16	51	2.24	0.30±0.43	0.11	30	0.48±1.16	0.15	43	1.63
Benzene	2.19±2.12	1.53	41	1.64±1.82	0.84	52	0.75	1.14±1.09	0.98	31	0.86±0.87	0.58	43	0.76
Cyclohexane	1.14±2.08	0.45	41	1.10±2.23	0.33	52	0.97	1.27±3.91	0.26	31	0.52±0.98	0.16	42	0.40
2-Methylhexane	0.75±1.40	0.32	41	0.69±0.86	0.27	51	0.92	0.48±0.64	0.24	31	0.45±0.87	0.27	42	0.93
2,3-Dimethylpentane	0.57±0.72	0.42	40	0.63±0.68	0.45	52	1.12	0.36±0.25	0.31	30	0.40±0.37	0.32	40	1.12
3-Methylhexane	1.75±1.55	1.10	41	1.73±1.58	1.36	52	0.99	1.47±1.42	1.09	31	1.93±2.21	1.02	43	1.31
2,2,4-Trimethylpentan	1.03±0.87	0.60	41	1.00±0.77	0.89	52	0.97	0.70±0.52	0.59	31	0.63±0.39	0.52	43	0.91
n-Heptane	0.67±0.81	0.40	41	0.61±0.64	0.30	52	0.91	0.63±0.86	0.37	31	0.51±0.64	0.33	43	0.81
Methylcyclohexane	0.28±0.28	0.19	41	0.26±0.29	0.16	52	0.93	0.38±0.50	0.19	31	0.16±0.15	0.10	43	0.41

Table 4.5 (Continued)

	Urban Station							Rural Station						
	Rainy Days			**Dry Days**				**Rainy Days**			Dry Days			
	Mean	Med.	N	Mean	Med	N	D/R	Mean	Med	N	Mean	Med	N	D/R
2,3,4-Trimethylpentn	0.19±0.15	0.14	41	0.24±0.30	0.11	51	1.28	2.16±6.22	0.11	31	0.37±1.44	0.09	41	0.17
Toluene	16.3±36.1	4.70	40	28.3±82.5	4.85	49	1.74	28.36±49.7	6.12	27	37.05±89.2	2.70	32	1.31
2-Methylheptane	0.48±0.42	0.31	37	1.04±2.54	0.37	48	2.20	10.4±47.06	0.20	26	0.23±0.27	0.19	40	0.02
3-Methylheptane	0.62±0.65	0.36	40	1.16±2.09	0.26	52	1.87	0.41±0.58	0.19	31	0.43±0.65	0.12	42	1.03
n-Octane	0.53±0.78	0.28	41	0.44±0.47	0.30	51	0.82	0.52±0.65	0.28	31	0.36±0.35	0.25	43	0.69
Ethylbenzene	2.88±10.4	0.72	41	2.17±7.35	0.59	52	0.75	1.73±3.10	0.38	31	0.74±1.00	0.40	43	0.43
m,p-Xylene	2.66±10.2	0.41	41	2.04±7.55	0.41	50	0.77	3.66±7.28	0.59	31	1.27±1.96	0.55	42	0.35
Styrene	1.56±2.10	1.02	41	1.04±1.33	0.60	52	0.67	1.03±1.56	0.51	31	0.88±0.90	0.63	43	0.86
o-Xylene	3.74±11.4	0.96	41	2.76±8.65	0.96	52	0.74	2.55±4.60	0.60	31	0.95±1.19	0.59	42	0.37
Nonane	0.72±1.12	0.33	41	0.49±0.88	0.26	52	0.69	1.07±1.99	0.27	31	0.52±1.12	0.24	43	0.49
Isopropylbenzene	0.41±0.51	0.18	41	0.30±0.44	0.14	50	0.73	0.28±0.32	0.18	30	0.21±0.16	0.18	41	0.74
n-Propylbenzene	0.56±0.94	0.25	41	0.47±0.66	0.18	51	0.83	0.32±0.32	0.24	31	0.40±0.79	0.16	42	1.23
m,p-Ethyltoluene	0.39±0.53	0.14	28	0.35±0.36	0.27	27	0.92	0.28±0.30	0.15	16	0.25±0.35	0.15	17	0.89
1,3,5-Trimethylbenz.	1.01±1.41	0.56	41	1.09±1.68	0.54	50	1.07	1.09±1.89	0.36	31	0.51±0.60	0.33	42	0.47
o-Ethyltoluene	0.84±1.27	0.34	40	0.82±1.24	0.45	50	0.97	0.51±0.48	0.33	30	0.37±0.59	0.19	39	0.73
1,2,4-Trimethylbenz.	1.04±1.13	0.63	41	1.11±1.94	0.46	51	1.07	0.63±0.68	0.49	31	0.64±0.64	0.46	41	1.01
n-Decane	1.12±1.50	0.65	41	1.99±3.16	0.63	50	1.79	2.05±6.18	0.46	31	0.95±1.26	0.41	42	0.46
1,2,3-Trimethylbenz.	5.39±6.46	3.46	41	3.64±3.93	2.37	52	0.68	1.38±1.36	0.97	31	2.05±2.28	1.33	42	1.49
p-Diethylbenzene	1.28±1.36	0.92	41	1.65±1.88	1.10	51	1.29	0.52±0.56	0.41	29	0.64±0.84	0.40	42	1.24
n-Undecane	3.02±2.41	2.49	41	2.55±2.62	1.78	52	0.84	1.33±1.51	0.86	31	1.24±1.66	0.58	42	0.93
n-Dodecane	9.37±7.89	7.38	41	7.83±7.05	5.80	52	0.84	5.39±7.15	2.16	31	4.45±5.24	2.61	42	0.82

*D/R refers to dry days to rainy days concentration ratio

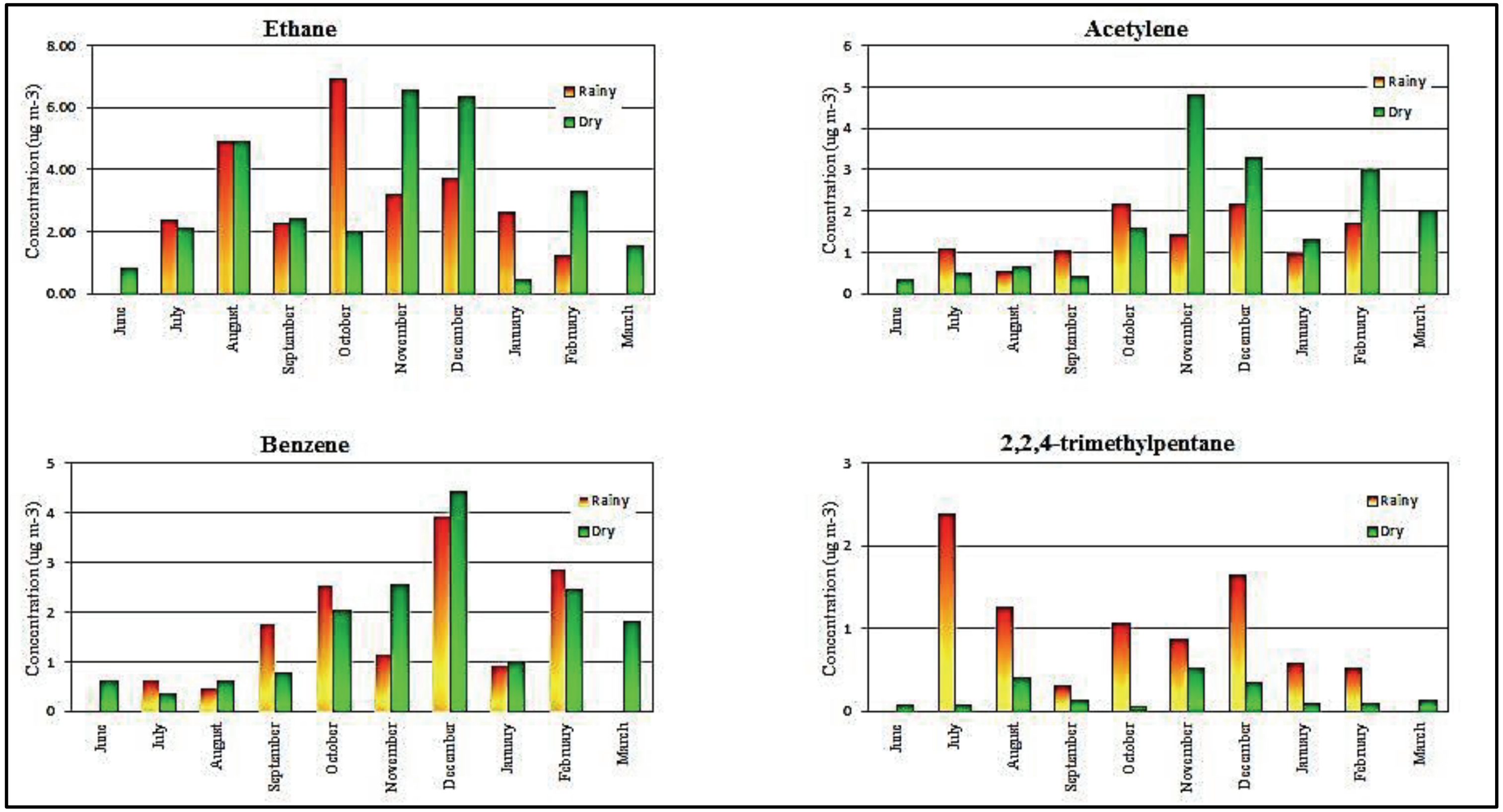


Figure 4.15 Effect of rainfall on monthly average concentrations of selected VOCs at urban station

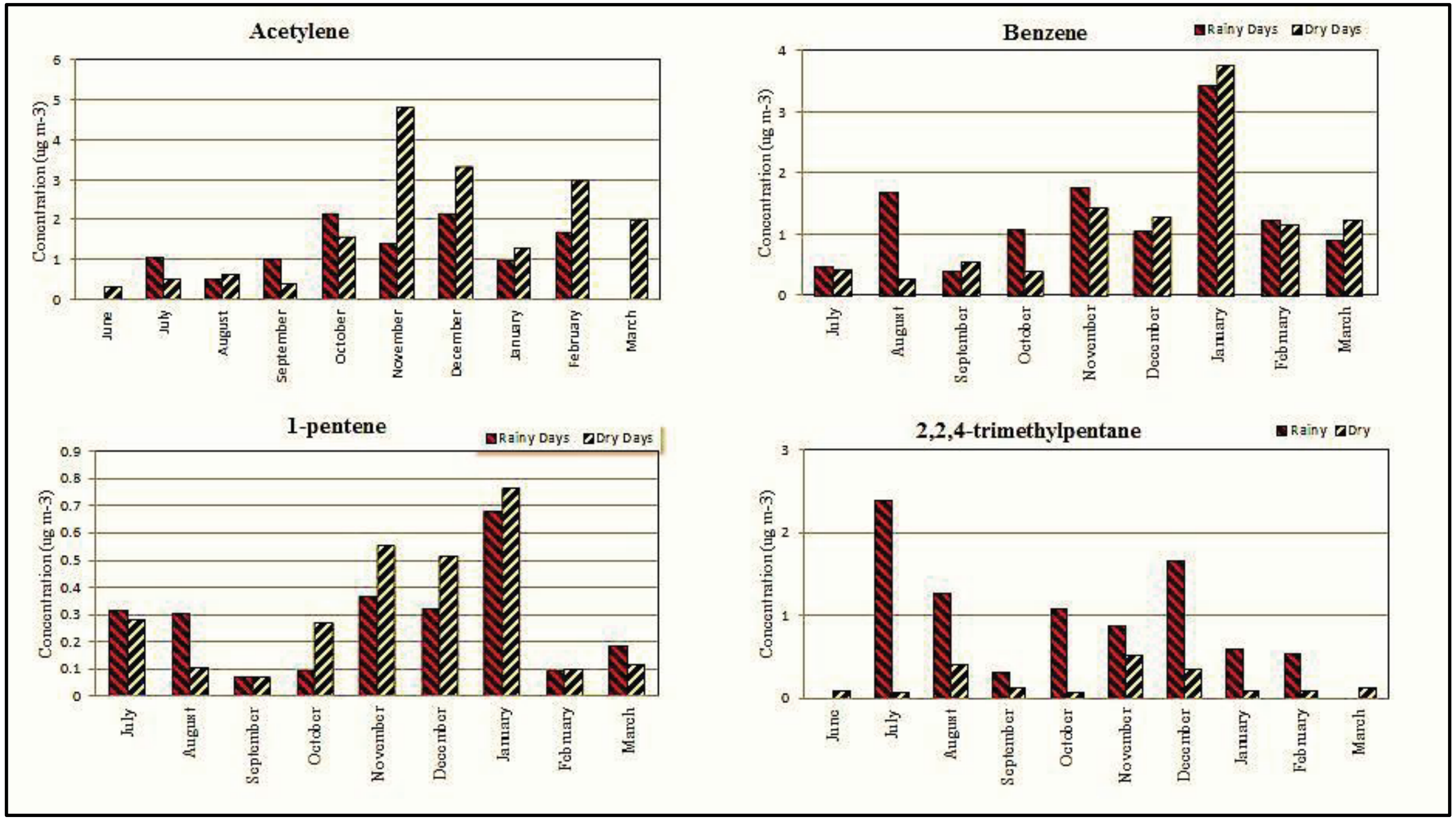


Figure 4.16 Effect of rainfall on monthly average concentrations of selected VOCs at rural station

4.5.4 Effect of mixing height on measured VOCs concentrations

As it was stated in the Section 4.1, mixing height is very important meteorological parameter that is used for interpretation of obtained data set. It refers to the distance between layer and ground level which released air pollutants can be vertically dispersed and mixed properly because of convection, or mechanical turbulance (Seibert, 2000). If mixing height is low, it means high atmospheric stability and limited vertical transportation of any pollutant. On the contrary, when mixing height is high, pollutants are diluted and their concentrations decrease consequently(Vega, et al., 2011). Correspondingly, it is expected that pollutant concentration is high when mixing height is low. Thus, it is known that mixing height is lower in winter than in summer, and concentrations of target air pollutants increase in winter (Majumdar,et al.,2011). Mixing height values, which were measured twice a day, were obtained from General Directorate of Meteorology. And, hourly mixing height values were obtained using these twice daily data and PCRAMMET programme, which was developed by USEPA in order to calculate hourly mixing height values. Consequently, average values of obtained hourly mixing height data was used to investigate variations of measured VOCs concentrations with mixing height for both stations and, obtained results were shown in the Figure 4.17 for some selected compounds.

Two groups of behaviour was determined among target VOCs. First group consisted decreasing concentrations of VOCs with increasing mixing height values, such as benzene and acethylene. This group included VOCs that had constant amount of emissions in summer and winter months mostly. Another group consisted VOCs that not show an apparent variation with mixing height values, such as undecane and dodecane. The underlying reason of this stationary state in concentrations with mixing height is their presence in solvents. Concentrations of VOCs which emits from solvents, or one of thier source is solvent, are prominently high in summer. Additionally, due to mixing height is high in summer, expected amount of decrease in concentration of solvent related VOCs can be substituted for increasing emission amounts. So, it can be generalized that there is not an appearent relationship between mixing height and concentration of solvent related VOCs that are measured in summer.

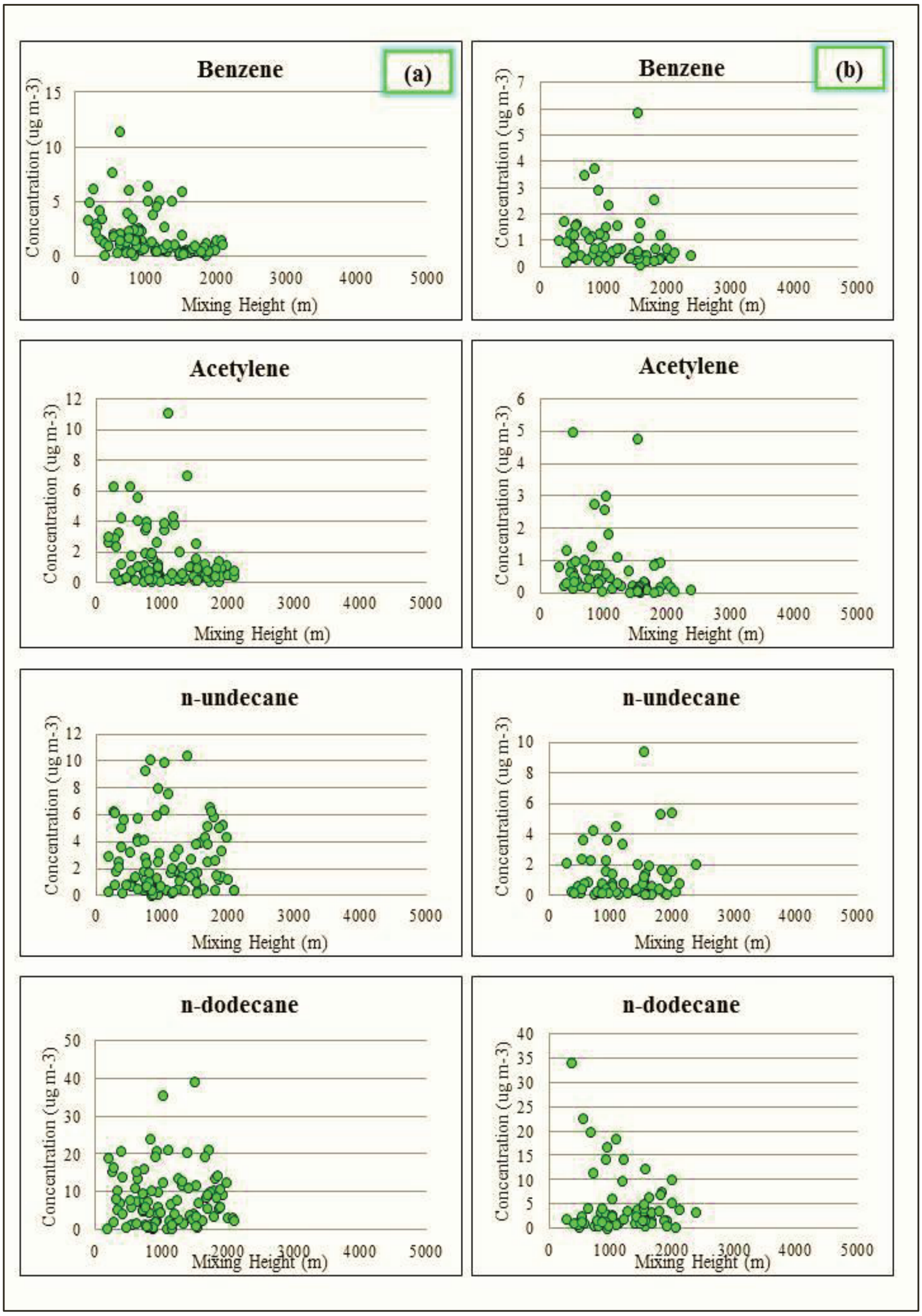


Figure 4.17 Effect of mixing height on concentrations of selected VOCs at (a) urban and (b) rural stations

4.5.5 Effect of ventilation coefficient on measured VOCs concentrations

Ventilation coefficient is another important meteorological parameter which should be taken into consideration while making interpretation of obtained data sets because of its effect on variations of concentrations of any air pollutants. It is considerably related with mixing height and wind speed. Moreover, it was calculated by multiplication of mixing height and wind speed values (Deng, et al., 2012).

Ventilation coefficient is the product of mixing height data with the relevant wind speed data. For this study, hourly ventilation coefficients were calculated through the multiplication of hourly mixing heights with the corresponding wind speeds. Ventilation coefficient is important as it gives information on the assimilative and ventilation capacity of the atmosphere (Lu et al., 2012). It also has an effect on the dilution of the pollutant concentrations in the atmosphere and takes role during the removal of the compounds from the air (Lu et al., 2012). As it was stated before, high ventilation coefficients together with high mixing heights dilute and hence lower the specie concentrations in the atmosphere.

In this study, hourly mixing height values were calculated as stated in the previous section. After that, obtained results were multiplied by related wind speed data, and ventilation coefficient was produced hourly. Finally, daily average values were calculated and in order to investigate its effect on measured concentrations, ventilation coefficient versus VOCs concentrations graphs were plotted for all target VOCs, then some of them were selected, and showed in the Figure 4.18. Ventilation coefficient causes to similar trend with mixing height in variations of pollutant concentreations in the atmosphere. Namely, high ventilation coefficients reduce pollutant concentrations through influence on dilution of concentrations (Seibert, 2000). And, as it can be seen in the Figure 4.18, this expected pattern was achieved.

As in the case with mixing height, two groups of behaviour was determined for variation of target VOCs concentrations with ventilation coefficient values. Concentrations of some VOCs which have relatively constant emission amounts, such as benzene and acethylene, decrease with increasing values of ventilation coefficient. Main reason of this situation is both further dispersion of pollutants in a larger volume with increase in ventilation coefficient, and being more effective ventilation due to wind speed.

The second group is solvent related VOCs whose both summer concentrations and ventilation coefficients are high. So, it can be stated that there is not an appearent relationship between ventilation coefficient and concentration of solvent related VOCs as in mixing height.

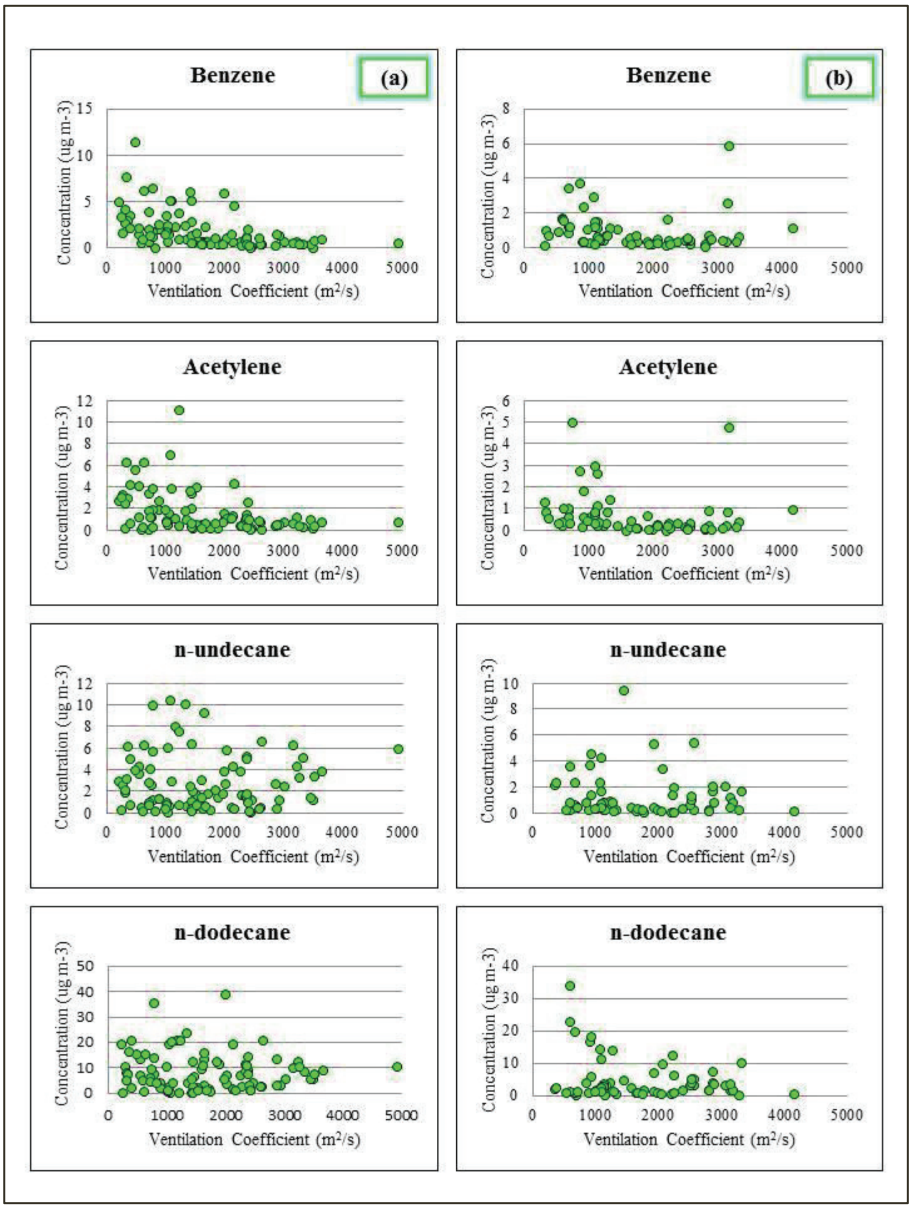


Figure 4.18 Effect of ventilation coefficient on concentrations of selected VOCs at (a) urban and (b) rural stations

4.6 Variation of VOCs concentrations with wind direction : contribution of power plants

As it was mentioned in previous sections, there are two high emitting power plants in Kütahya, namely Seyitömer and Tunçbilek Thermal Power Plants (TPP). The starting point of this study was determination of whether there is an effect of these thermal power plants in Kütahya or not, so investigation of variations of VOCs concentrations with wind direction is an important part of the study.

The main question is how thermal power plants (PPs) affected air quality of Kütahya, because of this, relationship between wind direction and concentration of VOCs is important to be able to answer this question. Correspondingly, if measured concentrations of VOCs in both stations were affected from thermal power plants, concentrations from the wind sectors that the thermal power plants reside in should be higher than other sectors. Actually, this cannot be a conclusive evidence to explain contribution of thermal power plants in VOCs concentrations, but it can demonstrate us that thermal power plants are one of the source of VOCs at least.

It is expected that effects of Seyitömer and Tunçbilek PPs on concentrations of VOCs are different in urban and rural stations. Seyitömer TPP and Tunçbilek TPP reside on the side of NNW and WNW sectors according to urban station respectively and distance between PPs and urban station is approximately 20 km and 50 km respectively. As for rural station, Seyitömer and Tunçbilek TTPs located on the side of ENE and NNW sectors respectively, and distance between PPs and rural station is approximately 42 and 18 km respectively.

As it was stated in the Section 4.1 that dominant wind directions in the region were N and NNW. In this case, it is expected that Seyitömer TPP affects concentrations that were measured in urban station mostly due to distance between them and also wind sector that Seyitömer TPP reside in. Similarly, it is expected that rural station affects from Tunçbilek TPP mostly, because this station is downwind of this TPP.

In this study, relationship between concentration of VOCs and wind directions were investigated using three different ways. First of all, the average concentrations of the pollutants in each wind sector were calculated and pollution roses were prepared.

In order to show the relation between concentrations of pollutants in the air and wind direction that was recorded throughout sampling period, pollution roses are very practical figures. They give information about location of their potential sources. In this sttudy, using average concentrations of target VOCs in each wind sector were calculated and pollution roses were created for all of them. To give an exapmle of them, Figure 4.19 was prepared with selected compounds for both stations. For urban station, n-pentane and ethyltoluene, and for rural station trans-2-pentene and 3-methylpentane were given as examples of coming from the wind sectors that the Seyitömer TPP locates in with high concentrations.

In urban station, when all sector contributions are considered, it is understood that VOCs with higher concentrations are coming from NNW sector mostly, and the main reason of this situation may be Seyitömer TPP. When all pollution roses were observed, in addition to selected VOCs, trans-2-pentene, m,p-ethyltoluene, and 1,3,5-trimethylbenzene show similar trend, so their concentrations are higher in NNW sector than those of others. A remarkable point is that concentrations of n-pentane and trans-2-pentene are not high only in NNW sector where Seyitömer TPP resides in, but also high in WNW sector where Tunçbilek TPP are located. It shows that both TPPs may affect measured concentrations.

In order to show effects of Tunçbilek TPP on VOCs concentrations in both stations, Figure 4.20 was prepared. 2,4-dimethylpentane and 2-methylpentane were selected to illustriate dominant wind sector contribution on concentrations that were measeured in urban station, also n-pentane and 2,2-dimethylbutane were selected to illustriate wind sector contribution trend in rural station. In common with Figure 4.19, typical VOCs were shown in the Figure 4.24. Actually, there are some VOCs that act in same manner in both stations.

In addition to the two VOCs in urban station which can be seen in the Figure 4.20, concentrations of propylene, n-pentane, trans-2-pentene, 2,2-dimethylbutane, 2-methylpentane, 3-methylpentane, toluene, isopropylbenzene, m-ethyltoluene are high in WNW sector where Tunçbilek TPP resides in. So many VOCs seems in the impact direction of Tunçbilek TPP. Indeed, this was not a much-expected result due to distance between urban station and the power plant. Because of this, it was thought that there may be a source in this direction. And as a remarkable point is that traffic related sources, such as acethylene and benzene, are not very high in WNW direction, so mentioned possible source should not be result from traffic emissions.

It seems that concentrations of approximately all target VOCs are higher in N and NNE sectors than that in others in rural station. The most approximate examples of these compounds can be sorted as ethylene, isopentane, n-pentane, 2,2-dimethylbutane, cyclohexane and n-heptane. This situration shows that impact of Tunçbilek TPP on VOCs concentration is very distinct in rural station. Due to availability of more emission sources around urban station, difference between concentrations of VOCs which come from related sectors where thermal power plants reside in and other sectors were not high as much as in rural station.

District of Tavşanlı is located between rural station and Tunçbilek TPP. For this reason, it is difficult to make a decision how much of high concentrations in N and NNE sectors come from the power plant or Tavşanlı. However, absence of well-known traffic related markers, such as benzene and acetlhylene, shows that source of high concentrations in these sectors is resulted from Tunçbilek TPP with high degree of probability than that from Tavşanlı.

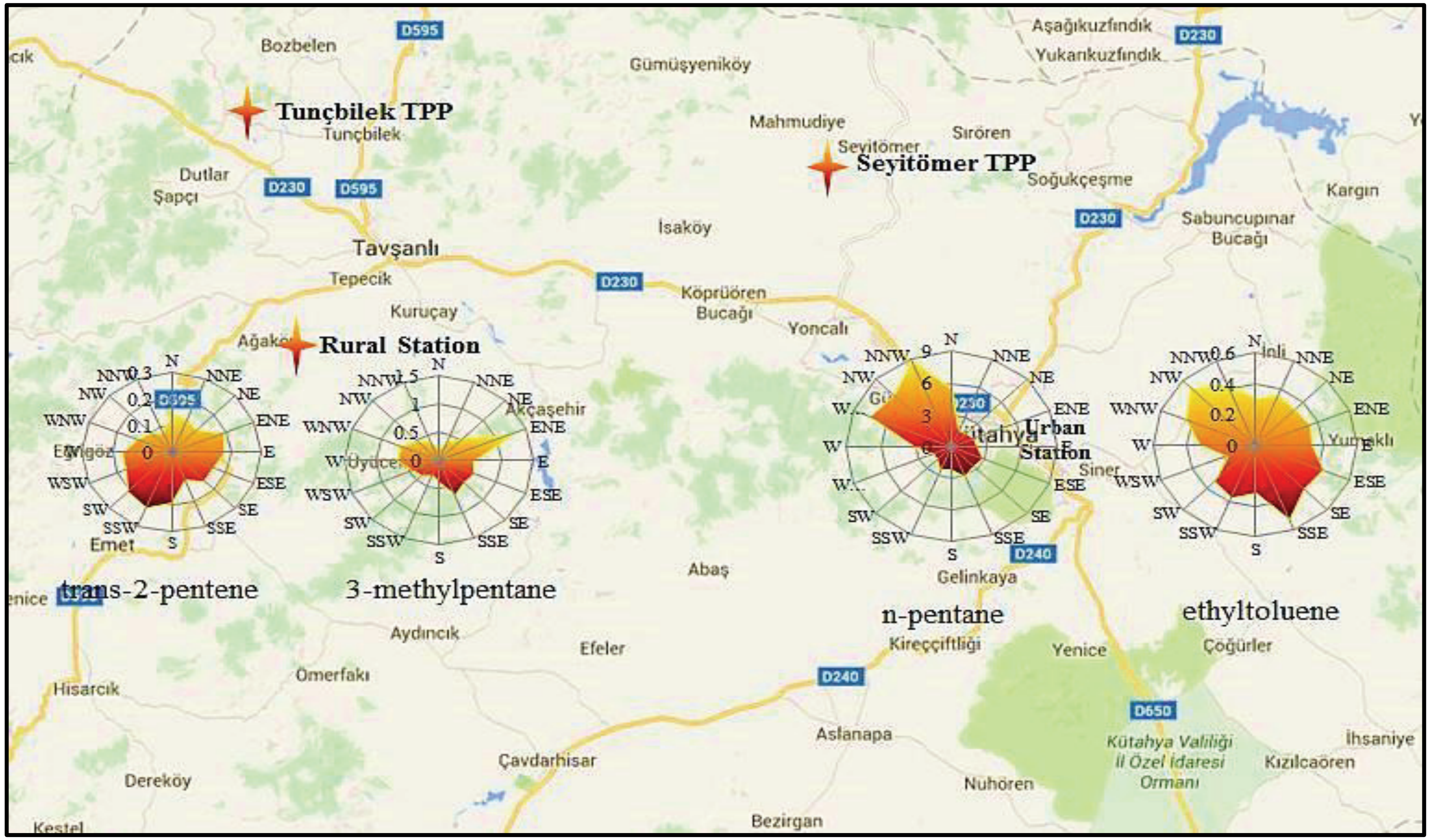


Figure 4.19 Average concentrations of selected VOCs which concentrations are affected from emissions from Seyitömer Power Plant at rural and urban stations

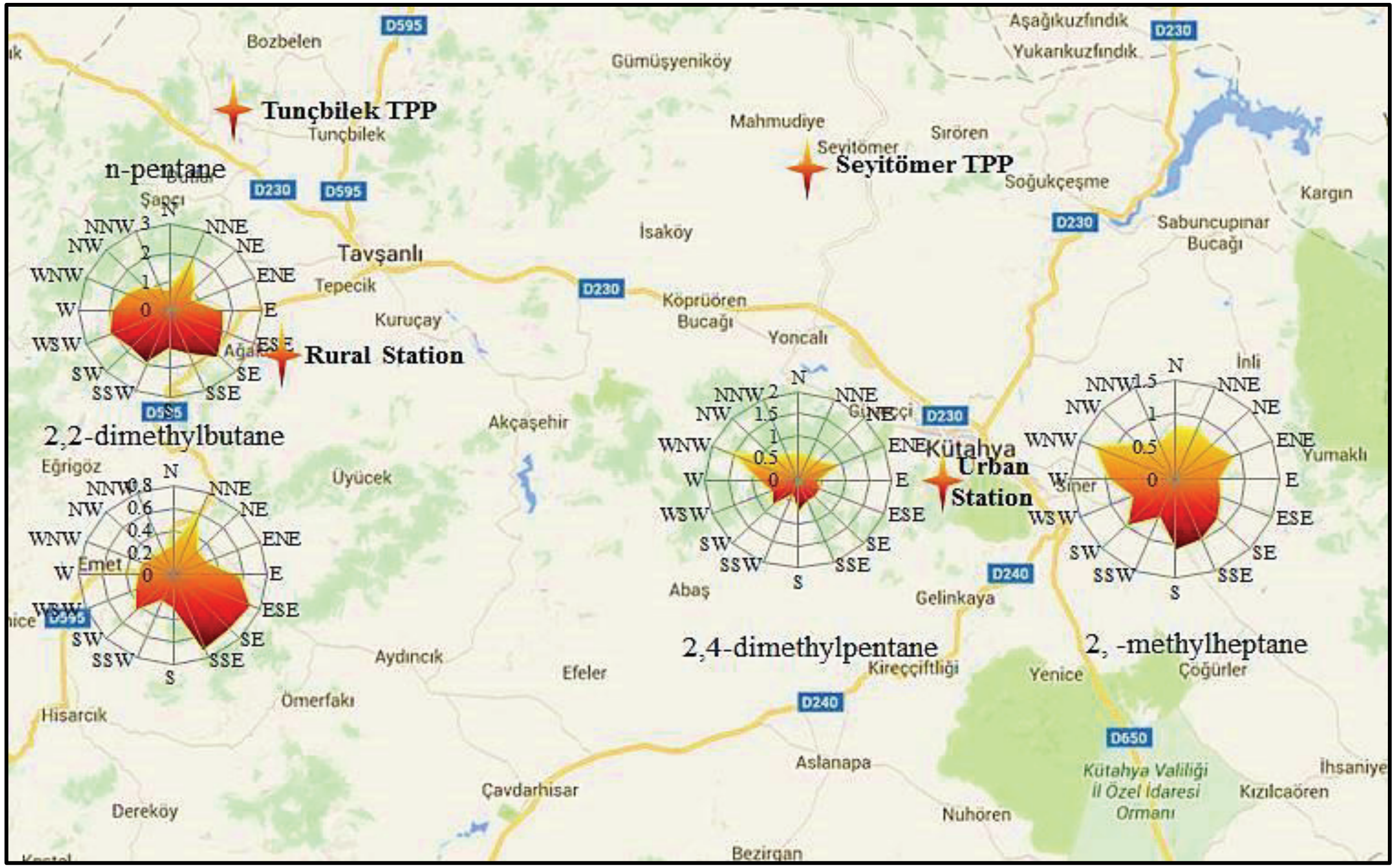


Figure 4.20 Average concentrations of selected VOCs, which concentrations are affected from emissions from Tunçbilek Powerplant at rural and urban station

As it was stated in the beginning part of this section, average concentrations of VOCs in wind sectors give information about their sources, but they cannot be sufficient to determine how much effects of power plants on concentrations by themselves. Because, this effect depends on not only wind direction, but also frequency of blowing from wind sectors where thermal power plants located in. For example, huge amount of VOCs may be released by Seyitömer TPP to Kütahya atmosphere. But, if wind did not blow properly to be able to transport emissions to Kütahya, contribution of the related emissions on measured VOCs concentrations will be out of the question. For this reason, in order to make an interpretation about the effect of TPP on measured concentrations, amount of wind blowing in a sector should be take into consideration.

For the mentioned reason above, "conditional probability function (CPF)" were calculated for all wind sectors. CPF is a purposive method to describe wind sectors taking into account of each possible source classes. It is identified as the following equation ;

$$\mathrm{CPF} = \frac{m_\theta}{n_\theta} \qquad \text{Equation (1)}$$

m_θ represents the amount of samples which are higher than an accurate concentration limit, which was specified as 60th percentile of whole obtained data (Doğan, 2013 ; Ashbaugh, et al.,1985) in both stations, in the related wind sector "θ", and n_θ represents total amount of samples in the same wind sector (Xie & Berkowitz, 2006).

In this study, in order to obtained more representative results about wind sector contributions on measured VOCs concentration, essential calculations were done and wind direction effects of both TPPs distribution of CPF among sectors in urban and rural stations were shown in the Figure 4.21 and Figure 4.22. As such in prepared pollution roses using average VOCs concentrations, designated VOCs are examples one for each in the figures that were prepared to illustrate distribution of CPF values of them in wind sectors. Besides these compounds, some other VOCs shows similar behaviour in both stations.

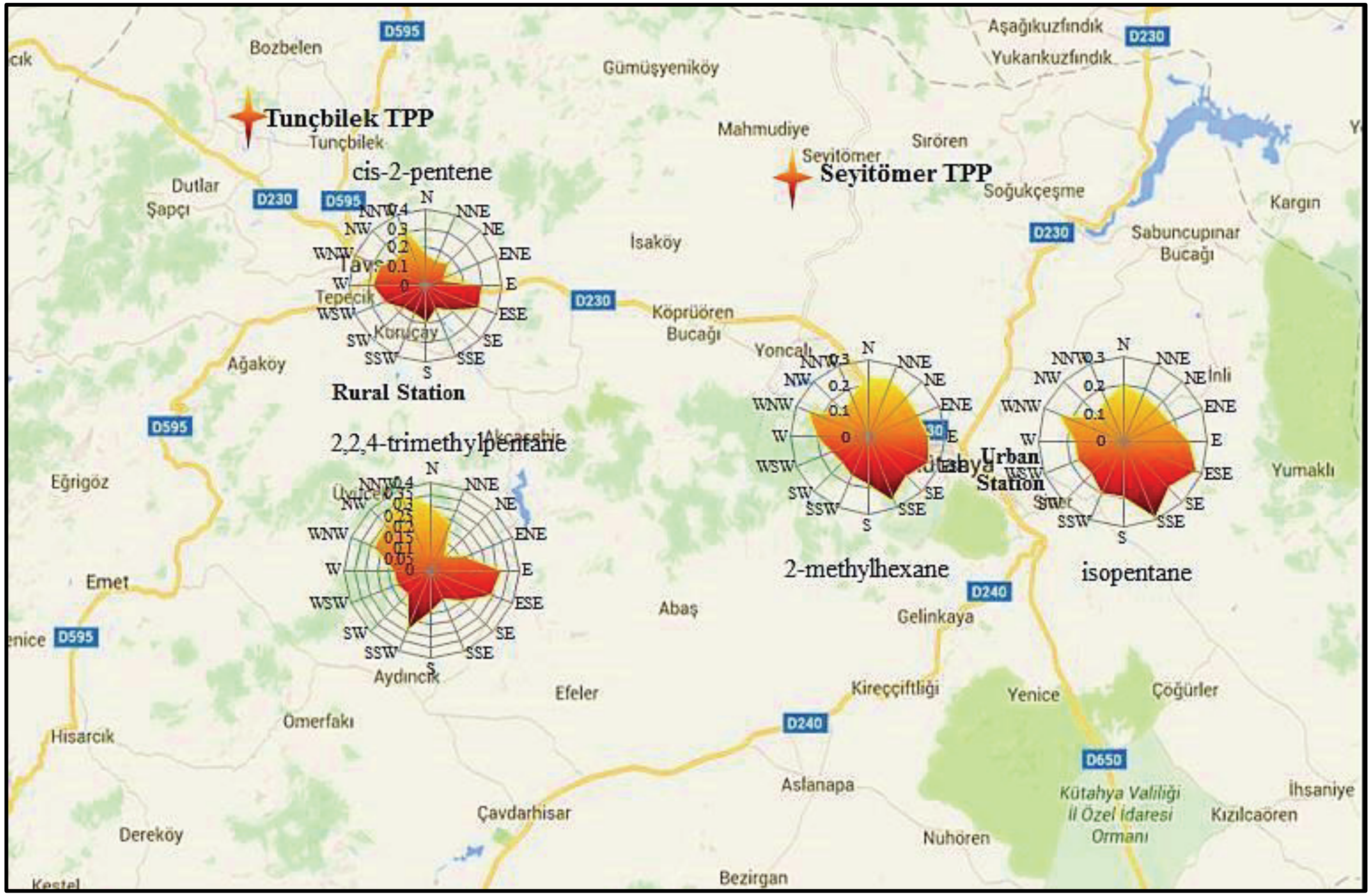


Figure 4.21 Distribution of CPF values of selected VOCs in wind sectors: VOCs those are affected from Tunçbilek power plant

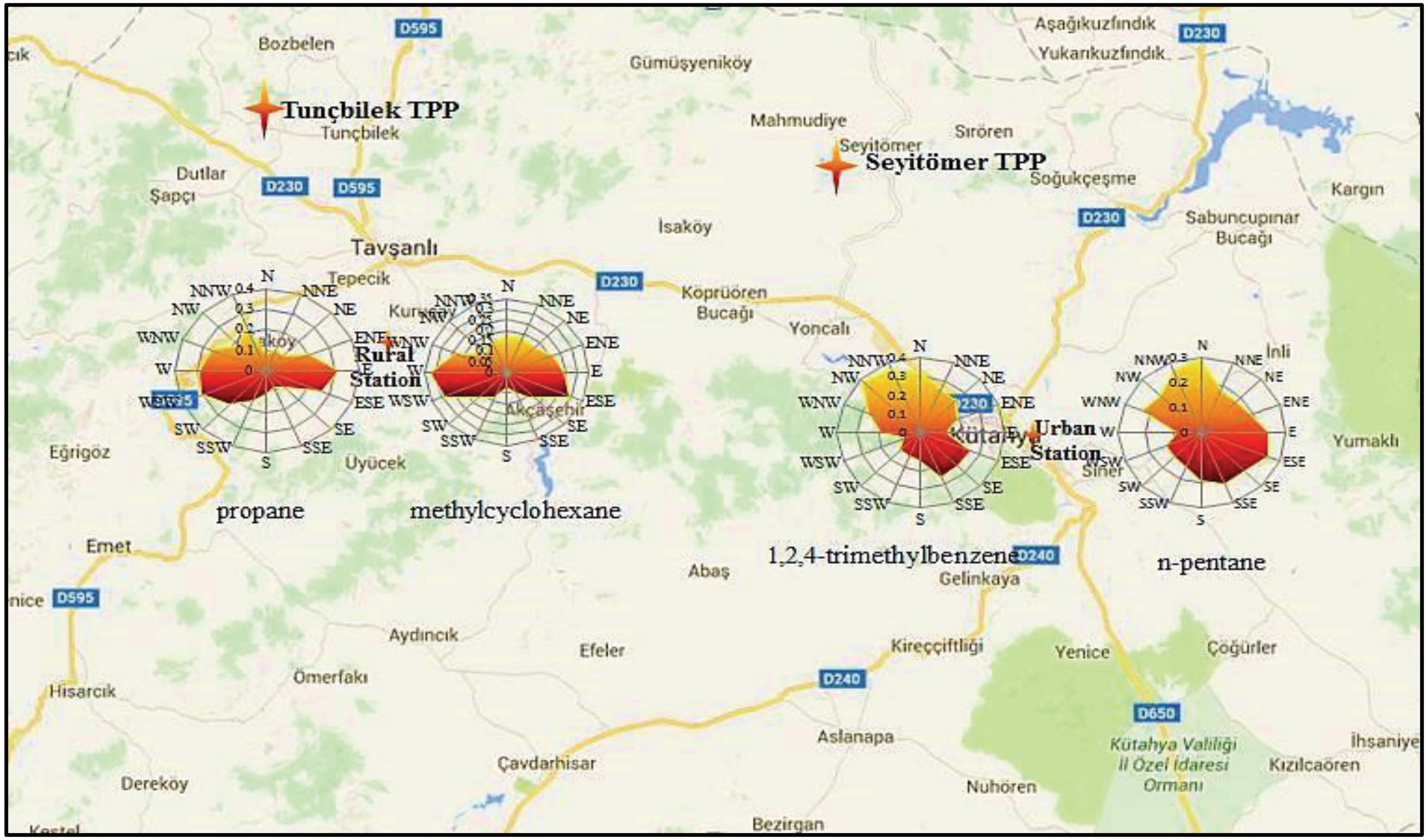


Figure 4.22 Distribution of CPF values of selected VOCs in wind sectors: VOCs those are affected from Seyitömer power plant

In urban station, CPF values of n-pentane, trans-2-pentene, cis-2-pentene, nonane, n-propylbenzene, m,p-ethyltoluene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene are high in NNW sector, whereas in rural station, CPF values of trans-2-pentene and 2,4-dimethylpentane are high in ENE sector where Seyitömer TPP resides in, except VOCs that were shown in the figures.

Here is a remarkable point again. When it was considered average concentrations in rural station, several VOCs which designate Seyitömer TPP were observed. However, it was realized that few VOCs with high concentrations came from ENE sector, when CPF calculations were evaluated. The reason is that may be when wind blew from ENE sector, concentrations of some VOCs were high. But, wind did not blow from this sector frequently, and this case shows that CPF values of these VOCs are low.

In urban station, VOCs with high average concentrations in the direction of Tunçbilek TPP are same VOCs that have high CPF values.

In common with average concentrations in rural station, CPF distribution of a clear majority of VOCs are high in N and NNW sectors where Tunçbilek TPP located in. Especially, trans-2-butane, 1-pentene, 2,2,4-trimethylpentane, 2,methylheptane, 3-methylheptane, ethylbenzene, m,p-xylene, o-xylene, isopropylbenzene,n-propylbenzene, o-ethyltoluene, n-undecane and n-dodecane are the main examples to mentioned VOCs that have high CPF distributions in N and NNW sectors. It was obviously understood that contributions of NNW,NNE and N sectors were high in rural station. But, it is not easy to decide how much of obtained contributions result from Tunçbilek or Seyitömer TPP, or emissions in Tavşanlı strictly.

Furthermore, as it is known that emissions in urban parts of Kütahya may be condiserable sources of VOCs around it. So, in order to be able to understand how to be effected VOCs concentrations that were measured in rural station by emissions in Kütahya province, VOCs with higher concentrations in E and ESE sectors comparing with other sectors were considered. In the Figure 4.23, two VOCs, 2,2-dimethylbutane and cyclohexane, were selected as an example to mentioned effect. In addition to selected compounds, E and ESE contributions in concentrations of several VOCs were high, so it can be obviously said that measured concentrations in rural station are affected by emissions due to urban sites of Kütahya.

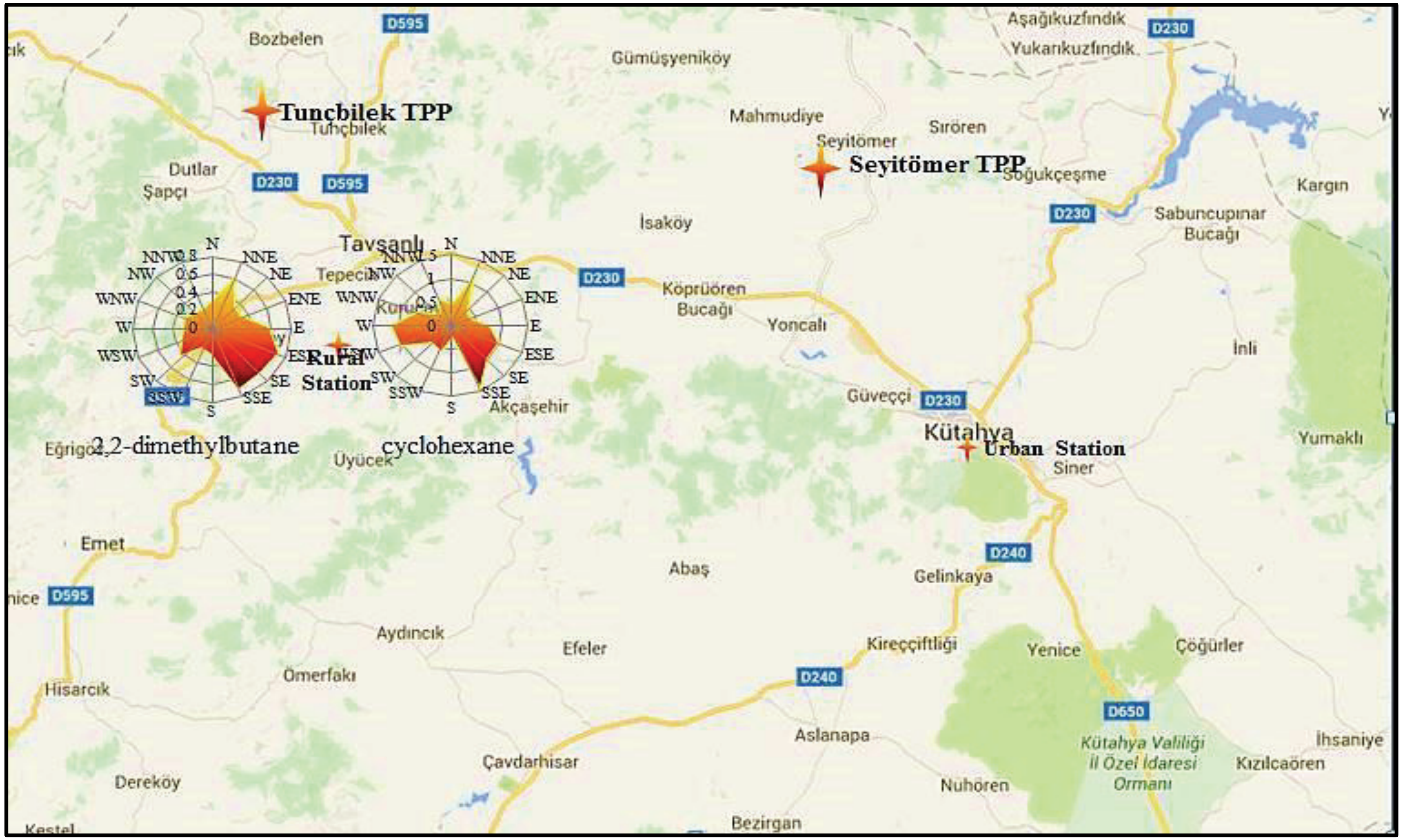


Figure 4.23 Distribution of concentrations of selected VOCs that are influenced from emisions at Kütahya, among wind sectors, at the rural station

4.7 Comparison of Obtained VOCs Concentrations in This Study with Urban and Rural Station in the Same Period

Although in the almost all previous sections of Chapter 4, especially in Section 4.4, obtained results from both sampling stations were compared and discussed in detail, in this section ,comparison of obtained concentrations in urban and rural stations were summerized correlatively in general terms.

In the Figure 4.24, median concentrations of all target VOCs that were measured in both stations compared with each other. As it is expected that majority amount of compounds are higher in urban station than that in rural station. As in aforementioned discussions, it was evaluated as an expected situation due to existence more emission amounts and sources in urban locations than that in rural ones.

In order to show episodic alterations in concentrations of all target VOCs, time series plots were prepared and relevant discussions were made in the Section 4.1.1 for both stations and as a conclusion, meteorological parameters, especially mixing height and ventilation coefficient variations, were held responsible for these abrubt changes potentially in both stations.

In Section 4.2.2, variations of weekday (WKDY) and weekend (WKEND) concentrations were investigated in urban and rural stations. Concentrations of majority amount of VOCs were measured as higher in weekdays than that at the weekends in both stations. In urban station, average concetrations of almost all VOCs were higher in weekday than at the weekend and average value of WKDY/WKEND ratio was calculated as 1.4 ±0.4. Whereas, concentrations of only almost half of target VOCs were higher in weekdays in rural staion and average value of WKDY/WKEND ratio was calculated as 1.0 ± 0.5. This is an expected result because of lower amount of differences in human activities between weekaday and weekend in urban locations.

Furthermore, when seasonal variations of concentrations were taken into consideration, it was seen that almost all of measured VOCs concentrations were higher in winter than in summer as it is expected. All possible reasons were stated in the Section 4.4.3 in detail. However, summer concentrations of some VOCs were higher than that of in winter. In urban station, S/W ratio of just only 10 of all target VOCs are greater than or equal to 1.0. As for rural station, S/W ratio of 9 VOCs are greater than 1.0. That means, related VOCs emission amounts should be considerably higher in the summer than that in winter. However, there is a difference between the reason of increasing in summer concentration of relevant species. Namely, the increase in amount of emissions should be out of question in rural station on the contrary to urban station, and due to the fact that differences in concentrations between summer and winter cannot result from emission changes in there. Seasonal variations on the side of dominant wind direction may cause more frequent transportation of pollutants to rural station, so concentrations of mentioned VOCs that are measured in summer may increase.

As it was mentioned quite a lot times earlier, local meteorology plays a significant role on variations of pollutant concentrations in the atmosphere, especially in urban locations. In this study, similar behaviours in VOCs concentrations that were shown in both stations according to variations in temperature, wind speed, rainfall, mixing height and ventillation coefficient. Although, this consequence may appear interesting at first sight, it is meaningful principally. Variations in concentrations can be anticipated in urban sites with local meteorology and due to changes in emission amounts. However, there are not any specific emission sources near to rural station, in other words, VOCs transport to rural station from somewhere. During this transportation, air masses passing over the several small, or large settlements. And, it was thought that VOCs that measured in rural station from some urban locations. For this reason, similar variations with local meteorology in urban station can be shown in the rural station.

Finally, effect of wind direction on the variaton of VOCs concentrations were discussed in the Section 4.6. And also, contribution of power plants to measured concentrations were examined using provided pollution roses and CPF calculations in both stations. First of all, dominant wind sectors, on the side of where Seyitömer and Tunçbilek TPP reside in, were determined. Seyitömer and Tunçbilek TPP are on the side of NNW and WNW sectors according to urban station respectively, while according to rural station they are located on the side of ENE and NNW sectors respectively. A more detailed comparison between two stations and discussion were made in the Section 4.6. As a summary it can be said that effects of TPP on concentrations in rural station may be more explicit than in urban station, because of the existence of more emission sources around urban station.

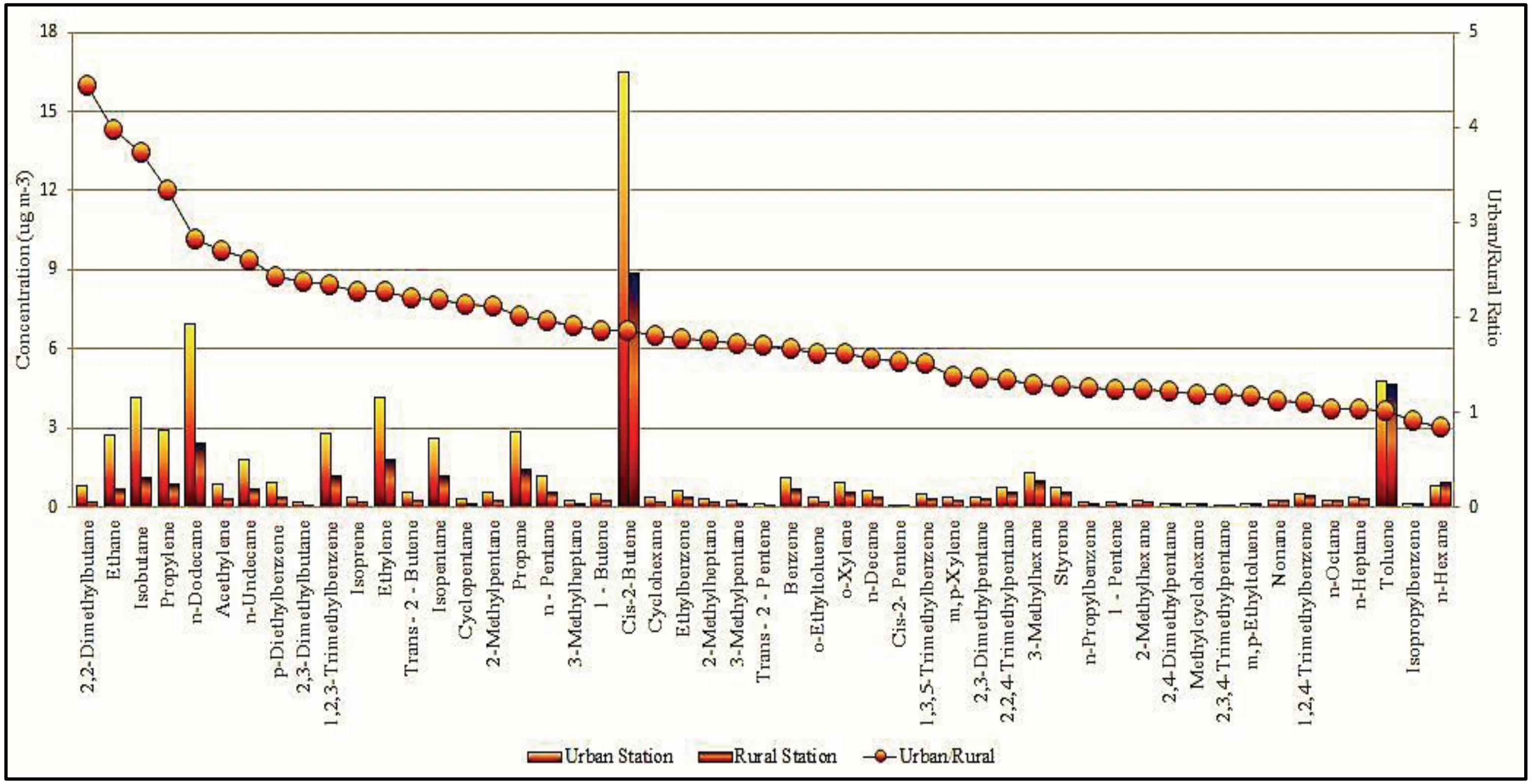


Figure 4.24 Median concentrations of measured VOCs at urban and Rural stations, urban to rural ratios

4.8 VOCs Ratios

Ratios of some VOCs are significant indicatiors to get information about possible emission sources of them. In the literature two VOCs ratio are used very commonly. These are toluene-to-benzene (T/B) and xylene-to-ethylbenzene (X/E) ratios (Na, et al, 2004 ; Nelson & Quigley, 1983).

T/B ratio represents traffic related emissions mostly, for this reason, this ratio is used for investigation of concentrations that are measured in urban locations generally. In some studies in the literature, this ratio was reported as about between 1.5 and 2.0 near to highways. Also, based on solvent usage, it was reported that this ratio may increase in some studies (Kuntasal, 2005 ; Elbir, et al.,2007). All VOCs have a different atmospheric reactivity. Concentration of a more reactive compound is lower than a less reactive one because of photochemical reactions in the atmosphere. Reactivity of benzene is slightly lower than reactivity of toluene, but toluene can be removed from atmosphere more rapidly due to higher reaction rates with hydroxyl radicals (Elbir, et al., 2007).

In addition to get information about possible emission sources of VOCs, by using some ratios “age of hydrocarbons in the ambient air” (Nelson & Quigley, 1983) can be determined. For this aim, X/E ratio is used as an indicator (Guo, et al., 2007). X/E ratio that is emitted by possible sources presumed as constant, but due to atmospheric reactions, lifetimes of xylenes are shorter than that of ethylbenzene in the ambient air. Consequently, xylenes removes from the air faster, and X/B ratio decreases (Doğan, 2013).

In this study, T/B ratio was calculated in urban and rural station, and variations of T/B ratio during sampling period were shown in the Figure 4.25 for both stations. As it can be seen from the figure, there is not a suggestive variation in T/B ratio during sampling period. Additionally, median value of T/B ratio was calculated as 3.16 and 3.94 in urban and rural stations respectively. Due to T/B ratio defines as an indicator of traffic related emissions, it is expected that this ratio is mostly higher in urban locations than that of rural locations. But in this study there is not a great differences between T/B ratios that were measured in urban and rural stations.

But, if it is compared with literature, this may be an acceptable result for both stations. In some different studies in the literature, T/B ratio was reported as between 1-6, and about 2 in a suburban and in an urban location where near to roadside, respectively (Hartmann,et al.,1997). In another study which was conducted in Hong Kong, T/B ratio was reported as between 5 and 6 (Guo, et al., 2004). The ratio may differ according to using fuel compositions, seasons, and toluene included solvent usage around sampling stations. For instance, unleaded gasoline that is enriched with aromatic hydrocarbons are cause to lower T/B ratio (Gee & Sollars, 1998). Additionally, rural station is near to Tavşanlı-Simav road and according to Figure 4.3 wind is blowing from where the Tavşanlı-Simav road located in. And, another dominant wind sector is ESE sector and downtown of Kütahya is located in this directon. So, one of the reason of close T/B ratios between urban and rural stations may be prevailing dominant wind sectors in rural station.

Also, average of T/B ratio was calculated in urban station as 3.53 and 2.73 in summer and winter respectively, and in rural station these values were calculated as 4.64 and 4.52 in summer and in winter respectively. As it can be seen, summer T/B ratios are higher than winter ratios. This is an expected result, because benzene is an important marker for residental heating related emissions (Elbir, et al., 2007), as well as traffic emissions. And, it is relatively high in winter, so T/B ratio that were calculated in summer is greater than that of in winter. Correspondingly, obtained lower T/B ratios in winter may result from residental heating.

In the Figure 4.26 wind sector dependence of T/B ratios in both stations were investigated. In urban station, as it is seen that T/B was affected by sources that were reside in almost all wind sectors, but especially N, NNW and WNW sector contributions are seen higher. As it was stated in the Section 4.1 that dominant wind directions in the urban region were N and NNW during sampling period. Furthermore, Seyitömer TPP and Tunçbilek TPP reside on the side of NNW and WNW sectors according to urban station respectively. Because of this fact, at the first sight it may look as if TPPs are responsible for higher T/B ratios. However, it is not a conclusive indication, since there is no evidence about toluene emitted by thermal power plants. It is known commonly as a good marker of solvent usage.

While in rural station, contribution of W and WSW wind sectors in T/B ratios are higher than other sectors. As it was shown in the Figure 4.3, wind is blowing from W and ESE sectors dominantly in rural station. And, Tavşanlı-Simav road is located in W side of the rural station, so it may be the main reason of high T/B ratio in W wind sector. Additionally, toluene concentrations were measured very high in some days, so to make more precise interpretation, effects of amount of wind blowing in related sectors CPF calculations were done. And, according to CPF calculatitons which were conducted in rural station, contribution of N sector is very distinct. Tavşanlı-Kütahya road is in the side of N sector and very near to rural station So, high toluene concentrations may result from this district. For this reason, it is difficult to make a certain decision how much of T/B ratio in N sector result from power plants or emissions in Tavşanlı-Kütahya road.

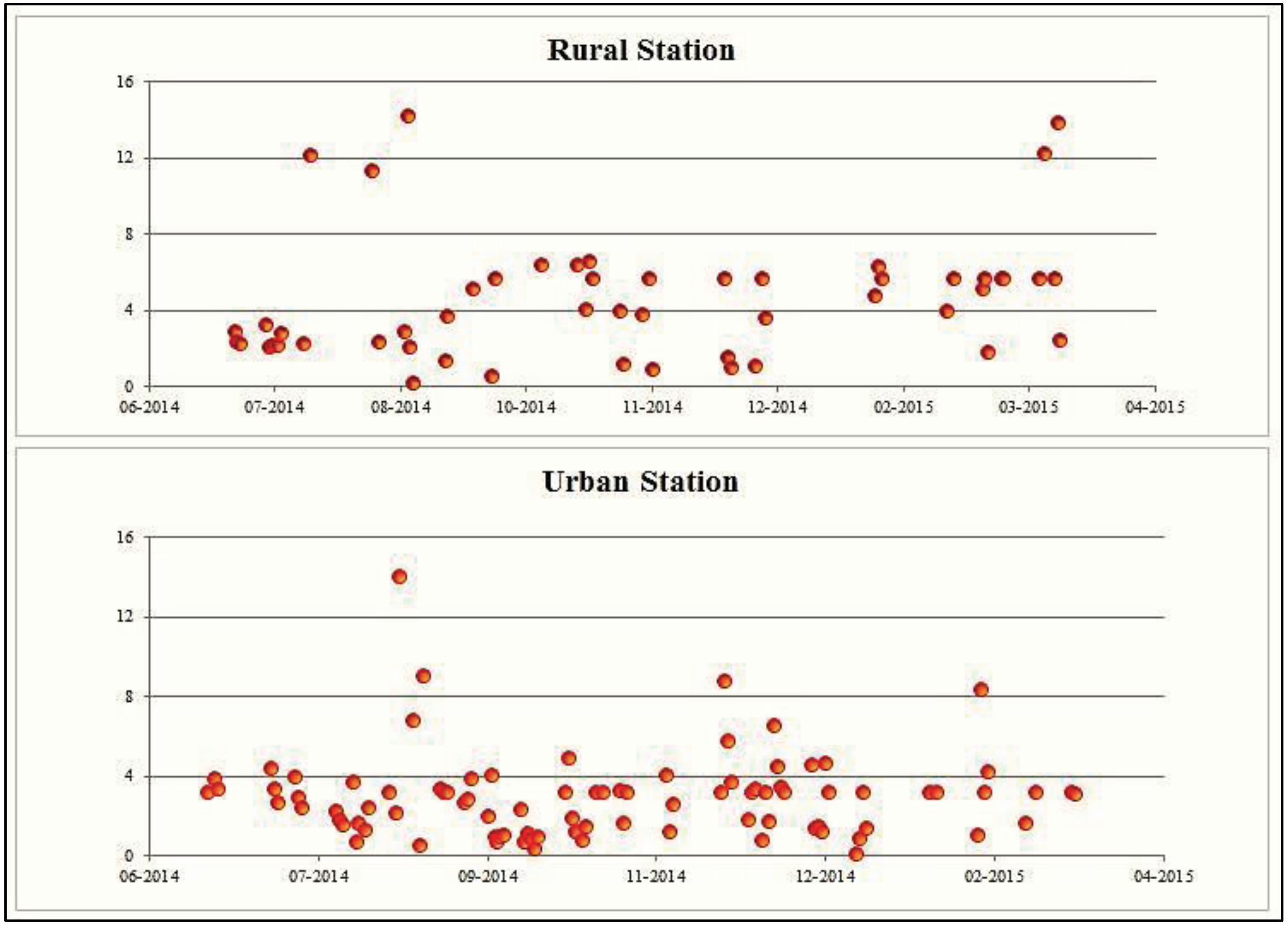


Figure 4.25 Variations of T/B ratio in urban and rural station during sampling period

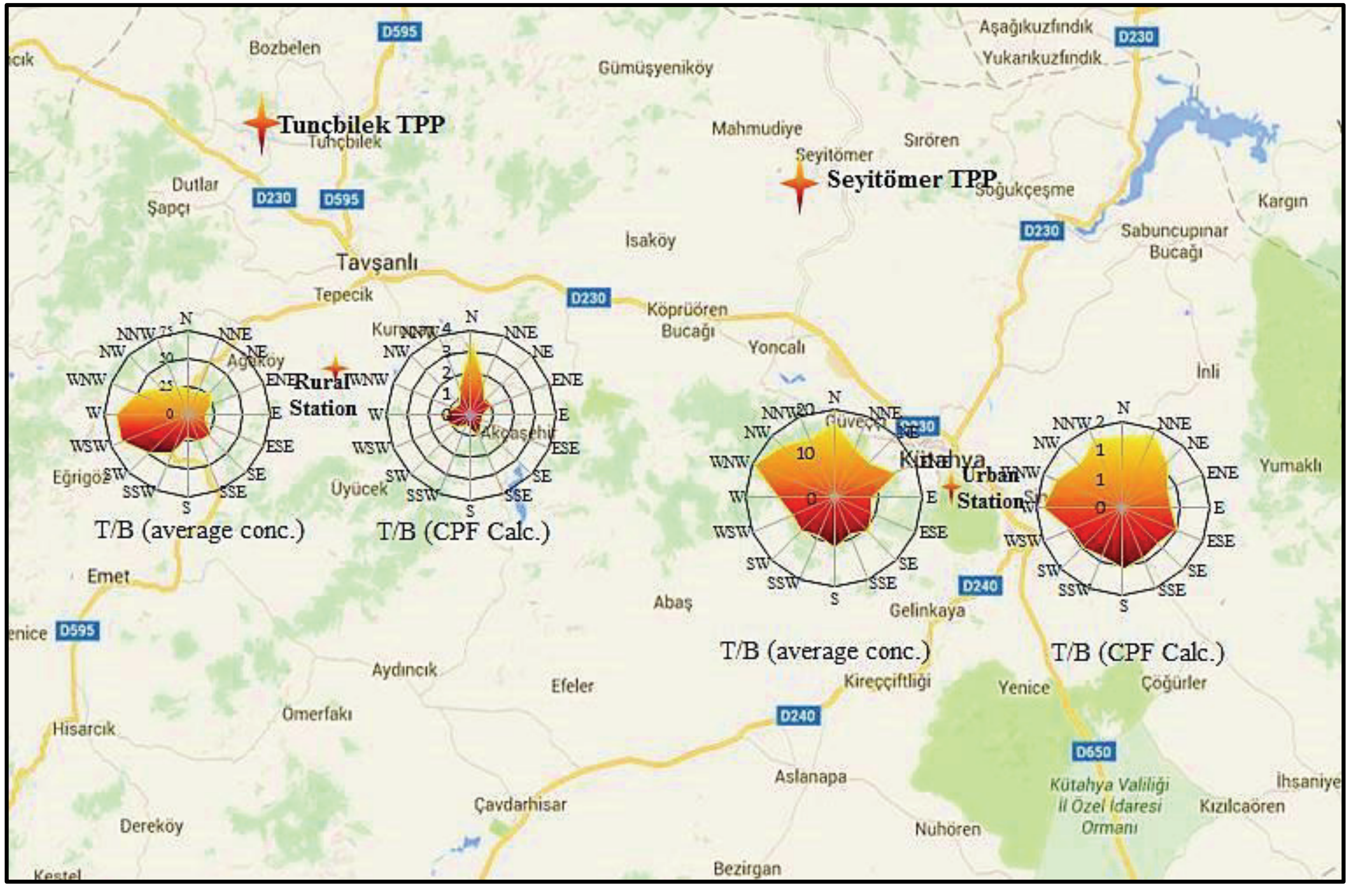


Figure 4.26 Wind sector dependence of average concentration and CPF calculations of T/B ratios in both stations

In addition to T/B ratio, same studies were conducted in order to investigate variations and wind sector dependence of X/E ratio in both stations. X/E ratio is used as an indicator to determine hydrocarbon age in the ambient air, or “age of air mass" (Nelson & Quigley, 1983). In other words, distance between sources of the relevant species and sampling site can be estimated considering X/E ratio. The main sources of xylenes and ethylbenzene are diesel fuel oil, gasoline, coal combustion and traffic (Cai, et al., 2010 ; Schauer, et al.,2001). As it was stated in the beginning part of this section, xylenes removes from the air faster than benzene, and due to this fact X/E ratio decreases if the source is far from the sampling site (Doğan, 2013).

Variations of X/E ratio during sampling period were shown in the Figure 4.27. As it can be seen from the figure there is not a suggessive statistical variation in X/E ratio during sampling period. And, median concentrations of the ratio was calculated as 0.76 and 0.82 in urban and in rural station respectively. As it was stated earlier, X/E ratio used for determining the age of air mass, and xylenes are removed more quickly than ethylbenzene. Accordingly, X/E ratio that were calculated in polluted air mass which come from much polluted locations should be lower than that of in less polluted locations.

Also, seasonal factors effects X/E ratio. Atmospheric reaction rates accelerate due to high temperatures (Kuntasal Ö. , 2005), so species should be removed from the atmosphere more quickly in the summer. This inference was obtained in both stations, average concentrations that were measured in summer was higher than that in winter.

Furthermore, in order to investigate whether there are any contributions of wind sectors where TPPs reside in on X/E ratio, Figure 4.28 was prepared. According to the figure, it is not possible to mention a certain contribution of TPPs to X/E ratios in both stations.

Fundamentally, investigation of VOCs ratio can be defined as preliminary source identification for some species. However, they can not be sufficient to be able to determine contributions of all possible sources. The most powerful tools are receptor modelling studies for this aim, and in the subsequent section of the study, all possible source contributions to concentrations of VOCs that were measured in both stations will be discussed in detail.

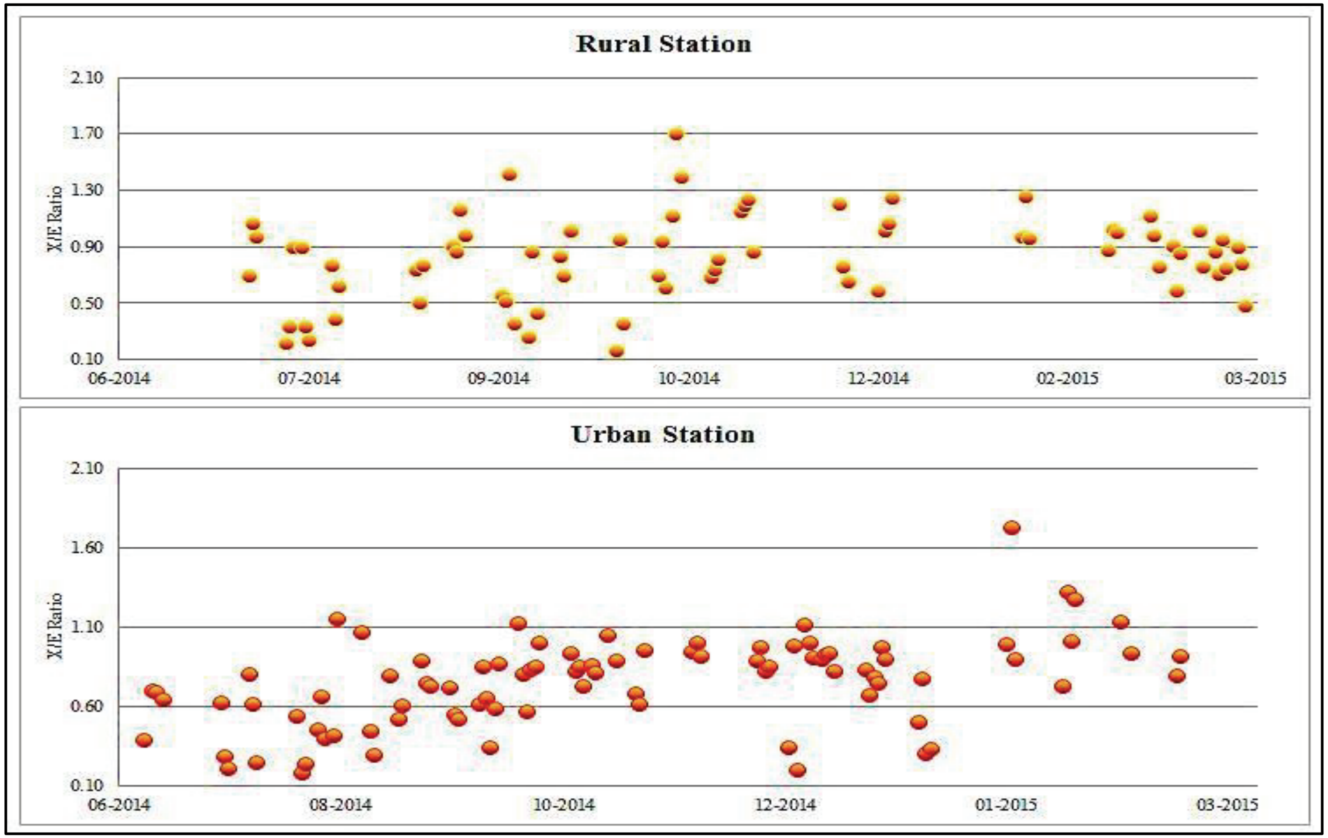


Figure 4.27 Variations of X/E ratio in urban and rural station during sampling period

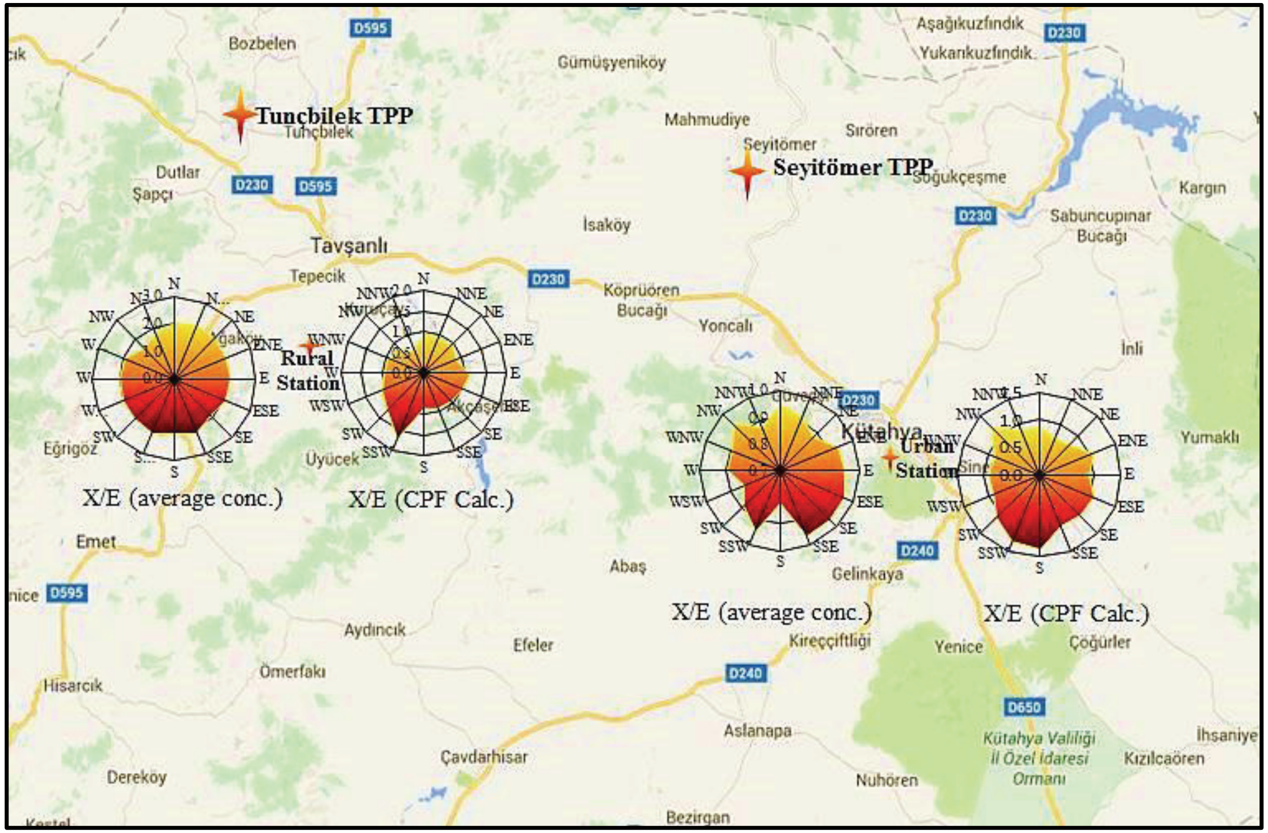


Figure 4.28 Wind sector dependence of average concentration and CPF calculations of X/E ratios in both stations

CHAPTER 5

SOURCE APPORTIONMENT

5.1 Positive Matrix Factorization (PMF) in Rural Station

After several trials, 8 and 9 factor solutions were evaluated in detail according to an approach which was explained in the Section 3.6, and 8 factor solution was found to be most explainable. The $Q_{theoretical}$ and Q_{robust} values were 1812 and 4281, respectively. The ratio of Q_{robust}-to-$Q_{theoretical}$ was 2,4 indicating a reasonable quality of the model fit. Factor loadings and percentage of measured VOC concentrations in factor profiles are given in Tables 5.1 and 5.2, respectively.

Table 5.1 Measured VOC concentrations in factor profiles for rural station

	F1	**F2**	**F3**	**F4**	**F5**	**F6**	**F7**	**F8**
				(µg/m^3)				
Ethane	0.07	0.00	0.78	0.02	0.06	0.06	0.00	0.07
Ethylene	1.96	0.00	0.24	0.13	0.47	0.21	0.16	0.25
Propane	0.34	0.12	0.14	0.20	1.20	0.07	0.13	0.20
Propylene	0.67	0.00	0.02	0.08	0.62	0.14	0.07	0.22
Isobutane	0.84	0.00	0.04	0.13	0.91	0.19	0.00	0.32
Acethylene	0.20	0.21	0.05	0.01	0.11	0.00	0.01	0.01
Trans - 2 - Butne	0.00	0.00	0.08	0.00	0.12	0.00	0.13	0.02
1 - Butene	0.06	0.00	0.01	0.02	0.18	0.02	0.08	0.03
Cis-2-Butene	1.24	0.08	0.23	0.88	2.68	0.84	6.59	0.38
Cyclopentane	0.03	0.00	0.01	0.01	0.11	0.00	0.04	0.02
Isopentane	0.50	0.06	0.14	0.03	0.30	0.28	0.11	0.40
n - Pentane	0.13	0.08	0.03	0.09	0.05	0.18	0.08	0.08
Trans - 2 – Pentn	0.02	0.00	0.01	0.02	0.02	0.00	0.01	0.01
1 - Pentene	0.03	0.00	0.05	0.02	0.05	0.00	0.07	0.01
2-Methylpentane	0.00	0.23	0.02	0.00	0.02	0.16	0.02	0.04
Isoprene	0.04	0.00	0.03	0.00	0.16	0.01	0.09	0.03
n-Hexane	0.00	0.79	0.00	0.00	0.00	0.69	0.18	0.16
2,4-Dimethylpen	0.00	0.08	0.04	0.00	0.01	0.09	0.01	0.02
Benzene	0.23	0.20	0.00	0.18	0.20	0.02	0.04	0.01
2-Methylhexane	0.02	0.06	0.00	0.04	0.04	0.06	0.08	0.04
3-Methylhexane	0.08	0.10	0.00	0.04	0.13	0.10	0.78	0.04
n-Heptane	0.05	0.05	0.01	0.06	0.08	0.03	0.10	0.03
2,3,4-Trimethylp	0.01	0.02	0.01	0.02	0.01	0.00	0.02	0.01
Toluene	1.68	0.00	0.00	0.00	1.18	12.36	0.00	1.86

Table 5.1 (Continued)

	F1	F2	F3	F4	F5	F6	F7	F8
				(μg/m^3)				
n-Octane	0.05	0.04	0.01	0.02	0.11	0.05	0.07	0.04
Ethylbenzene	0.10	0.02	0.03	0.03	0.12	0.12	0.07	0.61
m,p-Xylene	0.20	0.04	0.03	0.03	0.23	0.21	0.07	1.37
Styrene	0.08	0.07	0.04	0.09	0.02	0.03	0.25	0.04
o-Xylene	0.13	0.11	0.02	0.09	0.12	0.10	0.10	0.86
Nonane	0.02	0.02	0.01	0.03	0.12	0.06	0.03	0.21
Isopropylbenzene	0.00	0.04	0.03	0.04	0.00	0.02	0.02	0.03
n-Propylbenzene	0.01	0.03	0.01	0.05	0.02	0.02	0.02	0.02
1,3,5-Trimethyb	0.03	0.04	0.00	0.07	0.17	0.06	0.02	0.18
1,2,4-Trimethylb	0.00	0.06	0.03	0.11	0.03	0.02	0.08	0.04
n-Decane	0.00	0.02	0.09	0.05	0.20	0.10	0.00	0.14
n-Dodecane	0.03	0.18	0.00	3.62	0.03	0.12	0.39	0.18

Table 5.2 Percentage of VOC concentrations in factor profiles that were obtained in rural station

	F1	F2	F3	F4	F5	F6	F7	F8
Ethane	6.79	0	72.87	2.21	5.55	5.79	0	6.78
Ethylene	57.52	0	6.90	3.72	13.85	6.14	4.55	7.30
Propane	14.15	4.91	5.91	8.40	49.93	3.04	5.23	8.43
Propylene	36.72	0.22	1.18	4.37	33.97	7.82	3.80	11.9
Isobutane	34.73	0.00	1.54	5.25	37.50	7.95	0.00	13.0
Acethylene	33.19	34.87	8.78	1.68	17.83	0.00	1.84	1.81
Trans - 2 - Butne	0.00	0.00	23.23	0.00	33.76	0.00	38.4	4.56
1 - Butene	15.00	0.71	3.53	4.82	44.57	4.09	19.4	7.86
Cis-2-Butene	9.59	0.62	1.80	6.80	20.76	6.50	50.9	2.95
Cyclopentane	11.55	1.90	5.81	5.40	48.76	0.69	18.4	7.43
Isopentane	27.31	3.42	7.43	1.79	16.48	15.39	6.07	22.1
n - Pentane	18.08	11.47	4.64	12.07	7.14	25.17	10.9	10.5
Trans - 2 – Pentn	19.09	3.89	15.73	24.62	21.06	1.41	7.47	6.73
1 - Pentene	14.71	1.80	21.86	7.72	20.27	1.72	28.7	3.18
2-Methylpentane	0.00	46.93	4.39	0	3.30	33.70	3.65	8.03
Isoprene	12.08	0.00	7.88	0	45.42	2.05	25.0	7.57
n-Hexane	0.00	43.53	0.00	0	0	37.74	9.89	8.83
2,4-Dimethylpen	0.00	31.74	15.90	0	2.41	38.01	4.78	7.17
Benzene	25.44	22.67	0.00	20.50	22.96	2.16	4.75	1.52
2-Methylhexane	6.94	17.52	0.00	11.51	11.67	17.22	22.5	12.6
3-Methylhexane	6.06	7.95	0.00	3.41	10.12	7.69	61.7	3.03
n-Heptane	11.89	12.04	1.79	15.22	19.63	6.85	25.3	7.32
2,3,4-Trimethylp	7.75	21.39	7.65	21.77	11.82	0	18.6	10.9
Toluene	9.82	0	0	0	6.89	72.39	0.00	10.9
n-Octane	12.45	10.88	2.13	4.84	28.38	12.05	18.9	10.4
Ethylbenzene	9.08	2.15	2.49	3.08	10.88	10.74	6.18	55.4
m,p-Xylene	9.22	1.71	1.51	1.22	10.44	9.79	3.09	63.0
Styrene	13.37	11.70	6.78	13.88	3.44	5.05	40.0	5.78
o-Xylene	8.35	7.16	1.63	5.77	7.78	6.79	6.55	55.9
Nonane	4.81	4.64	1.07	6.93	23.93	11.05	5.66	41.9
Isopropylbenzene	0.00	20.89	17.35	20.16	2.48	9.43	13.4	16.3
n-Propylbenzene	3.94	15.76	7.36	25.94	11.57	11.51	10.5	13.4
1,3,5-Trimethyb	6.08	6.23	0.15	13.09	29.78	10.67	2.87	31.2
1,2,4-Trimethylb	0.00	16.01	9.01	28.21	8.26	6.53	21.2	10.8
n-Decane	0.00	4.07	14.72	7.97	33.45	17.08	0	22.7
n-Dodecane	0.59	3.89	0	79.76	0.60	2.72	8.54	3.90

At the beginning of the PMF studies, it was expressed that an approach was developed in order to obtain a successive result from PMF. According to this approach, poorly modelled compounds were removed from the PMF input taking into consideration their replacement amounts, S/N ratio, residual analysis, and r^2 values. As it was stated earlier, due to high amount of missing data values, 3-methylpentane, 2-methylheptane and m,p-ethyltoluene were removed from PMF input files. And, in rural station, 12 more compounds were removed and they were cis-2-pentene, 2,2-dimethylbutane, 2,3-dimethylbutane, cyclohexane, 2,3-dimethylpentane, 2,2,4-trimethylpentane, methylcyclohexane, 3-methylheptane, o-ethyltoluene, 1,2,3-trimethlybenzene, p-diethylbenzene, and n-undecane. Thus, an acceptable Q_{robust}-to-$Q_{theoretical}$ ratio was obtained.

Diagnostic figures for Factor 1 are depicted in Figure 5.1. These figures included factor loadings, which are the concentrations of VOCs in that particular factor. Percentage of the concentration of each specie accounted by that factor. Monthly average factor scores and average scores at each wind direction. Similar plots were prepared for each factor and discussed in this section. Among these diagnostic plots we find percentage of VOCs accounted by factors, which corresponds to explained variance in conventional factor analysis, more useful than factor loadings. Species can have high concentration in a factor, but it does not mean that that particular VOC is highly associated with or correlated with that factor. For example toluene in factor 1 has the second highest concentration in F-loadings. However, factor 1 account for only 10% of its modeled concentration. Approximately 60% of the measured concentration of toluene is accounted for by factor 6. This is true, not only for toluene, but also for most of the VOCs. Consequently fraction of VOC concentrations accounted for by each factor provides a better mean to identify physical meaning of factors than factor loadings.

Factor 1 explains > 30% of the concentrations of ethylene, propylene, isobutene and acetylene. It also explains approximately 20% of the concentration of isopentane and benzene. These are light hydrocarbons generally associated with gasoline exhaust (McCarthy et a., 2013; Shaoa et al., 2014; Selia et al., 2001) and evaporative emissions from vehicles (Watson et al., 2001; Kota et al., 2014). The profiles for evaporative emissions and gasoline exhaust are very similar and difficult to differentiate. Factor 1 includes isobutene, which is well documented tracer for evaporative emission from cars (Watson et al., 2001; McCarty et al., 2013). 1-butane and Cis-2-butane, which are associated with factor 1, are also good tracers of evaporative emissions from gasoline powered vehicles (Ho et al., 2009)

Factor 1 was identified as evaporative emissions from gasoline powered vehicles. However, it is probably mixed with exhaust emissions, because factor 1 also accounts for a high fraction of the concentrations of combustion products, such as propylene and acetylene, which normally occur in exhaust emissions, but not in evaporative emissions. Consequently, factor 1 represents a mixture of VOCs originating from evaporation in the engine and tailpipe.

Monthly averages of factor scores indicate that the factor is more effective in winter. This seasonal pattern is common for exhaust emissions and generally attributed to seasonal variations in mixing height (Kuntasal et al., 2013) and faster reactions that destroy hydrocarbons in summer (Jia et al., 2016). Evaporative emissions also follow the same seasonal pattern. Please note that evaporative emissions from car and gasoline evaporation, which dominates VOC concentrations in gas stations, have differences in terms of their seasonal pattern. Magnitude of evaporative emissions depends on engine temperature, whereas magnitude of gasoline evaporation in gas stations depends on ambient temperature and thus higher in summer season (Kuntasal et al., 2013).

Wind sector dependence of factor scores, which is shown in Figure 5.1, indicates that factor scores are fairly uniformly distributed in all directions except slightly higher values in WNW, W, WSW, SW, SSW and S directions. The roads that can affect traffic related VOCs in rural station lies to the north (the road that connects Tavşanlı to Kütahya) and west (The road that connects Tavşanlı to Simav). Higher scores at WNW, W and WSW sectors may be due to contribution of Tavşanlı – Simav road.

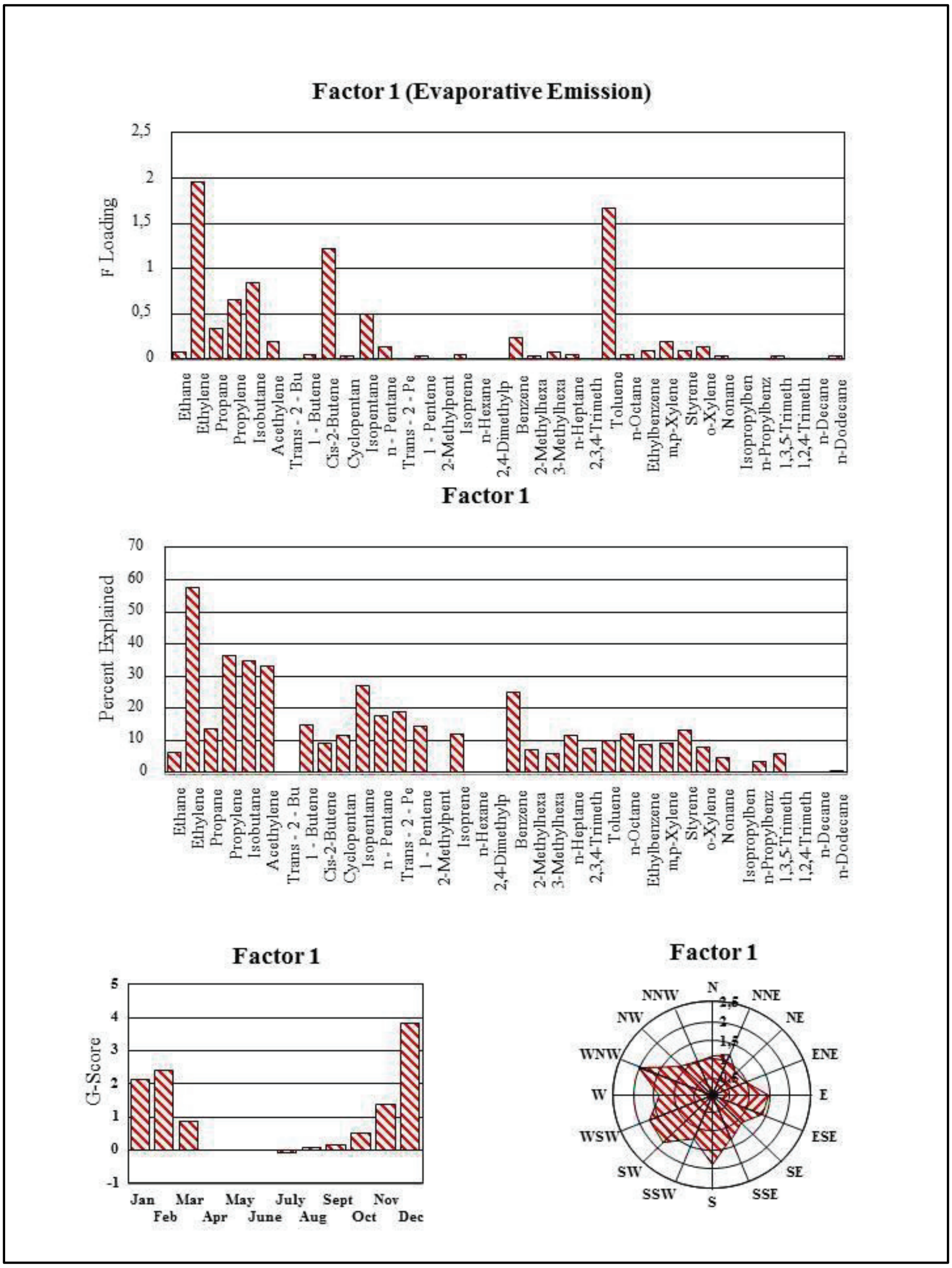


Figure 5.1 Diagnostic figures for factor 1 in rural station

For factor 2, F-loading, percent explained, seasonal variation of factor scores and wind sector dependence of the scores are depicted in Figure 5.2. Factor 2 is also loaded with C_4–C_8 hydrocarbons, including acetylene, propane, n-pentane,2-methylpentane, hexane, 2,4-dimethylpentane, benzene2-methylhexane, n-heptane, 3-methylhexane, 2,3,4-trimethylbenzene, isopropylbenzene, and 1,2,4-trimethylbenzene.

Most of the VOCs included in factor 2, such as 2-methylpentane, n-hexane, benzene, 3-methylhexane, 1,2,4-trimethylbenzene are marker species for light duty vehicle exhaust (Watson et al., 2001; Shaoa et l., 2008; Ho et al., 2009). Acetylene included in this factor is a combustion product and a good marker for light duty vehicle exhaust and is not expected to occur in evaporative emissions. Based on these arguments factor 2 was identified as light-duty vehicle exhaust emissions.

Seasonal variations in factor 2 scores closely resemble to seasonal variation observed in factor 1 scores, with higher scores in winter season. Scores are slightly higher in WNW and W sectors, which may be due to traffic activity on Tavşanlı-Simav road.

Diagnostic figures prepared for factors 1 and 2 closely resemble each other. It is well documented that emissions from tailpipe and engine evaporation have very similar compositions (Leuchner & Rappengluck, 2010). There are differences only in few VOCs. Differentiation of evaporative and exhaust emissions as factor 2 and factor 1 was based on the presence of lighter VOCs, and specific evaporative emission markers like butanes and particularly isopentane in factor 1 ,and not in factor 2. Generally combustion products, like propylene, acetylene, which are supposed to be associated with exhaust emission, but not with evaporative factor. However, in our case they exist in both factors 1 and factor 2. When the station is not in immediate vicinity of the source, VOC's from different sources can mix with each other and do not give a clear signal (or fingerprint of the source) (Srivastava, et al., 2005). This is probably what happened and evaporative emissions are mixed with tailpipe emissions and generated the profile in factor 1.

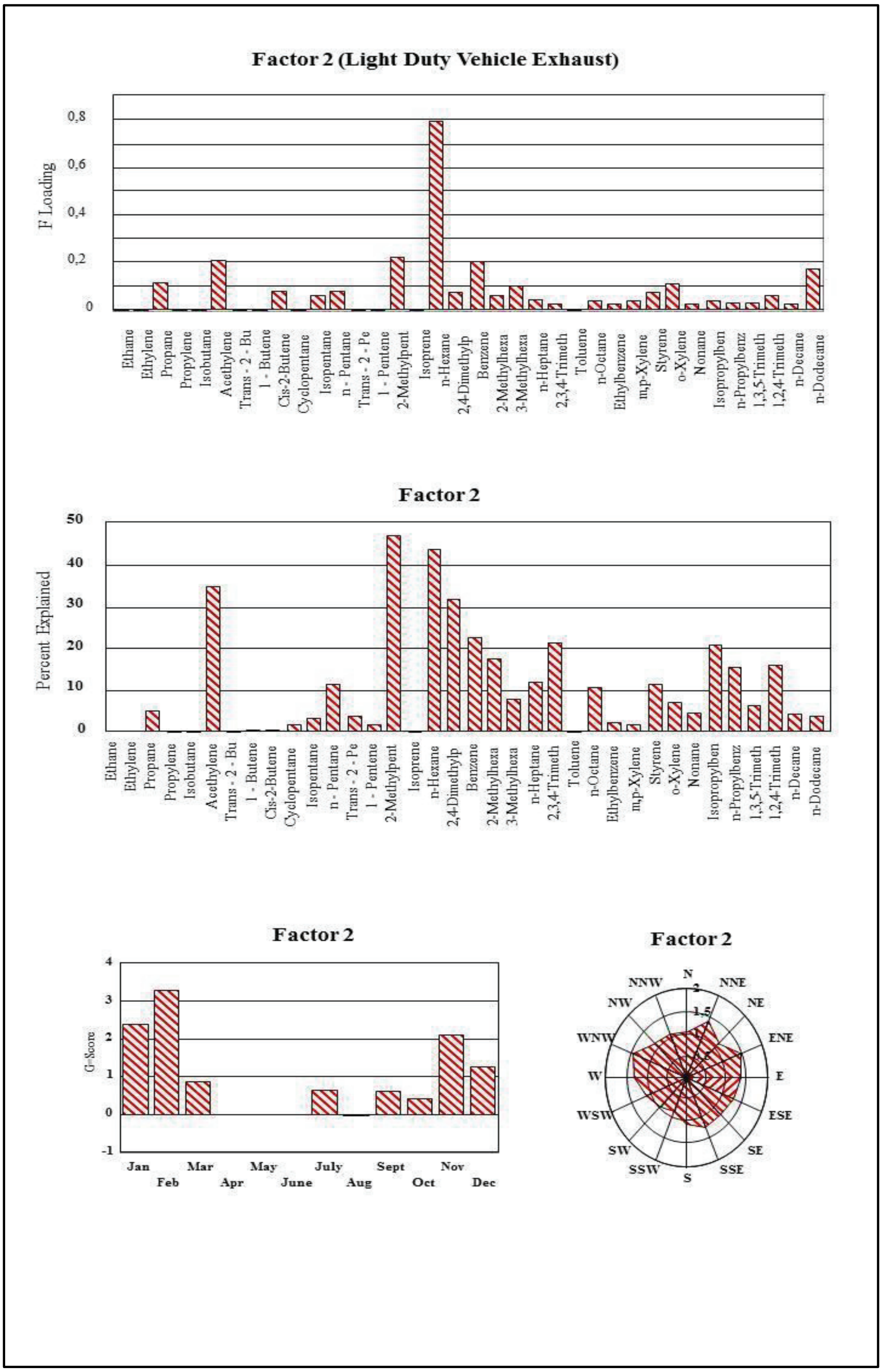
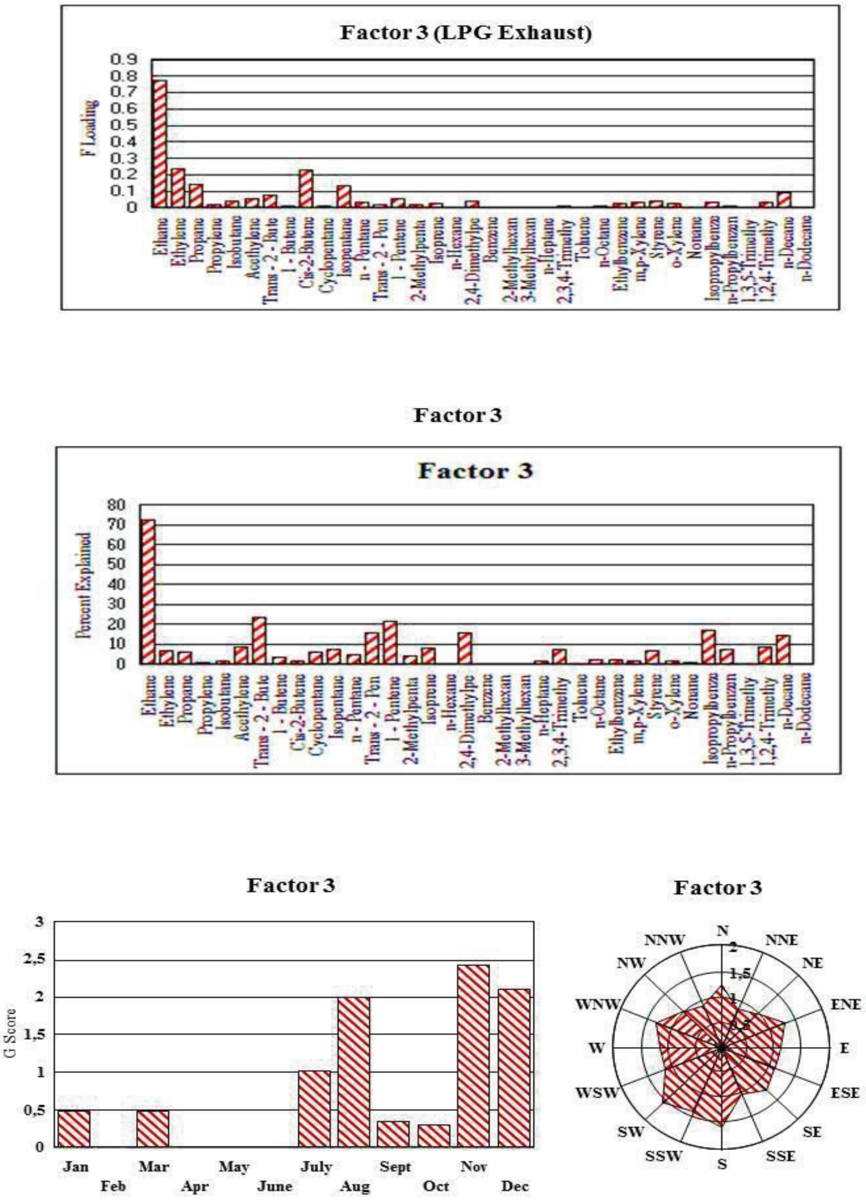


Figure 5.2 Diagnostic figures for factor 2 in rural station

Diagnostic plots for Factor 3 are given in Figure 5.3. Factor 3 is heavily loaded with ethane. It accounts for approximately 75% of measured ethane concentration. VOCs ethylene, propane trans-2-butane, 1-pentane are also associated with factor 3. These light hydrocarbons can be emitted from LPG vehicles and from natural gas (Watson et al., 2001; McCarthy et al., 2013; Jia et al., 2016). However, presence of combustion products such as ethane and ethylene favors LPG vehicle exhaust rather than natural gas.

Factor 3 scores do not depict a well-defined seasonal pattern, probably indicating that seasonal pattern is determined by both seasonal variations in emissions and meteorology. Please note that seasonal variations in factor scores which are determined by meteorology alone generally have lower G-score values in summer.

Factor 3 scores have higher values in WNW, N and ENE sectors. These are the sectors that include roads that connect Tavşanlı village to Simav and Kütahya. Based on these arguments, Factor 3 is assigned as emissions from exhausts of LPG vehicles.



Factor 5.3 Diagnostic figures for factor 3 in rural station

Diagnostic figures for factor 4 are given in Figure 5.4. Factor 4 is loaded with heavy hydrocarbons. Dodecane is the dominating VOC in this factor. Factor 4 accounts for approximately 80% of the dodecane concentrations measured at the rural station. The factor also accounts for >20% of the measured concentrations of 1,2,4-trimethylbenzene, n-propylbenzene, isopropylbenzene, 2,3,4-trimethylbenzene, benzene and trans-2-pentane. All of these VOCs, particularly dodecane are markers for diesel exhaust emissions (Watson et al., 2001; Shaoa et al., 2014; Ho et al., 2009; McCarthy et al., 2013; Schauer et al., 1999). Thus, Factor 4 is a clear diesel exhaust emission factor.

Factor scores do not show a clear seasonal pattern. This unexpected because concentration of species emitted from diesel vehicles are expected to be similar to the seasonal variations observed in Factors 1 and 2 for gasoline powered vehicles. It should be noted that monthly average values of factor scores (and monthly average concentrations of VOCs themselves) have high uncertainties due to small number of samples collected at rural station. We have a total of 75 samples collected in the course of 8 months of sampling. This means that we have approximately 10 samples in a month. However, since these samples are not distributed homogenously in 8 months, we ended up having few samples in some of the months. Unexpected seasonal patterns observed for some of the factors (and for concentrations of some of the VOCs) may be at least partly due to lack of sufficient data in some of the months.

Higher contribution of WNW sector may be due to Tavşanlı – Simav road in that direction. Similarly, higher values of the scores in N and NNE directions may be due to presence of Tavşanlı – Kütahya road in that sector. Obviously, as in Factor 1 and Factor 2, distribution of scores around the station is determined by orientation of roads around the station.

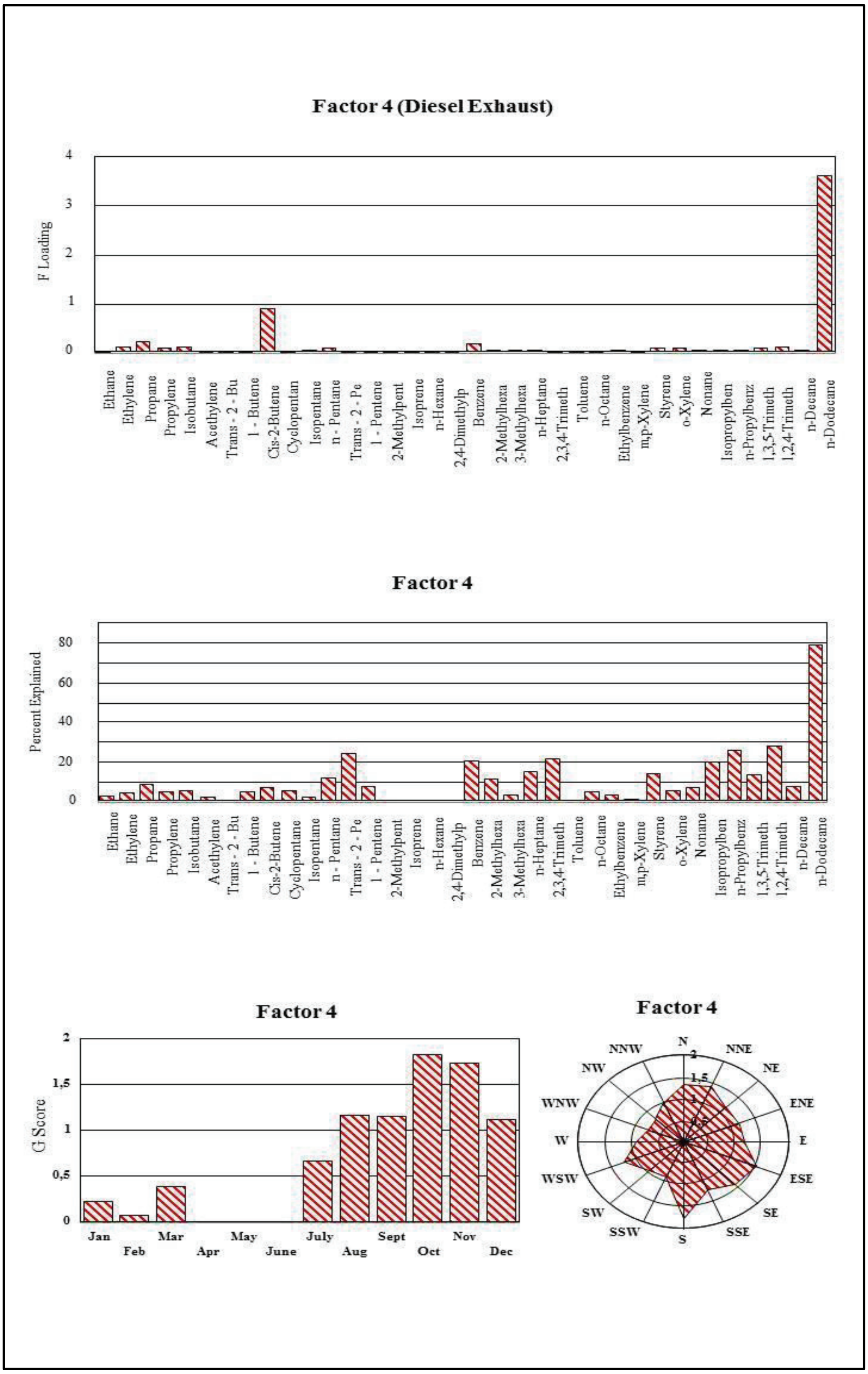


Figure 5.4 Diagnostic figures for factor 4 in rural station

Factor loadings, percentage of concentrations explained by factor, monthly average factor scores and average scores in each wind sector for factor 5 are given in Figure5.5. Factor 5 accounts for 50% of the concentrations of propane and cyclopentane, >40% of the concentrations of 1-butane, cylopentane and isoprene, <30% of the concentrations of propylene, isobutene, trans-2-butane and >20% of the concentrations of cis-2-butane, trans-2-pentane, Benzene, n-heptane, n-octane, nonane, 1,3,5-trimethylbenzene, n-decane.

Factor 5 seems to represent a mixture of sources, because it includes markers for very different source. For example markers for gasoline evaporation (isobutene, t-2-butane), gasoline exhaust (propylene, benzene, 1-butane), solvents (1-pentane), diesel exhaust emissions and/or asphalting activities all merged into one factor. Factor 5 is a mixed factor.

Factor 5 scores are very high in January, but this may be due to occurrence of only three factor score values in this month. One very high value (24) resulted in high January average. Sector dependence of factor 5 scores has a very clear signal from E. East is the wind sector in which Kütahya is located. Factor 5 is identified as the urban plume from Kütahya intercepted at our rural station.

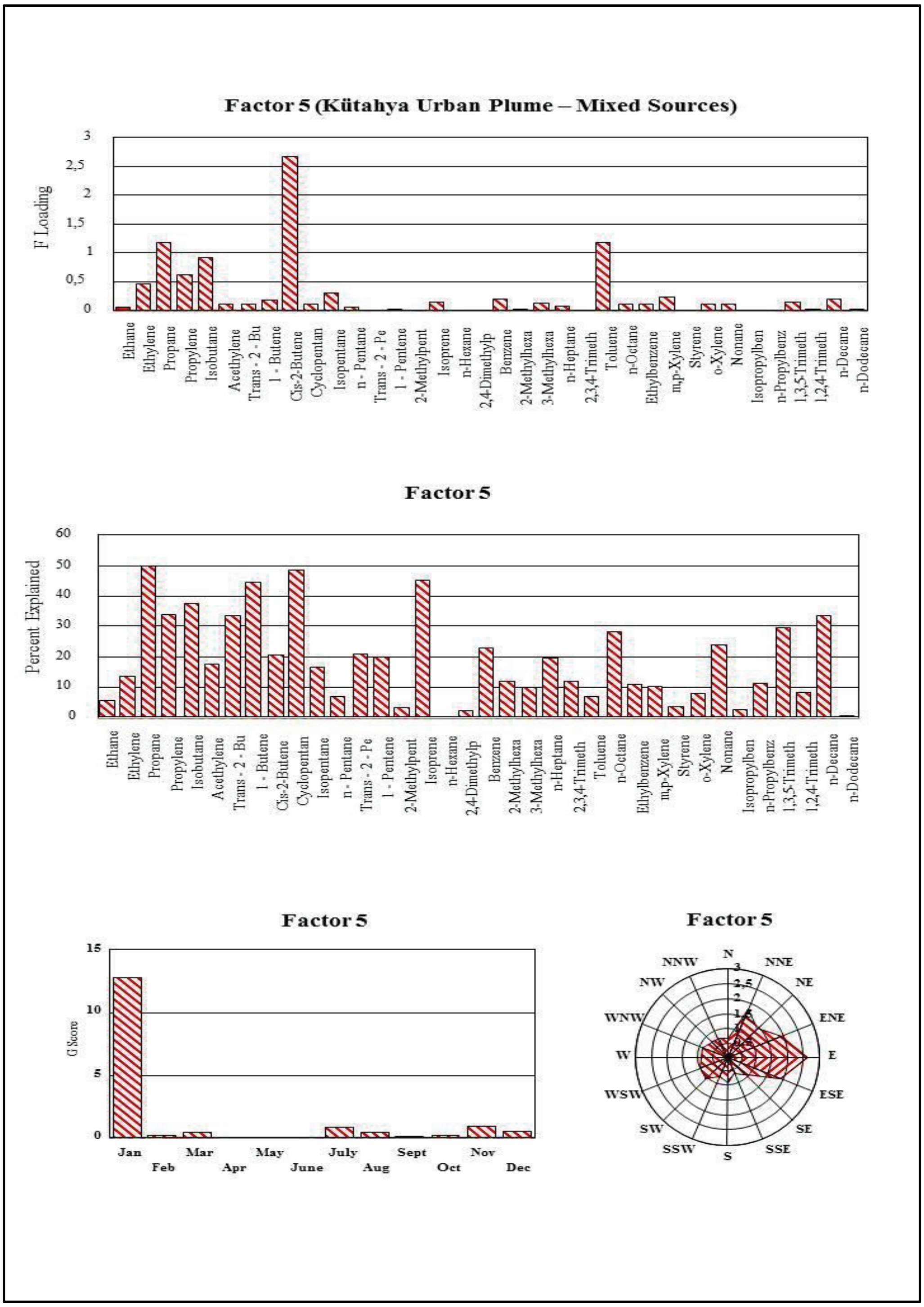


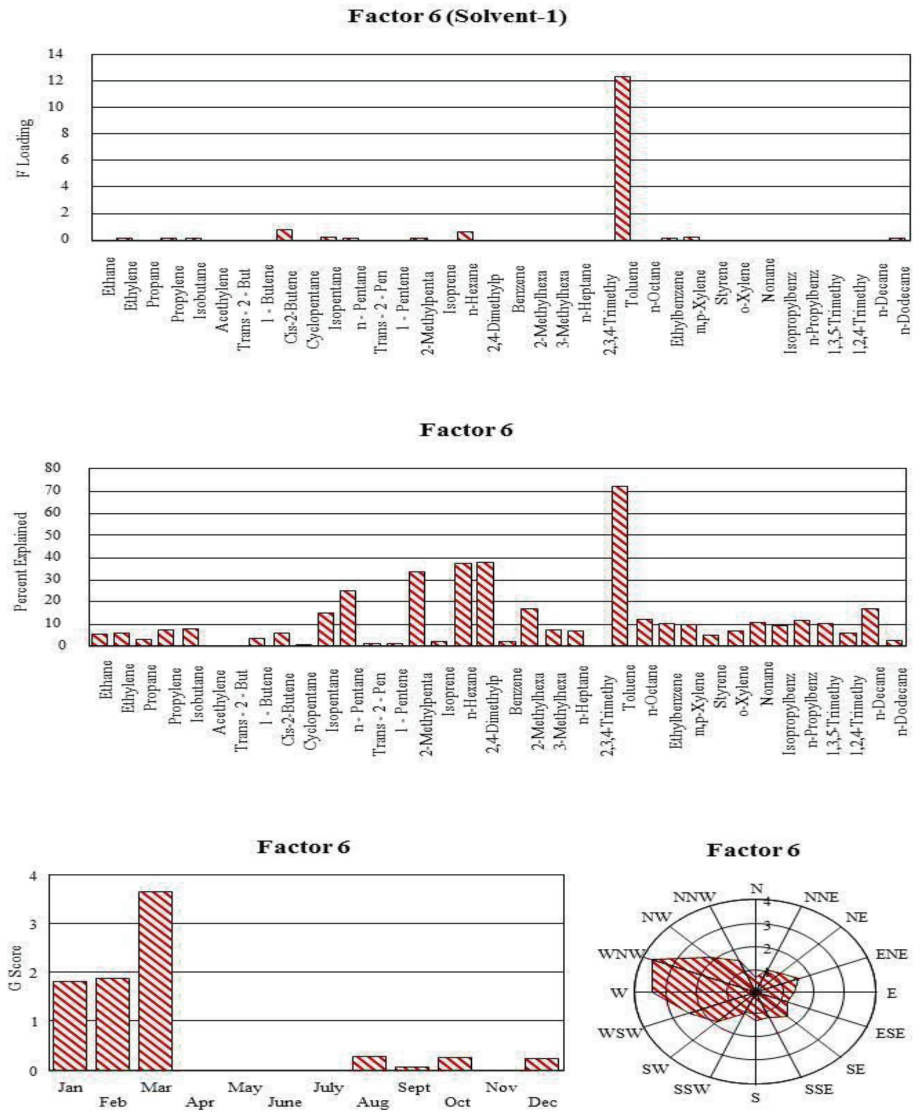
Figure 5.5 Diagnostic figures for factor 5 in rural station

Diagnostic figures for factor 6 are given in Figure 5.6. Factor 6 is a clear solvent factor. It accounts for approximately 70% of toluene concentration measured at rural station. In addition to toluene, factor 6 also accounts for 30% to 40% of the concentrations of 2,4-dimethyl pentane, n-hexane, 2-methylpentane and >20% of the concentration of n-pentane. These are all well documented markers of solvent evaporation (McCarthy et al., 2013; Ho et al., 2009; Jia et al., 2016; Kuo et al., 2014).

Sector average concentrations of factor 6 scores depicted a clear signal that the source generated Factor 6 lies in W and WNW sectors relative to station. However, there is no such a source in those sectors. We believe that Factor 6 represents solvent use activities in the premises of our rural station. No matter how small that solvent use activity is, it generated a strong signal in our PMF exercise, because it is very close to sampling point.

Diagnostic figures for Factor 7 are given in Figure PMF-2. This factor accounts for >50% of the measured concentrations of 3-methylhexane and cis-2-butane. The factor also accounts for >30% of the concentration of trans-2-butane, styrene, >20% of the concentrations of 1-butane, 1-pentane, cyclopentane, isoprene, 2-methyl hexane, n-heptane, n-octane, 1,2,4-trimethylbenzene.

Factor 7 is a mixed factor like in factor 5 (Kütahya urban plume). It includes VOCs which are good tracers of evaporative and gasoline exhaust (t-2-butane, 1-butane, isoprene, trimethylhexane), solvent use (pentanes, octane), emissions from paint (styrene, n-propylbenzene), diesel exhaust (1-butane, 1,2,4-trimethylbenzene). Wind sector averages of factor 7 scores have the highest values in N sector. This factor is identified as urban plume from Tavsanlı. Although Tavsanlı is not a highly populated city (population is about 62.000) it is fairly close to our rural station (distance is approximately 5 km). Due to this close proximity of the town to our rural station, urban plume from Tavşanlı generated a clear signal in our PMF exercise.



Factor 5.6 Diagnostic figures for factor 6 in rural station

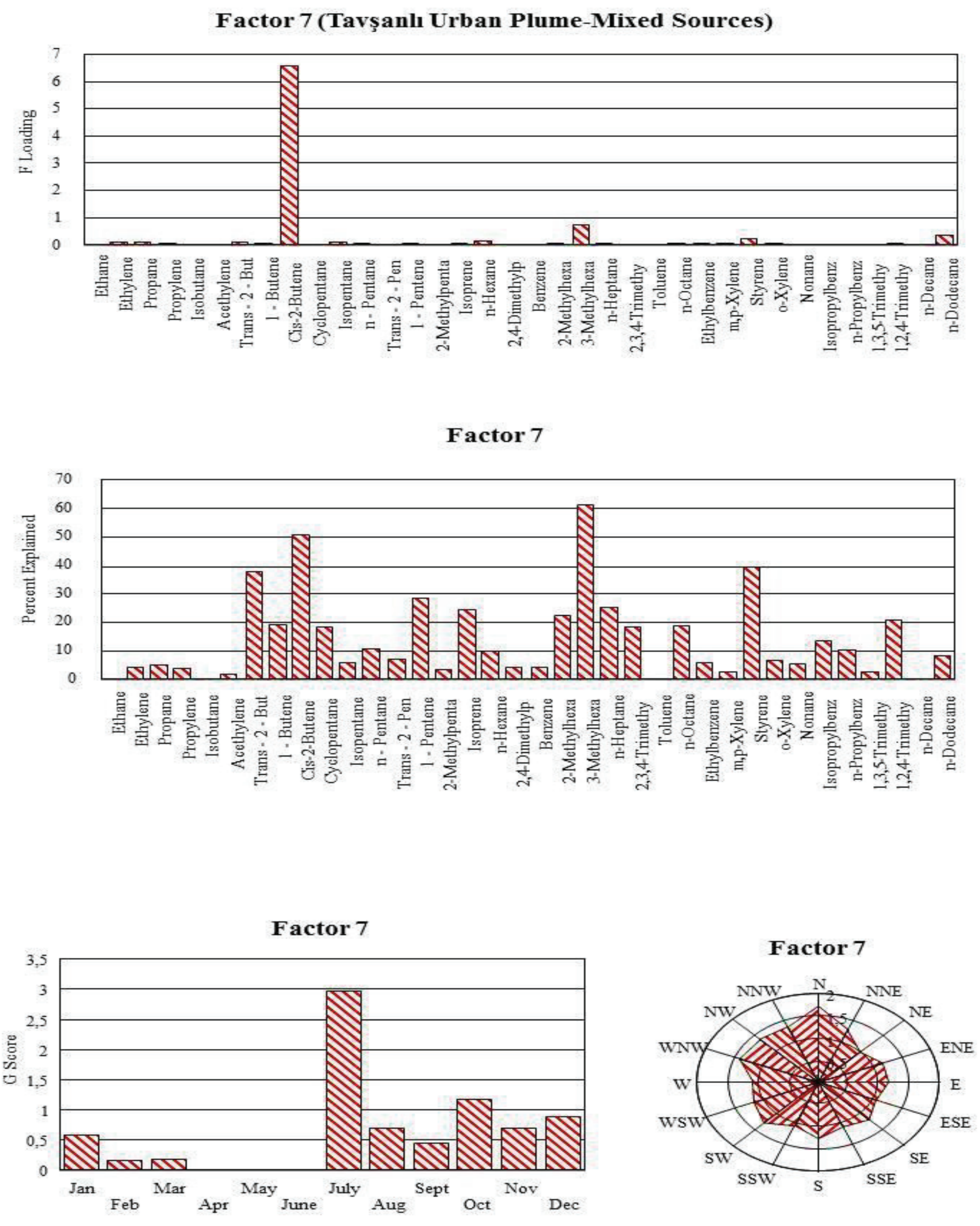


Figure 5.7 Diagnostig figures for factor 7 in rural station

Diagnostic figures for factor 8 are given in Figure 5.8. Factor explains more than 50% of the measured concentrations of ethylbenzene, m,p-xylene, and o-xylene concentrations. The factor also accounts for >20% of the concentrations of isopentane, nonane and 1,3,5-trimethylbenzene. This composition suggests that Factor 8 is a second solvent factor affecting our station. Although main source of ethylbenzene, m,p-xylene, o-xylene, which are among BTEX compounds, is emissions from gasoline exhaust, they are also known to be emitted from solvent use. This is also confirmed by very high toluene-to-benzene ratio (137) in Factor 7 loadings. The T/B ratio was 7 and 6 in factors 1 and 2, respectively and it was approximately 600 in factor 6, which was also a solvent factor. However, location of the source of this solvent source is not clear, because the average concentration of factor 8 scores in wind sectors do not depict a clear pattern.

Contribution of each factor to total VOC concentration is given in Figure 5.9. In the PMF exercise we identified a total of eight components in total VOC concentration. Four of these eight source categories were related to traffic emissions (Evaporative emissions, gasoline exhaust, LPG vehicle exhaust and diesel vehicle) total contribution of vehicle emissions to total VOC concentration at rural stations is approximately 30%. The mixture of evaporative emissions and light duty vehicle exhaust emissions (which is factor 1) makes up largest fraction of traffic contribution to total VOC mass, which is followed by diesel emissions, gasoline exhaust and LPC vehicles.

The local solvent use has the second important contribution to total VOC concentration after traffic. It accounts for approximately 26% of total VOC concentrations. The occurrence of this source in the immediate vicinity of the station should be the main reason fir it high contribution.

Kütahya and Tavşanlı urban plumes have 15% contribution to total VOC. The regional solvent factor (factor 8) accounts for approximately 12% of the total VOC concentration at the rural station.

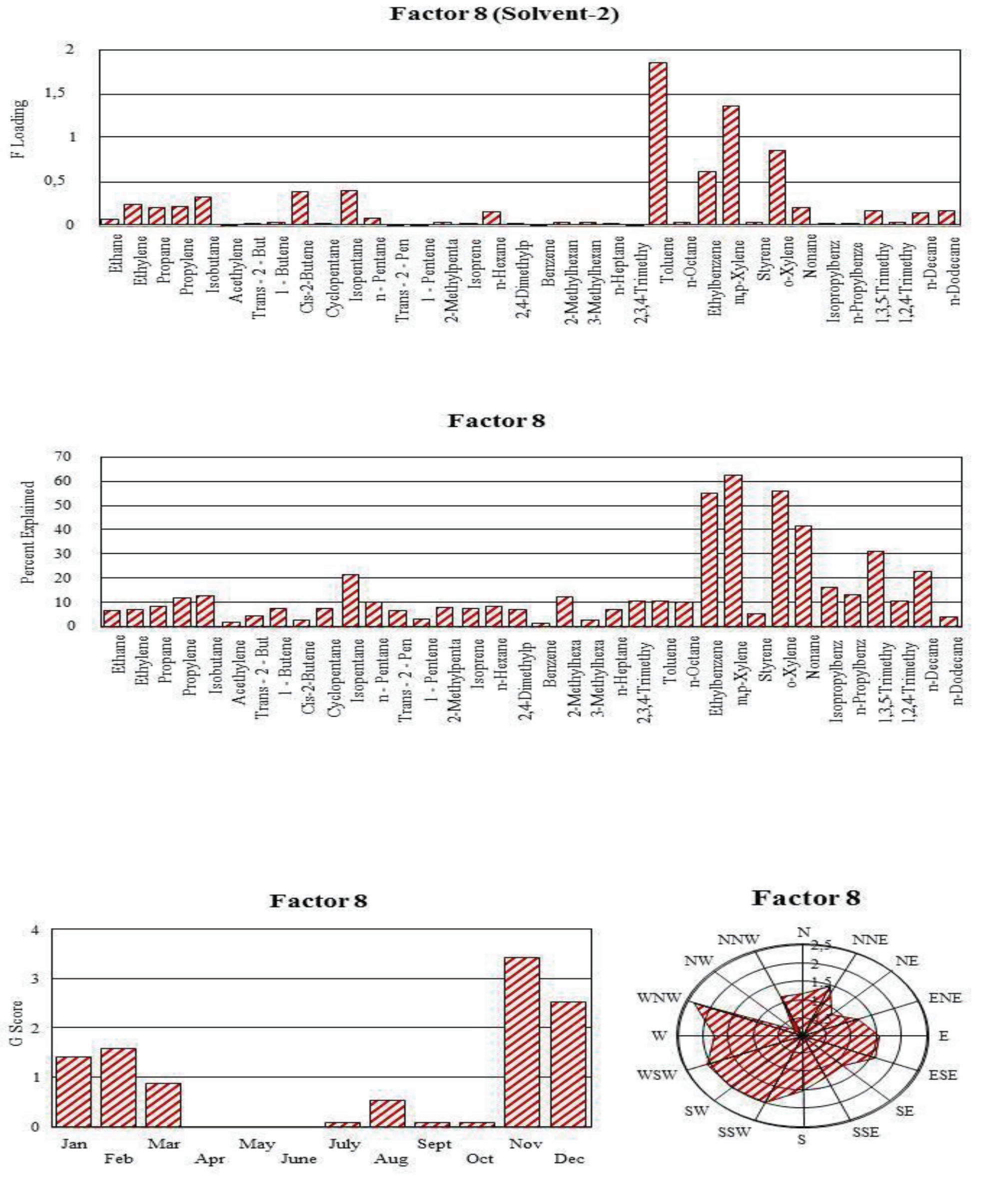


Figure 5.8 Diagnostic figures for factor 8 in rural station

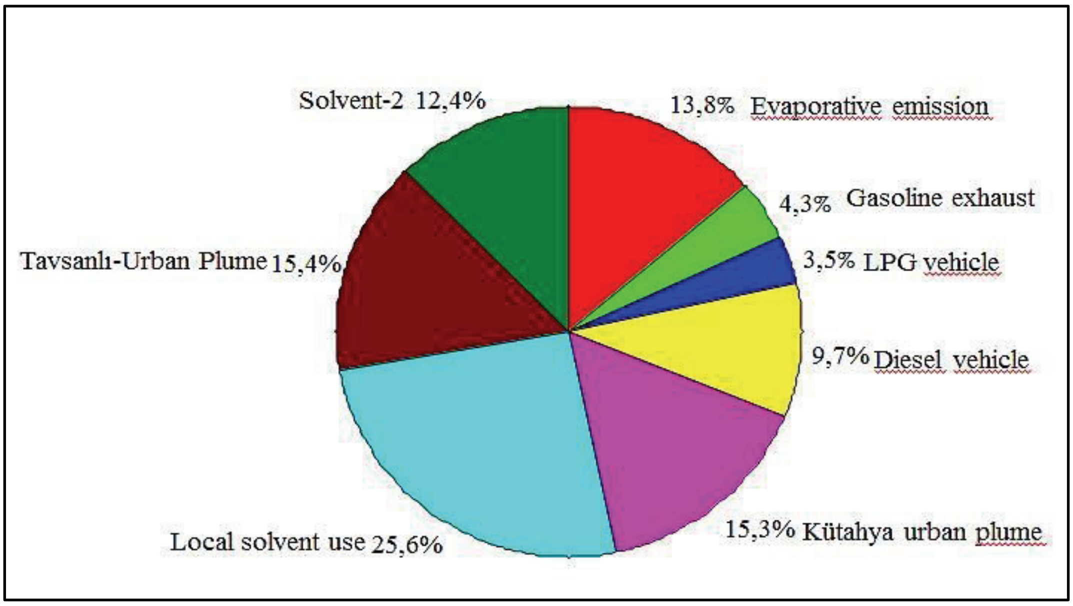


Figure 5.9 Contributions of factors to total VOC concentration in rural station

5.2 Positive Matrix Factorization (PMF) in Urban Station

The source apportionment in urban station using PMF resulted in 8 factors as well. After optimization Q_{robust} and $Q_{theoretical}$ values were 4700 and 1800, respectively, resulting in a $Q_{robust}/Q_{theoretical}$ ratio of 2.6, which indicates a reasonably good fit in the model. Factor loadings and percentage of measured VOC concentrations in factor profiles are given in Tables 5.3 and 5.4, respectively.

As in rural station, to obtain meaningful results from PMF, poorly modelled compounds were removed from the input of the model. In urban station 18 VOCs were removed using the same approach in rural station, and these compound were cis-2-butene, cyclopentane, n-pentane, trans-2-pentene, 1-pentene, cis-2-pentene, 2,3-dimethylbutane, 2,4-dimethylpentane, 2-methylhexane, 2,3-dimethylpentane, methylcyclohexane, 2,3,4-trimethylpentane, 3-methylheptane, n-octane, isopropylbenzene, o-ethyltoluene, 1,2,4-trimethylbenzene and n-decane.

Figures related to factor 1 are given in Figure 5.3. Factor 1 in urban PMF exercise has more than 20% contribution to dodecane, p-diethylbenzene, 1,2,3- trimethyl benzene, 1,3,5-trimethylbenzene, n-propylbenzene and n-heptane. This factor is one of the two factors, which are loaded with heavy hydrocarbons. Although factor one resembles Factor 4 in rural PMF exercises, which was assigned as diesel emissions, there are some minor differences. The most notable difference is the lack of VOCs like ethane, propylene and acetylene, which are combustion products and indicate exhaust emissions from both gasoline-powered and diesel-powered vehicle exhaust. Also contribution of Factor 1 on total VOC concentrations is less than what we expect to see from a diesel exhaust emissions. Factor 1 is assigned as asphalting operations a source, which is also associated with heavy hydrocarbons.

Although we did not pay too much attention to monthly average factor scores owing to small number of data at each month, monthly average Factor 1 scores make sense with asphalt source. Factor 1 scores are significantly higher in August than in all other months which are in agreement with asphalt source, because asphalting activities is only possible in summer. Wind sector dependence of factor 1 scores demonstrates that asphalting operations occurred around the station without a preference for a particular wind direction.

Table 5.3 Measured VOC concentrations in factor profiles for urban station

	F1	F2	F3	F4	F5	F6	F7	F8
				(μg/m^3)				
Ethane	0.03	0.01	0.15	2.48	0.00	0.23	0.21	0.40
Ethylene	0.00	0.10	0.07	1.40	0.25	3.38	2.80	0.00
Propane	0.03	0.09	0.44	0.48	0.18	1.06	2.34	0.40
Propylene	0.00	0.44	0.00	0.71	0.36	1.37	2.42	0.37
Isobutane	0.04	0.12	0.01	0.98	0.55	1.95	3.38	0.50
Acethylene	0.00	0.01	0.17	0.19	0.04	0.97	0.37	0.00
Trans - 2 - Butene	0.04	0.01	0.00	0.10	0.01	0.03	0.26	0.15
1 - Butene	0.01	0.02	0.07	0.04	0.03	0.15	0.41	0.10
Isopentane	0.08	0.57	0.10	0.65	0.59	0.74	1.71	0.26
2,2-Dimethylbut.	0.01	0.05	0.06	0.13	0.03	0.20	0.46	0.17
2-Methylpentane	0.00	0.28	0.05	0.15	0.12	0.11	0.23	0.08
Isoprene	0.01	0.02	0.14	0.08	0.03	0.07	0.26	0.06
n-Hexane	0.08	0.68	0.03	0.27	0.33	0.36	0.09	0.15
Benzene	0.00	0.04	0.03	0.13	0.09	0.98	0.50	0.09
Cyclohexane	0.00	0.15	0.04	0.14	0.27	0.17	0.05	0.03
3-Methylhexane	0.06	0.07	1.53	0.14	0.11	0.00	0.10	0.18
2,2,4-Trimethylp.	0.05	0.06	0.04	0.06	0.05	0.07	0.07	0.45
n-Heptane	0.11	0.02	0.02	0.06	0.05	0.10	0.14	0.08
Toluene	0.00	14.07	0.16	0.32	4.93	1.93	0.00	0.70
Ethylbenzene	0.06	0.04	0.06	0.05	1.68	0.18	0.19	0.17
m,p-Xylene	0.00	0.03	0.06	0.08	1.66	0.18	0.10	0.08
Styrene	0.13	0.01	0.07	0.00	0.23	0.08	0.22	0.36
o-Xylene	0.09	0.04	0.12	0.16	2.07	0.32	0.09	0.26
Nonane	0.07	0.01	0.02	0.02	0.14	0.10	0.08	0.05
n-Propylbenzene	0.36	0.00	0.01	0.01	0.04	0.02	0.04	0.02
1,3,5-Trimethylb.	0.22	0.01	0.03	0.00	0.19	0.19	0.12	0.14
1,2,3-Trimethylb.	0.60	0.03	0.14	0.23	0.24	1.03	0.14	0.36
p-Diethylbenzene	0.30	0.03	0.06	0.14	0.02	0.07	0.01	0.24
n-Undecane	0.07	0.00	0.20	0.21	0.03	0.24	0.08	2.05
n-Dodecane	1.20	0.04	0.57	0.96	0.00	0.11	0.20	4.15

Table 5.4 Percentage of VOC concentrations in factor profiles that were obtained in urban station

	F1	**F2**	**F3**	**F4**	**F5**	**F6**	**F7**	**F8**
Ethane	0.9	0.2	4.4	70.8		6.4	5.9	11.3
Ethylene	0.0	1.2	0.9	17.5	3.1	42.3	35.0	0.0
Propane	0.5	1.8	8.8	9.6	3.6	21.0	46.6	8.0
Propylene	0.1	7.7	0.0	12.4	6.4	24.2	42.6	6.6
Isobutane	0.5	1.6	0.1	13.0	7.2	25.9	44.9	6.7
Acethylene	0.0	0.8	9.7	10.9	2.4	55.1	21.0	0.1
Trans - 2 – But.	7.0	2.3	0.5	16.6	1.2	5.2	42.8	24.4
1 - Butene	0.7	2.6	8.5	4.8	3.6	18.5	49.8	11.7
Isopentane	1.7	12.1	2.1	13.9	12.6	15.7	36.5	5.6
2,2-Dimethylbut	1.0	4.6	5.2	11.8	2.7	17.9	41.2	15.6
2-Methylpentan	0.0	27.1	4.9	14.8	11.5	11.1	22.4	8.2
Isoprene	1.4	3.2	21.0	12.0	5.1	10.3	38.1	8.9
n-Hexane	4.2	33.8	1.7	13.6	16.7	17.8	4.6	7.7
Benzene	0.1	2.3	1.7	6.7	4.9	52.7	26.6	5.0
Cyclohexane	0.1	18.2	4.2	16.1	31.7	20.6	6.0	3.2
3-Methylhexane	2.7	3.2	69.8	6.4	5.1	0.0	4.5	8.2
2,2,4-Trimthylp.	6.4	6.7	4.2	6.9	6.3	7.9	8.7	52.8
n-Heptane	19.1	2.7	2.8	10.5	8.4	17.1	25.1	14.3
Toluene	0.0	63.6	0.7	1.5	22.3	8.7	0.0	3.2
Ethylbenzene	2.4	1.7	2.5	2.2	69.0	7.5	7.7	7.1
m,p-Xylene	0.2	1.4	2.6	3.6	75.7	8.3	4.6	3.5
Styrene	12.0	1.0	6.7	0.0	20.5	7.4	19.8	32.6
o-Xylene	2.8	1.2	3.9	5.1	65.6	10.2	2.9	8.2
Nonane	14.6	1.9	4.2	5.0	29.2	20.1	15.8	9.2
n-Propylbenzene	69.8	0.5	2.4	1.7	8.4	4.7	7.7	4.9
1,3,5-Trimethylb	24.4	1.5	2.8	0.0	21.9	20.9	13.1	15.2
1,2,3-Trimethylb	21.6	0.9	5.2	8.2	8.8	37.3	4.9	13.1
p-Diethylbenzen	34.4	3.2	6.9	16.2	2.8	7.8	1.3	27.4
n-Undecane	2.5	0.0	6.9	7.3	1.2	8.2	2.8	71.1
n-Dodecane	16.6	0.5	7.8	13.3	0.0	1.5	2.8	57.4

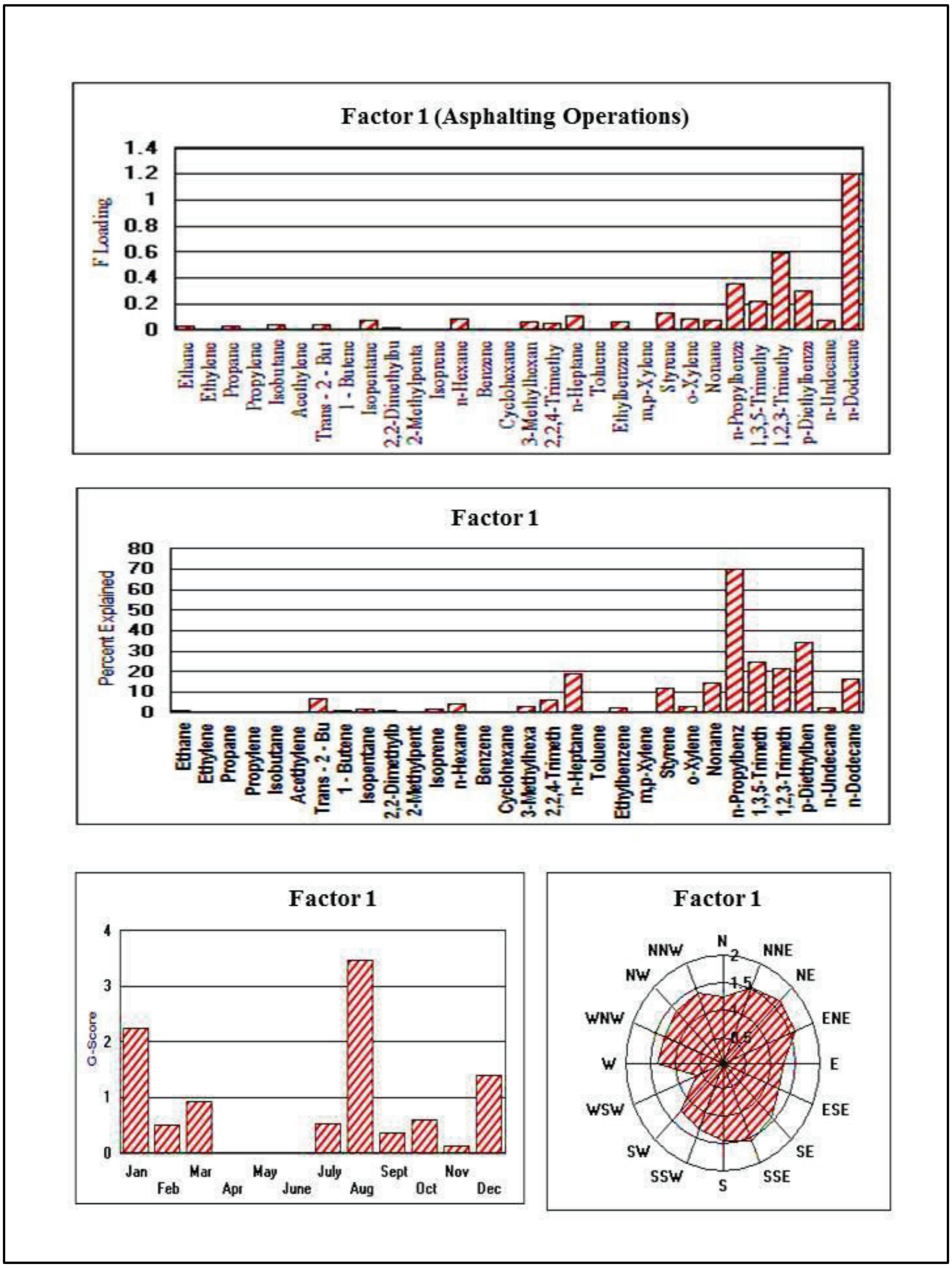


Figure 5.10 Diagnostic figures for factor 1 in urban station

Factor 2 loadings, percentage of concentrations accounted by Factor 2, monthly average factor 2 scores and average concentration of Factor 2 scores in each wind sector are presented in Figure 5.4. Factor 2 is a clear solvent source. It closely resembles Factor 6 in Rural PMF, which was identified as solvent use at the premises of the station. Thus, Factor 2 is identified as solvent use in Kütahya. Higher factor 2 scores in July, August and September also confirms solvent source due to higher temperature in these months. Wind sector averages of Factor 2 demonstrate that solvent use is more pronounced in WNW and ENE sectors.

Diagnostic plots for Factor 3 are depicted in Figure 5.5. Factor 3 is dominated by 3-methyl hexane. The factor accounts for approximately 70% of the 3-methyl hexane concentrations in the city. The factor also includes smaller loadings of isopentane, p-diethylbenzene, n-undecane and dodecane. The factor is not positively identified, but tentatively assigned as a second solvent use. Heavy hydrocarbons like do decane and undecane are good markers for sources like diesel emissions, asphalting operations, but they are also emitted from industrial solvent use activities (Watson et l., 2001; McCarty et al., 2013; Ho et al., 2009). Monthly average Factor 3 scores, which are higher in July, August and September also supports a solvent source.

Sector averages of Factor 3 scores show a very clear signal from SE and ESE directions. Indicating that the source is located in those directions.

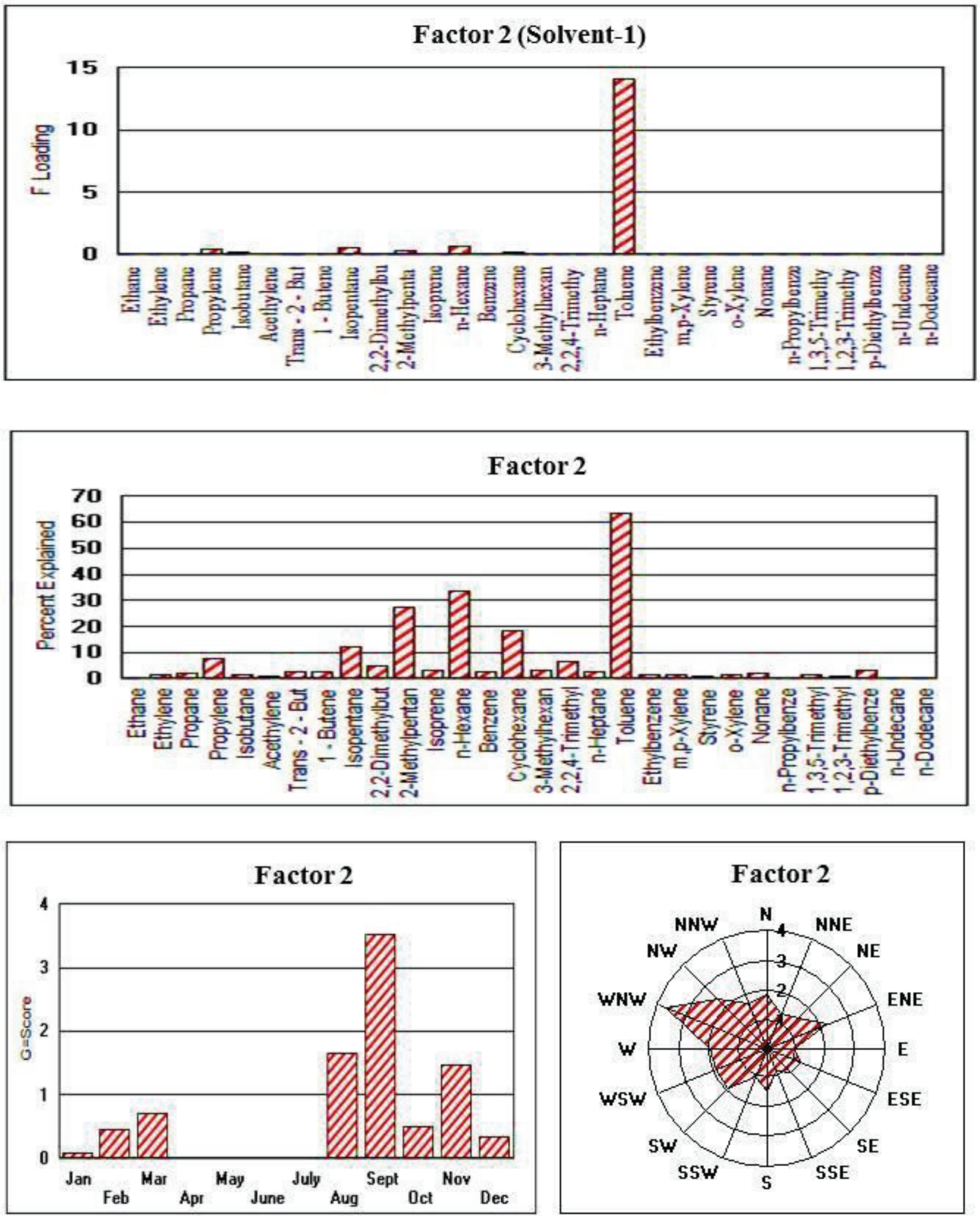


Figure 5.11 Diagnostic figures for factor 2 in urban station

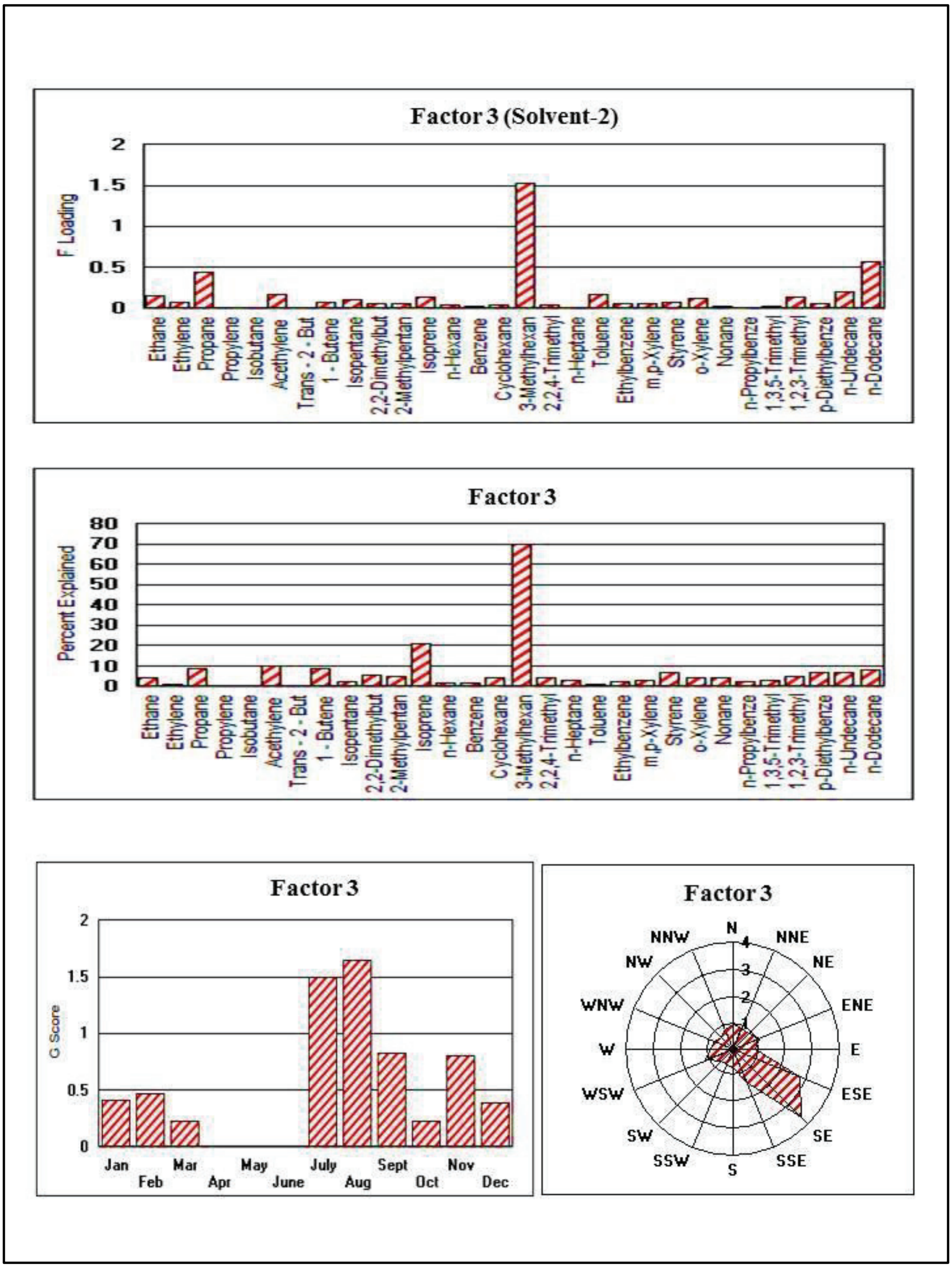
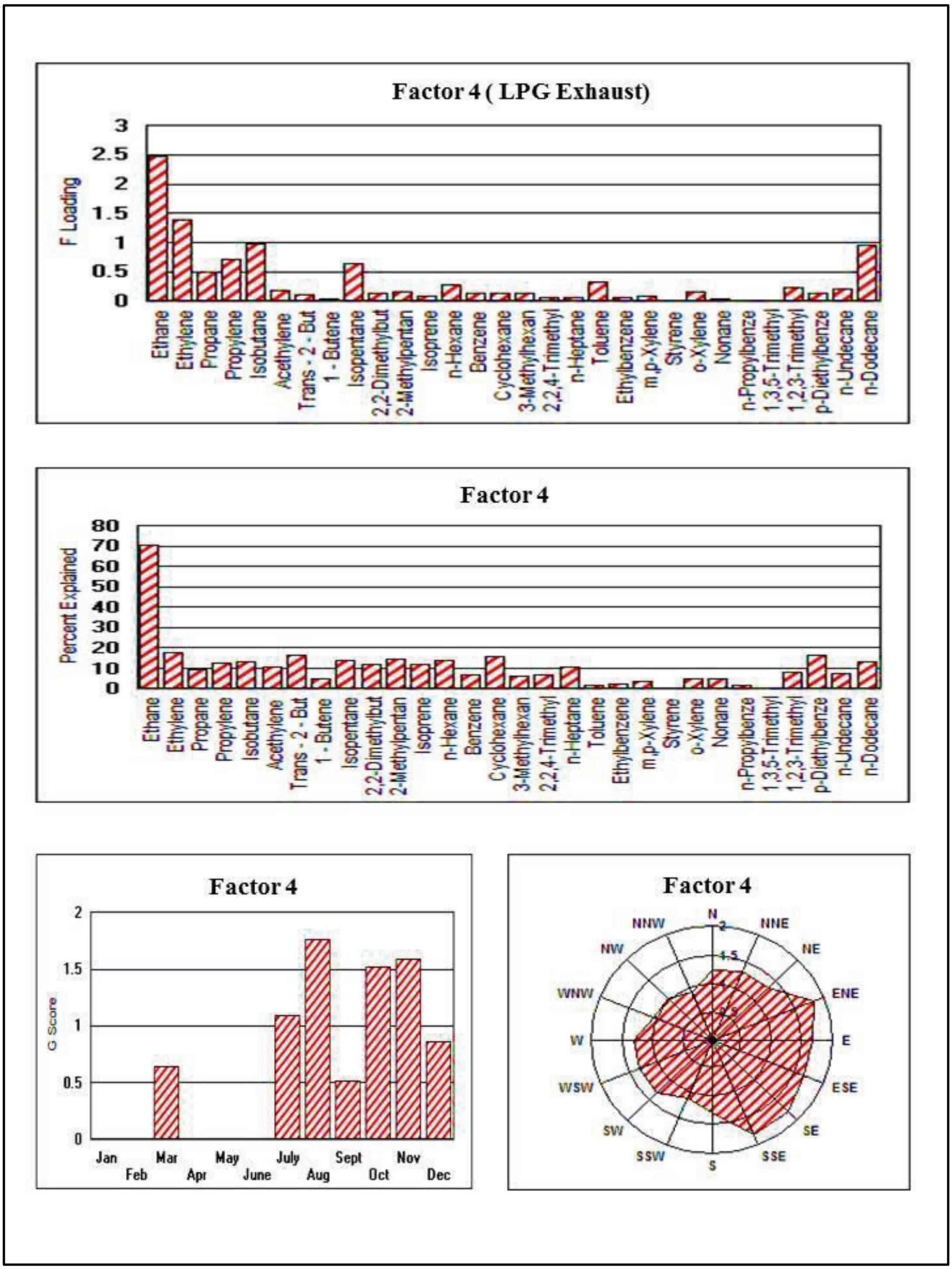


Figure 5.12 Diagnostic figures for factor 3 in urban station

Plots related to Factor 4 are given in Figure 5.6. Factor 4 is almost identical with Factor 3 in Rural PMF, which was identified as LPG vehicle exhaust. Distribution of score values around the station indicates that the sector between ENE and SSE have higher contributions to concentrations measured at urban station. This pattern is quite similar to the pollution rose patterns obtained in other traffic related factors as will be discussed later in the manuscript.

Diagnostic plots for Factor 5 are given in Figure 5.7. The factor accounts for large fraction of the concentrations of toluene, ethylbenzene, m,p-xylene, o-xylene (TEX compounds), nonane and cyclohexane. Composition of this factor is very similar to composition of Factor 8 in rural PMF, which was also attributed to solvent source. Consequently, Factor 5 in urban PMF is also a solvent source.

The pollution rose for this factor is very pointed. In other words solvent sources that generated this factor are located to the SSE, SE, SSW and NW of the station.



Factor 4 (LPG Exhaust)

Factor 4

Factor 4

Factor 4

Figure 5.13 Diagnostic figures for factor 4 in urban station

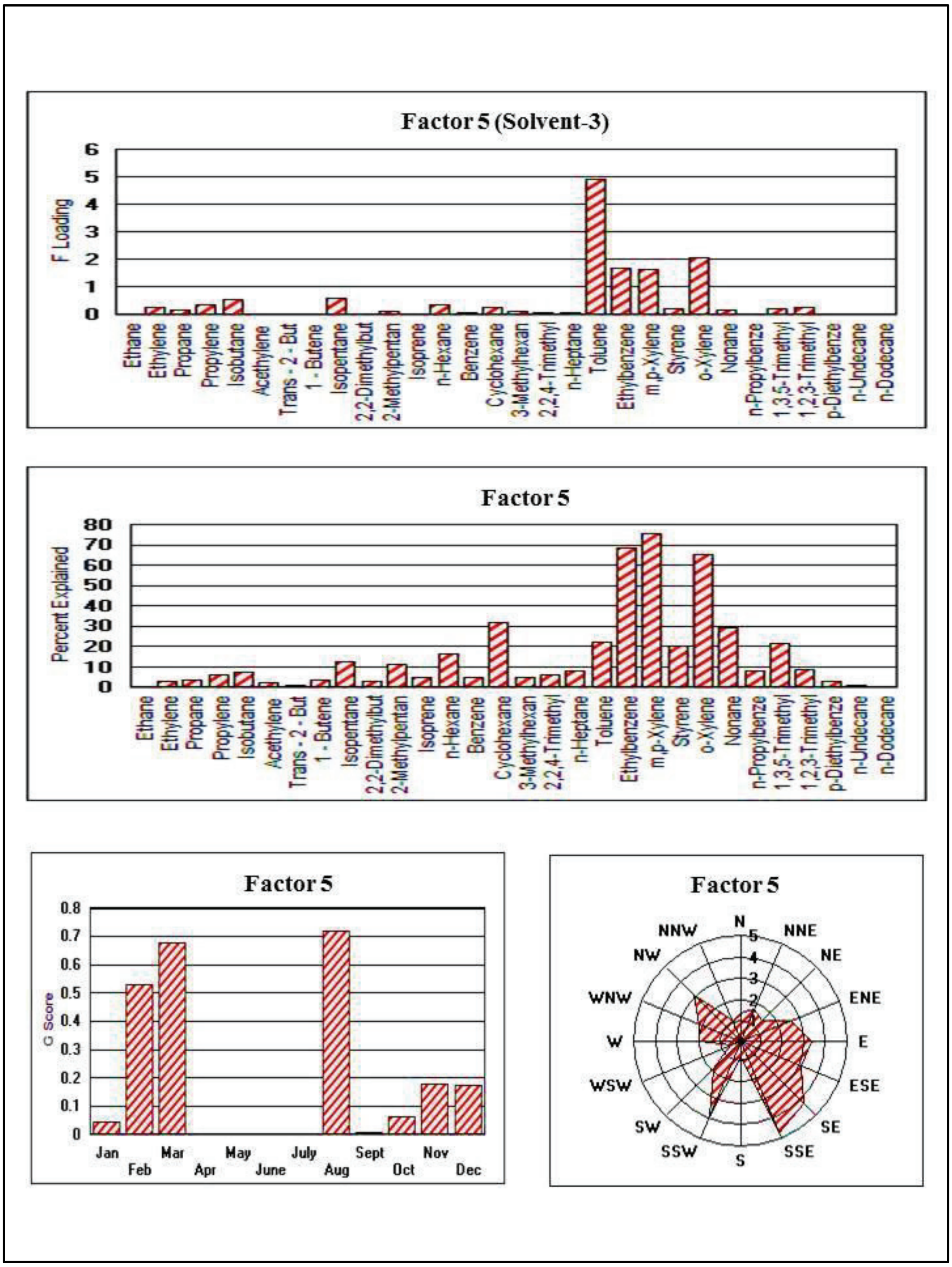


Figure 5.14 Diagnostic figures for factor 5 in urban station

Factor loadings, fractions of concentrations accounted by factors monthly average factor scores and distributions of factor scores around the station are given in Figures 5.8, 5.9 and 5.10 for factors 6, 7 and 8, respectively.

Both factors 6 and 7 are loaded with light hydrocarbons. The difference between the two factors is the association of Factor 7 with lighter fraction of C_2-C_8 hydrocarbons. It includes isopentane, which is a well-documented marker for evaporative emissions. This factor is similar to factor 1 in rural PMF and identified as evaporative emissions from light-duty vehicles. However, as in rural PMF, presence of combustion sources like ethylene and propylene in the factor suggests some mixing with exhaust emissions.

Factor 6 on the other hand includes heavier fraction of the C_2-C_8 hydrocarbons. The factor also includes most of the gasoline exhaust markers (for example BTEX compounds 1-butane, n-heptane etc.) and combustion products, namely ethylene, propylene and acetylene). The factor show close resemblance with factor 2 in rural PMF and identified as gasoline exhaust.

Scores of both factors have the highest average values in ESE, SE and SSE sectors. This is similar to the distribution observed in Factor 4 (LPG vehicle).

Factor 8 is loaded with most of the heavy hydrocarbons, like dodecane, undecane, diethylbezene, trimethylbenzene. These are all diesel markers. The factor resembles Factor 1, which was identified as asphalting activities. The main difference between the two is presence of VOCs which are combustion products in Factor 8 and their absence in Factor 1. Factor 8 is similar to Factor 4 in rural PMF and thus assigned as diesel vehicle source of measured VOC concentrations at Kütahya.

The score rose for Factor 8, which is shown in Figure 5.17 is similar to similar plots for factors identified as LPG vehicle, gasoline exhaust and evaporative emissions. Obviously distributions of scores among wind sectors are determined by the geometry of the roads around the station, which is similar for each traffic related factors.

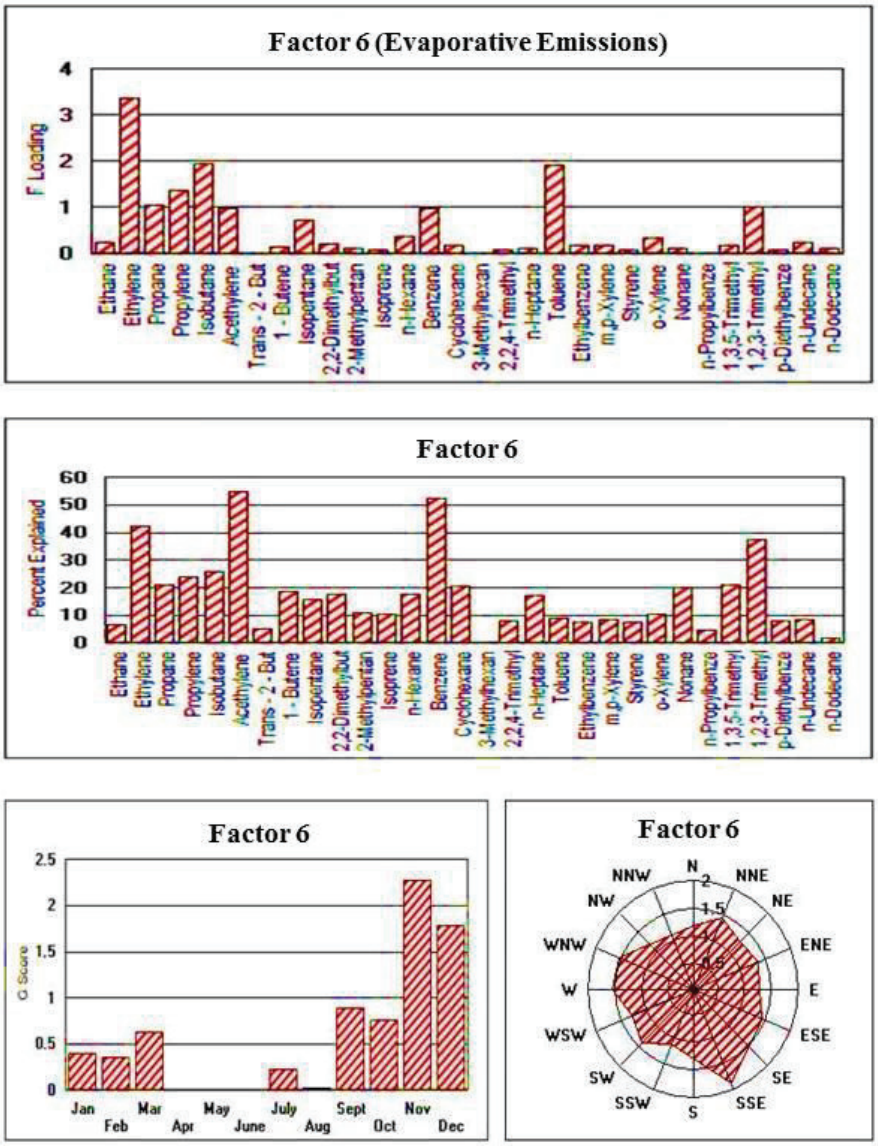


Figure 5.15 Diagnostic figures for factor 6 in urban station

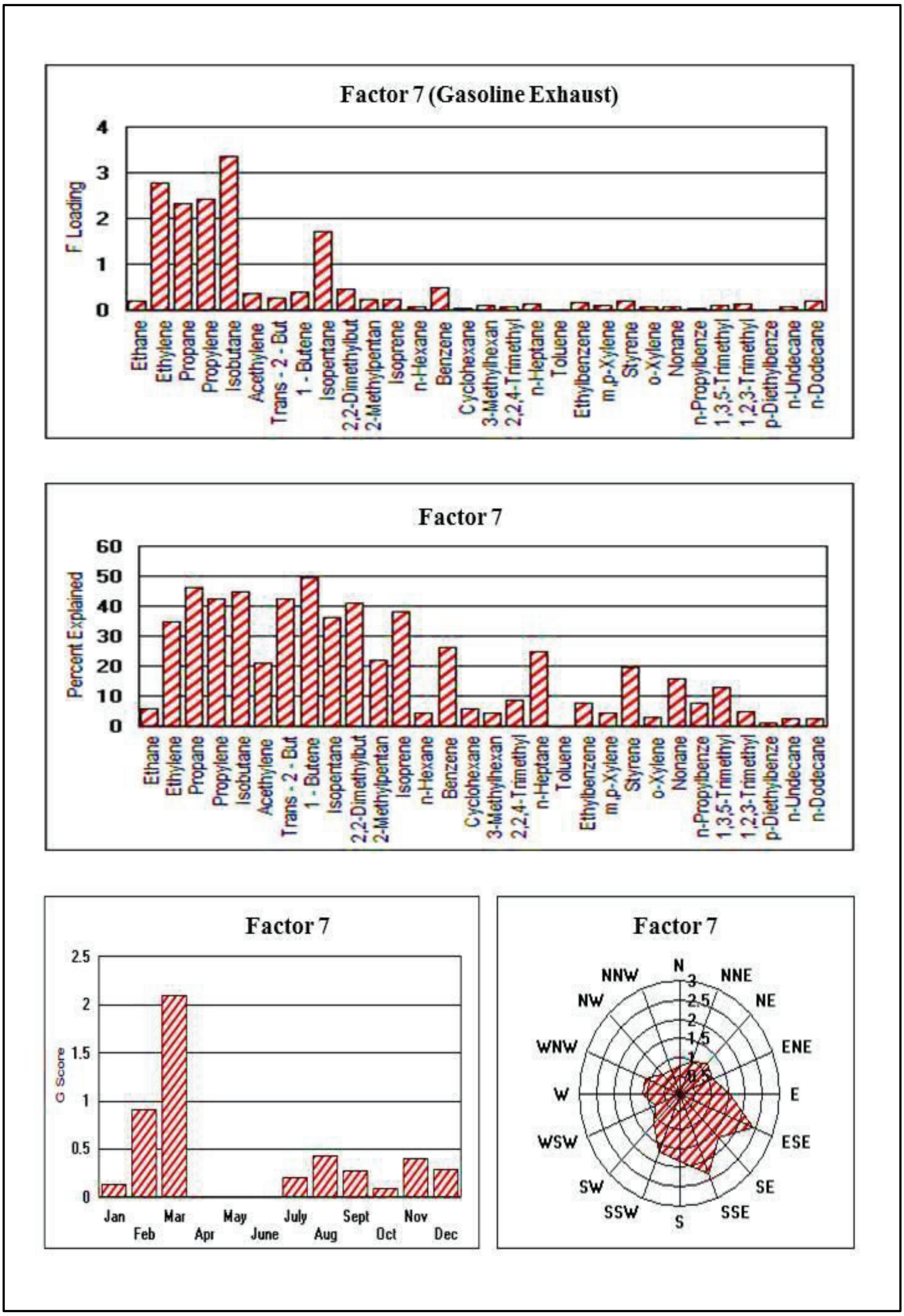


Figure 5.16 Diagnostic figures for factor 7 in urban station

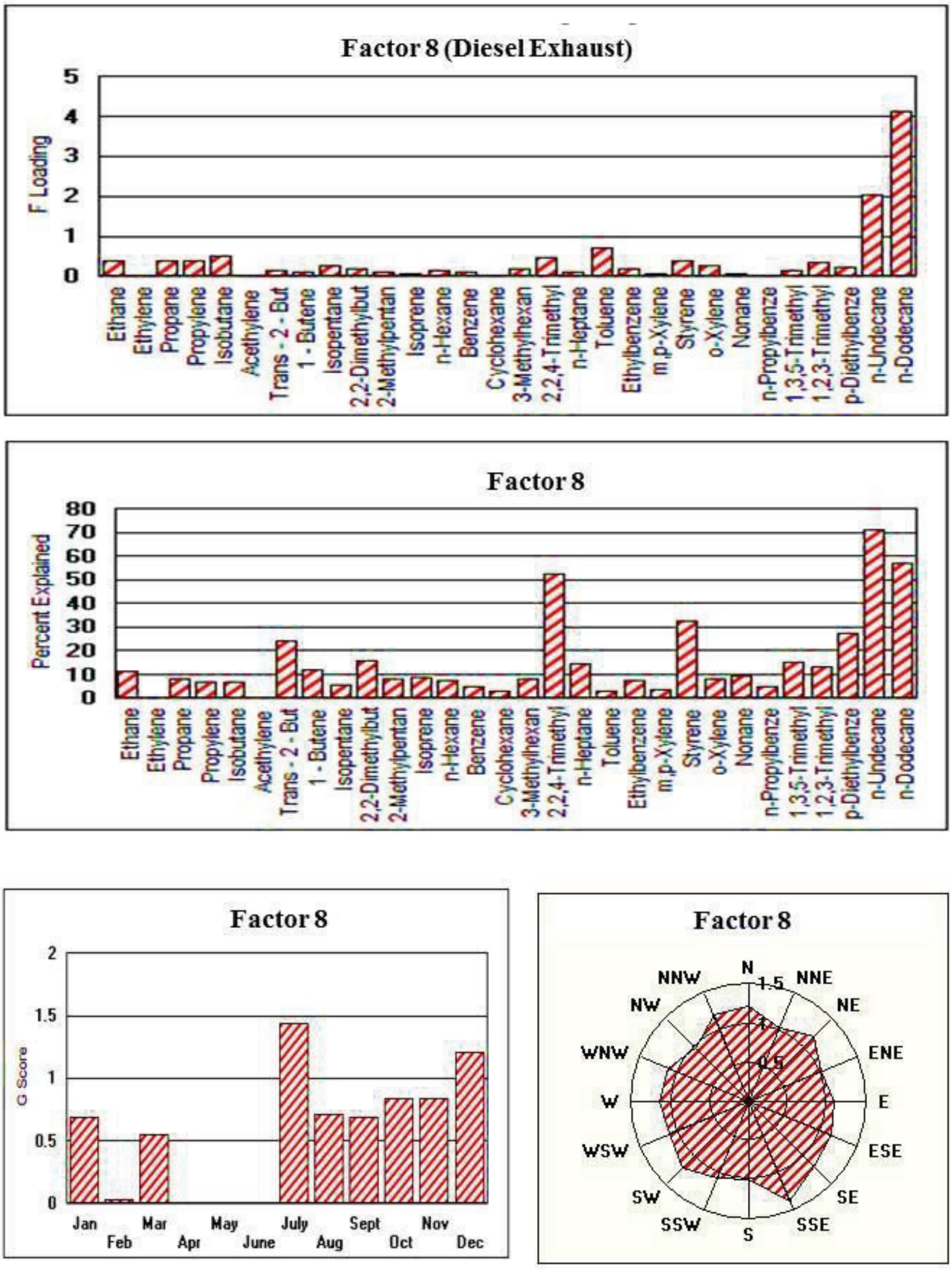


Figure 5.17 Diagnostic figures for factor 8 in urban station

Contribution of each factor on total VOC concentrations in Urban PMF exercise is given in Figure 5.11. Asphalting operations (factor 1) accounted for a small fraction of the total VOC concentrations measured at Kütahya. This was one of the (but not all) of the criteria we used to difference between asphalting and diesel factors. These two factors are very similar in composition. However, 4% contribution of diesel exhaust on total VOC is not realistic, but is reasonable composition for asphalting operations.

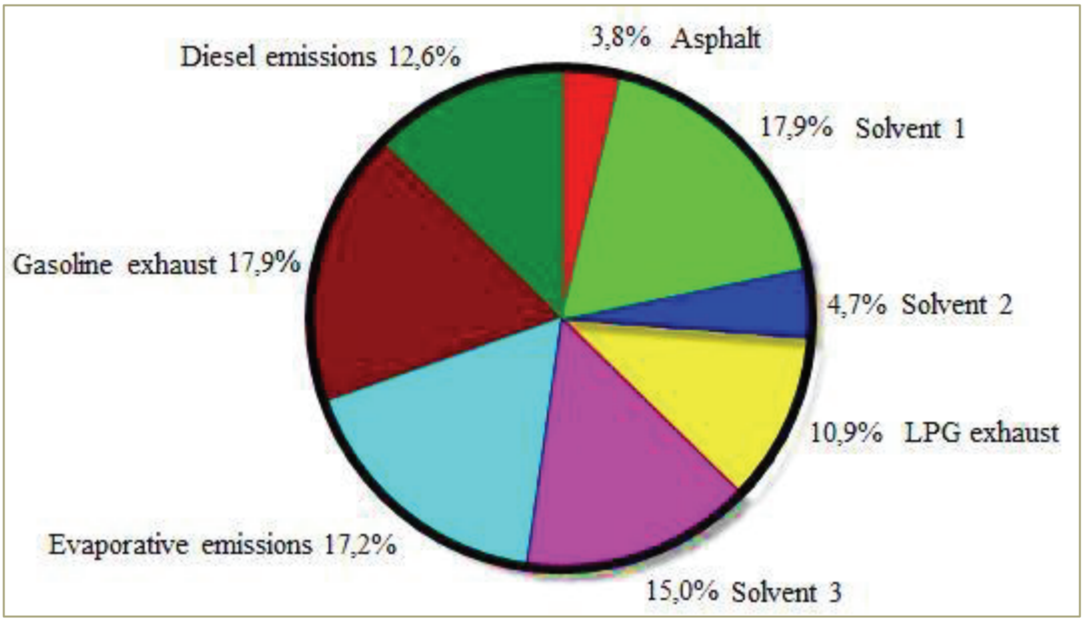


Figure 5.18 Contribution of sources to total VOC concentration in urban station

There are three solvent sources affecting VOC levels at Kütahya (Factor 2, Factor 3 and factor 5). They together accounted for approximately 38% of total VOC levels. As in rural PMF, traffic component at Kütahya VOC concentration consist of four sources, including gasoline exhaust, evaporative emissions from gasoline-powered vehicle, LPG vehicle exhaust and diesel exhaust. They together accounted for 59% of the total VOC concentrations. This is significantly higher than contributions of traffic related factors in rural PMF (approximately 31%). Higher contribution of traffic on total VOC levels at Kütahya is due to closer proximity of traffic emissions to the station.

In rural PMF diesel exhaust was the highest contributor to total VOC concentration. However, at urban station, it ranks third after gasoline exhaust and evaporative emissions. This observation is reasonable, because heavy duty vehicles accounts for a larger fraction of traffic in rural areas.

One very important conclusion of PMF exercise in this study is that there are same factors with almost identical composition in both urban and rural VOC mass. These are evaporative emissions which is Factor 6 in urban and factor 1 in rural PMF results, Gasoline exhaust (factor 7 in urban and factor 2 in rural), LPG vehicle exhaust (factor 4 in urban and factor 3 in rural), Diesel exhaust (factor 8 in urban and factor 4 in rural) and a solvent (factor 3 in urban and factor 8 in rural) sources. These sources are regionally effective in determining total VOC concentration and concentrations of individual organic compounds.

In addition to these common sources there are also sources unique for each site. These are urban plumes of Kütahya and Tavşanlı and local solvent source for rural station and two different solvent sources and an asphalt source for the urban site. It is interesting to note that asphalt source is fairly common in urban PMF or factor analysis studies. Its contribution is not very large, but it is always there.

Another significant conclusion in this study is that it is difficult, if not impossible; to differentiate power plants from other VOC sources. This indicates that VOCs are not appropriate parameters to apportion power plant sources.

CHAPTER 6

CONCLUSIONS

6.1 Conclusions

This study is a part of a large scaled TUBITAK project which was conducted in Kütahya. There are two high emitting power plants in the region, which are namely Tunçbilek and Seyitömer Thermal Power Plants. Possibility of contribution of these plants on VOCs concentrations have been suspected for a long time, however it is never evaluated comprehensively. In this study, in addition to common sources of VOCs, such as motor vehicle exhaust, solvent usage, space heating etc., it was investigated whether the concentrations of VOCs in the city is affected by mentioned thermal power plants.

For this aim, 51 PAMS VOCs were measured in an urban and a rural location of the Kütahya. Samples were collected using 6L electropolished stainless steel canisters, and the same brand integrated passive air sampling kits with 24-hour time intervals. At the beginning of the study, sampling period was determined as two campaigns as summer and winter, but due to some challenges in sampling sites summer and winter campaigns were combined and months between summer and winter were added to sampling period. In urban station, sampling period was between 27th June, 2014 and 13th March, 2015, while in rural station this period was started 7th July, 2014 and maintained until 27th March, 2015. Throughout sampling period, 93 and 75 samples were collected from urban and rural sampling stations respectively. And, all collected samples were analyzed with GC-FID system.

In urban station, average concentration range is between 23 $\mu g/m^3$ and 0.12 $\mu g/m^3$ for toluene and cis-2-pentene respectively. Correlatively, in rural station this range is changing between 33 $\mu g/m^3$ and 0.06 $\mu g/m^3$ for same compounds respectively. Toluene had the highest concentration in both stations.

Median and geometric mean values were very close to each other, while average concentrations of each compound were approximately two times higher than both median and geometric mean values. It means that whole VOCs show a right-skewed distribution prominently. Fundamentally, several frequency distribution models show right-skewed distribution. However, in order to understand which distribution is applicable, "goodness of fit test" were performed. And the most common distribution models were log-normal and loglogistic.

Obtained data set were compared with some studies in the literature which were conducted in Turkey and around the world. Consequently, it was decided that concentrations of VOCs in Kütahya is lower than both other provinces of Turkey and also around the world.

In order to make a more comprehensive interpretation, temporal and seasonal variations of VOCs concentrations were investigated. To show episodic alterations in VOCs concentrations during sampling period, time series plots were prepared for all target compounds. It was decided that the main reason of sudden episodic changes in concentrations may be alterations of meteorological parameters, especially mixing height and ventillation coefficient, in the related day comparing to former or the next day. Then, WKDY/WKEND ratios were calculated, which represent the traffic related emssions. In urban station, average concetrations of almost all of VOCs, were higher in WKDAY than WKEND Thus, most of the WKDY/WKEND ratios was calculated as 1.4 ±0.4. While in rural station this ratio is 1.0 ± 0.5. All of these situations showed us an expected result that were not significant differences between WKDY and WKEND concentrations in rural station. Because, traffic related emissions do not abundant in rural locations, and also VOCs concetrations that were measured in there effected by pollutant transportation so, local activities effect them little or nothing. Meteorological conditions are much more determinative factors than changes in emission amounts around the sampling location on concetrations of transported pollutant. For this reason, seasonal variations and meteorological parameters were taken into consideration.

In both stations, almost all of measured seasonal VOCs concentrations were higher in winter than in summer as expected. Actually, this result has been obtained in several different studies for many years. There may be three reasons of this outcome; higher emission amounts, this reason is applicable for urban station mostly , and decreasing of mixing height and ventilation coefficient in winters or, due to higher temperature and more effective sunlight, reaction rates increase in summer, so VOCs are removed from atmosphere and summer concentrations decrease(Lee, et al., 2002).

Another important part of the study was effects of local meteorology on measured VOCs concentration in both stations. For this aim, effect of temperature, wind speed, rainfall, mixing height and ventillation coefficient were investigated. VOCs showed significant behaviours according to these parameters seperately. As a conclusion, concentrations of VOCs may be affected by local meteorology, especially that were measured in urban station.

Wind direction is another important part and it can be defined as a preliminary study to determine the power plants contributions on concentrations of VOCs. Conducted evaluations indicated that Seyitömer TPP affects concentrations that were measured in urban station mostly due to distance between them and also wind sector where Seyitömer TPP reside in, wihile concentrations that were measured in rural station was affected by Tunçbilek TPP mostly, because this station is downwind of this TPP.

Finally, in order to apportion possible VOCs sources, PMF was used. In both stations all required quality control studies were conducted after several trials, 8 factor solutions were found to be most explainable in both stations. The Q_{robust}-to-$Q_{theoretical}$ ratio was calculated 2,4 and 2,6 in rural and urban stations respectively and reasonable quality of the model fit was observed. Using factor loadings, percentage of the concentration of each species accounted by that factor, monthly average factor scores and average scores at each wind direction a comprehensive evaluation were made and all possible sources were determined.

In rural station main sources were evaporative emissions from gasoline powered vehicles(factor 1 : 13.8%), light duty vehicle exhaust (factor 2 : 4.3%), LPG vehicles (factor 3 : 3.5%),diesel vehicles (factor 4 : 9.7%), urban plume of the Kütahya (factor 5 : 15.3%), local solvent use (factor 6 : 25.6%), Tavşanlı-urban plume (factor 7: 15.4%), and another solvent usage (factor 8 : 12.4%). While in urban station, main sources were determined as asphalting operations (factor1: 3.8%), solvent usage (factor2:17.9, factor 3: 4.7% and factor 5: %15), LPG exhaust (factor 4: 10.9%), evaporative emissions (factor 6: 17.2%), gasoline exhaust (factor 7: 17.9%), and diesel emissions (factor 8: 12.6%).

All possible sources were defined as common VOCs sources. As a conclusion of PMF study is that it is difficult, if not impossible, to differentiate power plants from other VOC sources. So, it was decided that VOCs are not appropriate parameters to apportion power plant sources.

6.2 Recommendations for Future Studies

In this study, 93 and 75 samples were collected from urban and rural station respectively. To be able to make more statistical interpretation, sampling period should be extended.

During this study, some problems were encountered because of sampling kits that were using for collecting air samples into the canisters during 24 hours. They were continually and quickly fouling and sampling was interrupted several times. So, in order to conduct a continuous sampling alternative samplers may be suggested.

Contamination is the major problem in air pollution studies, for this reason much attention should be paid to carrying out a proper cleaning throughout sampling and analysis process. Additionally, leakage is another important problem during sampling period, for this reason pressure of canisters should be checked regularly.

Canisters should be placed in a shelter in order to collect air samples as safely as possible in case any contamination occur due to dust around sampling station, or meteorological events, such as rain.

As it was stated in Chapter 4 and Chapter 5, VOCs concentrations were not measured as high in Kütahya and, as a result of source apportionment study, it was decided that VOCs are not convenient pollutants to apportion power plant sources. However, it has been long known that thermal power plants contribute to air pollution substantially. For this reason, concentrations of other air pollutants, such as concentration of particulate matters, SO_2, and NO_x, should be investigated.

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