DETERMINATION OF AMBIENT LEVELS AND SOURCES OF VOLATILE ORGANIC COMPOUNDS IN İZMİR-ALİAĞA REGION

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ABSTRACT

DETERMINATION OF AMBIENT LEVELS AND SOURCES OF VOLATILE ORGANIC COMPOUNDS IN İZMİR-ALİAĞA REGION

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In this study, atmospheric levels and sources of VOCs at Aliağa industrial area was investigated. For this, VOC concentrations were measured at two monitoring stations through winter and summer campaigns in 2005 and 2006. Sampling stations were located in downtown Aliağa and downwind of industrial facilities, approximately 500 m to the south east of Horozgediği village. After the summer sampling, another temporary station was installed in between PETKİM and TÜPRAŞ, named as TÜPRAŞ Station to generate TÜPRAŞ and PETKİM profiles. More than 50 species were measured in all stations.

In all stations, toluene has the highest contribution to total VOC concentration. Toluene is followed by m,p-xylene and benzene. While higher concentrations of traffic related VOCs were measured at Aliağa station, VOCs from industrial solvents and industrial processes were higher at Horozgediği station.

The concentration levels in Aliağa and Horozgediği are found to be comparable to the other industrial regions reported in the literature. Investigation of episodes, diurnal variations of VOCs and meteorological parameters showed that PETKİM and TÜPRAŞ emissions affect the concentrations levels at Horozgediği and Aliağa stations.

Source profiles of PETKİM and TÜPRAŞ are determined by using the TÜPRAŞ station data set. 2-methyl-hexane, benzene and 2,2,3-tri-methyl-butane+2,3-di-methyl-pentane are found to be good markers of PETKİM emissions.

Ten different VOC sources were identified in the region. These were gasoline exhaust, diesel exhaust, natural gas use, gasoline evaporation, industrial emissions-1, natural gas construction, non-industrial solvent use, industrial emissions-2, PETKİM emissions, and mixed emissions from PETKİM and shipbreaking facilities.

Keywords: VOC, on-line GC, Aliağa, industrial sources, source apportionment

ÖZ

İZMİR-ALİAĞA BÖLGESİNDEKİ UÇUCU ORGANİK BİLEŞKLERİN ORTAM HAVASINDAKİ SEVİYELERİNİN VE KAYNAKLARININ BELİRLENMESİ

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Bu çalışmada, Aliağa bölgesinde ortam atmosferindeki VOC seviyeleri ve kaynakları incelendi. Bunun için 2005 ve 2006 yıllarında yaz ve kış saha çalışmaları ile iki gözlem istasyonunda ölçümler yapıldı. Örnekleme istasyonlarından birisi Aliağa şehir merkezinde, diğeri ise Horozgediği köyünün yaklaşık 500 m güney doğusuna kuruldu. Yaz örneklemesi sonunda, PETKİM ve TÜPRAŞ'ın arasına bir geçici istasyon kurulmuş ve bu istasyon, TÜPRAŞ İstasyonu olarak adlandırılmıştır. Her istasyonda 50'den fazla bileşik ölçüldü.

Toluen, bütün istasyonlarda VOC konsantrasyonlarına toplam katkısı en yüksek olan bileşiktir. Tolueni m,p-ksilen ve benzen takip etmektedir. Aliağa istasyonunda trafik kaynaklı bileşikler daha yüksek gözlenirken, Horozgediği istasyonunda endüstriyel solvent ve endüstriyel proseslerden kaynaklı bileşiklerin daha yüksek olduğu görülmüştür.

Aliağa ve Horozgediği istasyonlarındaki VOC düzeyleri literatürde bildirilen diğer sanayi bölgelerinde rapor edilen değerlerle karşılaştırılabilir düzeylerdedir. Episodlar, VOClerin gün içindeki değişimleri ve meteorolojik parametreler incelendiğinde PETKİM ve TÜPRAŞ emisyonlarının Aliağa ve Horozgediği istasyonlarında ölçülen değerleri etkilediği görülmüştür.

TÜPRAŞ istasyonu veri seti kullanılarak PETKİM ve TÜPRAŞ kaynak profilleri belirlenmiştir. 2-metil-heksan, benzen ve 2,2,3-tri-metil-butan +2,3-di-metil-pentane bileşiklerinin PETKİM'in emisyonları için iz bileşikleri olduğu (tracer) görülmüştür.

Bölgede on farklı VOC kaynağı belirlenmiştir. Bunlar, benzinli araç egzozu, dizel araç egzozu, doğal gaz kullanımı, yakıt buharlaşması, endüstriyel emisyon-1, doğal gaz inşaatı, endüstriyel olmayan solven kullanımı, endüstriyel emisyon-2, PETKİM emisyonları ve PETKİM ve gemi söküm tesislerinden kaynaklı karışık emisyondur.

Anahtar Kelimeler: Uçucu organik bileşikler, on-line GC, Aliağa, endüstriyel kaynaklar, kaynak belirleme

To My Parents

and

to Altay…

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INTRODUCTION

Volatile organic compounds (VOCs) have large impact on atmospheric chemistry contributing to ground level ozone formation, stratospheric ozone depletion, and secondary particle formation. In addition to these organic compounds in the atmosphere also have health effect, because many of them are carcinogens or suspected carcinogens. Volatile organic compounds also enhance global warming. Some of these compounds, not volatile ones, are persistent in the atmosphere and thus accumulate in various compartments. They have numerous sources, but the most important one is light and heavy duty traffic. Solvent use in paint applications, in laboratories, combustion of solid, liquid and gaseous fossil fuels, waste storage and industrial processes can be counted among non-traffic sources. Refineries and petrochemical complexes are at the top of this list. Aliağa is an important industrial region with a large number of industries, including a petrochemical complex (PETKİM) and a refinery (TÜPRAŞ).

The overall objective of this study is to understand levels and temporal behavior of volatile organic compounds at an industrial airshed. The study is aimed at understanding concentrations and temporal variations with the goal of revealing factors and sources affecting temporal variations of VOCs. The “industrial airshed” in this study is the Aliağa industrial region, located approximately 70 km to the north of İzmir. As a result, the effect of industrial emissions to an urban site is evaluated.

This study is a part of a more extensive work which was completed in 2007 through a TÜBİTAK project (project number 104Y276). The part of the study, which included hourly measurement of approximately 50 VOCs was the topic of this work

Half hourly and hourly measurements of VOCs were performed at two stations located at downtown Aliağa and Horozgediği village, which is downwind of the industrial area, For each of these two stations approximately 3 months of winter and 3 months of summer data were generated. During these sampling campaigns VOCs were measured and analyzed using on-line gas chromatographs. Aside from these two stations, another temporary station was established between PETKİM and TÜPRAŞ. The station (TÜPRAŞ station) was equipped with the same instrument that was used in Horozgediği station. Fifteen days of hourly sampling was performed in this temporary station after the sampling in Horozgediği was completed.

Integration of chromatographs was the most sensitive and time-consuming part of the study due to large number of chromatograms and almost 50 compounds per chromatogram. Throughout this study, three data sets constituted of nearly 375000 VOC data points in total has been investigated from the hourly and half hourly measurements. The data set generated for this thesis is the most extensive one in terms of number of sampling locations, instruments used and data quantity that has ever been developed in Turkey.

The other objectives of this study are:

- To determine and compare the levels of VOCs in downtown Aliağa and Horozgediği village, downwind of industrial region,

- To determine factors leading to seasonal, diurnal, weekend-weekday variability of VOCs and
- To identify and quantify sources contributing to ambient VOC levels.

CHAPTER 2

LITERATURE REVIEW

2.1. Earth’s Atmosphere and Volatile Organic Compounds

The Earth’s atmosphere is divided into four layers defined primarily by various reactions taking place at different altitudes that yield temperature differences between the layers (Figure 1). The outermost two layers, ionosphere and chemosphere, are of interest to scientists mainly due to their absorption and scattering of solar energy. The stratosphere is the second closest layer to ground and of interest to air pollution scientists because global transport of pollution and debris from volcanic eruptions and absorption and scattering of harmful ultraviolet solar radiation by ozone both occur in this layer.

The troposphere is the innermost layer of the atmosphere. In the troposphere, temperature decreases with increasing altitude, from an average of 13^{o}C at ground level to -60^{o}C at the tropopause. In the atmosphere, pressure decreases monotonically with increasing altitude, from an average of 1013 millibar (mb) at the Earth's surface to 140 mb at 14 km (Atkinson, 2000). Anthropogenically released chemicals are generally emitted into the troposphere. The troposphere is the most complex chemical processor of the atmospheric layers wherein partial or complete degradation of almost all pollutants emitted into atmosphere from natural and anthropogenic sources occurs (Derwent, 1995).

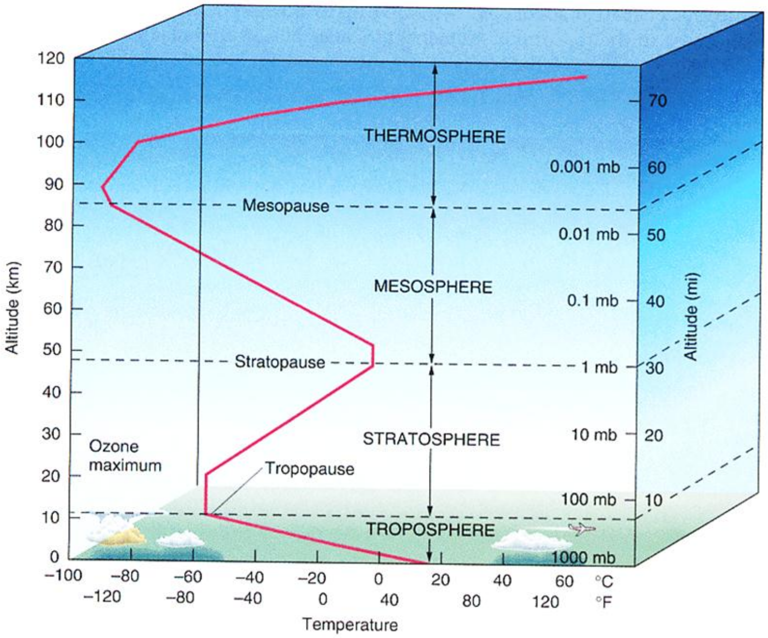


Figure 1 Structure of Earth’s atmosphere
(Mihos, 2009)

The physical and chemical properties of a released material influence its interactions with the other pollutants in the atmosphere, its removal mechanism and its direct and indirect effects to human health, vegetation, forests, animals and structures. The interactions of a pollutant and its effects are different whether the released pollutant is gas or particulate matter.

Particulate matter (PM) is a complex mixture of extremely small particles and liquid droplets. PM is made up of components including acids, organic chemicals, metals and soil particles (US EPA, 2012). Average particle compositions vary with size, time, and location reflecting the particles' diverse origins and atmospheric processing. A considerable amount of work has been carried out in different locations of the world to define the chemical characteristics of PM under different environments and to estimate the atmospheric inputs and parameters yielding such compositions. Results of these studies have shown that aside from primarily emitted particles, particles formed from inorganic and organic gases, so called secondary organic aerosols (SOA), also play an important role in the composition of PM. The effect of inorganic gases on PM formation has been known for decades. The most important inorganic gases that have been focused on by researchers are sulfur dioxide (SO_2) and oxides of nitrogen (NO_x). The effects of these gases on the composition of PM and their influence on the environment are very well-known. However, the formation of PM by SOA and organic gases is a new concept that has developed over the last decade.

The reactions of organic gases with NO_x play important role in tropospheric chemistry. Organic gases are compounds of primarily carbon and hydrogen. These compounds include reactive organic gases, also known as Volatile Organic Compounds (VOCs), in addition to low reactivity compounds and organics that have aerosolized. There are many definitions of VOCs. The most common definition of VOC is that carbon containing gases and vapors whose vapor pressure at 20^oC is less than 760 torr (101.3 kPa) and greater than 1 torr (0.13 kPa) excluding carbon dioxide, carbon monoxide, methane and chlorofluorocarbons. They are typically classed as containing up to 12 carbon atoms per molecule (Derwent, 1995; Blake and Blake, 2002).

2.2. Sources of Volatile Organic Compounds

The most important sources of VOC emissions are motor vehicles, organic solvents, the oil and chemical industries, combustion sources and natural sources. Other minor VOC sources include food and drink manufacturing, the metals industries, waste disposal, and straw and stubble burning. Natural and biogenic processes produce significant amounts of VOCs (Derwent, 1995; Passant, 1995). A recent estimate of anthropogenic non-methane VOC emissions indicates a global release of about 140 Tg y^{-1}. However, natural sources make a significantly larger contribution to total emissions, with about 1150 Tg y^{-1} (Blake and Blake, 2002).

Emissions from motor vehicles can be divided into two categories. These are emissions as a result of incomplete fuel combustion (exhaust emissions) and emissions due to losses of fuel prior to combustion (evaporative emissions).

A major use of solvents is in the formulation of industrial coating materials such as paints, inks and adhesives. Solvent evaporation after application is the most important emission source. Through coating processes, some part of the emission is controlled and this is referred as a fugitive emission; handling and storage of coating materials, washing of equipment, and spillages. Solvents are also used in other industrial processes, for instance the extraction of vegetable oil from oil seeds, the cleaning of metal and plastic components, and dry cleaning of textiles. Another important use of solvents is in the formulation of products for use by consumers, for example aerosols, cosmetics and household paints.

Major emissions from crude oil production are flaring and venting of gases from production facilities, together with displacement of vapor during loading of crude oil tankers. Oil refineries and chemical plants also emit enormous quantities of VOCs. Emissions occur from storage of volatile materials, venting and flaring of gases and fugitive emissions from valves and pumps. The distribution of fuel is another important source of VOCs; emissions occurring during loading of road tankers, filling station storage facilities and during vehicle refueling. Emissions from stationary combustion sources are much less significant.

Natural and biogenic sources, trees, plants, wild animals, natural forest fires, and anaerobic processes in bogs and marshes, also contribute significantly to VOC emissions (Derwent, 1995). Estimates of biogenic emissions vary considerably; still, biogenic emissions represent a high fraction of total emissions in some regions (Passant, 1995).

2.3. Effects of VOCs on Atmosphere and Biota

Although there are thousands of organic compounds in the natural and polluted troposphere that meet the definition of a VOC, most measurement programs have concentrated on the 50 to 150 most abundant hydrocarbons depending upon the characteristics of the specific environment and the effects of the VOCs to both the environment and the human. VOCs have a large impact on atmospheric chemistry contributing to:

- stratospheric ozone depletion
- ground level photochemical ozone formation
- secondary particle formation
- toxic or carcinogenic human health effects
- enhancing the global greenhouse effect
- accumulation and persistence in the environment

These effects are briefly reviewed in the following subsections.

2.3.1. Stratospheric Ozone Depletion

Some of the organic compounds are stable enough to resist tropospheric removal processes and reach the stratosphere. If the compound has a bromine or chlorine group, stratospheric photolysis processes and hydroxyl radical destruction may lead to active ozone-destroying reactions. These reactions lead to further stimulation of ozone layer depletion. Many chlorinated and bromine containing solvents have been identified as stratospheric ozone layer depleting compounds (Derwent, 1995).

2.3.2. Ground Level Photochemical Ozone Formation

In the troposphere, ozone initiates oxidation reactions through the formation of hydroxyl radical $^{\bullet}OH$. Volatile organic compounds together with NO_x control the rate of ground level ozone production in the presence of sunlight (Wang and Austin, 2006).

Ground level ozone negatively affects human health, crops, plants and trees. The contribution that organic compounds make to the exceedence of environmental criteria set to protect both human health and natural ecosystems for ozone is now well documented across Europe (EEA, 2012a). Organic compounds which produce photochemical ozone in the troposphere are within the scope of the Geneva Convention on Long Range Transboundary Air Pollution. This convention requires the reductions in emissions of ozone producing VOCs (Derwent, 1995).

Every VOC has a different ozone forming potential. Carter (1994) calculated VOCs' photochemical reactivities and their impacts on peak ozone concentrations under VOC-sensitive conditions. Under such conditions, the ozone forming potential of a VOC is called the Maximum Incremental Reactivity (MIR). The ozone forming potential of a compound is calculated by multiplying MIR value with the concentration of that compound (Na et al., 2007). 1,3-butadiene, 1,3,5-trimethyl-benzene, *trans*-2-butene and *cis*-2-butene have MIR values greater than 10, i.e. more than 10 g of ozone is produced from one gram of compound (Carter, 1994).

2.3.3. Secondary Particle Formation

The photochemistry of aromatic compounds can lead to the formation of SOA, which are known to be harmful to human and ecosystem health. In fact, studies have shown that the atmospheric organic aerosol formation potential of gasoline vapor can be accounted for solely by the aromatic fraction of the fuel. As emissions of aromatics are concentrated in urban areas, where many people live and work, the formation of secondary organic aerosols becomes a more acute problem (Barnes and Becker, 2002).

2.3.4. Toxic or Carcinogenic Health Effect

Some VOCs have direct effects on human health. They may exert a narcotic effect and certain other species are toxic. An indirect impact of VOCs to human health is through photochemical ozone formation. Additionally, particular interest is given to those VOCs which can cause cancer in the human population. The most important VOCs which are considered carcinogenic or toxic are benzene and 1,3-butadiene, both potential leukemia inducing agents (Derwent, 1995).

2.3.5. Global Greenhouse Effect

Some of the longer lived organic compounds accumulate in the troposphere. Compounds that absorb solar or terrestrial infrared radiation may contribute to the greenhouse effect (Derwent, 1995). Such compounds are classified as radiative active gases. These compounds are generally VOCs with a halogen component and are known as chloro-floro-carbons (CFCs) (Midgeley, 1995).

Organic compounds can behave as secondary greenhouse gases either by reacting to produce ozone in the troposphere or by affecting $^{\bullet}OH$ concentration and hence affecting methane distribution (Derwent, 1995).

2.3.6. Accumulation and Persistence

Semi-volatile organic compounds have a tendency to become adsorbed onto the surface of PM. In this form they can be long-range transported and may be removed in rain. After their deposition, they may re-evaporate back into the atmosphere and begin another cycle. Finally, these compounds may reach sinks in colder environments in polar regions. Biological accumulation of these pollutants can reach to toxic levels for humans and animals. Accumulating and persistent VOCs are not considerably identified (Derwent, 1995).

2.4. Fates of Organic Compounds

The removal processes of VOCs are similar to each other and include the following:

- Photochemical oxidation by hydroxyl ($^{\bullet}OH$) radicals in the troposphere
- Photolysis
- Deposition and uptake at the Earth's surface
- Reactions with other reactive species

Some of the VOCs' lifetimes with certain compounds are given in Table 1. As depicted from Table 1, the overall impact of these fate processes is significantly dependent upon the physical and chemical properties of the individual organic compound (Derwent, 1995). VOCs are generally degraded by photolysis and/or chemical reaction with $^{\bullet}OH$ radicals, $NO_3^{\bullet}$ radicals, and ozone. These degradation processes transform VOCs to more polar products which often have fewer carbon atoms than the parent compound. The degradation of secondary products continues until the compound has been degraded to CO_2 and H_2O or the products are removed from the atmosphere by wet and/or dry deposition. Through this degradation process, gas to particle conversion may occur, triggering wet and/or dry deposition (Atkinson, 1995).

2.4.1. Photochemical Oxidation by Hydroxyl Radicals in the Troposphere

Hydroxyl radical, which oxidizes trace gases in the atmosphere, is the most important specie of tropospheric chemistry. Hydroxyl radical oxidation is a sink for organic compounds. This oxidation rate determines the atmospheric lifetimes for the majority of VOCs. The lifetimes of VOCs from oxidation by hydroxyl radicals have a wide range. Alkanes with 3 or more carbon atoms have lifetimes of about 2-30 days. Methane and ethane have lifetimes of 10 years and 120 days, respectively. Alkenes have the shortest lifetimes. Their lifetimes range from about 6 hours to 4 days. Lifetimes of alkanes and alkenes generally decrease as the molecular weight increases. Except for benzene, with a lifetime of 10 days, aromatic hydrocarbons show lifetimes in 3 hours to 2 days range (Atkinson, 2000).

Table 1 Lifetimes for selected VOCs with respect to reactions with the $^{\bullet}OH$ radical, the $NO_3^{\bullet}$ radical and with ozone (Atkinson, 2000)

Compounds	**$^{\bullet}OH$**	**$NO_3^{\bullet}$**	**O_3**
Propane	10 day	~7 yr	>4500 yr
n-Butane	4.7 day	2.8 yr	>4500 yr
n-Octane	1.3 day	240 day	
2,2,4-Trimethylpentane	3.2 day	1.4 yr	
Ethene	1.4 day	225 day	10 day
Propene	5.3 h	4.9 day	1.6 day
trans-2-Butene	2.2 h	1.4 h	2.1 h
Isoprene	1.4 h	50 min	1.3 day
a-Pinene	2.6 h	5 min	4.6 h
Limonene	50 min	3 min	2 h
Benzene	9.4 day	>4 yr	>4.5 yr
Toluene	1.9 day	1.9 yr	>4.5 yr
m-Xylene	5.9 h	200 day	>4.5 yr
1,2,4-Trimethylbenzene	4.3 h	26 day	>4.5 yr
Styrene	2.4 h	3.7 h	1 day
Phenol	5.3 h	9 min	
Formaldehyde	1.2 day	80 day	>4.5 yr

2.4.2. Photolysis

Photolysis is a significant removal process for ketones and aldehydes. Photolysis lifetimes of aldehydes and ketones in the troposphere may be on the order of several days depending on sunlight (Atkinson, 1995).

2.4.3. Deposition and Uptake at the Earth's Surface

Dry deposition of VOCs is only significant when molecules are present in the atmosphere close to a region where biological uptake can trap the compound at the surface. There has been little research into the frequency or characteristics of dry deposition. The uptake rate of VOCs by soil is low. For example, the time it takes for soil to completely uptake methane has been reported to be 160 years.

Wet deposition is important for readily water-soluble VOCs. The most VOCs are not in this category. The highly polar carboxylic acids and alkyl hydroperoxides are the only classes of organic compounds which may be removed from the atmosphere via wet deposition mechanisms (Atkinson, 1995).

2.4.4. Reactions with Other Reactive Species

During night-time in the unpolluted atmosphere, $NO_3^{\bullet}$ radicals build up through reactions of ozone with nitrogen dioxide. Nitrate radicals may react with the reactive alkenes to form nitrato-carbonyl compounds by addition reactions. For the vast majority of VOCs, nitrate radicals are not reactive enough to contribute significantly to atmospheric removal. Ozone reactions appear to be as significant as $NO_3^{\bullet}$ radical reactions in the case of reactive alkenes (Atkinson, 1995).

2.5. VOC Emission Control Legislations

There is currently only one international agreement signed for decreasing VOC emissions or their transboundary fluxes: Protocol to the 1979 Convention on Long-Range Transboundary Air Pollution Concerning the Control of Emissions of Volatile Organic Compounds or Their Transboundary Fluxes. This protocol is an extension of 1979 Geneva Convention on Long Range Transboundary Air Pollution.

2.5.1. 1979 Geneva Convention on Long Range Transboundary Air Pollution

The Convention on Long-range Transboundary Air Pollution is one of the important milestones for the protection of the environment. This convention has considerably contributed to the growth of international environmental law and has created a crucial framework for controlling and reducing the damage to human health and the environment caused by transboundary air pollution.

In response to acute regional pollution problems, a High-level Meeting within the Framework of the Economic Commission for Europe on the Protection of the Environment was held at the ministerial level in November 1979 in Geneva. The meeting resulted in the signature of the Convention on Long-range Transboundary Air Pollution by 34 Governments and the European Community (EC). The Convention was the first international legally binding instrument to deal with problems of air pollution on a broad regional basis.

The Convention on Long-range Transboundary Air Pollution entered into force in 1983. The convention was ratified by 51 countries including Turkey (UNECE, 1999).

2.5.2. Protocol to the 1979 Convention on Long-Range Transboundary Air Pollution Concerning the Control of Emissions of Volatile Organic Compounds or Their Transboundary Fluxes

The protocol concerning the control of emissions of VOCs or their transboundary fluxes was signed in 1991 by the 23 parties given in

Table 2. The protocol entered into force in 1997. The main aim of this protocol was to put certain limitations on VOC emissions and their transboundary fluxes. The protocol consists of 18 articles and 4 annexes. Article 2, Article 3, Article 5 and some parts of the annexes are summarized below.

Article 2 stated the basic obligations of the protocol. Parties were obligated to decrease and control their VOC emissions in order to reduce their transboundary fluxes and the fluxes of the resulting secondary photochemical oxidant products so as to protect human health and the environment from adverse effects. The parties agreed to take measures to reduce their annual national emissions of VOCs by at least 30% using 1988 levels as a basis or any other annual level during the period 1984 to 1990.

According to Article 2, parties should have:

- Applied appropriate national and international emission standards to new stationary and mobile sources based on the best available technologies which are economically feasible.
- Taken measures at either national or international level for products that contain solvents, promoted the use of products that are low in or do not contain VOCs and labeled the products to specify their VOC content.
- Fostered public participation in emission control programs through public announcements, encouraged them to use best transportation modes and promoted traffic management schemes.

Within five years from the date of entry of the protocol into force, economically feasible best available technologies should have been applied to existing stationary sources and new techniques should have been applied to reduce the emissions from oil redistribution and motor vehicle refueling operations where national or international tropospheric ozone standards are exceeded or where transboundary fluxes originate or are expected to originate.

Parties should also have cooperated in order to establish:

- More detailed information on the individual VOCs and their photochemical ozone creation potential (POCP) values;
- Critical levels for photochemical oxidants;
- Reductions in annual emissions of VOCs;
- Control strategies to obtain overall cost effectiveness to achieve agreed-upon objectives;
- Measures and a timetable commencing no later than 1 January 2000 for achieving such reductions.

The other obligations that the parties within Article 2 are listed below:

- The VOCs for which the parties should consider decreasing the emissions of are the VOCs which have highest POCP.
- Parties shall take appropriate steps to ensure that toxic and stratospheric ozone-depleting VOCs in current use are not simply replaced with other harmful VOCs.
- Parties, no later than six months after the date of entry into force of the protocol, should start negotiations to decrease their national emissions.
- Parties will start to negotiate for conducting similar measures for the reduction of methane emissions.

Table 2 Status of ratification of the 1991 Geneva Protocol concerning the Control of Emissions of Volatile Organic Compounds or their Transboundary Fluxes as of 22 April 2008

Party	Signature	Ratification
Austria	19.11.1991	23.08.1994
Belgium	19.11.1991	31.10.2000
Bulgaria	19.11.1991	27.02.1998
Canada	19.11.1991	
Croatia		03.03.2008
Czech Republic		01.07.1997
Denmark	19.11.1991	21.05.1996
Estonia		07.03.2000
Finland	19.11.1991	11.01.1994
France	19.11.1991	12.06.1997
Germany	19.11.1991	08.12.1994
Greece	19.11.1991	
Hungary	19.11.1991	10.11.1995
Italy	19.11.1991	30.06.1995
Liechtenstein	19.11.1991	24.03.1994
Lithuania		22.05.2007
Luxembourg	19.11.1991	11.11.1993
Monaco		26.07.2001
Netherlands	19.11.1991	29.09.1993
Norway	19.11.1991	07.01.1993
Portugal	02.04.1992	
Slovakia		15.12.1999
Spain	19.11.1991	01.02.1994
Sweden	19.11.1991	08.01.1993
Switzerland	19.11.1991	21.03.1994
Ukraine	19.11.1991	
United Kingdom	19.11.1991	14.06.1994
United States	19.11.1991	
European Community	02.04.1992	

Article 3 of the protocol included further measures that could be taken for sustainable development and for regulatory actions to control other air pollutants. As stated in the article, the parties signing the protocol should also take measures to reduce total gaseous emissions that may contribute significantly to climate change, to the formation of tropospheric background ozone or to the depletion of stratospheric ozone or that are toxic and carcinogenic.

Article 5 described the research and monitoring objectives of the protocol. According to the protocol, each party should have sought to:

- Identify and quantify effects of VOCs, both anthropogenic and biogenic, and photochemical oxidants on human health, environment and materials.
- Determine geographically sensitive areas.
- Develop emissions and air quality monitoring and model calculations.
- Improve estimates of the performance and costs of technologies for control of emissions of VOCs and record the development of improved and new technologies.
- Develop VOC emission strategies and obtain overall cost-effectiveness to achieve agreed objectives.
- Improve accuracy of emissions inventories of VOCs.

- Improve their understanding of the chemical processes involved in the creation of photochemical oxidants.
- Identify possible measures to reduce emissions of methane.

There were four annexes in the protocol. Annex I of the protocol summarized the tropospheric ozone management areas specified for the purposes of this protocol. Annex II and III provided the parties to the convention with guidance in identifying best available technologies applicable to both stationary and mobile sources to enable parties to meet the obligations of the protocol. Annex IV summarized the information available about photochemical ozone creation potential of VOCs (UNECE, 1979).

2.5.3. VOC Regulations in Turkey

For the last ten years, air quality standards of Turkey improved parallel to European Union directives. In 2008, Air Quality Assessment and Management Regulation (AQAMR) was renewed (T.C. Resmi Gazete, 2008). Benzene (C_6H_6) was the only VOC that was directly considered in this new regulation. In Europe the benzene proportion of oil is approximately 2 percent. Population exposure to benzene mainly arises due to vehicle exhaust emissions. EU Directive 2000/69/EC and AQAMR established an annual average limit value of 5 $\mu g/m^3$ for ambient benzene levels (EP and CEC, 2000; T.C. Resmi Gazete, 2008).

Although a measurement strategy for benzene was defined in this new regulation, the Ministry of Environment and Urbanization have not installed any equipment to quantify benzene levels in Turkey (EEA, 2012b).

In Appendix II of AQAMR (T.C. Resmi Gazete, 2008), measurement of ozone precursor species were considered. The main aim of this appendix is to provide guidance for the determination of emission sources, to check the consistency of emission inventories, to control the efficiency of emission decreasing strategies and to analyze the trend of ozone precursor pollutants. In this appendix, 30 VOCs were listed. However, there is still no measurement of VOCs consistent with the the requirements of this regulation reported in the literature.

2.6. VOC Emission Control Techniques

Volatile organic compounds are emitted from a wide variety of sources and have a wide variety of individual components, each with its own properties. In order to decrease any kind of emissions, including VOCs emissions, an emission inventory study must be conducted. Then successful reductions in anthropogenic VOC emissions from sources can be accomplished by following methods, either one at a time or in combination (Passant, 1995):

- resource management
- product reformulation
- process modification
- end-of-pipe treatment

2.6.1. Resource Management

Resource management covers all the activities to improve the management and control of processes to minimize emissions and wastage. A chief example of resource management relates to solvent management. There is an understanding that solvents are cheap supplies and little care has been paid to limiting fugitive emissions. In order to avoid fugitive emissions from stationary sources, the Commission of the European Community proposed plan for plant operators to estimating their fugitive emissions by developing a “Solvent Management Plan”.

Fugitive emissions can be estimated from the difference of all input solvent in to the plant and all outputs (Passant, 1995).

2.6.2. Product Reformulation

Product reformulation approach includes the reduction or elimination of organic solvents from products such as coatings used in a process. Oil based paints harden by the evaporation of VOC solvents, whereas water based paints are concentrated oil based paints and are emulsified in water. After the evaporation of water, the small amount of organic solvent in the remaining paint must also evaporate for the paint to harden. The use of water based paints instead of oil based paints reduces the emissions of VOCs from painting (de Nevers, 2000; Passant, 1995).

2.6.3. Process Modification

Process modification includes activities for reduction of VOC emissions from a process by improving or making modifications to the equipment used. Replacing gasoline-powered vehicles with electric powered vehicles is a form of process modification (Passant, 1995).

Tanks containing liquid VOCs emit VOC vapors during filling and emptying activities. These emissions are minimized by attaching a pressure vacuum valve to the vent of the tank. These valves remain shut when the pressure difference across them is low. They open for significant flows of vapor in and out that are caused by filling and emptying (de Nevers, 2000).

EPA regulations states that for storage vessels with a capacity greater than or equal to 151 m^3 of fluid with a vapor pressure of 5.2 kPa at the maximum monthly temperature at the site must use floating roof (EPA, 1987).

2.6.4. End-of-Pipe Treatment

End-of-pipe abatement systems are processes to eliminate VOC emissions through particular technologies which either destroy or capture the emission.

Incineration is the most commonly used method for stationary sources. Incineration can be used to treat all VOCs. However, incineration of chlorinated VOCs may be form acidic by-products that must be treated further (Passant, 1995).

Certain microorganisms break organic compounds via biofilters. Biofiltration is the most frequently used biodegradation application. In a biofilter, there is a bed of material through which the waste gas flows. The bed is kept moist and microorganisms grow on the bed material to form biofilms. Organic pollutants dissolve into the water and microorganisms degrade them. Alcohols and alkanes generally degraded well with biofilters. Biofilter technology is an inexpensive treatment technology, though the efficiency may be low (Passant, 1995).

A very frequently applied method for the recovery of VOCs is adsorption; attachment of molecules to the surface of a solid. Activated carbon is usually used as the adsorbent. Adsorption is useful for batch processes as the capacity of the adsorbent is limited. Desorption of VOCs is done by heating the adsorbent or by stripping the stream (Passant, 1995; de Nevers, 2000).

Other recovery techniques for stationary sources are absorption, the dissolution of molecules within a collecting medium (de Nevers, 2000), and condensation. Absorption is most applicable for organic pollutants having reasonably high boiling points relative to ambient conditions. Condensation is also a possible recovery alternative however freezing of water vapor and VOC may create problems in cooling coils (Passant, 1995).

Treatment of VOCs from gasoline engine mobile sources relies on the three way catalyst which oxidizes unburned VOCs to carbon dioxide and water. Evaporative emissions from cars can be controlled through use of carbon canister (Passant, 1995).

2.7. Analytical Methods Used for the Determination of VOCs

Generally, measurement programs include monitoring of C_2 to C_{14} aliphatic hydrocarbons, aromatic hydrocarbons from benzene to naphthalene, isoprene and halogenated hydrocarbons. Depending upon the purpose of the sampling program, a variety of sampling equipment and analysis instruments are required as these VOCs cover wide range of concentration, polarity and volatility (Woolfenden, 1997).

Volatile organic compounds emissions are monitored by national outdoor ambient air VOC monitoring networks that have been in place in the USA, Canada, Europe and the UK. Sampling results from national monitoring programs are used by regulatory agencies to evaluate overall exposure of VOCs to atmosphere and biota. Correct identification of VOC emissions affect the evaluation procedure. Accurate VOC determination relies on the quality of the monitoring data, including monitoring strategies and sampling/analytical methods used. There is considerable amount of variation in the sampling methods (Wang and Austin, 2006).

Appropriate method selection depends upon one or more of the following; target compounds, concentration range, required level of sensitivity, accuracy, and precision, selectivity and the presence of possible interfering substances, sampling conditions, such as temperature and humidity, type of sample required (grab, time integrated, or real-time sampling), availability of sampling and analytical equipment, required level of training and expertise required to operate the equipment, and cost (Wang and Austin, 2006).

Analytical methods for measuring VOCs in ambient air generally involve sampling with sorbent tubes or containers (whole air sampling), which are then transported to a laboratory for analysis using the combination of gas chromatography (GC) with a flame ionization, photoionization, mass spectrometry detector in single mode or in tandem mode, (Badjagbo et al., 2007) or combination of detectors depending upon the target compounds. GC methods have proven reliability on low concentration levels with high accuracy and precision (Badjagbo et al., 2007; Wang and Austin, 2006).

Sorbent tubes are suitable for determination of C_3 hydrocarbon polar and apolar VOCs. However, these tubes do not supply good media for collecting highly volatile compounds such as C_2 hydrocarbons at ambient temperatures. Other advantages of sorbent tubes are listed below:

- Sorbent tubes are cheaper than passivated canister.
- Sorbent tubes do not require cleaning after thermal desorption GC analysis.
- Only a pump is needed in case of an active sampling. For passive sampling, pump is not required.
- Sorbent tubes can usually be reused at least 1000 times before the sorbent needs to be replaced.
- Multi-liter air samples may be collected depending upon the required sensitivity.
- Tubes are small. It is useful for both personal and static monitoring.

Sorbent selection is also important for sampling. Considering volatility range, sorbent stability and artifact formation, the following sorbents can be used singly or in combination to sample most VOCs: Tenax, Carbotrap (Carbopack B), Spherocarb, Carboxen 1000 (Carbosieve SIII) (Woolfenden, 1997), XAD-2, Porapak, Activated charcoal and Ambersorb-XE (Wang and Austin, 2006). Breakthrough, humidity, sampling volume, sampling rate, tube dimensions are important parameters that must be optimized before use (Woolfenden, 1997).

Collection of a sample to a container is referred to as container or “whole air” sampling (e.g., tedlar/teflon bag, passivated canisters). A sampling system consists of a prefilter, pump, flow controller, and flow restrictor. Advantages of container sampling include:

- No breakthrough of target compounds
- No thermal or solvent desorption necessary
- Multiple aliquots for replicate analysis
- Grab or time integrated sampling is possible

A common technique for container sampling is the passivated canister method. Additional advantages of passivated canisters are:

- No degradation of trapping materials
- Detection and measurement of a wide range of polar and nonpolar VOCs
- Sample stability for weeks or months, depending of the nature of the sample
- Easy cleaning
- Consistent recoveries
- Reduced contamination
- No electrical power needed

However, there are potential problems that must be solved when taking container sampling (Wang and Austin, 2006):

- Possible sample instability
- Surface reactions
- Sample permeation
- No exclusion of non-target compounds
- Condensation
- Volume of container
- Transportation

Though GC methods are essential for detection of low concentration compounds, they are time consuming due to sampling, sample shipping, analyte desorption and preconcentration, chromatographic separation, detection and data transmission. In addition to that, they provide only a time-averaged concentration that excludes temporal variations of VOC concentrations. The techniques that use GC are considered off-site techniques and are not useful in emergency situations, such as when fast-response evaluation is critical for decision that may have to be made, especially when the community may be under threat because of exposure to high concentrations of harmful VOCs. Some continuous and real-time air sampling and monitoring techniques are available for determination of VOCs in real-time. These methods give rapid and reliable results (de Blas et al., 2011; Badjogbo et al., 2007).

Direct sampling-mass spectrometry (DS-MS) is one of the real-time gas analysis approach. This technique involves minimal sample preparation and no prior chromatographic separation before analysis by mass spectrometry (MS). A pump is used to draw air sample continuously to the inlet where the sample is extracted and transferred to the MS (Badjagbo et al., 2007). This technique can be used in monitoring the emissions from incinerator stacks, chemical process streams, exhausts, vents and also fugitive emissions (Wise et al., 1997).

Differential Optical Absorption Spectroscopy (DOAS) have been applied to determine especially monocyclic hydrocarbons (Benzene, Toluene, Ethyl-benzene and Xylene) levels in ambient air. The principle of the DOAS technique is based Lambert-Beer's Law. The DOAS equipment is composed of three parts: an emitter, a receiver and an analyzer. The emitter sends to the receiver a light beam containing a range of wavelengths from ultraviolet to visible. Different VOC molecules absorb light at specific wavelengths along the path between the emitter and the receiver. The analyzer (spectrophotometer) continuously measures the light absorbance within the wavelength interval of interest. Each compound is determined by comparing its specific wavelength absorption in the measured spectrum with the reference spectra that are prerecorded from pure standard gases. A computer converts the differential absorbance into concentrations for each of the VOCs monitored (de Blas et al., 2011; Badjogbo et al., 2007).

Low Pressure Chemical Ionization Tandem Mass Spectrometry (LPCI-MS^2) is another spectrometric method for the determination of VOCs. VOC molecules with proton affinity higher than water clusters in the air sample, are ionized through proton transfer reactions. VOCs that have ionization potential lower than water undergo simple charge exchange with the other primary reagent ions producing molecular ions. The precursor ions are then selected in the quadrupole and submitted to collision-induced dissociation with argon atoms in the second quadrupole. The subsequent product ions are then separated according to their m/z ratios by the third quadrupole. VOCs are determined by matching the fragmentation patterns of the precursor (Badjogbo et al., 2007).

Proton-Transfer Reaction Mass Spectrometry (PTR-MS) is an alternative method for real-time identification of VOCs. PTR-MS comprises an ion source to produce primary reagent ions (H_3O^+), a flow-drift tube and a mass spectrometer to detect and to quantify ions (Badjogbo et al., 2007).

Many mobile laboratories are equipped with field-able analytical instruments GC-FID, GC-PID or GC-MS. These mobile devices are useful where the use of GC technology is needed for low concentrations or where fast response and/or monitoring of temporal variations of VOC concentrations are needed. These systems are not as fast as other real-time sampling techniques as sample desorption and chromatographic separation steps take time (Badjogbo et al., 2007).

Another way for determination of VOCs is passive (or diffuse) sampling followed by thermal desorption GC analysis. In passive sampling, gases adsorbed onto the surface of an adsorbent through air movements. VOCs are adsorbed on the passive tubes based on Fick's First Law (Civan, 2010). According to Fick's First Law, under steady state conditions, amount of analyte adsorbed is a function of diffusion coefficient and concentration gradient of the analyte.

2.8. Source Apportionment Techniques Applied to VOC Datasets

Source apportionment is the assessment of the contributions to the airborne species that are emitted from natural and anthropogenic sources. In order to identify sources, data analysis tools are applied to derive information on the sources of species from the measured concentrations.

There are two main receptor modeling approaches that are widely used for source apportionment. The first one is receptor oriented models. These models use the chemical composition data. In such cases, the outcome is the identification of the pollution source types and estimates of the contribution of each source type to the observed concentrations (Hopke, 2001).

The second modeling approach is a source oriented model called Chemical Mass Balance (CMB). The CMB model is applicable to cases that have reliable localized source profiles and some ambient samples measured at receptors (Watson et al., 2001).

Whatever the approach is, the essential rule in source apportionment is that mass is conserved and a mass balance analysis can be used to define and apportion sources. The fundamental assumption is that the determined concentrations are the outcome of a summation of the mass contributions of a number of independent sources or factors. Hence, for all *m* chemical species in the *n* samples, a mass balance equation can be formulated as contributions form *p* sources.

$$x_{ij} = \sum_{p=1}^{p} g_{ip} f_{pj} + e_{ij} \qquad \text{Equation 1}$$

where x_{ij} is the measured concentration in the *i*th sample of the *j*th specie, g_{ip} the contribution of the *p*th source to the *i*th sample, f_{pj} the concentration of the *j*th species in the material emitted by source p, and e_{ij} the un-modeled part of the specie (Hopke, 2009).

There are set of natural physical restrictions on the system that must be considered in apportioning the sources:

- The model must reproduce the original data and describe the observations.
- A source or specie cannot have a negative contribution.
- The sum of the predicted mass contributions of species for each source must be less than or equal to the total measured mass for each specie (Hopke, 2009).

There are also basic assumptions for source apportionment modeling:

- Compositions of source emissions are constant over the period of ambient and source sampling.
- Chemical species do not react with each other.
- The number of sources or source categories is less than or equal to the number of species.
- Measurement uncertainties are random, uncorrelated, and normally distributed (Watson et al., 2001).

2.8.1. Receptor Oriented Models

If the number and the profiles of the sources in the region are not exactly known, then receptor oriented models are useful for source apportionment studies. Receptor oriented methods are multivariate models that analyze a series of observations simultaneously in an attempt to determine the number of sources, their chemical compositions and their contributions to each observations (Guo, et al., 2004). Source identification depends upon the prior knowledge on the tracers. In some cases, additional source identification techniques such as pollution rose, conditional probability function and potential source contribution function can be used with the source contribution output of the model.

2.8.1.1. Principle Component Analysis

In Principle Component Analysis (PCA), source apportionment of a data set is performed under orthogonal constraints for both source contribution and source profile (loading). Additionally, loadings are also normalized and forced to be in the direction of explaining maximum variance. Under such restrictions, PCA provides a unique solution (Tauler et al., 2008).

In order to quantify the contributions of all sources to measured pollutants, the Absolute Principle Component Score (APCS) method is used (Thurston and Spengler, 1985). To estimate each identified source's mass contribution, APCS values were used for the regression of sample mass concentrations (Guo et al., 2004b).

2.8.1.2. UNMIX

The UNMIX model is a newer version of PCA that is geometrically constrained to generate source profiles and contributions with the physically meaningful attribute of non-negativity (Hopke, 2009; Jarquera and Rappenglück, 2004).

If there are N sources, the data space can be reduced to an N-1 dimensional space. In UNMIX, it is assumed that for each source there are some data points where the contribution of a source is not present or negligible compared to the other sources. These data points are called edge points. Each edge defines the points where a single source is not contributing. If there are N sources, then the intersection of N-1 of these edges defines a point that has only one source contributing. Thus, this point gives the source composition. In this way, the profiles of the N sources are found, and then the source contributions of each data point are calculated (EPA, 2007).

2.8.1.3. Positive Matrix Factorization

Positive Matrix Factorization (PMF) uses the least square approach to solve Equation 1 by integrating non-negative constraints into the optimization process and using the error estimates for each data value. The main advantage of PMF over other source apportionment tools is that in PMF, missing data and below-detection limit data can be handled more effectively by assigning them higher error estimates. Although replacements in the data file give the corresponding data a lower weight, this gives an opportunity to use more samples in the analysis. Quantitatively, the mass profile factors produced by the PMF model are better at describing the source structure than those derived by the other receptor oriented methods (Pekey and Doğan, 2013).

2.8.2. Source Oriented Models (Chemical Mass Balance)

When the number and the source profiles of the sources are known in the region, then the only unknown is the mass contribution of each source to each sample. Equation 1 is solved using an effective least square approach that is also known as Chemical Mass Balance (CMB) model. CMB model is useful for primary emissions. Secondary pollutants are difficult to identify as they are formed in the atmosphere (Hopke, 2009).

The essentials of CMB modeling are identification of the contributing source types; selection of chemical species to be involved in the modeling; estimation of source profile of in each source type; and estimation of the uncertainty in source profiles and ambient concentrations (Watson et al., 2001).

Assumptions of CMB model, other than those listed in general assumptions for source apportionment models are:

- All sources are identified.
- The emission profiles of the sources are significantly different from each other (Watson et al., 2001).

2.8.3. VOC Source Tracers

The VOC tracers for each source are not identically same in every study. This is mainly because of VOCs measured in each study are different (Watson et al., 2001). However there are some commonly referred compounds in the literature for the identification of certain sources. In this section, these commonly referred compounds are summarized.

Most abundant compounds emitted from motor vehicle emissions are ethene, acetylene, propane, propene, 1-butene, isobutene, isopentane, n-pentane, hexane, benzene, toluene, m&p-xylene and 1,2,4-trimethylbenzene. However, depending on the type of the vehicle, exhaust emission varies. Acetylene, isobutene, isopentane, n-hexane are enriched in gasoline exhaust. However, in diesel exhaust the abundant compounds are propene, propane, 2,2-dimethylbutane, n-decane and n-undecane. Heavy VOCs are used for the discrimination of diesel exhaust from gasoline exhaust. These compounds are well enriched in diesel exhaust (Wastson et al., 2001).

Liquid gasoline emissions are generally characterized with the same compounds of gasoline vehicle exhaust. However, in liquid gasoline, the combustion products, ethane, ethene and acetylene, are not observed. Similar to liquid gasoline emissions in evaporated gasoline emissions, combustion products and heavy VOCs with low vapor pressure are less enriched. Isobutane, n-butane, t-2 butene, and isopentane are the dominant VOCs in evaporated gasoline emissions (Watson et al., 2001).

Petroleum refineries are characterized by ethane, propene, propane, n-pentane, t-2-hexene, benzene, n-heptane, toluene and n-octane. Most of these compounds are also abundant in liquid and evaporated gasoline vapors (Watson et al., 2001).

Large components of VOCs are emitted from solvent usage in paints and in industries. The emissions from solvent use are depleted in compounds emitted from fuel manufacturing and use. Styrene, n-decane and other heavy VOCs are enriched in solvent sources (Watson et al., 2001). Printing ink solvents are enriched especially with toluene, styrene, n-nonane and 1,2,4-trimethylbenzene and other heavy VOCs (Wadden et al., 1995).

Coal fired power plants emit small quantities of VOCs. The tracers of coal fired power plants are toluene, benzene, xylenes, ethylbenzene and tetrachloroethane (Watson et al., 2001; Garcia et al., 1992). VOCs from household combustion of biomass and coal are mainly acetylene, ethylene, propylene, ethane, propane, benzene and toluene. Methyl chloride (Liu et al., 2008c) and 1,2-dicholoethane (Cai et al., 2010) are typical species from biomass burning and coal combustion, respectively. Emissions from coal combustion primarily depend on the coal type (Liu et al., 2008c).

Biogenic emissions are generally characterized by isoprene and terpenes. However, the main difficulty in biogenic emissions is that source profile varies with vegetation type, ambient temperature, seasonal growth cycles and humidity (Watson et al., 2001).

2.9. Review of VOC Studies in Industrial Regions

For the last three decades, there has been tremendous effort to characterize levels of VOCs in industrial areas in whole over the world. Some studies focus on BTX compounds. In many studies passive or container sampling methods are used followed by GC analysis. In some studies online measurement systems have also been used. In several of the studies, source apportionment tools were applied to understand the source regions. Some example applications to determine and to identify the sources of VOCs are given below.

Volatile organic compound concentrations at five locations around industrial areas of Bombay, India were measured (Rao et al., 1997). The samples were collected using tedlar gas sample bags for a period of 3 h from 06:00 to 09:00. The air sample was then transferred into an evacuated stainless steel canister. The samples were concentrated using cryogenic preconcentration and analyzed with GC-FID. C_2-C_5 hydrocarbons were higher at the refinery area.

Concentrations of VOCs at Ulsan industrial area were determined using stainless steel canister as samplers (Na et al., 2001). Analysis was performed with GC-FID. The light hydrocarbon fraction at Uslan industrial site was higher that other industrial areas in the literature. This suggests that the fugitive emissions of light VOCs (C_2-C_5) in Uslan industrial area might be higher than those of other industrial areas.

Five VOCs were analyzed and classified in a study conducted at two sites in Kaohsiung, Taiwan (Liu et al., 2008a). The samples were collected using stainless steel canisters. A portion from the sample was taken and preconcentrated. After the thermal preconcentration, the sample was injected into a GC-MS system. Samples were analyzed for 56 compounds. In the industrial site, toluene, ethylbenzene, styrene, o-xylene and benzene were found to be the highest concentration VOCs.

Seasonal variations of VOCs at Kwun Tong industrial area in Hong Kong was investigated (Ho et al., 2004). Stainless steel canisters were used for the sampling. Samples were preconcentrated using cryogenic concentrator and were analyzed with GC-MS. A total of 37 VOCs were identified. Toluene concentration in Kwun Tong was approximately three times higher in summer than winter.

Eight hour time weighted average samples were collected in stainless steel canisters in Harris Country, Texas (Conley et al., 2005). A total of 53 compounds were quantified using a GC-MS coupled to a cryogenic preconcentrator. It was concluded that butane, isobutane, 2-methyl butane and pentane are chemical signatures of petrochemical industrial processes.

The chemical mass balance receptor model was applied to define the sources of 58 VOCs measured at seven sites in Pearl River Delta, China (Liu et al., 2008b). One of the sampling stations was located at an industrial site, Dongguan. Canisters were used for the sampling. Analyses were performed with GC-MS/FID system. Solvent usage was found as the highest contributing source in Dongguan.

Airborne concentrations and sources of thirteen VOCs were evaluated in two urban areas in Illinois (Sweet and Vermette, 1992). Canister sampling followed by GC-MS analysis was performed. CMB and PCA were applied to data. These analyses indicated that most of the VOCs were from vehicle exhaust, evaporative emissions and solvent emissions.

In Changchun, China, VOCs were measured at five different locations (Liu et al., 2000). Samples were collected in bags. The sample was then pulled from the bag to an adsorption tube. The analysis was performed with GC-MS-FID system. The diurnal variation of the total mean VOC concentrations showed two peaks related with traffic density for three sites and a single peak for the industrial area.

Seasonal variations of VOCs in Edmonton, Alberta-Canada, were analyzed at two sites (Cheng et al., 1997). One of the stations was located in downtown whereas the other station was in an industrial area. Samples were collected in canisters an subsequently subjected to GC- MS and GC-FID analyses. Eighty-five VOCs were determined. Major VOC contributors in industrial area were butane, propane and isopentane. Distinct seasonal variations in VOC were not observed at the industrial site. This was because the sampling station was dominated by nearby sources. The total lifetime VOC-related cancer risk in downtown was triple than at the industrial site.

Kume et al. (2008) measured 27 VOCs in an industrial city Fuji, Japan. Passive samplers were used to sample VOCs at 33 sampling sites. The sorbent used in the passive samplers was activated charcoal. Samples were extracted and analyzed with GC-MS. Toluene was found to be most abundant VOC in the area. The mean toluene to benzene ratio for the three campaigns was found around 8.7.

In Daliao and Tzouying, southern Taiwan, 52 VOCs were monitored near an industrial district (Hung-Lung et al., 2007). Petrochemical, paint and resin industries were located around Daliao station and oil refining was the closest industry to Tzouying station. Air samples were collected using stainless steel canisters. Samples were analyzed with GC-MS. Ozone formation potentials of VOCs were calculated using MIR values for each site. Concentrations of n-pentane, isopentane, 1-butane and isoprene were higher in Daliao and 1-butene and undecane were observed to be higher in Tzouying. In Daliao, major OFP species were reported as toluene, propene and isoprene whereas in Tzouying, toluene, propene and 1-butene were the three major OFP compounds.

Two VOC measurement campaigns were carried out in an industrial city, Dunkerque, France, using passive samplers at 40 and 36 sites in during summer and winter campaign, respectively (Roukos et al., 2009). A total of 174 compounds were identified using thermal desorption GC-FID and MS. High BTX concentrations influenced the two industrial plants. For the winter period, BTX concentrations are mainly due to a local pollution mixed to oceanic air masses. The summer campaign was characterized by VOC ratios greatly influenced by photochemical activity and continental aged air masses.

Passive samplers were used to sample air at 34 locations in Shizuoka, Japan (Ohura et al., 2006). Samples were extracted and analyzed with GC-MS. Spatial distributions and emission sources for the VOCs were created. The lifetime cancer risks were calculated. Significantly higher cancer risk was observed in winter than in summer. Risk was derived mainly from benzene.

In Mumbai, India, VOCs were sampled using active sampling onto sorbent tubes (Srivastava, 2004). The samples were analyzed by thermal desorption followed by GC-MS. CMB model was used to identify the sources. It was observed that the main source of VOCs in Mumbai was evaporative emissions.

Volatile organic compounds near a petroleum refinery in Corinth, Greece were sampled onto adsorption tubes (Kalabokas et al., 2001). Adsorption tubes were filled with Tenax-TA and flow rate of the sampling was 100 ml/min. Samples were analyzed with a thermal desorption unit connected to GC-FID. A total of nine VOCs were monitored. The average values of saturated hydrocarbons for the May and September periods were three times higher than the corresponding values for the February and October periods.

In Dunkerque, France, another study was conducted by another group to determine the temporal variation (diurnal and seasonal) of VOCs in the area (Badol et al., 2008). Sampling was done using online GC-FID. Hourly measurements were made for a one year period for C_2 to C_9 hydrocarbons. A total of 330 000 data points were generated. VOC to acetylene ratio with wind direction showed the influence of industrial emissions and natural gas leakage.

Continuous online measurements of C_2-C_{10} VOCs were performed at Houston, USA (Leuchner and Rappenglük, 2010). Automated GC-FID was used for the sampling and analysis. VOCs were sampled for every hour for 40 min and preconcentrated on a cold trap at -30°C.

Subsequently, the sample was desorbed at 325^{o}C in a backflush mode thermal desorber and injected into a GC. PMF was applied to the data set. PMF analyses showed that traffic, industrial and biogenic sources were the major sources contributing to VOC mass. The conditional probability function, used to identify the location of source, showed that Houston Ship Channel emissions account for approximately two-thirds of the VOC mass contributions.

On-line air sampling was used to determine hourly levels of VOCs in Bilbao, Spain (Durana et al., 2006). Samples were analyzed with automated GC-FID. 62 VOCs were measured. Diurnal variations showed that vehicle emissions were the dominant source of VOCs.

Quasi-continuous measurement of VOCs in the range of C_4-C_{12} was carried out in Santiago, Chile (Jorquera and Rappenglück, 2004). The measurement application consisted of a two double stage preconcentration procedure using adsorbent and cryofocusing. Then the compounds were thermally desorbed rapidly and injected into two specific columns mounted in series. UNMIX and PMF models were applied to the results to apportion the sources of VOCs. At the residential site, transported gasoline exhaust and local gasoline exhaust were found to be the most dominant sources. It was stated that both models showed good performance at discriminating sources. However, PMF was able to find better and cleaner source profiles that did UNMIX.

2.10. Review of VOC Studies Conducted in Turkey

The studies conducted in Turkey on VOCs started last decade. VOC sampling and analyses with different methods have been tried by different research groups. Certain studies focused on the effects of VOCs on humans in different microenvironments. Several source apportionment studies have also been conducted to understand the main sources and diurnal variations of VOCs.

An active sampling method with charcoal tubes was used for the collecting airborne VOCs in İzmir (Müezzinoğlu et al., 2000). VOCs were extracted into vials and then analyzed with GC-FID. Toluene was found to be the most abundant VOC in the urban air followed by xylenes and benzene, respectively. BTX concentrations were found higher than the values in the literature. Significant correlations between benzene and other compounds were observed. This indicated that VOC levels were mainly affected by motor vehicle emissions.

In another study conducted in İzmir, VOCs were collected at urban and suburban sites (Elbir et al., 2006). Samples were collected on a tube filled with activated carbon via pump. 5 night and 5 day time samples were collected from each site. Samples were then extracted and analyzed with a GC-MS for 28 VOCs. Toluene (40.6%) was the most abundant compound in suburban site and was followed by benzene (7.4%) and o,m-xylene (6.5%). In the urban site, toluene (30.5%), p-xylene (14.9%), o,m-xylene (11.4%), and ethyl benzene (7.2%) were the dominating compounds in summer. PMF was applied to the data set. Six source factors (gasoline vehicle exhaust, diesel vehicle exhaust residential heating, paint production/application, degreasing, dry cleaning, and an undefined source) were extracted.

The composition of odorous gases emitted from a municipal landfill was investigated in İzmir (Dinçer et al., 2006). Samples were taken into special bags and transferred into adsorbent tubes. The analyses were performed with thermal desorption GC-MS. Up to 53 VOC compounds in different classes (mono-aromatics, halogenated compounds, aldehydes, ketones, esters, and volatile fatty acids) were identified and quantified.

The relationship between odor concentrations and chemical concentrations was also studied as a continuation of the previous study (Dinçer et al., 2006) at three locations in İzmir (Dinçer and

Müezzinoğlu, 2006). Results showed different characteristics of the odorous gases and air in and around the urban and industrial sources.

Another landfill study was carried out in İZAYDAŞ (Waste and Residue Treatment, Incineration and Recycling Inc.) landfill, Kocaeli (Durmuşoğlu et al., 2010). Samples were collected onto adsorbent tubes via active sampling. The samples then analyzed with GC-FID. Health risk was calculated using BTX concentrations. The mean cancer risk over a period of 70 years was estimated to be 67.5 per million, primarily due to inhalation of benzene.

A third landfill study was conducted in an İstanbul municipal solid waste landfill site (Saral et al., 2009). The odorous effects of 22 VOCs and H_2S were investigated. Industrial Source Complex v3 Short Term (ISCST3) model was used to estimate hourly concentrations of VOCs over the nearest residential area. Results showed that short-term averages of three odorous VOCs, ethyl mercaptan, methyl mercaptan and hydrogen sulfide, exceeded their odor thresholds.

Interaction patterns of major photochemical pollutants were studied in İstanbul (İm et al., 2008). The sampling included the measurement of ozone, nitrogen oxides and VOCs at two urban districts in Karaköy and Saraçhane. VOCs were measured with a total hydrocarbon instrument. Results showed that high levels of O_3 were observed mostly under relatively anti-cyclonic conditions with considerably low-wind speeds. VOC-NO_x ratios at both stations showed that the chemistry was NO_x-sensitive.

Levels of BTEX compounds were determined at Dilovası and Gebze Institute of Technology campus (GYTE), Kocaeli (Ergenekon et al., 2009). Active and passive tube sampling methods were used for sampling. BTEX levels were determined with thermal desorption GC-FID system. BTEX concentration ratios were calculated as (5.4; 9.1; 1.0:3.1) at Dilovası and (6.1; 7.5; 1.0; 2.2) at GYTE using passive sampling results. Active samples taken in the morning at Dilovası showed significant correlation among BTEX compounds suggesting the effect of traffic related VOC pollution at the site while GYTE suffered from polluted aged air masses.

Pekey and Yılmaz (2011) used passive samplers to determine levels of VOCs at 49 locations in Kocaeli, Turkey. Samples were analyzed using thermal desorption GC-FID. Among all VOCs, concentrations of *m*- & *p*-xylene and toluene were found to be highest. Source apportionment by PCA identified four sources. Use of industrial solvent and industrial process losses were the two industrial related emission sources.

Levels and sources of VOCs were determined in a study conducted in Bursa, (Civan et al., 2011). Passive sampling was carried out at 40 points over two sampling periods. Thermal desorption GC-FID was used for the analysis of the samples. Thirty four VOCs were identified in Bursa atmosphere. PCA was conducted to determine the sources of VOCs. Three sources were identified: vehicular exhaust, industrial emissions and evaporative emissions.

Sources and variability of approximately 30 VOCs in suburban Ankara were determined (Yurdakul et al., 2013). VOCs were sampled for 6 months on adsorbent via active sampling. Analyses were performed using thermal desorption GC-FID. Four sources were identified by PMF; gasoline exhaust, diesel exhaust, solvent evaporation and local laboratory emissions.

Indoor concentrations of VOCs and their associated health risk were determined at three primary schools in İzmir (Sofuoğlu et al., 2011). Active sampling was applied for VOCs on Tenax TA tubes. VOCs were analyzed in a thermal desorption-GC-MS system. Formaldehyde was classified as the primary concern among the VOCs measured followed by benzene, naphthalene, and toluene.

Human exposure to VOCs in Kocaeli was investigated in different microenvironments (Pekey and Arslanbaş, 2008). Passive sampling with adsorbent tubes was used. The analyses were done using thermal desorption GC-FID. Personal exposure and indoor concentrations were generally markedly higher than outdoor levels. Compared with the findings of earlier studies, the level of target analytes in indoor air were higher for several target VOCs, indicating a possible trend toward increased inhalation exposure to these chemicals in residential environments.

The effect of diurnal changes in strengths of VOC sources on the performances of PMF and PCA was investigated using ambient measurement results that were taken during daytime and nighttime hours within Davutpaşa Campus of Yıldız Technical University, İstanbul (Demir et al., 2012). Forty-five VOC species were measured in the samples. A total of six source groups were extracted from each dataset: solvent use, general industrial paint use, gasoline and diesel vehicle exhausts, and biogenic as well as evaporative emissions. The results suggested that extraction of possible sources by PCA depends greatly on the number of samples and the strength of the sources, while PMF produced stable results regardless of number of samples and source strengths.

There are couple of ongoing projects that our research group involved. The first one of those was on-line sampling and analysis of VOCs at Bursa. Hourly chromatographs were generated and analyzed. Sampling was completed by the year 2006. This study is expected to be completed in 2013 by Sema Yurdakul.

The other study was the sampling of VOCs in Balıkesir atmosphere via canister and passive sampling. VOC sampling was carried out by our research group. The sampling and analyses were completed in 2012. Dr. Lokman Hakan Tecer is responsible for this project.

2.11. Review of Other Studies Conducted in Aliağa Region

Various studies have been conducted in Aliağa region. Most of the studies conducted have tried to explain the current composition of the Aliağa atmosphere and soil. Species of different organic and inorganic groups were investigated in the region. The selected articles are summarized in this section.

There has been only one VOC analysis conducted previously in Aliağa region. In the study, air samples were collected at three sites around petrochemical complex and oil refinery (Çetin et al., 2003). Samples were collected on a carbon tube by a vacuum pump. The samples were then extracted in an ultrasonic bath and centrifuged. After sample extraction, analyses were performed by GC-FID. VOCs measured were n-hexane, ethyl alcohol, acetone, ethyl acetate, n-butyl alcohol, methyl isobutyl ketone, butyl acetate, and ethylene dichloride. VOC concentrations were 4-20 times higher than those measured at a suburban site in İzmir (Çetin, 2002). The total VOC concentrations were reported to increase with temperature. The highest concentrations were measured in summer. The authors indicated that this was probably due to the increased evaporation of VOCs as a result of higher temperatures.

Atmospheric concentrations of polychlorinated biphenyls (PCBs) and trace elements were determined at two site stations (industrial and urban) located around the Aliağa industrial region (Çetin et al., 2007). Average PCB concentration in the industrial area was found to be higher in summer whereas in the urban site, winter concentrations were higher. The elemental composition of the industrial site was dominated by terrestrial elements and trace elements emitted by the iron-steel plants. PCA results showed that the steel industry, fuel oil combustion or vinyl chloride process and soil were important PCB sources.

Both gas and particle phase atmospheric concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) in Aliağa were investigated (Bozlaker et al., 2008a). Average PAH concentrations in summer were found higher than those observed in winter. PAH concentrations in soils taken from 50 locations were also determined. It was determined that urban Aliağa, steel plants, the petroleum refinery and the petrochemical plant are the dominant sources of PAHs in the region. One other important outcome of this study was regarding the role of soil for PAH distribution. It was concluded that soil was a secondary source to the atmosphere for low molecular weight PAHs in summer and a sink for the higher molecular weight ones in both seasons.

Similar to the PAH study, Polychlorinated Biphenyls (PCBs) concentrations were determined in ambient air, dry depositions and soil in Aliağa region (Bozlaker et al., 2008b). Summer PAH concentration in ambient air was found to be higher than winter. This could be due to increased volatilization with temperature. The spatial distribution of average PAH soil concentrations showed that the iron steel plants, shipbreaking facilities, refinery and petrochemicals complex were the important sources in the region.

Soil and atmospheric concentrations, dry deposition and soil-air gas exchange of organochlorine pesticides (OCPs) were also investigated in Aliağa region (Bozlaker et al., 2009). The OCP concentrations in the ambient air were found to be higher during summer due to volatilization at higher temperatures and regional use of pesticides.

PAH and aliphatic hydrocarbons in sediment of the Aliağa Bay were investigated to formulate an environmental risk assessment from PAH contamination (Neşer et al., 2012). Aliphatic and PAH diagnostic ratios were shown to be mainly petroleum-originated and pyrolitic contaminations, respectively. Further analysis suggested that Aliağa sediments are likely contaminated by acutely toxic PAH compounds.

CHAPTER 3

MATERIALS AND METHODS

3.1. Sampling Locations

3.1.1. General Features of Aliağa Region

Aliağa is located 50 km north of İzmir on the coast of Aegean Sea. The town is surrounded by the Dumanlı Mountains and Yunt Mountains. Aliağa's municipality land area is 412.5 km^2. The town located along D550 Çanakkale - İzmir highway. Typical Mediterranean climate is observed in the town. Almost all of the precipitation events occur during winter. Northerly winds dominate during winter whereas local sea breezes (etesian winds) are particularly effective on summer afternoons. Average daily temperatures are 25^{o}C and 7^{o}C in summer and winter, respectively (Municipality of Aliağa, 2009).

The economy of Aliağa, which was based on agriculture until early 1960's, has gained an industrial character after the 1970's as the town was declared as a "heavy industrial zone" in the first five year development plan. Aliağa Organized Industrial Zone was established in 1977 and Aliağa became an industrial center. Today, Aliağa produces 1-1.3% of Turkey's gross national product per capita (Aliağa Chamber of Commerce, 2011). The population of Aliağa municipality according to 2007 statistics is approximately 60 000 and is expected to rise to 300 000 by 2015 (Turkish Statistical Institute, 2012).

Various industrial facilities in different production sectors were established, once the Organized Industrial Zone was established. These include refinery (TÜPRAŞ), petrochemical complex (PETKİM), petroleum products storage and filling facilities, iron steel industries, power plants, shipbreaking facilities, pulp and paper factory, and fertilizer factory. Locations of major facilities are given in Figure 2.

The crude oil demand of Turkey is about 694 000 tons and one third of this demand is processed by TÜPRAŞ. A natural gas fired thermal power plant, with a capacity of 1520 MWh was built by ENKA in 2002. Another major industry in Aliağa is the petrochemical complex, PETKİM, which became operational in 1985. PETKİM has production capacity of 3.2 million tons. Aside from these three major complexes, a number of harbors, including PETKİM terminal, Nemrut Port, Refinery Port, Port of Aliağa, and ship breaking facilities played significant roles in the development of the area. These harbors are especially important for the transportation of crude oil, distilled products, petrochemical products and various chemicals to and from the region. The scrap for iron steel industry, ammonia and phosphoric acid for fertilizer factories, pulp for paper industry and raw materials for petrocokes industry are also supplied from these harbors. There are 25 ship breaking units are located in the shoreline of the Nemrut area. Approximately 10 iron and steel factory are located in the Horozgediği area. These factories use the steel and iron recovered from ships and metals recovered from metal recovery factories.

Figure 2 Sampling Site

Major pollution sources in the Aliağa area, their capacities and types of pollution are summarized in Table 3 (Müezzinoğlu, 2000). Based on this table PM from iron and steel plants, SO_2 from all combustion sources and VOCs from refinery and petrochemical complex are main pollutant types affecting air quality in the region. However, it should be noted that emissions of both PM and SO_2 from these industries decreased significantly in last 10 years. Reduction in PM levels was due to actions taken by iron and steel plants and reductions on SO_2 levels were due to use of natural gas for energy production and in industrial processes. How VOC emissions and levels changed in time is not known as there were no VOC measurements in the past decades.

Table 3 Major pollution sources in the Aliağa area
(modified from Müezzinoğlu, 2000)

Type	Production	Annual Capacity	Pollution Type
Steel mills	Various	8.5 million tons*	PM, SO_x, NO_x, CO, PCB, **VOCs**,
Rolling mills	Various	7.35 million tons*	PM, CO, SO_x and NO_x
Petroleum refinery	Various	8.9 million tons	Mercaptanes, H_2S, SO_x, NO_x, **VOCs**, PM, CO, PCB
Petrochemicals	Various	3.2 million tons	SO_x, NO_x, **VOCs**, PCB, PAH
Metal foundry	Special alloy casting	1.2 million tons	CO, PM, **VOCs**
Petrocokes	Drying imported petrocokes	25 600 tons dry cokes*	CO, PM, **VOCs**, SO_x, NO_x, PAH
Solvent distillers	Various chemicals	450 000 tons*	**VOCs**
Petrochemical Storage	Storage	79 000 tons*	**VOCs**
Concrete production	Concrete	24 000 m^3 tons	PM
Pulp and paper mill	Paper	23 000 tons	PM, NO_x, SO_x and CO
Fertilizer	Chemical fertilizer	330 000 tons	PM, acid, NO_x, SO_x, NH_3
Ship breaking	Iron and steel	195 000 tons	PM, NOx, **VOCs**, Asbestos
Gas fired power plant	Electricity	12.4 billion KWh	PM, **VOCs**, CO, NO_x and SO_x
Harbors	Transportation and Storage	34 million tons	PM, **VOCs**, CO, NO_x and SO_x
Highway	Transportation	6.54 million vehicle	PM, **VOCs**, PAH, CO, NO_x, SO_x
Coal storage and packing	Coal	580 000 tons	PM
Metal recovery	Iron, steel and aluminum	Not reported	PM
Solvent recovery	Various	Not reported	PM, **VOCs**, CO, NO_x and SO_x

*Data does not include productions of all facilities in the region.

3.1.2. Stations

In order to quantify the contribution of industrial facilities to Aliağa region and downtown Aliağa VOC concentrations, sampling was conducted at two monitoring stations through winter and summer campaigns. One of the sampling stations was located in downtown Aliağa and the other one was established approximately 500 m to the south east of Horozgediği village. Stations consisted of containers with dimensions 4m x 6m x 2m and equipped with a bench, an air conditioner and uninterruptible power supply (UPS). After the summer sampling, another temporary station was installed in between PETKİM and TÜPRAŞ, named as TÜPRAŞ Station. Further details on station characteristics and sampling equipment are given in following sections.

3.1.2.1. Aliağa Station

According to 2007 census, downtown Aliağa had a population of 52 000 (Turkish Statistical Institute, 2012). Aliağa station was located at the Demokrasi Square in downtown Aliağa (38^{o}48'N, 26^{o}58'E). This station will be referred as Aliağa Station throughout the manuscript. A detailed map and photos taken from the Aliağa station are given in Figure 3 and Figure 4, respectively.

Various commercial and non-commercial facilities, including a municipality building, restaurants, banks, grocery stores and offices of non-governmental organizations and lawyers were located around the square. Bankalar Street and İstiklal Street were two frequently used road in the town. These two streets were also used for parking. The station was located 50 m and 30 m from İstiklal Street and Bankalar Street, respectively. It was also approximately 500 m from the Aegean Sea. The distance between D550 Çanakkale-İzmir highway and station was 300 m. The closest industries to the sampling site were TÜPRAŞ and PETKİM, which were located 2 km to the west and 3.3 km to south west of the station, respectively. A paper and pulp factory was located approximately 4 km to northwest of the station. The station was also approximately 5.5 km from the Nemrut Bay.

VOCs were not the only species measured in this station. In addition to organic compounds, daily trace element samples were also collected using a dichotomous sampler and trace elements in collected samples were analyzed using x-ray fluorescence (XRF) technique. Inorganic pollutants, namely SO_2, NO, NO_2, O_3 and PM_{10} mass were also measured on an hourly basis along with the VOCs. Results of these non-VOC measurements were not evaluated in this thesis. However, those data are occasionally used to support VOC data to explain certain points.

Figure 3 Detailed map of the Aliağa station

Figure 4 Photos from Aliağa Station

3.1.2.2. Horozgediği Station

Horozgediği Station was located 350 m north east of Horozgediği Village (38^{o}43'N, 26^{o}55'E). The location of the Horozgediği station and some views from the station are depicted in Figure 5 and Figure 6, respectively. The station was installed near an air quality monitoring station operated by ENKA gas-fired power plant. This was necessary, because data on air quality parameters, SO_2, NO, NO_2 and PM_{10} mass were obtained from their measurements. The station was 500 m south of Yeni Foça-İzmir road and 4.5 km west of D550 Çanakkale-İzmir highway. Industries were located to the north and northeast of the station. Horozgediği station was particularly close to iron and steel industries. There were 7 of these plants located between 640 m – 3900 m from the station. TÜPRAŞ and PETKİM are relatively further away. These two important VOC emitters are located approximately 7.5 km to the NW of the Horozgediği station. Sampling site is 2.7 km and 8.2 km away from Nemrut Bay and from Aliağa downtown, respectively. Çakmaklı, Cumhuriyet, Bozköy and Kozbeyli were other villages around the sampling site.

Figure 5 Detailed map of Horozgediği station

Figure 6 Photos from Horozgediği Station

3.1.2.3. TÜPRAŞ Station

TÜPRAŞ station was established between TÜPRAŞ and PETKİM to investigate similarities and differences between emissions from these two strong VOC emitters and to generate VOC profiles specific to them. Such profiles would be very useful for least-square based receptor modeling tools, where priory information on composition of sources is necessary. Since temporal variability (both seasonal and short-term) was not concern, measurements were performed for a shorter period compared to the campaigns in Aliağa and Horozgediği stations.

The station was established at an abandoned building in TÜPRAŞ (38°47'N, 26°56'E), located at the border between TÜPRAŞ and PETKİM. Location of the station is given in Figure 7. A picture of the station is not included in the thesis, because we were not allowed to take pictures in that area. Although the sampling period was not long, we feel that VOC fingerprints or profiles of TÜPRAŞ and PETKİM are invaluable as these two industries are the dominant VOC sources in the region. Downtown Aliağa was 3 km from TÜPRAŞ Station.

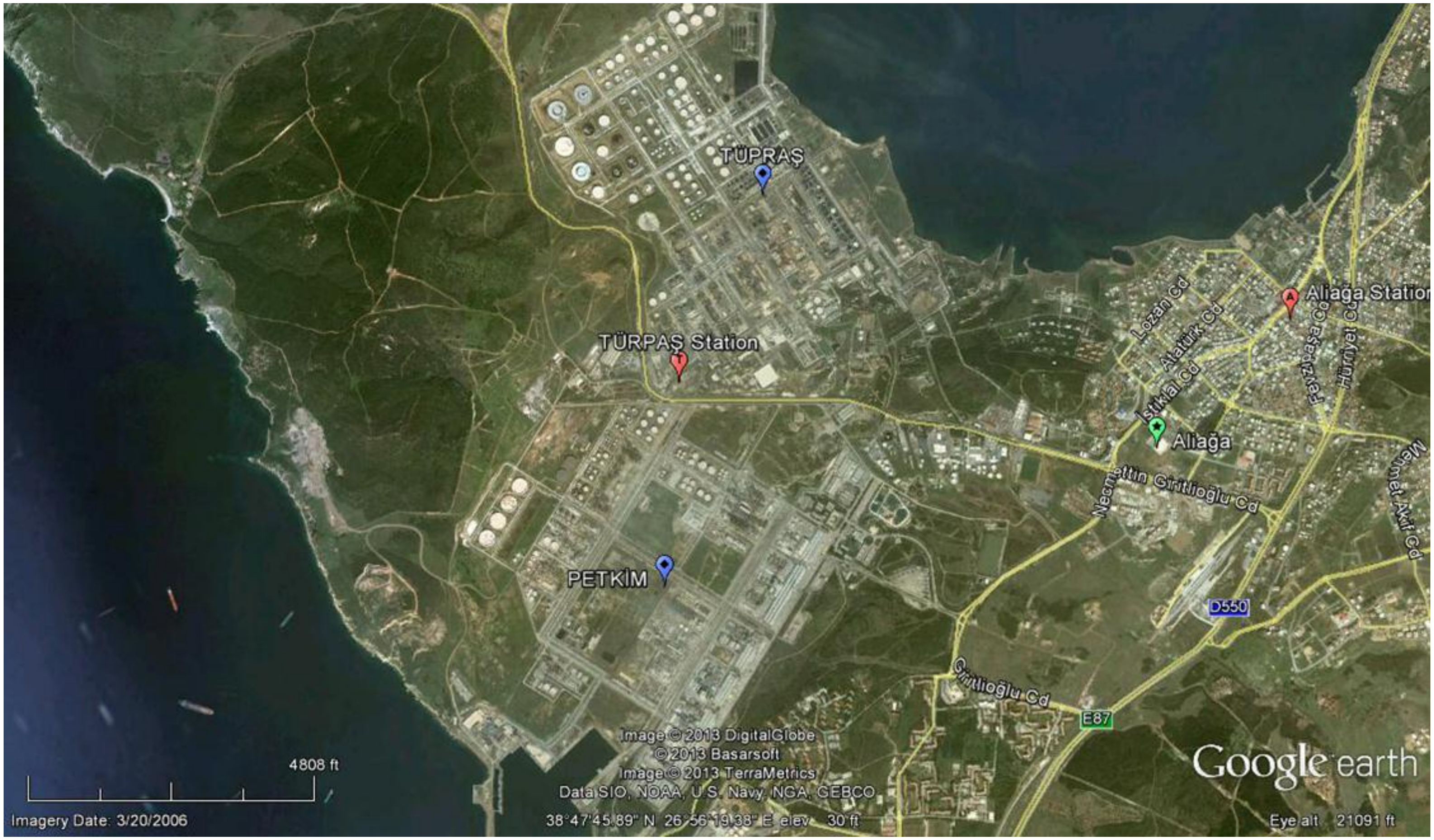


Figure 7 Detailed map of TÜPRAŞ station

3.2. VOC Measurements

As discussed in Section 2.7, VOCs in ambient atmosphere can be determined by a variety of methods. These include collection of VOC samples in some sort of container and subsequent analysis in the laboratory by gas chromatography. Containers that can be used for this purpose can be evacuated canisters, tedlar bags etc. Another approach is to collect samples on a solid adsorbent and again subsequent analysis by GC-MS or GC-FID systems. Adsorbents used can be inorganic material such as silica, various zeolites, carbon based material or organic polymers. Inorganic sorbents are not commonly used because they are hydrophilic and converting them hydrophobic requires some additional processing. Carbon based material which can be carbon molecular sieves, or graphitized carbon blacks and organic polymers are more widely used adsorbents for VOCs. Today most widely used adsorbents include activated charcoal, Chromasorp 106 (which is Styrene-divinyl-benzene-copolymer), Tenax TA (which is Poly-(2,6-diphenyl-)-p-phenylenoxide) and Carbopack, which is a graphitized carbon black. Adsorbents, no matter what type they are, cannot collect VOCs with carbon number less than four. Another common problem is that they do not let for long term sampling, because their active sites are quickly filled and VOCs start to leak.

The method used in this study was online gas chromatograph with FID and PID detectors. Online GC systems, which includes deploying a specially designed gas chromatograph equipped with a sampling system to field has few advantages compared to other sampling techniques, briefly described above. Main advantage is their capability of generating high resolution data. Hourly data or data with 30 min resolution can be generated. They also have lower detection limits and they can measure larger spectrum of VOCs than those measured in adsorbent or canister samples.

The working principle of online GC is composed of four steps. These are sampling, preconcentration, separation and quantitative analyses. During separation of VOCs, instruments are capable of sampling and preconcentrating the next sample.

Two different on-line GC systems, one located at the Aliağa station and the other one at Horozgediği station, were used in this study. Two field campaigns were conducted in 2006. Winter campaign was started in November 2005 and continued until March 2006. Summer campaign started in August 2006 and continued until October 2006. The samplings were carried out simultaneously in Aliağa and Horozgediği stations. After the summer sampling, the online-GC in Horozgediği Station was transported to TÜPRAŞ station in November 2006 for 15 days of sampling. Further details on sampling devices and VOCs measured in each station are given in next subsections.

3.2.1. VOC Measurements at Aliağa Station

At Aliağa Station, The Syntech Spectras GC955 series 600 and 800 online GCs were used. These two GCs were used in parallel and controlled with a single built-in computer. A single sample inlet was used for both of the instruments. General characteristics of two GCs are given in Table 4 (Syntech Spectras, 2005).

Table 4 General characteristics of the Syntech Spectras GC955 series 600 and 800 online GCs (Syntech Spectras, 2005)

Parameter	**GC955 series 600 (C_6-C_{10})**	**GC955 series 800 (C_2-C_5)**
Detector	PID	PID and FID
Column	DB1, 30 m, 0.32 mm ID, 1.8 µm film	AT5, 5 m and Al_2O_3, 10 m, 0.32 mm ID, 1.8 µm film
Temperature Program	55°C for 4 min then 2.25°C/min increase for 20 min	50°C for 3 min then 5°C/min increase for 10 min
Cycle Time	30 min	30 min
Carrier Gas	Nitrogen	Nitrogen
Other Gases	-	Hydrogen and Dry air
Gas Consumption	Nitrogen, 25 ml/min	Nitrogen, 25 ml/min Hydrogen, 20 ml/min Dry air, 250 ml/min
Detection Limit	0.4 µg/m^3 for benzene	0.4 µg/m^3 for butene
Volume of Air Sampled/Cycle	315 ml	315 ml

Picture of the GC955 is depicted in Figure 8. Flow diagram is given in
Figure 9.
Figure 9a shows the analysis and sampling and
Figure 9b shows the injection and stripping cycles. Sampling of both GCs is almost identical. In each cycle, the instrument took a fresh sample of air into a sample loop via small membrane pump. The pump is switched off when a volume of 35 ml sample gas is collected and sent to preconcentration tube. This procedure is repeated until enough sample material had been drawn. For both parts of the instrument, nine sampling cycles are conducted in 30 min sampling. A total of 315 ml (35 ml/cycle x 9 cycle) of air is sampled. Before each sampling, the pump is switched on again for a short time. The preconcentration tube is purged with carrier gas to remove oxygen.

The GC955 series 800 is used to analyze low molecular weight VOCs, i.e. VOCs with C_2-C_5. VOCs are preconcentrated on Carbosieves SIII at 5°C. Decreasing of temperature at the preconcentrator is achieved by radiation. To do this, the preconcentration tube is embedded in an aluminum block. This block is cooled on both sides by Peltier elements. Peltier elements acts as heat pumps and transport heat from one of their side to the other. The heat transferred to the other side of the plate is removed from the system by fans.

The sample is desorbed in a short time by heating the preconcentration tube quickly, while flushing it with carrier gas. Then, sample enters to the column. Column consists of two parts: a stripper column (5 m long AT5 column) and an analysis column (10 m long Al_2O_3 column). The use of two columns is to prevent a prolonged analysis, which is normally caused by the necessity of waiting for elution of the highest boiling compound. Therefore the time is set for the slowest eluting compound of interest to get through the column. After this time, the flow in the stripper column is reversed. The rest of the compounds are flushed back from the stripper column and removed from the system as seen with green line in
Figure 9b.

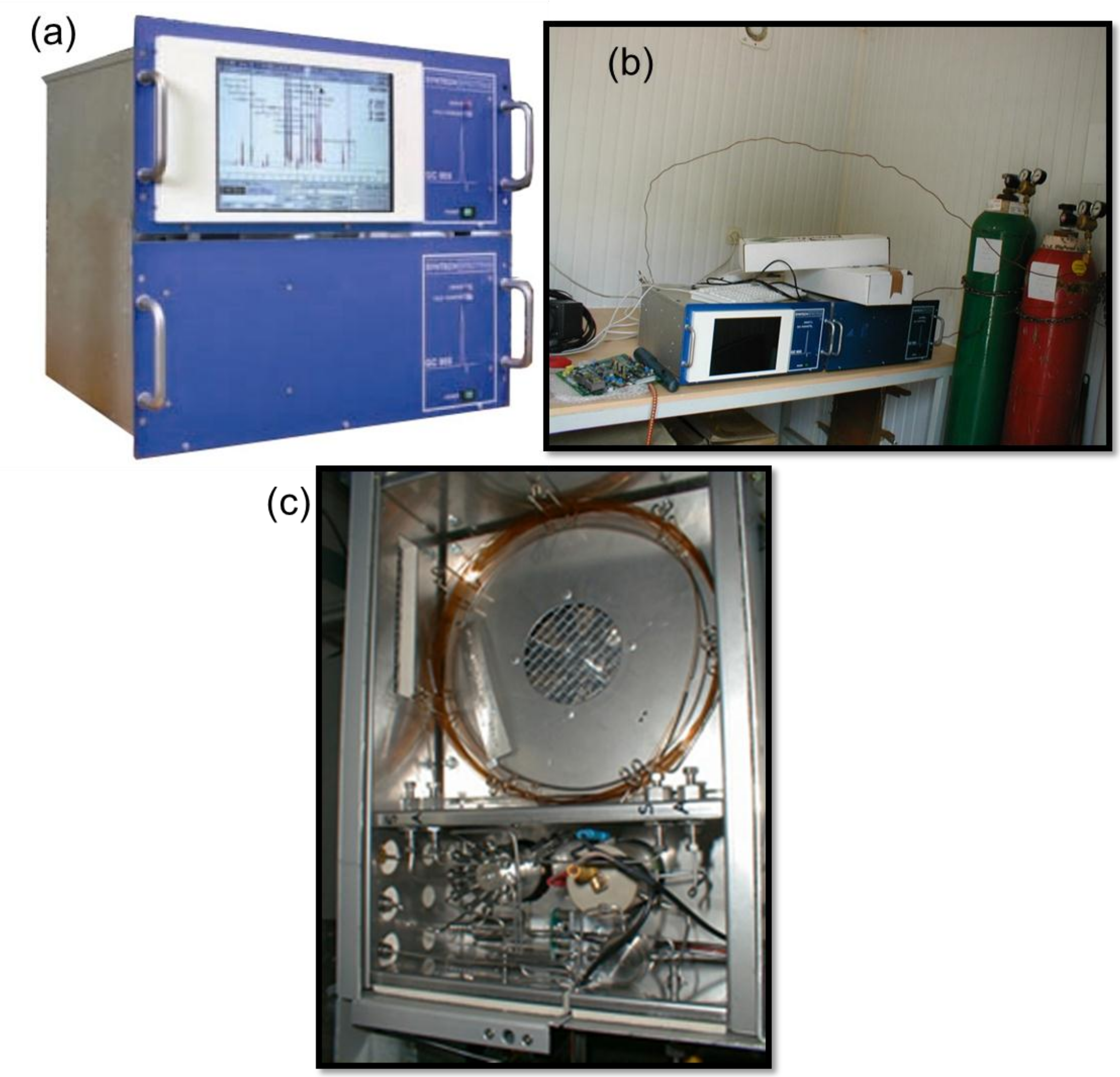


Figure 8 Appearance of GC955
(a) general appearance, (b) at Aliağa station and (c) top view

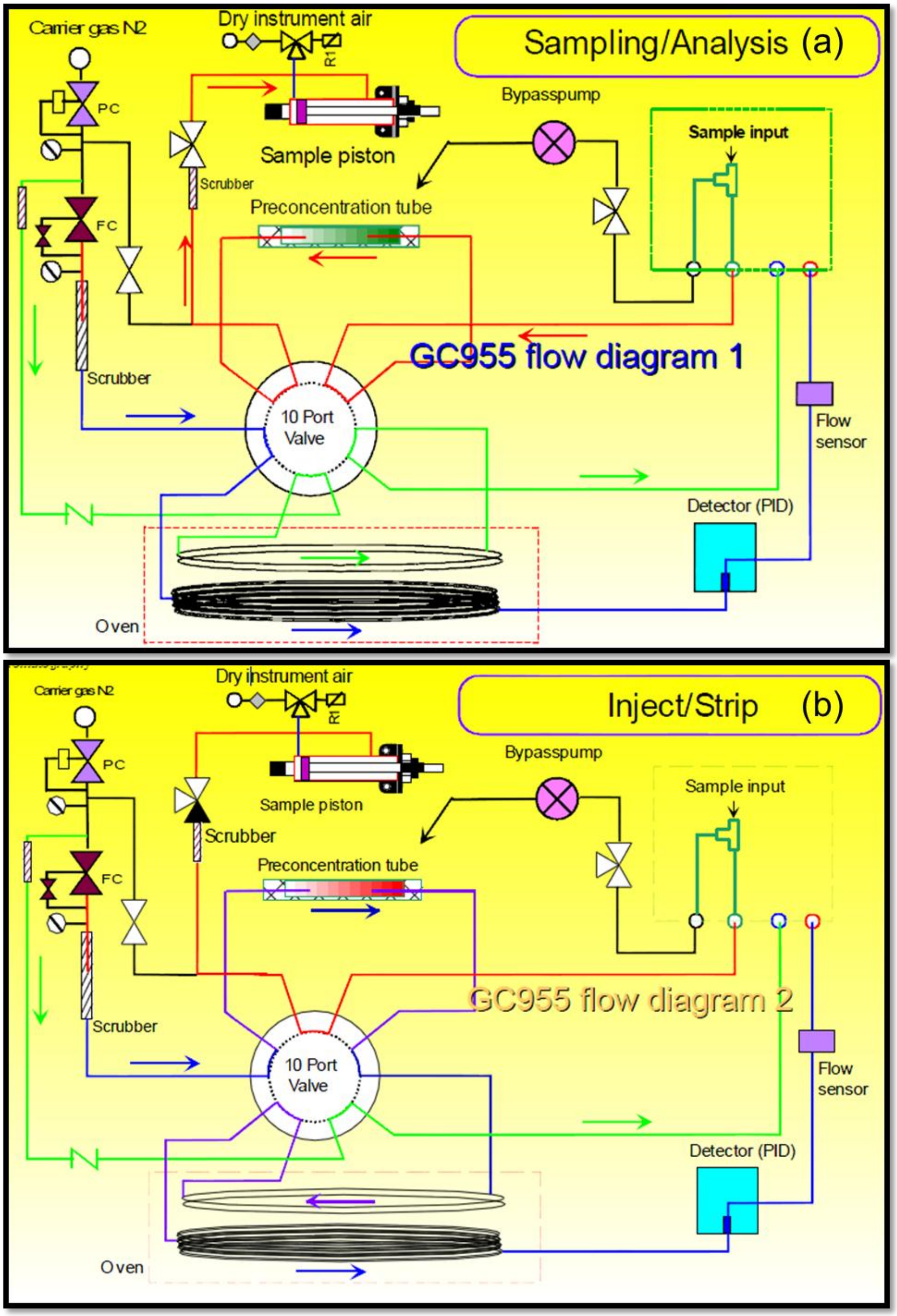


Figure 9 Cycles in GC955
(a) sampling and analysis cycle and (b) inject and strip cycle

The cycle time of the instrument is 30 min. The initial temperature of the oven is set to 50°C. This temperature is held at 50°C for 3 minutes. Then the oven temperature is increased with a rate of 5°C/min to 100°C and temperature is then kept constant for 10 minutes. After that the temperature of the oven decreased back to 50°C for the next analysis. Analysis is done by two detectors connected in series. The first detector is photo ionization detector (PID). The PID detector of series 800 is for the quantification of alkenes and methyl-alkanes. The second detector is flame ionization detector (FID). The FID detector is used for the analyses of alkanes.

The GC955 series 600 is used to monitor high molecular weight VOCs, i.e. VOCs with C_6-C_{10}. The working principle is approximately same with GC955 series 800. However, there are some differences in the materials used. Tenax GR is used as a preconcentrator. The columns used in this part are two identical DB1 columns. Both the stripper column and analysis column are 15 m long DB1 columns. PID is used for the quantification of C_6-C_{10} VOCs. The GC955 series 600 had a cycle time of 30 min. The initial temperature of the oven is 55°C and this temperature is kept constant for 4 minutes. Then the temperature of the oven is increased gradually with a rate of 2.25°C/min to 100°C. The temperature is retained at 100°C for a minute and then decreased back to 55°C for the next analysis.

3.2.2. VOC Measurements in Horozgediği and TÜPRAŞ Stations

An Agilent 6890N Network GC-FID system is used for Horozgediği and TÜPRAŞ measurements. In this system, sample is first passed through a selective membrane dryer and sent to cold trap. The selective membrane dryer separated water and low molecular weight compounds and removed them from the system. Thus, the negative effects of these compounds on FID were decreased. The samples are collected via an air server system. Samples are withdrawn continuously with a rate of 10 ml min^{-1} for 45 min. The withdrawn air is then captured in a cold trap at -15°C. Cold trap is cooled electronically. After the sampling is completed, the cold trap is heated for 6-8 seconds and gas phase analytes are introduced to the inlet of Al_2O_3 column of GC.

To obtain better resolution of the peaks with two different columns a Dean Switching system is used. This system is used for heart cutting of samples from one column to another without any pressure or flow fluctuations in any of the switch paths. Dean Switch is used when a secondary column is needed to separate components that cannot be resolved properly on the primary column. In this study, Dean Switch is used for the determination of C_6-C_{12} VOCs with the second FID detector. Heart cut time was determined by injecting a hexane standard onto the primary column. The retention time for hexane was determined as 13.40 min. Using the retention time of hexane, the heart-cutting time was determined as 13.20 min to 45.5 min. Then, this cut time is checked by using the same hexane standard and other calibration standards (Civan, 2010).

In Figure 10, Dean Switch application is shown. All compounds are sent through Al_2O_3 coated capillary column then compounds whose boiling point is less than hexane are diverted to restrictor column and then to first FID. This period is shown in Figure 10a where Dean Switch is in off position. As depicted in Figure 10b, after 13.20 min from the start of the run, the solenoid valve controlling the Dean Switch opens and Pressure Control Module (PCM) forces the effluent of the Al_2O_3 column to go the DB-1 column. After the separation of VOCs with boiling point greater than hexane in DB-1 column, a second FID detector is used for the detection of the compounds. Agilent GC system can differentiate more than 140 compounds and can give hourly average values of these compounds. General information about the Agilent GC system is given in Table 5.

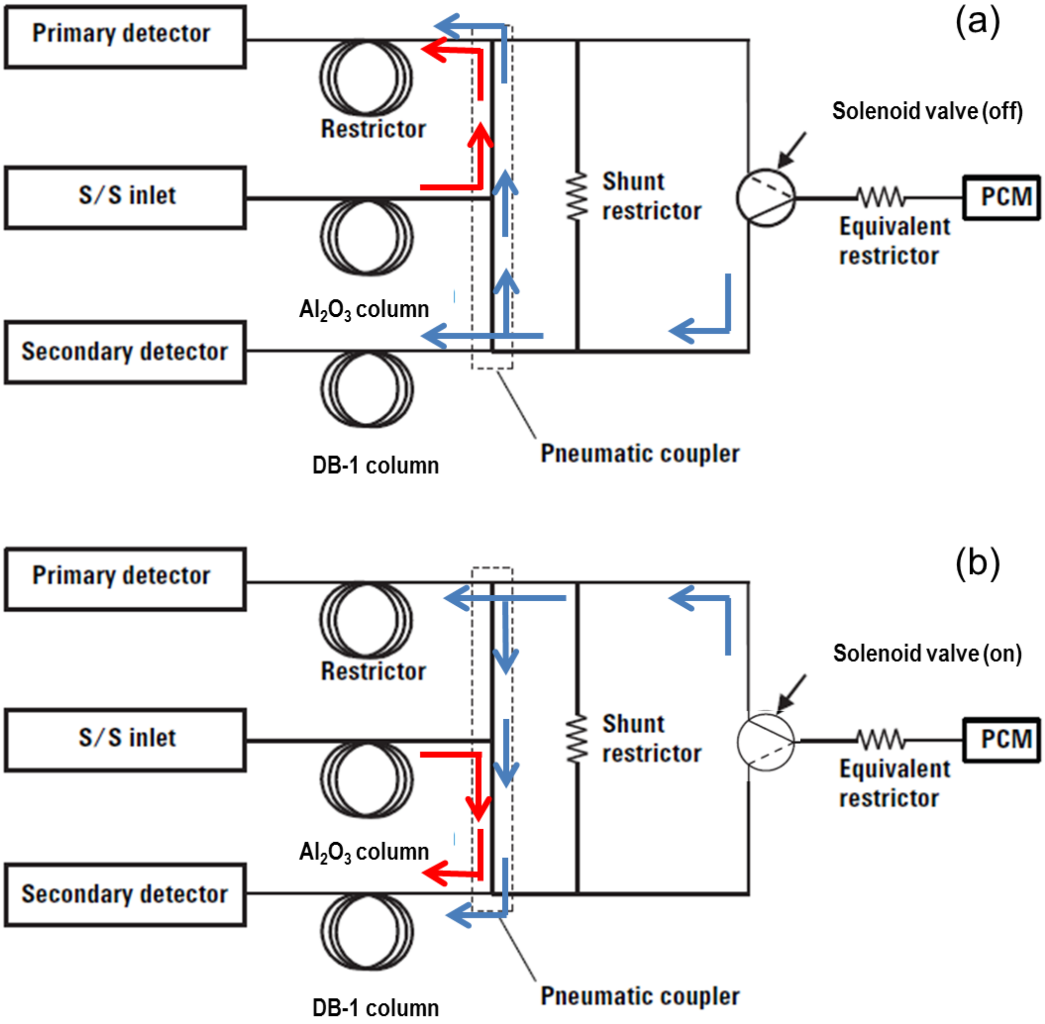


Figure 10 Dean Switch at Agilent 6890N Network GC-FID system
(a) solenoid valve is in off position and (b) solenoid valve is in on position

Table 5 General characteristics of Agilent 6890N Network GC-FID system

Parameter	Agilent 6890N Network GC-FID system
Detector	2 FID in Parallel, splitless injector mode
Column	Al_2O_3 Plot 50 m, 0.32 mm ID, 8 µm film (C_2-C_5) and DB-1 60 m, 0.25 mm ID, 1 µm film (C_6-C_{10})
Temperature Program	40^{o}C for 5 min, 5^{o}C/min for 31 min, hold at 195^{o}C for 10 min
Cycle Time	1 hour
Carrier Gas	Nitrogen
Other Gases	Hydrogen and Dry air
Gas Consumption	Nitrogen, 50 ml/min Hydrogen, 30 ml/min Dry air, 300 ml/min
Detection Limit	0.001 µg/m^3
Volume of Air Sampled/Cycle	450 ml

3.2.3. Data Completeness

The sampling periods, number of measurements and the number of compounds analyzed in each station are given in Table 6. Our objective before we start measurements was to measure VOCs for two months at each station. This objective was more or less accomplished at Aliağa station. 3082 thirty minute long measurements were performed in summer campaign (which corresponds to 64 days of uninterrupted measurements). In the winter campaign 2861 chromatograms were generated, which corresponds to 59 days of uninterrupted measurements.

We were not as lucky in the measurements performed in Horozgediği station. In the winter, there were very frequent power cuts and very severe fluctuations in the voltage. Although the GC was connected to an uninterrupted power supply (UPS), it did not operate properly throughout the campaign. This unfortunately was the combined effect of poor infrastructure in the area and poor quality of the UPS used in the station. Since there were 7 or 8 iron and steel plants in the area and they all melt scrap iron using electric furnaces, the voltage in the whole area drops substantially when these furnaces are charged. This was one of the reason. The other reason was the poor quality of the UPS used at Horozgediği station. Although it was brand new and purchased for that particular station, it failed most of the time when there were power-cuts or voltage drops. Because of this, we were able to generate chromatograms for only 233 hours, which corresponds to approximately 10 days. 233 measurements were enough to run statistics, but temporal coverage was poor. In the summer campaign, the UPS was changed, but power failure and voltage drops continued to be a problem. The new UPS handled voltage drops very nicely but there was nothing that could be done for power cuts that were longer than four hours. Approximately 900 hourly chromatograms, which correspond to 37 days, were generated during summer period.

Another problem that degraded data completeness was the breaking up of the one of GCs in the Aliağa station in summer campaign. The Syntech GC-PID-FID system operated at Aliağa station consisted of two GCs with common sampling port GC955-800 was used to measure light VOCs (C<5) and GC600 was used to measure heavy VOCs. Both GCs operated properly throughout the winter period, but GC 955-800 failed to operate in the summer campaign. Sending it to service for repair worsened the situation. Because of this, only GC955-600 was operated and heavy VOCs were measured in summer campaign.

Table 6 Sample amount, sampling periods the number of compounds analyzed for each station

Station	Sampling Period	Sample Amount (After QA/QC*)	Number of VOCs quantified
Horozgediği Winter	19.11.2005 02.01.2006	233 hourly data	52 compounds
Horozgediği Summer	09.08.2006 27.10.2006	862 hourly data	52 compounds
Aliağa Winter	11.01.2006 16.03.2006	2861 half hourly data	51 compounds
Aliağa Summer	05.08.2006 30.10.2006	3082 half hourly data	29 compounds
TÜPRAŞ	04.11.2006 22.11.2006	418 hourly data	47 compounds

*QA/QC: quality assurance and quality control

3.3. Quality Assurance and Quality Control

Assessment of the quality of data generated is becoming more and more important every day. With modern instruments we can measure many analytes in many samples. Number of analyte determined in studies and number of samples in which these analytes are measured are increasing with developments in instrumentation. In this study >50 species were measured in approximately 7500 measurement cycles (chromatograms). Some errors during generation of such vast data matrix is inevitable. That is why protocols which includes procedures to detect potential errors and thus to assist generating reliable data set, which is known as quality assurance-quality control is becoming more and more important.
In this study QA/QC protocol included:

- Estimation of detection limits and quantification limits
- Determination of the precision of the measurement system
- Parallel measurements using the two GC systems
- Proper calibration of the instruments
- Investigation of the role of below LOQ values on average and median concentrations
- Data quality control

All these activities, except for data quality control, are related to ensure accuracy of measurements but cannot identify potential errors that can occur during processing of chromatograms. The objective of the last step in the QA/QC protocol, namely “Data Quality Control” is to identify possible errors that can occur during manual determination of peak areas (peak fitting). Considering that approximately 375 000 peaks were fitted in this study (7500 chromatograph x 50 VOC in each chromatograph), data quality control was a very important component of the QA/QC program performed in this study. Each of these components in QA/QC protocol was discussed in following sections.

3.3.1. Quantification and Calibration

The quantification of VOCs was performed according to calibration curve method. The calibration curve method involves plotting response area against concentrations of the analyte in the standard. Calibration factor was calculated as the ratio of concentrations to response area. Sample concentration is then found by multiplying response area with calibration factor. It was not practical to repeat calibration very frequently (such as every day), because 5 chromatograms are collected for each five-point calibration. Collection of five chromatograms corresponds to approximately 30 hour of our sampling time per day. Consequently, instead of repeating full five point calibration, calibration checks were performed by injecting mid-point standard only and comparing responses of VOCs with the responses obtained in the previous full calibration. If there are deviations in responses then full calibration was run, but if the responses of VOCs are not significantly different from those obtained in previous calibration, a new calibration was not performed and previous calibration was assumed to be valid. Full calibrations were performed at the beginning of the campaigns. Calibration checks with mid-point standards were performed in every 15 days at Aliağa station and in the summer campaign at the Horozgediği station. However, during winter campaign there were very frequent power-cuts at Horozgediği and to avoid any deviation in retention times of VOCs, both full calibrations and mid-point calibration checks were performed much more frequently.

Both on-line GCs were calibrated before the start of analyses at the field. Certified gas standards were used for calibration of Agilent 6890 and Syntech GC955. For winter campaign, certified gas standard, which was obtained from Environment Canada, Science and Technology Laboratories, Analysis and Air Quality Division was used. 148 VOCs ranging from C_2 to C_{12} with 98% purity is present in this standard (Wang and Austin, 2006). The standard mixture is composed of aliphatic, aromatic hydrocarbons and halogenated hydrocarbons. Concentrations of VOCs in the calibration gas ranged between 2 - 20 $\mu g\ m^{-3}$. This was the standard of our choice, because VOCs in the standard were at ambient levels and can be directly fed to GC without diluting them. However, expiration date of standard mixture passed before the second campaign (summer campaign). Therefore, another certified gas from Scott Specialty Gas was obtained. This gas standard is composed of 57 VOCs, between C_2 to C_{12} that are used by EPA in their Photochemical Assessment Monitoring Stations (PAMS) network. Since PAMS standard did not include halogenated hydrocarbons, another standard, which includes 19 halogenated hydrocarbons was also obtained from Scott Specialty Gases Company. Concentrations of VOCs in these two standards, which were used during summer campaign, were 1 ppm. As in the winter campaign, a five point calibration curve was obtained for each compound. Correlation coefficients were 0.999 and higher for all compounds.

The calibration of Agilent GC system was carried out directly by using Unity thermal desorber coupled to the GC. The thermal desorber can withdraw specified amount of gas from calibration mixture and send it to GC-FID system. For winter campaign, calibration curve was obtained by withdrawing 100, 200, 300, 400 and 500 ml from calibration mixture obtained from Canada. During summer campaign, calibration was carried out using 1, 2, 3, 4 and 5 ml of samples withdrawn from Scott Specialty Gas PAMS and halogen standards. The reason of the volumetric difference is because of concentration differences in gas standards. Response-per-nanogram was calculated for each compound from the calibration curve prepared. The mass of each compound in a sample was then calculated by dividing response of each VOC to slope of the relevant calibration curve. Finally, concentration of a compound in a sample was calculated by dividing mass of the compound by the volume of sampled air.

According to EPA 8000b standard (EPA, 1996), when the variation in response is less than or equal to 20%, the use of the existing calibration curve is appropriate. During the sampling periods, the variation in response did not exceed 20%. Chromatographs of a calibration standard and a sample are given in Figure 11 and Figure 12, respectively. However, more frequent calibrations and calibration checks were performed due to frequent, unexpected power failures at the Horozgediği station.

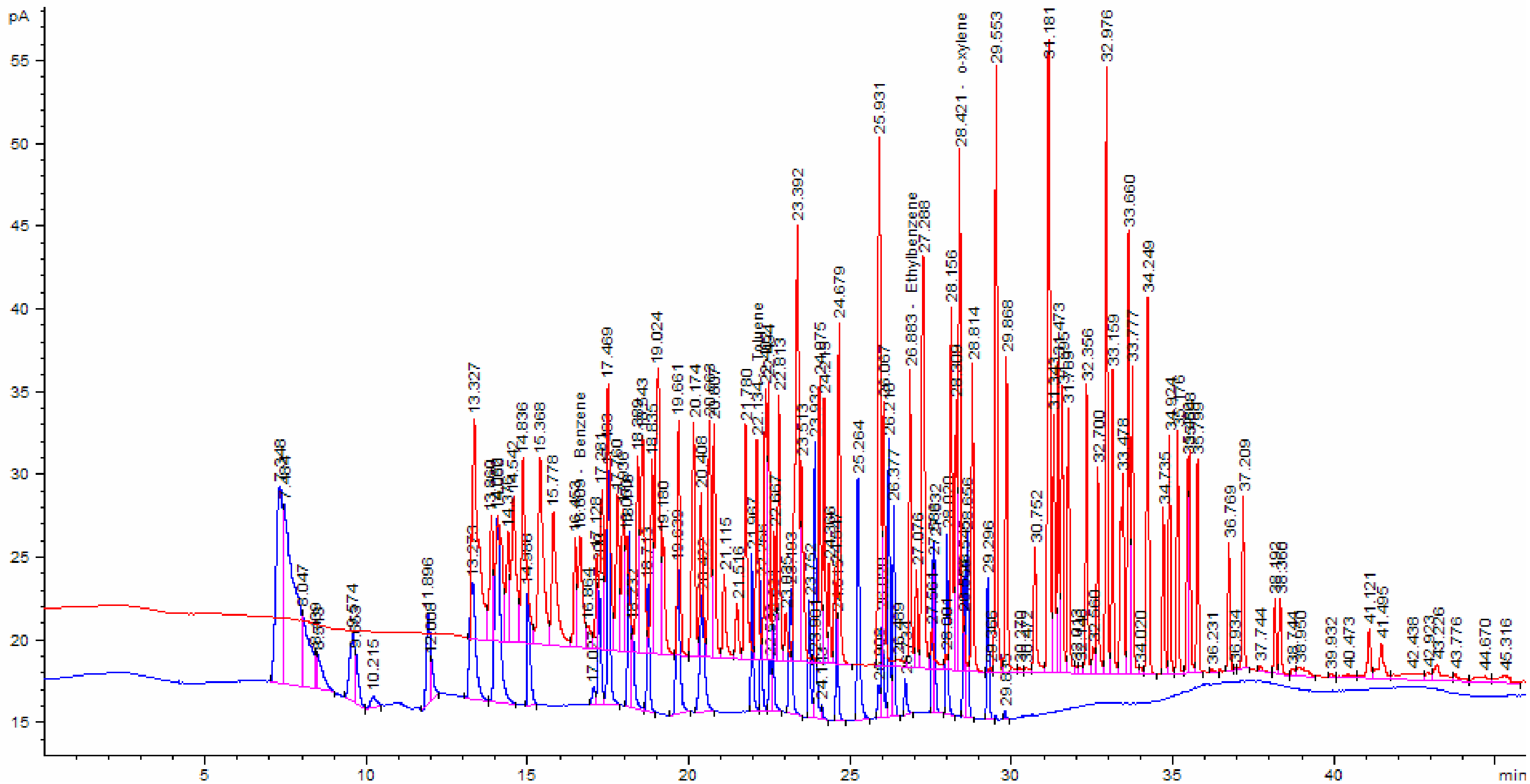


Figure 11 An example calibration chromatogram for Agilent GC system
(Blue chromatogram: C2-C5 VOCs, red chromatogram: C6-C12 VOCs)

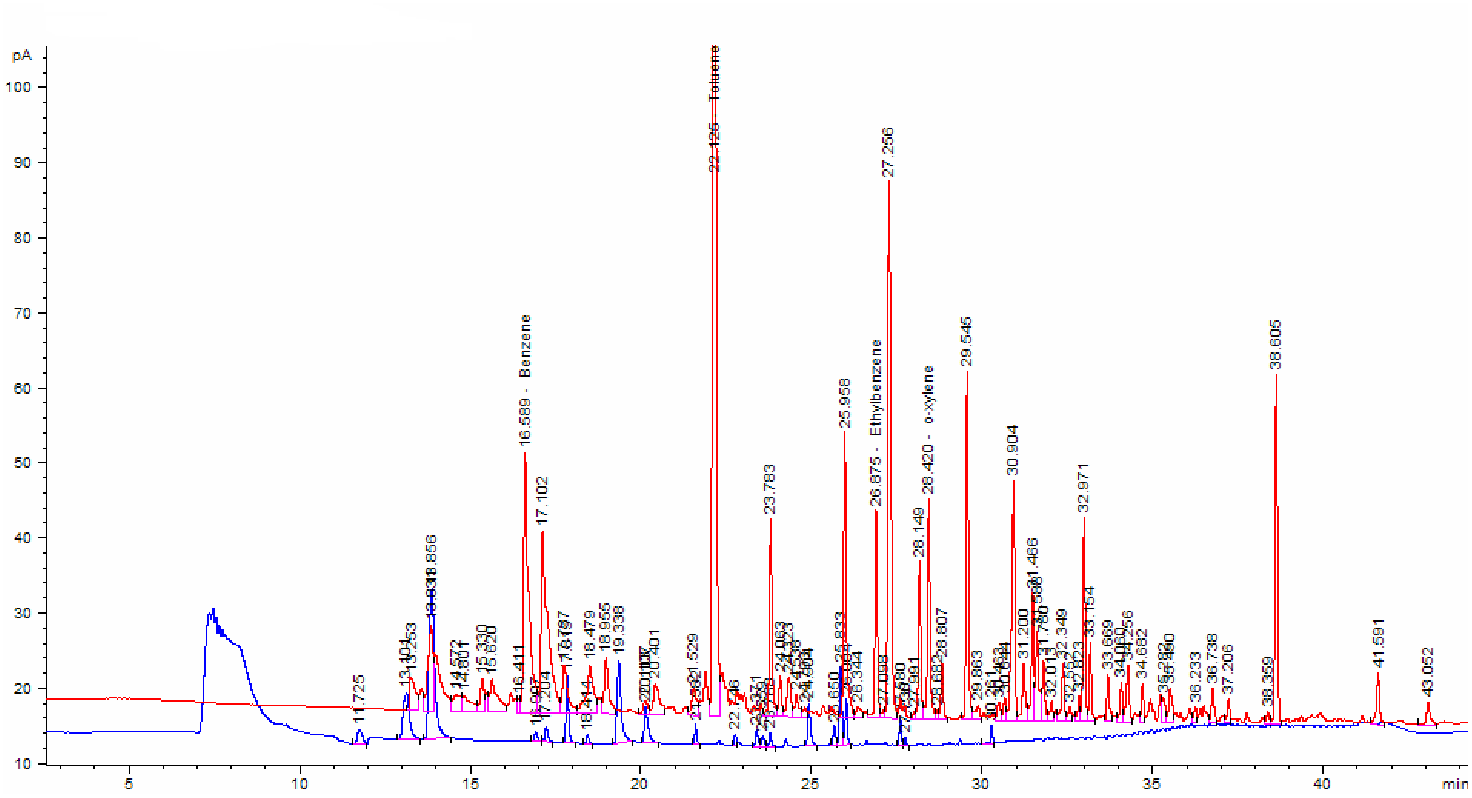


Figure 12 A sample chromatogram for Agilent GC system
(Blue chromatogram: C2-C5 VOCs, red chromatogram: C6-C12 VOCs)

The GC system used at Aliağa station was calibrated by PAMS standard obtained from Scott Specialty Gas company in both sampling campaigns. Although the standard obtained from Environment Canada was available during winter campaign, it was not possible to use it with Syntech GC955, because the GC had a shorter column than Agilent GC used at Horozgediği station and 145 VOCs in Environment Canada resulted in substantial peak overlaps which was difficult to resolve. Unlike in Environment Canada standard, concentration of all VOCs was 1 ppm in PAMS standard. Because of such high concentrations, calibration mixture was diluted with dry air and then injected to the Syntech GC system. Instrument was calibrated before each sampling campaign, and calibration checks were performed in every 15 days, as in the Horozgediği station. Chromatographs of a calibration standard and a sample are given in Figure 13 and Figure 14, respectively.

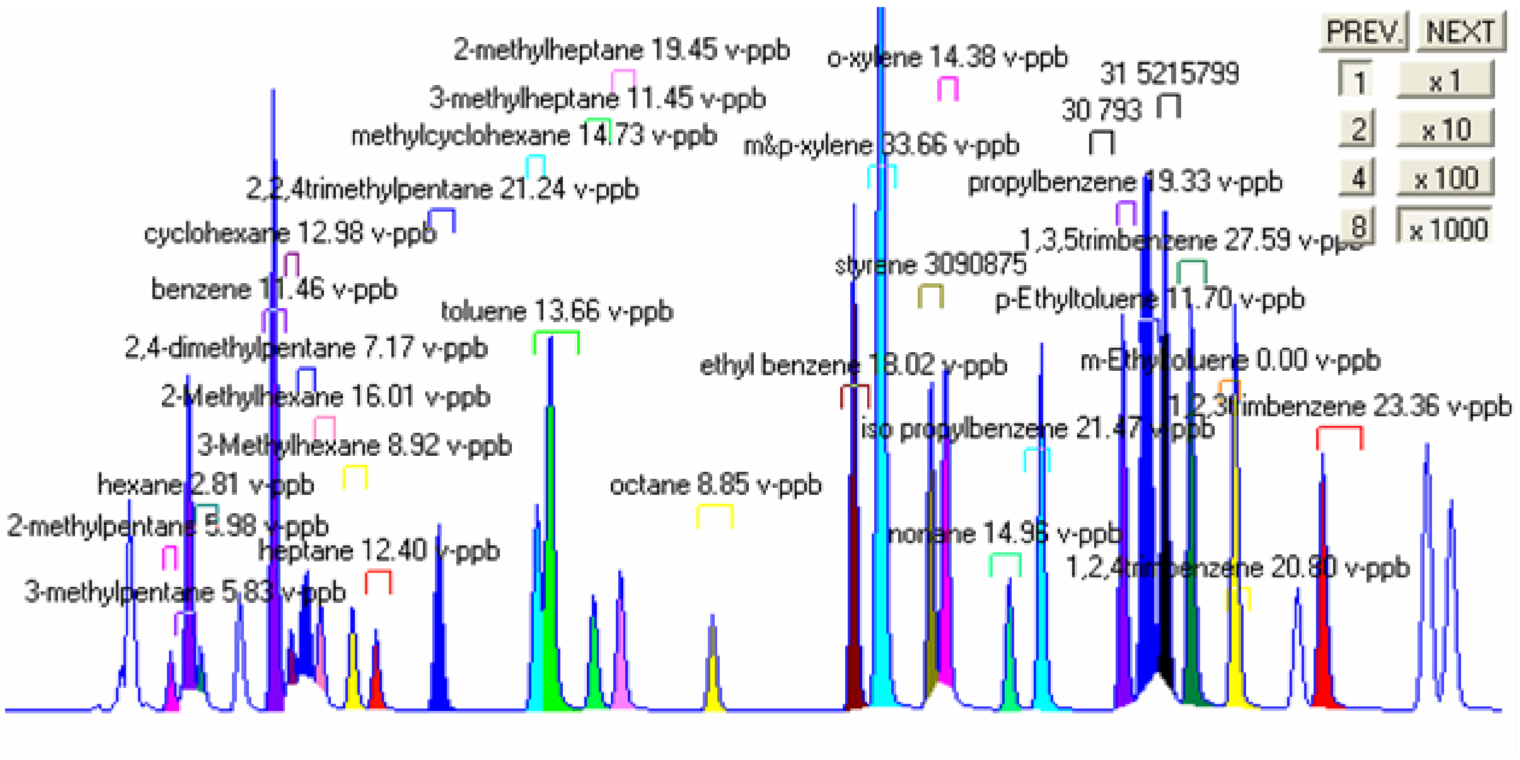


Figure 13 An example calibration chromatogram of C_6-C_{12} part of Syntech GC system

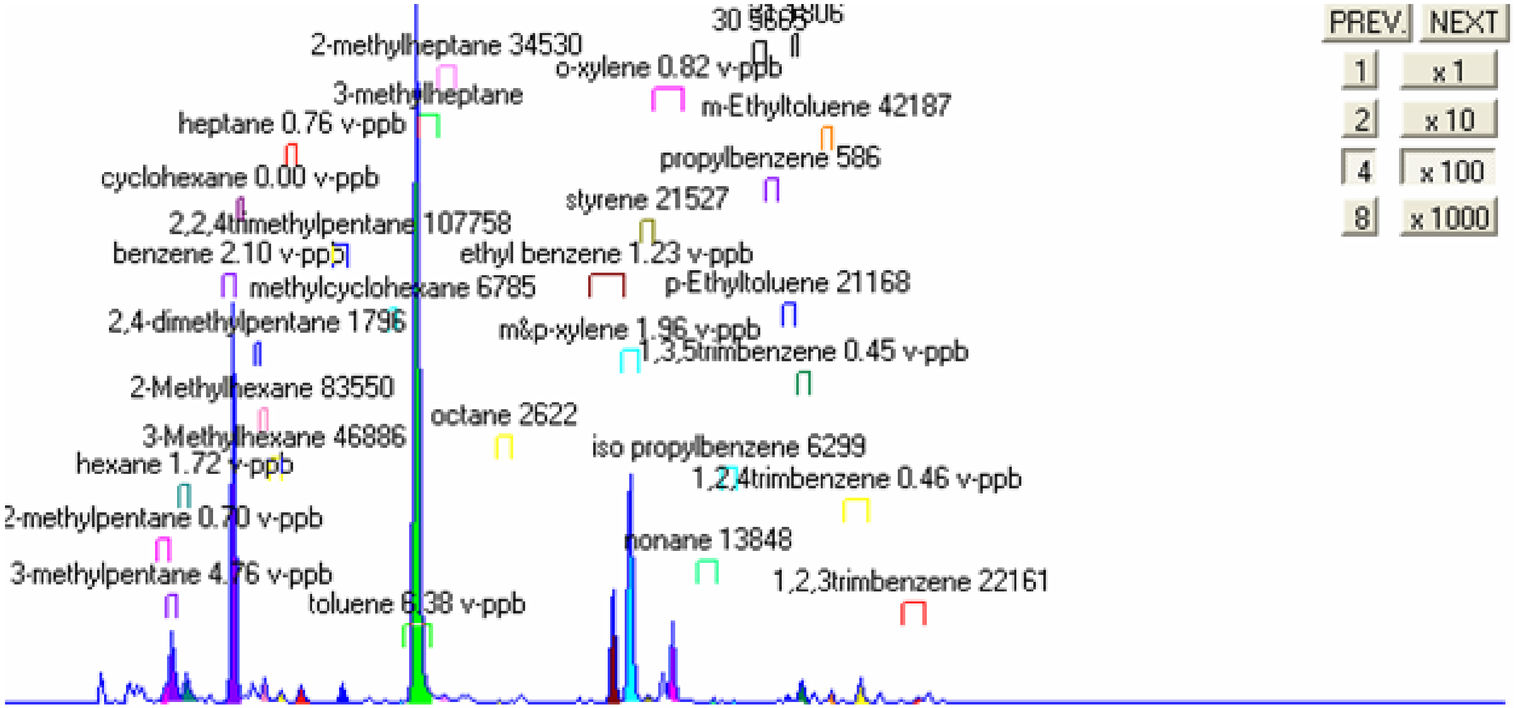


Figure 14 A sample chromatogram of C_6-C_{12} part of Syntech GC system

3.3.2. Detection Limits of VOCs

Manual integration of small peaks in chromatograms is a problem for accurate quantification. The peaks with an area of less than certain value for each instrument are not integrated. These values are determined by integrating different peak areas. The variations in the percent differences in integrated peak areas are compared and the low percent variation in peak areas is identified. The concentrations of corresponding areas are determined for every compound and these values are defined as limit of quantification (LOQ) values. LOQ values for every compound are given in Table 7. The precision of the system are calculated from six replicate measurements of the midpoint calibration standard. The relative standard deviation (RSD) values are given in Table 7. The RSD values are ranged from 0.39 to 11.97% with an average value of 6.55%.

Table 7 Limit of quantification and system precision of compounds

Compounds	LOQ (µg m^{-3})	System precision (%)
Ethylene	0.0311	
Ethyne (Acetylene)	0.0434	
Propane	0.0460	
Propylene	0.0323	
iso-Butane+n-Butane	0.0760	
t-2-Butene	0.0468	
1-Butene	0.0490	
n-Pentane	0.0339	0.83
Cyclo-Pentane	0.0227	3.84
2,2-Di-Methyl-Propane	0.0677	
1-Pentene	0.0562	3.25
n-Hexane	0.0627	0.39
2,2-Di-Methyl-Butane	0.0500	5.74
2,3-Di-Methyl-Butane	0.0515	4.33
2-Methyl-Pentane	0.0532	2.54
3-Methyl-Pentane	0.0956	3.67
Cyclo-Hexane+Cyclo-Hexene	0.1780	3.17
Methyl-Cyclo-Pentane+2,4-Di-Methyl-Pentane	0.0634	
Benzene	0.0543	1.35
n-Heptane+cis-3-Heptene	0.0564	5.22
2,2,3-Tri-Methyl-Butane+2,3-Di-Methyl-Pentane	0.0572	4.34
2-Methyl-Hexane	0.0543	4.58
3-Methyl-Hexane	0.0595	3.42
Methyl-Cyclo-Hexane	0.0558	5.48
Toluene	0.0517	5.82
Octane	0.0539	10.51
2,2,4-Tri-Methyl-Pentane	0.0409	
2-Methyl-Heptane	0.0564	4.18
4+3-Methyl-Heptane	0.1049	8.85
1-Octene	0.0515	9.85

Table 7cont. Mean detection limit, limit of quantification and system precision of compounds

Compounds	LOQ (µg m^{-3})	System precision (%)
c-1,2-Di-Methyl-Cyclohexane	0.2367	7.51
m+p-Xylene	0.0488	5.85
o-Xylene	0.0269	7.98
Ethyl-Benzene	0.0545	9.54
Styrene	0.0346	10.64
1,3,5-Tri-Methyl-Benzene	0.0522	8.94
n-Nonane	0.0553	9.02
n-Propyl-Benzene	0.0191	8.62
iso-Propyl-Benzene	0.0512	10.03
3-Ethyl-Toluene (m-Ethyl-Toluene)	0.0480	0.54
4-Ethyl-Toluene (p-Ethyl-Toluene)	0.0518	7.64
2-Ethyl-Toluene (o-Ethyl-Toluene)	0.0505	6.87
1,2,4-Tri-Methyl-Benzene	0.0253	9.54
1,2,3-Tri-Methyl-Benzene+p-Cymene	0.0576	8.74
n-Decane	0.0525	9.67
1,3-Di-Eethyl-Benzene	0.0517	10.21
n-Butyl-Benzene	0.0614	11.02
Naphthalene	0.0651	11.97
Undecene	0.0653	11.54
Di-Bromo-Methane+1,2-Di-Cloro-Propane	0.2388	4.43
c+t-1,3-Di-Chloro-Propene	0.0945	6.85

3.3.3. Parallel Sampling

The results of two online GC systems were compared by parallel sampling before the start of campaigns. For this, The GC955 are transported to Horozgediği station and operated side by side with the Agilent system for 3 hours.

The comparison was not limited to GCs but included all parameters measured. Inorganic gas analyzers, dichotomous samplers that operate at Aliağa station were also brought to the Horozgediği station for field comparison exercise. Photographs taken during these simultaneous measurements are given in Figure 15. BTX results measured by both systems are given in Table 8. The mean value results are compared with t-test. Differences in measured concentrations of other VOCs are not significantly different from differences observed in BTX compounds.

Table 8 Parallel sampling results of two GCs used in the study

Compounds	15:00 Agilent	15:00 Syntech	16:00 Agilent	16:00 Syntech	17:00 Agilent	17:00 Syntech
Benzene	1.15	1.25	1.60	2.11	1.77	1.92
Toluene	0.74	0.83	0.80	0.75	0.92	1.01
m,p-Xylene	0.76	0.82	0.54	0.64	0.61	0.63
Ethylbenzene	0.76	0.79	0.57	0.78	0.54	0.69
o-Xylene	0.61	0.64	0.43	0.47	0.33	0.40


[redacted]

Figure 15 Photos from parallel sampling at Horozgediği Station

3.3.4. Four Step QA/QC

Quality assurance and quality control (QA/QC) is essential for the preparation of a reliable data set. In this study, QA/QC can be applied both during measurement and to integration of chromatograms. In this type of work, quality checks for peak-fitting is essential, because there are thousands of chromatograms where peaks are manually fitted. It is very easy to make mistakes and those mistakes have to be identified by a post-processing QA/QC protocol.

In this study, a four step QA/QC protocol was applied after the integration of chromatographs. These steps included (Kuntasal, 2005; Civan, 2010):

- Control of VOC retention times (RT),
- Control of concentration variation of every compound separately,
- Control of concentration variations of 5-6 successively eluted compounds at the same time and
- Control from correlation plots.

The first step consisted of checking if there were any RT shifts in the chromatograms. This was necessary, because manual integration of thousands of chromatograms was a tedious task and took long time. Because of this, for some compounds, false integration might be inevitable. In order to eliminate this kind of error, variation in RT of each compound was compared with RTs of compounds' in different parts of the chromatogram. If a VOC shows a RT shift, while other VOCs do not, that chromatogram was re-integrated. Furthermore, if there is an abnormal deviation in RT of a VOC that chromatogram was re-integrated without looking to RTs of other VOCs.

In the second step, time-series plots of concentration of concentration of each VOC was prepared and searched for outliers. The chromatogram was reanalyzed if there is a very high or very low concentration for any of the VOCs. It should be noted that VOC concentrations in our data set are log normally distributed and an outlier does not necessarily mean a wrong value. It only implies that it should be checked. If high concentration does not change after re-integration process, that high concentration is kept in data set.

Third step in data QA/QC is related to second step. In this step, time-series plots of 5 or 6 correlated VOCs were investigated comparatively. Generally tare many VOCs that are highly correlated in the data set. The VOCs were grouped based on their correlation coefficients and time series plots of correlated ones are plotted together. An example of such VOC group, which is called "fingerprint-plot" is depicted in Figure 16. Since these compounds have high correlation coefficient, the peaks in time series should coexist. If there is a peak in one of the compounds but not in others, it is flagged and chromatogram was re-integrated. As in previous steps, existence a unique peak for a VOC does not necessarily indicate a faulty value. If that concentration remains after re-integration, that unique value is kept.

The final stage for the QA/QC consisted of investigation of binary scatterplots between correlated VOCs. Before preparing the correlation plots, data values below the Limit of Quantification (LOQ) values were replaced with one half of the LOQ value. Then, Pearson Correlation Coefficients (R) of compounds with respect to other compounds were calculated. The plots of correlations which have statistically significant Pearson correlation coefficient, R, values of above 0.8, were prepared. An example correlation plot is given in Figure 17. After the preparation of each graph, a linear trend line and a corresponding 95% confidence interval trend line were drawn. The data points outside the 95% confidence interval lines were reinvestigated.

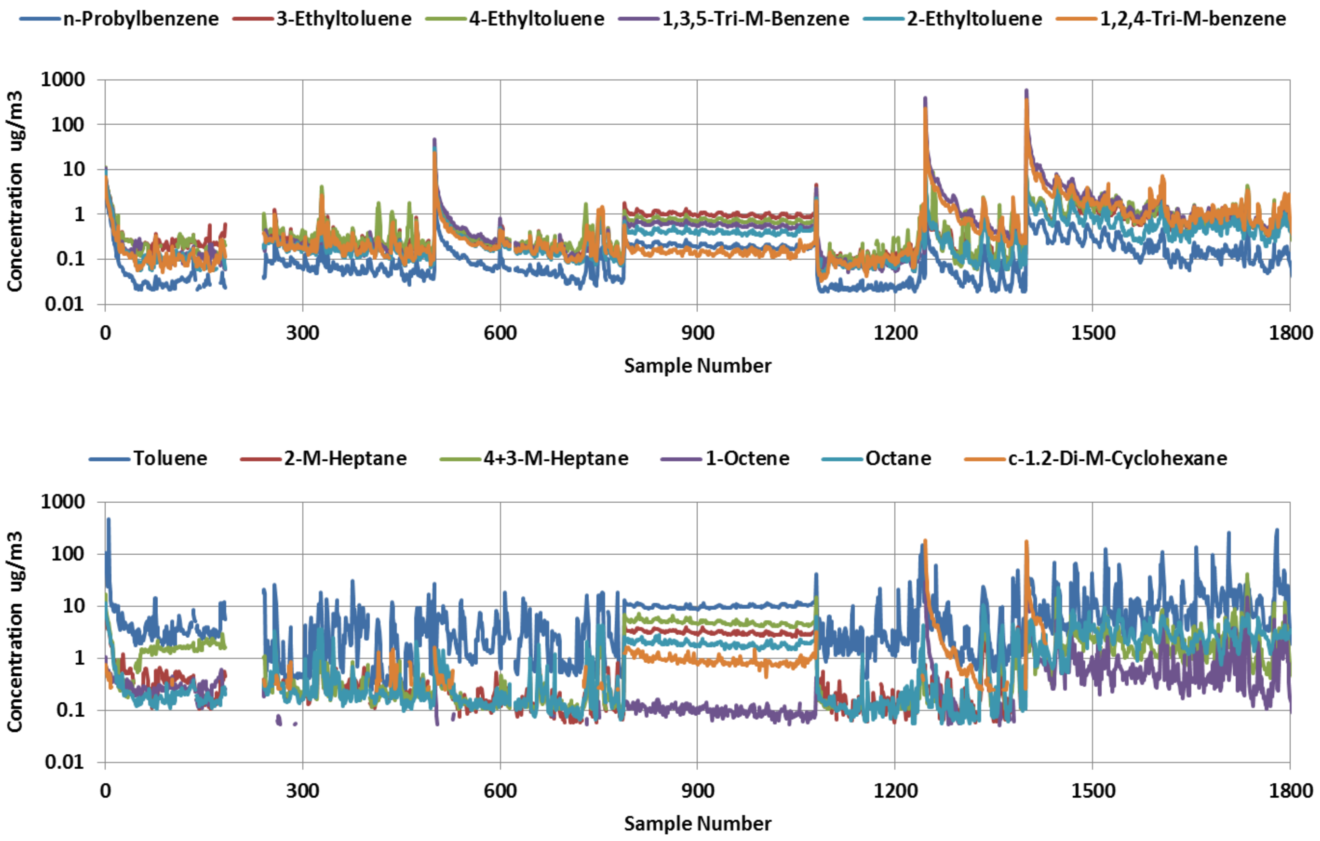


Figure 16 Fingerprint plots of selected compounds for QA/QC check

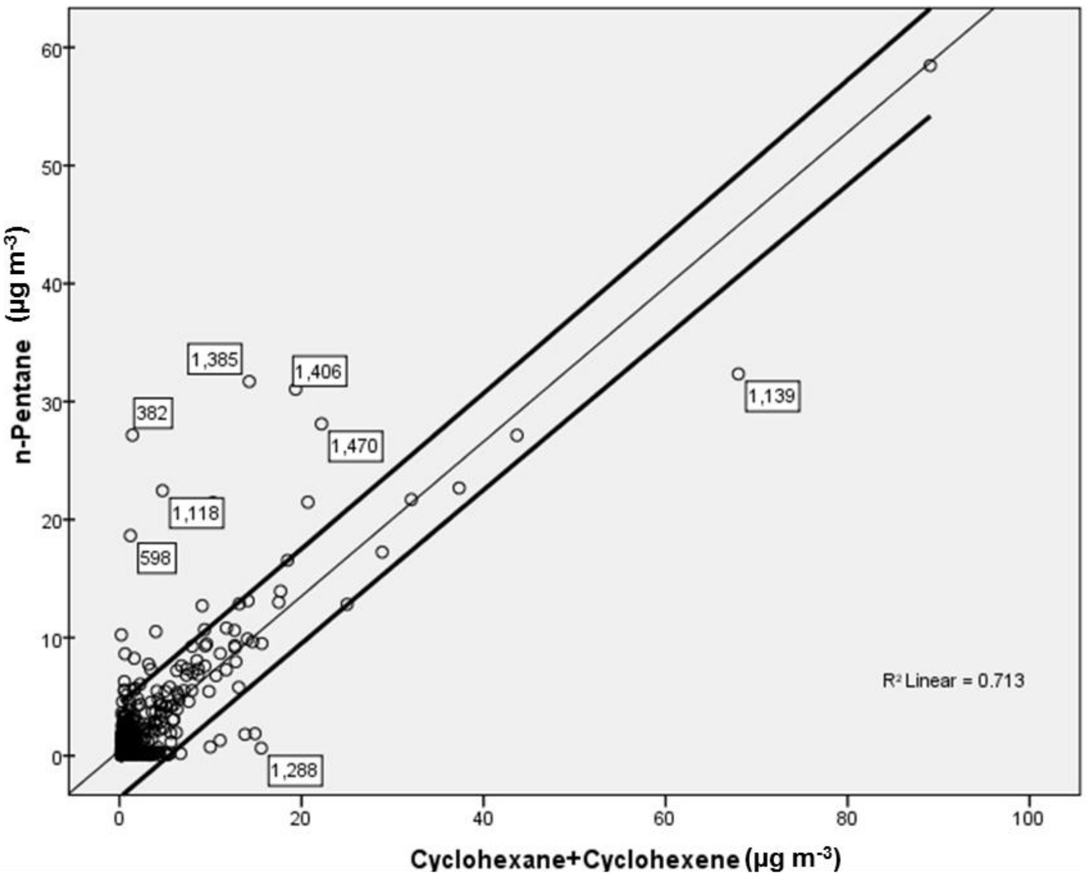


Figure 17 A correlation graph for determination of outliers
(bold lines represent 95% confidence intervals of linear trend line and numbers in the graph indicate the data point)

3.3.5. Influence of Handling Below Detection Limit Values by Replacing Them with ½LOQ on Mean Concentrations

Handling of below quantification values is always a problem in atmospheric data sets. It is a particular problem here, because many parameters are measured and some of the parameters used can have BLOQ values in large number of samples. Since this data will eventually be fed to a receptor model and in the receptor modeling exercise BLOQ values will be replaced with ½LOQ values, it may be a good idea how much average, geometric mean and median values will be affected by such replacement.

Horozgediği, Aliağa and TÜPRAŞ data set were used to investigate this. Data which were below LOQ values were replaced with ½LOQ. Mean, geometric mean and median concentrations of 20 most abundant VOCs were calculated (a) by leaving BLOQ values blank and (b) by replacing BLOQ values with ½LOQ value. Results for the Horozgediği station are shown in Figure 18. The effected compounds from the replacement in all three stations are given in Table 9.

Table 9 Compounds that effected LOQ replacement for below LOQ values

Aliağa Station	**Horozgediği Station**	**TÜPRAŞ Station**
Ethyne	1-Octene	n-Hexane
i-Pentane	c-1,2-Di-Methyl-Cyclohexane	Methyl-Cyclo-Pentane+2,4-Di-Methyl-Pentane
Cyclo-Pentane	Dodecene	Cyclo-Hexane+ Cyclo-Hexene
Isoprene		n-Heptane+cis-3-Heptene
2,2-Dimethyl-Butane		3-Methyl-Hexane
2,3-Dimethyl-Butane		c-1,2-Di-Methyl-Cyclohexane
2-Methyl-Pentane		
3-Methyl-Pentane		

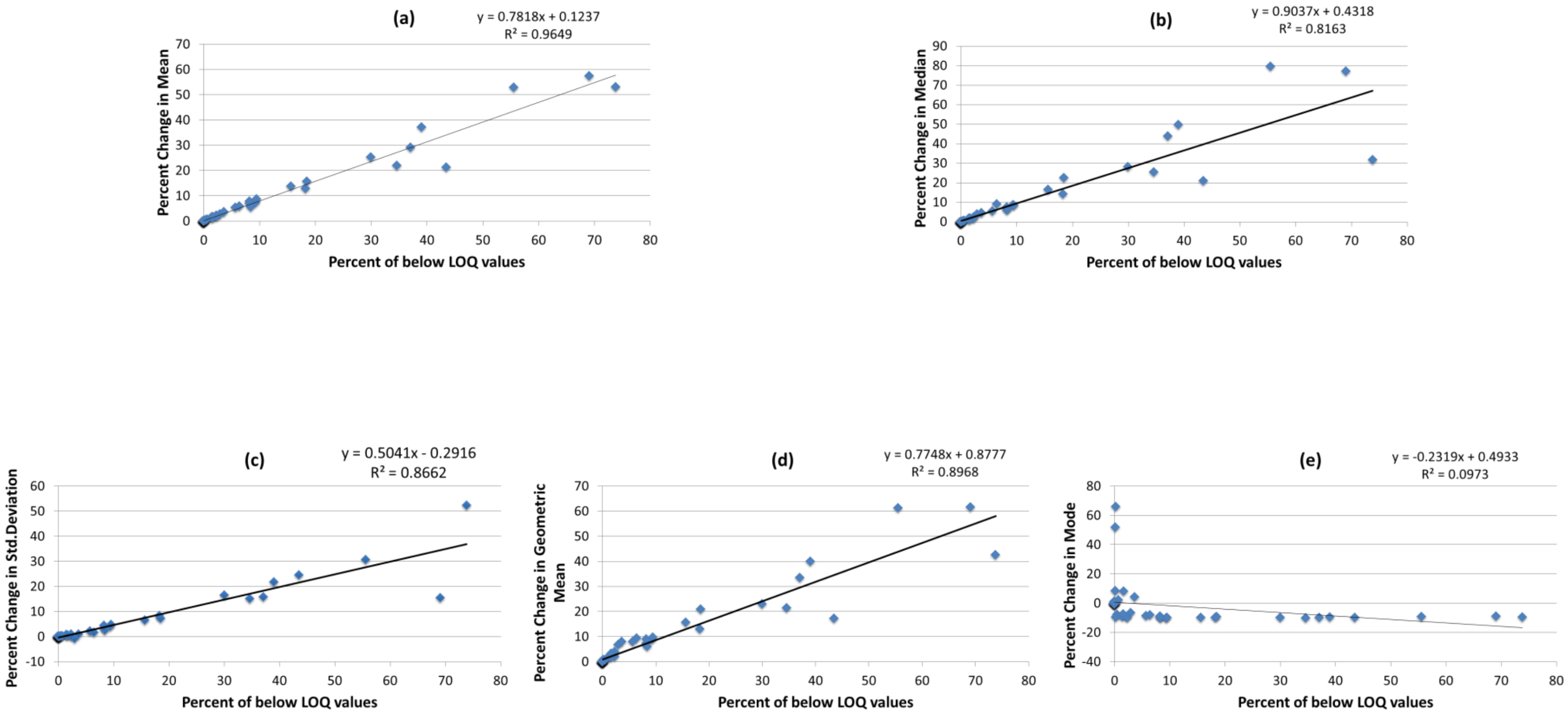


Figure 18 Effect of below LOQ value replacement
on (a) mean, (b) median, (c) standard deviation, (d) geometric mean and (e) mode

For most of the compounds replacing values below the LOQ with ½of the LOQ does not make a significant difference in their mean, median and geometric mean concentrations. Acetylene, butylbenzene are examples of such behavior at Horozgediği station. However, for a number of compounds, which includes Ethyne, i-Pentane, Cyclo-Pentane, Isoprene, 2,2-Dimethyl-Butane, 2,3-Dimethyl-Butane, 2-Methyl-Pentane, 3-Methyl-Pentane at Aliağa station, 1-Octene, c-1,2-Di-Methyl-Cyclohexane, Dodecene at Horozgediği station and n-Hexane, Methyl – Cyclo – Pentane + 2,4- Di-Methyl - Pentane, Cyclo – Hexane + Cyclo-Hexene, n-Heptane+cis-3-Heptene, 3-Methyl-Hexane, c-1,2-Di-Methyl-Cyclohexane at TÜPRAŞ station are significantly affected from replacements.

For some of these compounds, like cyclohexane in Figure 19, median and geometric mean concentrations are not affected strongly, but there is large difference in average values with and without ½LOQ replacement. On the other hand, for some of them like dodecane in Figure 19, all three parameters (mean, geometric mean and median) are strongly affected from ½LOQ replacement.

Effect of BLOQ replacement with ½LOQ value on mean median and geometric mean concentrations of VOCs is expected. Interesting point is such replacement effects only mean concentrations of some VOCs, median and mean concentrations of other group of VOCs and median, mean and geometric mean concentrations of yet another group. This gives the impression that the effect depends how many replacements is done. This is tested using Horozgediği data set. Results are depicted in Figure 18 where percent change in mean, median and mode were plotted against percentage of values replaced for different VOCs. It is clear from the figure that as the percent of below LOQ values that are replaced increases, percent change in statistical values also increases. Obviously, mean, median and geometric mean concentrations of species are affected strongly when there is high number of BLOQ values in the data set. When small number of BLOQ values are replaced with ½LOQ, only mean values are affected.

These conclusions can have a significant effect on receptor modeling application and suggest that least square based techniques, such as CMB, which operates on individual samples and multivariate techniques such as PMF, where contribution of each data on the model fit can be individually weighted are more suitable for data generated in this work than conventional multivariate techniques such as factor analysis (FA), principal component analysis (PCA) or cluster analysis (CA). Data have to be completed in those later techniques and most widely used way of filling missing data is to replace them by ½LOQ, which can have an impact on the results as demonstrated with 20 VOCs in Figure 19. In this study positive matrix factorization was used as a tool for source apportionment, which allowed us to weight individual points when it became necessary.

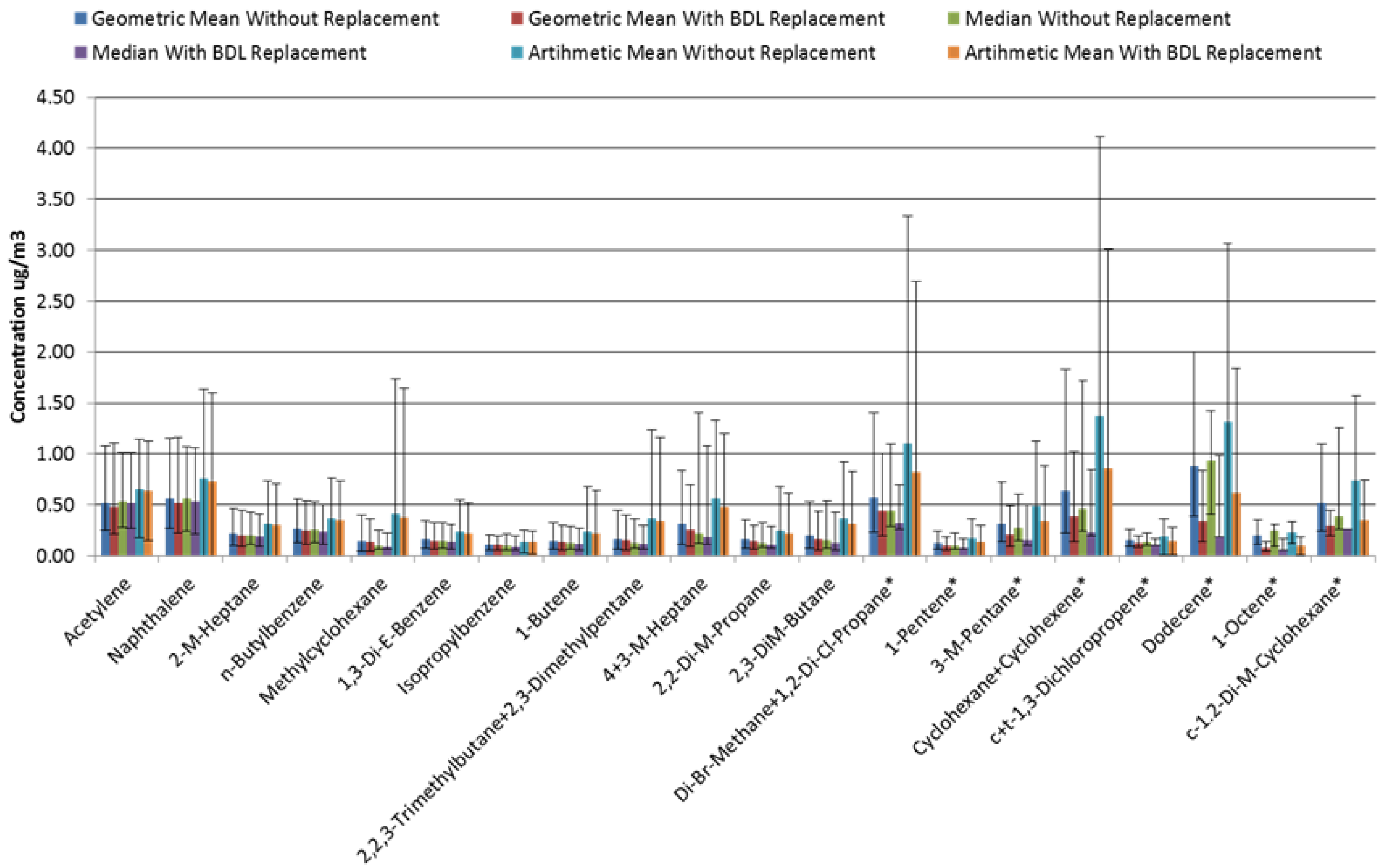


Figure 19 Statistical values variation of 20 most BDL valued VOCs
(error bars represents standard deviation)

3.4. Source Apportionment

As discussed in Section 2.8, different modeling techniques have been applied to identify and quantify the sources of VOCs. Source oriented method and CMB have been used to apportion sources in Delhi (Srivastava et al., 2005), Cario (Abu-Allaban et al., 2002), Helsinki and Jarvenpaa, Finland (Hellen et al., 2006); Pearl River Delta, China (Liu et al., 2008b); Mexico City, Mexico (Wöhrnschimmel et al., 2006); Seoul, Korea (Na and Kim, 2007); California, USA (Fujita et al., 1994); Kaohsiung, Taiwan (Lai et al., 2005) and Dunkerque, France (Badol et al., 2008).

The relatively old and well-known receptor oriented model, PCA, was used in many cases where either source profiles or number of sources were not exactly known: Bursa, Turkey (Yılmaz Civan, 2011); Hong Kong (Guo et al., 2007; Guo et al., 2004a); A Coruna, Spain (Perez-Rial et al., 2010); Kaohsiung, Taiwan (Liu et al., 2008a); Kocaeli, Turkey (Pekey and Yılmaz; 2011); Lin’an, China (Guo et al., 2004b) and Michigan, USA (Jia et al., 2008). UNMIX was used to identify VOC sources in New York, USA (Olson et al., 2007).

During the last decade, the newly developed and relatively advanced receptor model PMF has been applied extensively in identifying and quantifying sources contributing to VOC in ambient atmosphere at different locations in the world: Shanghai, China (Cai et al., 2010); Pearl River Delta, China (Ling et al., 2011); Houston, USA (Kim et al., 2005; Xie and Berkowitz, 2006; Buzcu and Fraser, 2006; Leuchner and Rappenglück, 2010); Ankara, Turkey (Yurdakul et al., 2013); Kocaeli, Turkey (Pekey et al., 2013); Donon, Peyrusse-Vieille, Tardiere, France (Sauvage et al., 2009) and Hong Kong (Lau et al., 2010).

In Helsinki, Finland, CMB and UNMIX models were compared (Hellen et al., 2003). Similar source contributions were observed.

In a study in Los Angeles (Brown et al., 2007), performances of PMF and CMB were compared. In Milan, Italy, Latella and his colleagues (2005) also compared the results of CMB and PMF analyses. In these two studies, no significant difference was observed in between CMB and PMF.

In a study conducted in Beijing, China, CMB, UNMIX and PMF were used to identify the sources of VOCs (Song et al., 2008). In this study, CMB model estimated gasoline related sources and LPG higher and petrochemical emissions lower than UNMIX and PMF. It was concluded that the VOC profiles used in the CMB model were for fresh emissions and the profiles extracted from ambient measurements by two receptor oriented models were aged.

In Santiago, Chile, two receptor oriented models, UNMIX and PMF, were applied to VOC dataset (Jorquera and Rappenglück, 2004). It was reported that PMF was able to find better and cleaner source profiles than UNMIX.

In another study, four receptor oriented source apportionment methods, PMF, CMB, UNMIX and PCA, were evaluated by applying them to simulate personal exposure data to select VOCs that were generated by Monte Carlo sampling from known source contribution profiles (Miller et al., 2002). The exposure sources modeled were paint emissions, cleaning and/or pesticide products, environmental tobacco smoke, gasoline vapors, wastewater treatment plant emissions and automobile exhaust. In that study, PMF-extracted factor profiles most closely represented the major sources used to generate the simulated data. However, sources that contributed less than 5% to the average total VOC exposure were not identified with any of the methods used.

Thus, the best applicable receptor model for the identification and quantification of VOCs in Aliağa region was determined to be PMF because:

- there were too many possible sources contributing to VOCs in the region,
- there were no complete source profiles available,
- aging of pollutants might generate problems in identification of sources,
- as stated in the literature, PMF resolves VOC sources better than other receptor methods.

3.4.1. Positive Matrix Factorization

Positive matrix factorization was developed as an alternative to the more conventional receptor oriented modeling approaches. PMF uses a weighted least-squares fit with the known error estimates of the elements of the data matrix used to derive the weights. It produces quantitative non-negative solutions. PMF provides a solution that minimizes an object function, Q, based upon uncertainties for each observation (Paatero, 1997; Polissar et al., 1998). This function is defined as:

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

where x_{ij} is a measured variable *j* in sample *i*, g_{in} is the contribution of source *n* to sample *i*, f_{nj} is 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).

The success of PMF strongly depends on the estimated uncertainties for each data value. The uncertainty estimation provides a useful tool for decreasing the weight of missing and below quantification limit data in the solution and to account for the variability in the source profiles. For the measured data values, the concentration values were used directly, and their uncertainty estimates were defined as 10% of the concentration value. In this study, values below the quantification limit were replaced by half of the quantification limit values, and their overall uncertainties were set at 5/6 of the quantification limit values. Missing values were substituted by the geometric mean of the measured values, and their accompanying uncertainties were set at four times these geometric mean values (Pekey and Doğan, 2013). Below quantification limit values were substituted by half of the LOQ and their accompanying uncertainties were set to 5/6 of the LOQ. In this study, EPA PMF v3.0 was utilized.

There are three output matrixes of PMF. These are factor profiles matrix (F or F loading), factor contributions matrix (G or G-score) and error matrix. Factor profile shows the mass of each species apportioned to the factor. The percent of each species apportioned to the factor is called explained variance. Factor profile and explained variance are used for the characterization of the source.

Each data point in factor contributions matrix shows the variation of contribution of each sample to each source. If the samples are collected hourly as in this case, then G score represents the hourly contribution of each source to the sample. G-scores are useful for the identification of source regions via conditional probability function (explained later in Section 3.5.2), pollution rose or potential source contribution function depending on location and duration of sampling. High G-score in a factor means, high contribution of that sample to that specific factor.

3.5. Supplementary Data

In order to identify sources of pollutants, supporting data might be useful. For this purpose, meteorological data and concentration of gaseous pollutants were used.

3.5.1. Air Quality Data

As mentioned in Section 1.12, this work was a part of a more extensive TÜBİTAK project. Measurement of inorganic gases (oxides of nitrogen, ozone and sulfur dioxide), automatic particulate matter and $PM_{2.5}$ and $PM_{2.5-10}$ sampling were also conducted within the scope of the TÜBİTAK Project. Those data were not under the scope of this thesis. However, for some discussions, inorganic gas results were used. The measurements of these inorganic gases were performed with automatic continuous measurement instruments. The measurement principles and devices used in the sampling in each station are given in Table 10.

Table 10 Instruments used for the monitoring inorganic gases

Parameter	Measurement Principle	Horozgediği Station	Aliağa Station
SO_2	UV florescent	Environnement AF21M	Thermo 43C
NO and NO_2	Chemiluminescence	Environnement AF31M	Thermo 42C
O_3	UV light absorption	Environnement AF42M	Thermo 49C

3.5.2. Meteorological Data

Meteorological data is used to understand the variations in concentrations of pollutants. In this study, the data from two meteorological stations were used. One of the stations was operated by Turkish State Meteorological Service at downtown Aliağa. The other meteorological station was located just nearby Horozgediği station and was operated by ENKA (power plant). The meteorological data was used to determine effect of temperature, relative humidity, wind speed, mixing height, ventilation coefficient and wind direction on concentrations of pollutants

Dependence of VOC concentrations in both stations on wind direction is investigated by calculating “conditional probability function” (CPF) for different wind sectors. The CPF estimates the probability that a given source contribution from a given wind direction will exceed a predetermined threshold criterion. The CPF is defined as:

$$CPF = \frac{m_{\Delta\theta}}{n_{\Delta\theta}} \qquad \text{Equation 3}$$

where $m_{\Delta\theta}$ is the number of occurrences from wind sector $\Delta\theta$ that exceeded the threshold criterion, and $n_{\Delta\theta}$ is the total number of hourly wind occurrences from the same wind sector. In this study, 16 wind sectors were used ($\Delta\theta$=22.5 degrees). Calm winds (<1 m/s) were excluded. The threshold was set as the highest 40% of the source contribution concentrations (Ashbaugh et al., 1985; Xie and Berkowitz, 2006).

Mixing height is the height to which the lower troposphere will undergo mechanical or turbulent mixing, producing a nearly homogenous air mass (NOAA, 2011). In this study, mixing height is calculated on an hourly basis using PCRAMMET software program. For PCRAMMET to run, wind direction, wind speed, dry bulb temperature, opaque cloud cover, cloud ceiling height, morning and afternoon mixing height data are supplied from meteorological station operated by General Directorate of Meteorology at Aliağa. Another meteorological parameters used in this study was “ventilation coefficient”. Concentrations of VOCs and other pollutants in an airshed are primarily determined by vertical and horizontal ventilation mechanisms. Horizontal ventilation occurs winds and vertical ventilation is caused by convective stability of the atmosphere. Wind speed and mixing height are two indicators for horizontal and vertical ventilation process. Because of this in many studies pollutant concentrations in airshed is found to be more strongly correlated with ventilation coefficient then wind speed and mixing height alone (Manju et al., 2002; Goyal and Rao, 2007; Genç et al., 2010). Ventilation coefficent is also considered as an indicator for assimilation capacity of the atmosphere (Goyal and Rao, 2007).

The effect of wind speed, relative humidity and temperature on VOC concentrations will also be discussed. The effect of these parameters on VOC concentrations are fitted to a model using a statistical program, Statgraphics v16.1 Centurion. The statistical program can fit data set to twenty-seven linear and nonlinear models. At first linear (y=ax+b) and logarithmic (y=lnx+b) models are tested. If there is a statistically significant relationship between the selected parameters, then these models are used. If there is no linear or logarithmic relation between the parameters, then rest of the nonlinear models are run and best R-squared valued model is selected.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. Descriptive Statistics

4.1.1. Meteorology of Aliağa

Alteration in the parameters of local meteorology is an important factor controlling the variation of pollutant concentration. In order to understand the regional transportation and dispersion of pollutants, meteorological parameters of Aliağa is investigated in this section. In this study, meteorological data used is from a meteorological station at Aliağa operated by General Directorate of Meteorology (GDM).

4.1.1.1. Wind Direction

The wind roses prepared for the sampling periods are presented in Figure 20. In this figure, wind roses prepared with the data obtained during summer and winter sampling campaigns and a total wind rose prepared from the combination of those data set. As depicted in the figure, the wind system effecting Aliağa is influenced by two wind components. First and dominating wind component is N and NNE sectors. The second and less frequent wind component is S and SSE sectors.

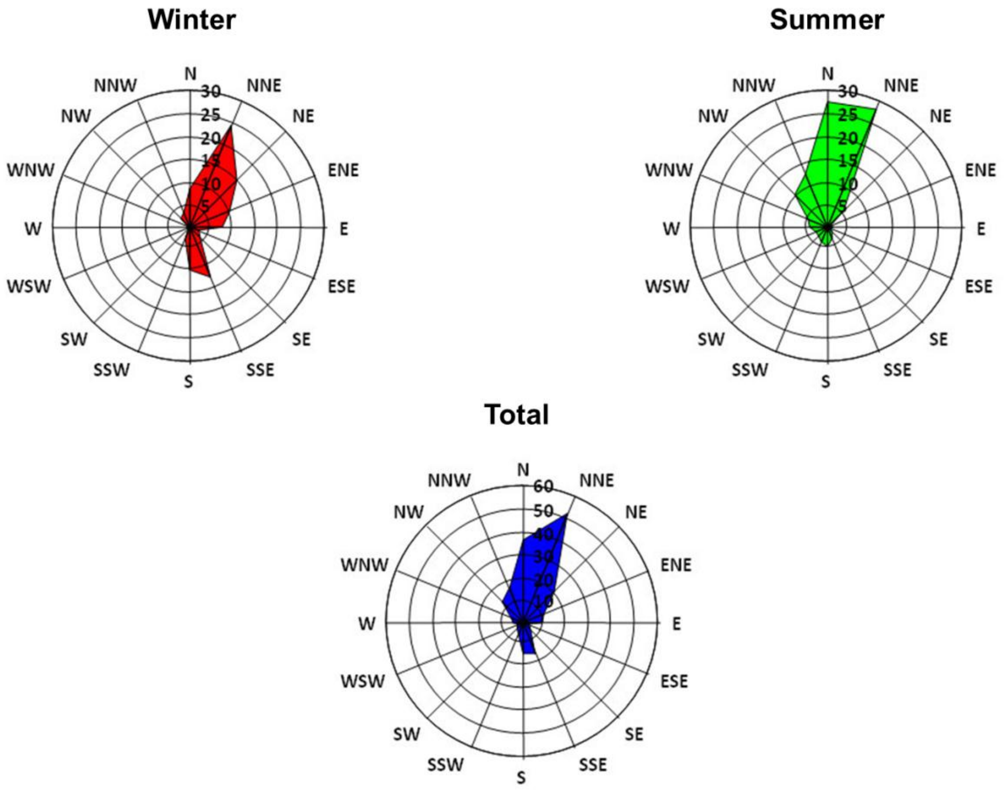


Figure 20 Wind roses prepared from the data obtained during sampling campaigns

As stated above, the wind roses given in Figure 20 are prepared from the meteorological data covering six month measurements during summer and winter sampling periods. A six month wind direction analysis is not enough to represent the actual meteorological condition of the region. In order to clarify this situation, the wind roses prepared in this study are compared with the seven wind roses prepared from one year observations in 1991 through Aliağa region.

In 1991, air quality and meteorological parameters were measured with automatic stations at seven locations for a project by Middle East Technical University Environmental Engineering Department. The wind roses of all stations prepared from these measurements are given in Figure 21. As depicted from the figure, there are certain similarities and differences in between wind roses. It was concluded that the main reason of the difference was due to topology of the region. However, the domination of N and NNE sectors are observed at four stations other than Kesik, Türkelli and Gerenköy stations which were affected from topology. Furthermore, a second wind component is also observed at all stations but in each station the wind direction is different. In a general perspective, it can be concluded that the wind roses generated 15 years ago are not very different from the wind roses generated in this study. This conclusion is based on the results of four stations, namely Foça, MKE, Samurlu and Çoraklar. The wind roses of Gerenköy, Kesi and Türkelli stations are not considered because these stations are far from the sampling region and they are affected from local topology.

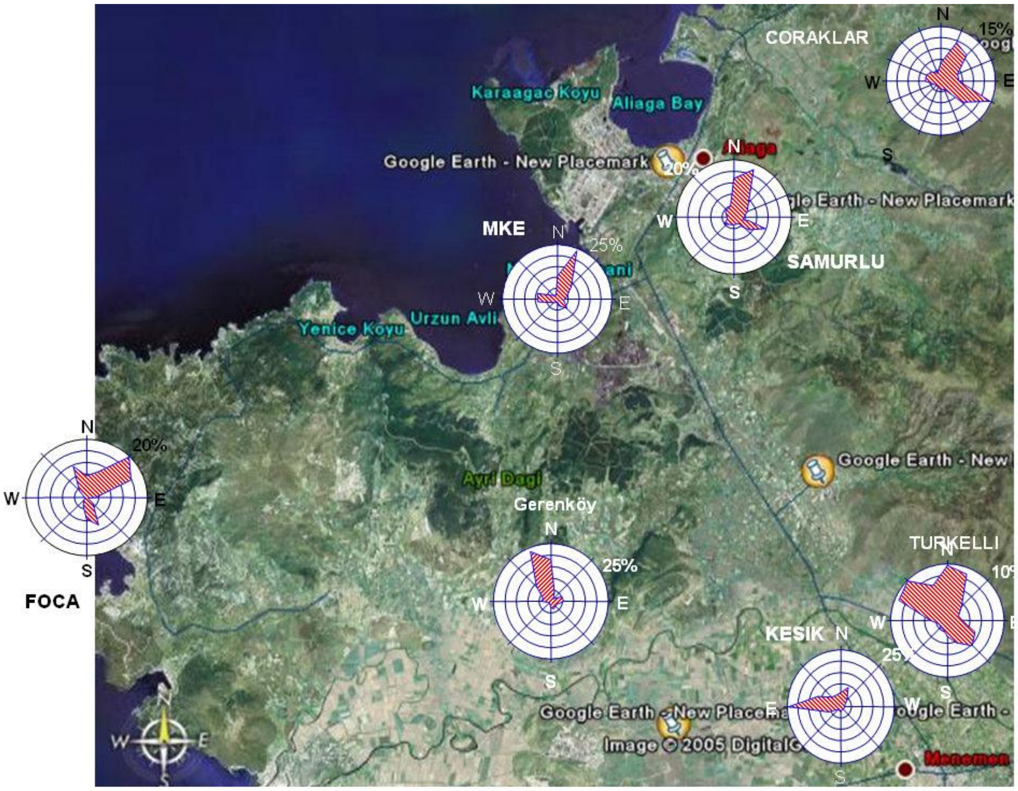


Figure 21 Wind roses of seven sampling stations of the year 1991

Annual average wind rose represent general wind pattern in the region. However, since the wind does not blow from the same direction through the day, annual average wind roses can be misleading about the pollution transport in that region. For this purpose, hourly wind roses are calculated by using the 2005 and 2006 Aliağa GDM data and given in Figure 22. Starting from 1:00 am till 7:00 am, wind blows dominantly from N and NNE, and less frequently from S and SSE directions. Throughout the day, wind blows from N and NNE components. However, after 7:00 am, a second wind component shows up and this component, blows from different direction at every hour. As depicted from the figure, the second component is from NNW at 07:00 and 08:00, from NW at 10:00, 11:00 and 12:00, from W at 13:00, from WSW, SW and SSW, from SSW and S at 15:00 and 16:00, from S at 17:00 and after 18:00 from S and SSE.

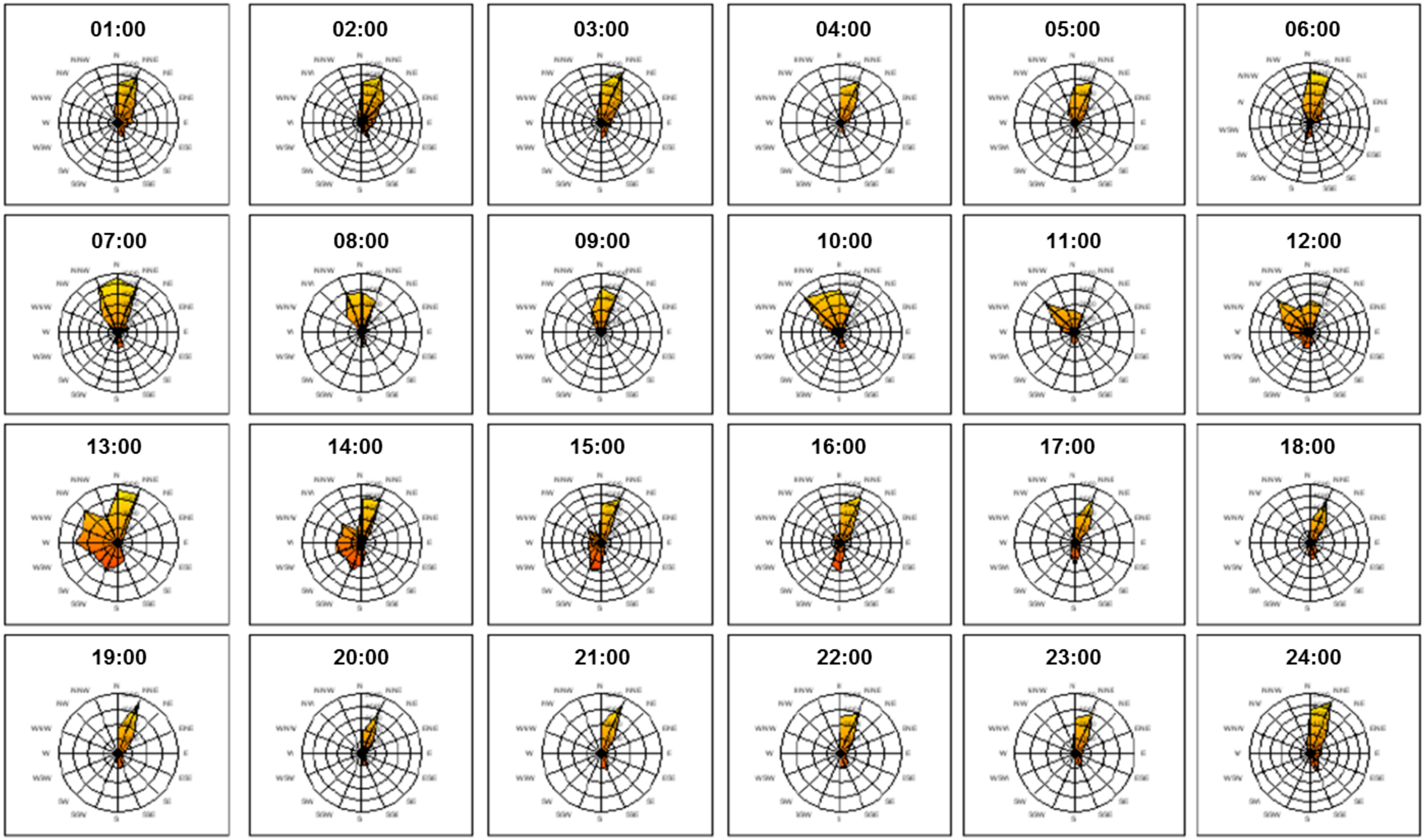


Figure 22 Hourly wind roses prepared for the Aliağa region

4.1.1.2. Temperature, Humidity and Wind Speed

Monthly average wind speed, temperature and humidity values reported during sampling campaigns are given in TABLEXXX. The temperature in the region varies between 16-37^{o}C and -4-23^{o}C during summer and winter campaigns, respectively. Monthly average temperatures are 23-27^{o}C during summer season and 6-11^{o}C during winter season.

The humidity values through the sampling campaigns are between 19% to 88% and 28% to 71% in summer and winter, respectively. Monthly average humidity values fluctuate between 46% to 50 % during summer and 68% to 69% during winter.

Wind speed measurements in Aliağa station showed that wind speed values during summer season are between < 1 m s^{-1} to 9.3 m s^{-1}. Average monthly wind speeds in this season are 4.9 m s^{-1}, 2.8 m s^{-1} and 3.7 m s^{-1} for July, August and September, respectively. During winter, the observed wind speed changes from < 1 m s^{-1} to 14 m s^{-1}. The monthly average values fluctuate in between 3.6 to 3.9 m s^{-1}.

Table 11 Measured temperature, humidity and wind speed values though the sampling campaigns at Aliağa region

	Temperature (^oC)			Humidity (%)			Wind Speed (m s^{-1})		
	Avg±STD	Max	Min	Avg±STD	Max	Min	Avg±STD	Max	Min
Summer									
July	26.5±3.5	34.6	18.7	46±11	75	20	4.9±1.6	9.3	0.5
August	27.1±3.8	36.9	17.7	53±15	88	20	2.8±1.6	8.2	0.0
September	23.4±3.7	32.8	16.2	50±16	87	19	3.7±1.6	7.2	0.0
Winter									
November	11.4±4.2	18.9	2.7	71±12	94	42	3.9±2.1	10.3	0.0
December	10.9±5.2	23.0	-2.0	68±13	98	29	3.8±2.3	13.9	0.0
January	6.3±5.2	17.1	-4.0	68±11	93	31	3.7±2.2	9.8	0.0
February	8.9±5.0	19.8	-3.9	69±12	95	33	3.6±2.2	10.3	0.0
March	10.4±3.9	18.9	0.8	68±13	96	28	3.9±2.7	12.3	0.0

4.1.2. Summary Statistics of VOC Concentrations at Aliağa, Horozgediği and TÜPRAŞ Stations

Summary of statistical information for Aliağa, Horozgediği and TÜPRAŞ stations are given in Table 12, Table 13 and Table 14, respectively. Tables include mean, standard deviation, median, geometric mean, minimum, maximum values as well as number of data points for each VOC. As will be discussed later in Section 0, VOCs measured in this study, without any exception, depicts a skewed frequency distribution which is best represented by "median" value. It is well documented that most environmental data follow log-normal distribution, which is best represented by geometric mean value. In this study both geometric mean and median concentrations of VOCs are listed, because although most of the VOCs have right-skewed distributions all of these distributions are not log-normal. Geometric mean value is specific to log-normal distribution whereas median is good for most of the right skewed distributions.

Approximately 50 VOCs are listed in each table. However, the VOCs detected at Aliağa and Horozgediği stations are not necessarily the same, because different GCs with different column and standards were used in those two stations. The on-line GC-FID/PID system used at Aliağa had a shorter column than the GC-FID system used at Horozgediği Station. Because of this, we were not able to use calibration standard used at Horozgediği which had 150 compounds in it. A different standard mix consisting of approximately 60 VOCs were used to calibrate the on-line GC at the Aliağa station. The observed difference in the VOCs detected in the two stations is largely due to this difference in standards. Since the same GC-FID system is used in Horozgediği and TÜPRAŞ stations, detected compounds are fairly similar in these stations. Thirty-one VOCs were common in all three stations. These include ethylene, ethyne (acetylene), propane, propylene, t-2-butene, 1-butene, n-pentane, cyclo-pentane, 1-pentene, n-hexane, 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, benzene, 2-methylhexane, 3-methylhexane, methylcyclohexane, toluene, 2,2,4-trimethylpentane, m+p-xylene, o-xylene, ethylbenzene, styrene, 1,3,5-trimethylbenzene, n-nonane, n-propylbenzene, isopropylbenzene, 2-ethyltoluene (o-ethyltoluene), 1,2,4-trimethylbenzene, n-decane. Twenty-one compounds including ethane, isobutane, n-butane, c-butene, 1,3-butadiene, i-pentane, t-pentene, c-pentene, isoprene, 2-methyl-1-pentene, cyclohexane, methylcyclopentane, heptane, 2,3-dimethylpentane, 2,4-dimetyhlpentane, 2-methylheptane/3-methylheptane, 2,3,4-trimethylpentane, m,p-ethyltoluene, 1,2,3-trimethylbenzene, m,p-diethylbenzene were detected at Aliağa Station, but not at Horozgediği and TÜPRAŞ. Most of these compounds were not detected at Horozgediği station because of their low concentrations there and their undetect values are not due to lack of these compounds in the calibration mixture used at the Horozgediği station. Twenty two compounds including isobutane+n-butane, 2,2-dimethylpropane, cyclohexane+cyclohexene, methylcyclopentane+2,4-dimethylpentane, n-heptane+*cis*-3-heptene, 2,2,3-trimethylbutane+2,3-dimethylpentane, octane, 2-methylheptane, 4+3-methylheptane, 1-octene, c-1,2-dimethylcyclohexane, 1,3,5-trimethylbenzene, 3-ethyltoluene (m-ethyltoluene), 4-ethyltoluene (p-ethyltoluene), 1,2,3-trimethylbenzene+pcymene, 1,3-diethylbenzene, n-butylbenzene, naphthalene, undecene, dodecene, dibromomethane+1,2-dicloropropane, c+t-1,3-di-chloropropene are measured at Horozgediği and TÜPRAŞ but not at Aliağa station. Most of these are compounds that are not included in the limited standard mix used at Aliağa. Compounds detected at Horozgediği and TÜPRAŞ measurements are more or less the same as the same GC-FID system and standard are used in both campaigns. Some of the compounds that are measured at Aliağa, but not detected at Horozgediği station are detected at TÜPRAŞ, demonstrating that at least some of the undetected chemicals at the Horozgediği station has nothing to do with the instrumentation and standard used.

Median concentrations of VOCs cover a wide range in all three stations. This range is between 0.05 μg m^{-3} for 2,2,4-trimethylpentane and 9.68 for n-butane at Aliağa station, between 0.05 μg m^{-3} for n-propyl benzene and 2.75 μg m^{-3} for n-butane at Horozgediği station and between 0.16 μg m^{-3} for n-propylbenzene and 47 μg m^{-3} for ethylene at the TÜPRAŞ station.

Table 12 Statistical summary of VOCs in Aliağa station (µg m^{-3})

Compounds	AVG±STD	Median	Geometric Mean	Min-Max	N**
Ethane	4.29±2.51	3.75	3.75	0.06-44.0	1604
Ethene	20.1±34.35	6.43	7.31	0.02-352	2106
Ethyne (Acetylene)*	2.99±6.96	0.02	0.21	0.02-95.7	1134 (2400)
Propane	6.38±8.7	4.14	4.03	0.03-110	1807
Propene	6.00±9.39	4.05	3.91	0.03-161	2225
iso-Butane	10.95±20.68	5.05	4.27	0.04-260	1838
n-Butane	17.5±23.52	9.68	8.72	0.06-239	1429
t-Butene	1.05±1.78	0.64	0.63	0.04-33.0	1593
1-Butene	2.77±3.14	2.07	1.56	0.04-42.4	2314
c-Butene	0.73±1.03	0.43	0.43	0.04-16.4	1853
1,3-Butadiene	2.43±3.92	1.10	0.97	0.03-50.3	1893
n-Pentane	4.68±13.8	0.42	0.62	0.05-282	1735
i-Pentane*	0.43±4.47	0.05	0.06	0.05-136	135 (2404)
Cyclo-Pentane*	0.07±1.01	0.04	0.05	0.04-48.9	20 (2404)
1-Pentene	0.54±0.62	0.31	0.32	0.05-5.81	1727
t-Pentene	0.42±0.76	0.23	0.24	0.04-12.5	1779
c-Pentene	0.51±0.84	0.26	0.29	0.04-23.4	1757
Isoprene*	1.59±7.50	0.04	0.20	0.04-162	1055 (2404)
Hexane	0.34±0.78	0.10	0.14	0.002-14.8	5101
2,2-Di-Methyl-Butane*	0.39±1.37	0.05	0.11	0.055-28.7	709 (2404)
2,3-Di-Methyl-Butane*	0.35±1.01	0.05	0.12	0.055-32.6	826 (2404)
2-Methyl-Pentane*	0.82±2.33	0.05	0.15	0.055-40.0	802 (2404)
3-Methyl-Pentane*	0.65±1.68	0.05	0.18	0.055-40.3	1174 (2403)
2-Methyl-1-Pentene	0.93±1.17	0.77	0.52	0.054-11.2	3549
Cyclo-Hexane	0.23±0.52	0.10	0.08	0.002-13.9	3098
Methyl-Cyclo-Pentane	1.36±1.24	1.13	0.86	0.016-13.7	5765
Benzene	2.39±3.86	1.3	1.16	0.004-78.3	5910
Heptane	1.97±5.96	0.24	0.31	0.01-69.5	3320
2,3-Di-Methyl-Pentane	1.82±4.00	0.83	0.83	0.01-76.9	5544
2,4-Di-Metyhl-Pentane	1.07±1.95	0.45	0.46	0.002-41.4	5733
2-Methyl-Hexane	0.49±0.57	0.30	0.30	0.005-7.70	4037
3-Methyl-Hexane	0.55±1.85	0.14	0.16	0.002-52.4	4911
Methyl-Cyclo-Hexane	0.34±0.97	0.09	0.08	0.001-21.7	3433

Table 12cont. Statistical summary of VOCs in Aliağa station (µg m^{-3})

Compounds	AVG±STD	Median	Geometric Mean	Min-Max	N**
Toluene	7.95±9.64	5.20	5.22	0.014-179	5879
2,2,4-Tri-M-Pentane	0.13±0.22	0.05	0.05	0.001-4	3373
2,3,4-Tri-M-Pentane	0.29±0.99	0.09	0.08	0-30.9	3431
2-M-Heptane+ 3-M-Heptane	2.97±16.85	0.5	0.64	0.002-685	5616
m, p-Xylene	1.65±2.92	0.95	0.93	0.004-60	5875
o-Xylene	1.13±1.51	0.67	0.65	0.003-21	5510
Ethyl-Benzene	0.75±0.95	0.46	0.47	0.007-19	5712
Styrene	0.69±1.4	0.23	0.28	0.001-22	5344
n-Nonane	0.65±0.98	0.35	0.34	0.002-17	3506
n-Propyl-Benzene	0.20±0.37	0.12	0.11	0.001-16	3820
Iso-Propyl-Benzene	0.99±2.23	0.37	0.42	0.002-18	5550
m,p-Ethyl-Toluene	0.39±0.45	0.27	0.25	0.001-8.0	4775
o-Ethyl-Toluene (2-Ethyl-Toluene)	0.31±0.48	0.15	0.16	0.002-9.9	4143
1,2,4-Tri-M-Benzene	1.03±1.14	0.70	0.66	0.004-17	4695
1,3,5-Tri-M-Benzene	0.39±0.8	0.18	0.19	0.003-18	5131
1,2,3-Tri-M-Benzene	0.28±0.34	0.17	0.16	0.001-6.1	3370
n-Decane	0.42±0.43	0.29	0.28	0.002-7.4	5251
m, p-Di-Ethyl-Benzene	0.27±0.35	0.14	0.12	0.001-3.5	3235
∑Saturated HCs	22.02±45.69	8.22	8.87	0.03-949	73688
∑UnsaturatedHCs	14.56±35.94	1.22	4.30	0.05-602	25600
∑ Aromatic HCs	18.77±20.76	12.32	12.61	0.05-212	80216
∑ VOCs	55.3±84.89	29.24	30.96	0.2-1430	179504

*****The statistical values of these species, except for median, are calculated after replacement of below LOQ values with half of quantification value (QV).

******Numbers in parenthesis shows the number of measurements used for statistical analyses after the replacement of below LOQ values with half of QV.

Table 13 Statistical summary of the VOCs in Horozgediği station (µg m^{-3})

Compounds	**AVG±STD**	**Median**	**Geometric Mean**	**Min-Max**	**N****
Ethylene	2.92 ± 5.74	1.37	1.43	0.1-60.8	854
Ethyne (Acetylene)	0.66 ± 0.48	0.53	0.51	0.04-4.48	1056
Propane	2.44 ± 8.44	0.51	0.67	0.11-105	1035
Propylene	1.37 ± 2.45	0.77	0.88	0.11-38.37	1090
iso-Butane+ n-Butane	5.20 ± 10.9	2.75	3.05	0.18-269	1090
t-2-Butene	0.26 ± 0.33	0.16	0.19	0.06-5.44	1089
1-Butene	0.23 ± 0.44	0.12	0.14	0.05-6.3	988
n-Pentane	1.05 ± 2.50	0.31	0.39	0.04-27.2	1090
Cyclo-Pentane	1.47 ± 3.01	0.42	0.61	0.09-37.7	1090
2,2-Di-Methyl-Propane	0.25 ± 0.43	0.12	0.16	0.07-5.73	890
1-Pentene	0.17 ± 0.19	0.10	0.12	0.06-2.26	711
n-Hexane	1.81 ± 3.76	0.74	0.86	0.08-44.8	988
2,2-Di-M-Butane	0.81 ± 1.81	0.23	0.31	0.05-29.5	1065
2,3-Di-M-Butane	0.36 ± 0.56	0.16	0.20	0.05-4.57	887
2-Methyl-Pentane	1.41 ± 2.80	0.49	0.64	0.08-32	1090
3-Methyl-Pentane	0.48 ± 0.64	0.27	0.31	0.1-6.55	683
Cyclo-Hexane+ Cyclo-Hexene	1.37 ± 2.74	0.46	0.63	0.18-31.3	560
M-Cyclo-Pentane+ 2,4-Di-M-Pentane	1.62 ± 5.59	0.23	0.36	0.06-72.2	973
Benzene	1.98 ± 5.43	0.76	0.86	0.14-59.9	988
n-Heptane+ cis-3-Heptene	1.00 ± 3.39	0.27	0.35	0.07-44.8	988
2,2,3-Tri-M-Butane+ 2,3-Di-M-Pentane	0.37 ± 0.87	0.12	0.17	0.06-9.47	884
2-Methyl-Hexane	0.49 ± 1.28	0.18	0.23	0.06-14.2	981
3-Methyl-Hexane	0.96 ± 2.45	0.43	0.51	0.19-30.9	988
Methyl-Cyclo-Hexane	0.41 ± 1.33	0.10	0.14	0.06-17.12	898
Toluene	4.25 ± 9.20	2.34	2.26	0.24-147	988
Octane	0.36 ± 0.81	0.16	0.20	0.06-10.4	983
2,2,4-Tri-Methyl-Pentane	0.83 ± 0.65	0.68	0.69	0.11-8.6	988
2-Methyl-Heptane	0.32 ± 0.41	0.20	0.22	0.06-4.07	874
4+3-M-Heptane	0.56 ± 0.77	0.22	0.31	0.1-8.98	816
1-Octene*	0.10 ± 0.09	0.06	0.08	0.05-0.6	232 (988)
c-1,2-Di-M-Cyclohexane*	0.35 ± 0.40	0.26	0.29	0.24-4.35	177 (985)

Table 13cont. Statistical summary of the VOCs in Horozgediği station (µg m^{-3})

Compounds	AVG±STD	Median	Geometric Mean	Min-Max	N**
m+p-Xylene	1.71 ± 3.45	0.85	1.05	0.23-57.5	988
o-Xylene	0.35 ± 0.45	0.21	0.24	0.06-3.66	988
Ethyl-Benzene	0.63 ± 0.65	0.42	0.49	0.15-5.32	988
Styrene	1.49 ± 1.63	0.84	1.05	0.17-9.37	988
1,3,5-Tri-Methyl-Benzene	0.35 ± 0.65	0.17	0.21	0.05-6.29	969
n-Nonane	0.36 ± 0.59	0.22	0.25	0.06-11.55	988
n-Propyl-Benzene	0.06 ± 0.04	0.05	0.05	0.02-0.36	963
iso-Propyl-Benzene	0.14 ± 0.11	0.10	0.11	0.05-0.98	896
3-Ethyl-Toluene	0.26 ± 0.21	0.22	0.22	0.05-2.71	988
4-Ethyl-Toluene	0.31 ± 0.31	0.24	0.24	0.05-4.14	934
2-Ethyl-Toluene	0.17 ± 0.15	0.13	0.14	0.05-2.35	971
1,2,4-Tri-Methyl-Benzene	0.31 ± 0.46	0.17	0.19	0.03-4.04	988
1,2,3-Tri-M-Benzene+ p-Cymene	0.61 ± 0.56	0.40	0.46	0.07-4.94	988
n-Decane	0.46 ± 0.71	0.31	0.33	0.08-13.46	988
1,3-Di-Ethyl-Benzene	0.23 ± 0.32	0.15	0.16	0.05-3.77	898
n-Butyl-Benzene	0.37 ± 0.40	0.26	0.27	0.06-4.14	918
Naphthalene	0.75 ± 0.88	0.56	0.56	0.07-11.63	946
Undecene	0.59 ± 0.84	0.43	0.43	0.08-16.29	970
Dodecene*	0.62 ± 1.22	0.19	0.34	0.17-12.51	378 (986)
Di-Br-Methane+ 1,2-Di-Cl-Propane	1.10 ± 2.24	0.44	0.58	0.24-19.16	660
c+t-1,3-Di-Chloro-Propene	0.19 ± 0.18	0.13	0.15	0.09-1.97	512
∑Saturated HCs	22.95 ± 51.55	9.53	11.33	2.04-793	22224
∑UnsaturatedHCs	8.69 ± 17.07	4.03	4.69	0.90-207	9310
∑Aromatic HCs	13.98 ± 24.90	7.88	8.56	1.55-328	16387
∑HaloganatedHCs	1.28 ± 2.42	0.57	0.73	0.33-21.12	1172
∑VOC	46.90 ± 95.94	22.01	25.31	4.82-1340	49093

*****The statistical values of these species, except for median, are calculated after replacement of below LOQ values with half of QV.

******Numbers in parenthesis shows the number of measurements used for statistical analyses after the replacement of below LOQ values with half of QV.

Table 14 Statistical summary of the VOCs in TÜRPAŞ station (µg m^{-3})

Compounds	AVG±STD	Median	Geometric Mean	Range	N**
Ethylene	50.5±37.01	46.97	35.27	0.74-335	251
Ethyne (Acetylene)	3.69±5.55	1.91	1.86	0.17-35.5	96
Propane	19.57±18.08	13.87	12.79	0.2-120	243
Propylene	20.49±18.13	17.41	14.08	0.08-189	335
iso-Butane+ n-Butane	56.97±66.2	42.55	37.11	0.63-734	340
t-2-Butene	5.35±5.18	3.93	3.09	0.06-38.1	346
1-Butene	5.99±5.63	4.44	3.51	0.05-39.9	344
n-Pentane	7.25±12.29	3.18	3.23	0.05-123	348
Cyclo-Pentane	7.12±9.33	3.80	3.99	0.1-68.7	350
2,2-Di-Methyl-Propane	5.67±5.34	4.13	3.43	0.08-35.3	342
1-Pentene	0.46±0.42	0.32	0.34	0.06-2.63	326
n-Hexane*	1.4±5.8	0.81	0.89	0.81-99.8	18 (346)
2,2-Di-Methyl-Butane	1.35±2.36	0.62	0.66	0.05-24.6	242
Cyclo-Hexane+ Cyclo-Hexene*	2.73±9.03	0.35	0.66	0.35-89.1	52 (221)
Methyl-Cyclo-Pentane+ 2,4-Di-Methyl-Pentane*	2.40±5.18	1.48	1.77	1.48-60.1	35 (209)
Benzene	10.53±15.09	4.50	4.42	0.1-86	194
n-Heptane+ cis-3-Heptene*	0.62±1.88	0.06	0.11	0.06-16.3	56 (210)
2,2,3-Tri-M-Butane+2,3-Di-M-Pentane	9.19±25.28	2.12	2.63	0.13-198	77
2-Methyl-Hexane	11.07±32.83	2.66	3.46	0.42-290	107
3-Methyl-Hexane*	1.26±5.4	0.11	0.22	0.11-58.3	58 (211)
Methyl-Cyclo-Hexane	3.14±5.38	1.35	1.62	0.2-54.6	335
Toluene	16.31±27.17	8.55	9.64	1.39-288	402
Octane	3.07±1.95	2.75	2.65	0.51-22.4	401
2,2,4-Tri-Methyl-Pentane	2.00±4.45	0.99	1.02	0.1-51.3	271
4+3-Methyl-Heptane	2.39±3.21	1.62	1.73	0.31-41.1	401
1-Octene	0.92±1.34	0.55	0.60	0.09-14.5	399
c-1,2-Di-M-Cyclohexane*	2.17±0.81	1.94	2.08	1.94-6.07	14 (143)
m+p-Xylene	12.67±16.17	7.67	8.37	2.35-122	402

Table 14cont. Statistical summary of the VOCs in TÜRPAŞ station (µg m^{-3})

Compounds	AVG±STD	Median	Geometric Mean	Range	N**
o-Xylene	2.06±2.02	1.46	1.47	0.3-17.2	402
Ethyl-Benzene	2.8±2.44	2.13	2.04	0.31-15.8	402
Styrene	1.74±1.64	1.18	1.39	0.45-13	402
1,3,5-Tri-Methyl-Benzene	1.98±2.04	1.17	1.43	0.43-12.9	402
n-Nonane	2.94±3.73	1.88	2.07	0.45-40.4	402
n-Propyl-Benzene	0.21±0.15	0.16	0.17	0.04-0.73	402
3-Ethyl-Toluene (m-Ethyl-Toluene)	1.13±0.63	0.98	0.99	0.26-4.17	402
4-Ethyl-Toluene (p-Ethyl-Toluene)	1.27±0.73	1.10	1.10	0.26-4.8	402
2-Ethyl-Toluene (o-Ethyl-Toluene)	0.7±0.45	0.60	0.60	0.19-3.42	402
1,2,4-Tri-Methyl-Benzene	1.72±1.43	1.23	1.33	0.29-8.22	402
1,2,3-Tri-Methyl-Benzene+ p-Cymene	1.24±0.83	1.05	1.08	0.41-8.46	402
n-Decane	2.02±1.7	1.56	1.63	0.44-13.2	402
1,3-Di-Eethyl-Benzene	1.10±1.64	0.59	0.68	0.16-14.82	397
n-Butyl-Benzene	2.00±1.02	1.77	1.83	0.78-10.26	402
Naphthalene	1.28±0.72	1.05	1.12	0.37-4.36	402
Undecene	1.56±0.93	1.34	1.36	0.47-8.41	402
Dodecene	2.00±3.52	0.55	0.81	0.18-22.3	390
Di-Bromo-Methane+1,2-Di-Cloro-Propane	18.53±26.56	8.31	9.83	0.45-196.11	89
c+t-1,3-Di-Chloro-Propene	2.28±1.72	1.86	1.72	0.36-9.76	398
∑Saturated HCs	242±319	161	144	9.3-2835	6664
∑UnsaturatedHCs	71.4±92.1	39.4	36.8	3.6-621	1153
∑Aromatic HCs	27.5±22.2	21.3	22.1	5.9-187	6029
∑HaloganatedHCs	2.28±1.72	1.86	1.72	0.36 - 9.76	398
∑VOC	343±435	223	204	19-3652	14244

*****The statistical values of these species, except for median, are calculated after replacement of below LOQ values with half of QV.

******Numbers in parenthesis shows the number of measurements used for statistical analyses after the replacement of below LOQ values with half of QV.

When 10 VOCs that are measured in all three stations and have the highest median concentrations in each of them are listed, it can be seen that six of these compounds are common in all stations. These VOCs with the highest concentrations at all stations include ethylene, propane, propylene, benzene, toluene and m, p-xylene.

The box and whisker plots of most abundant 30 measured VOCs at Aliağa, Horozgediği and TÜPRAŞ stations are depicted in Figure 23, Figure 24 and Figure 25, respectively. Box and whisker plots are convenient way of representing distribution of data population. In these graphs the bottom and top of the box are the 25th and 75th percentile (the lower and upper quartiles, interquartile range - IQR), respectively and the band near the middle of the box is always the 50th percentile (the median). The ends of the whiskers represent minimum and maximum values that are not outliers. An outlier is any value that lies more than one and a half times the length of the box from either end of the box (data point is below Q1 - 1.5×IQR or above Q3 + 1.5×IQR). Each outlier is denoted by a dot above or below whiskers.

Box and whisker plots for Aliağa and Horozgediği stations have the same appearance with large number of outliers at high concentrations, but no or very few outliers at low concentrations. This is typical for right skewed data where there is large number of data points 1.5xIQR above the third quartile.

The box and whisker plot for TÜPRAŞ station is different from the other two. The number of outliers is fewer and for compounds like ethylene and propylene there are outliers at low concentrations as well. This pattern is probably due to location of this station at the middle of VOC emitting industries. This increases the interquartile range and thus reduces the number of outliers. Smaller number of outliers suggests less skewed distributions of VOCs at TÜPRAŞ station.

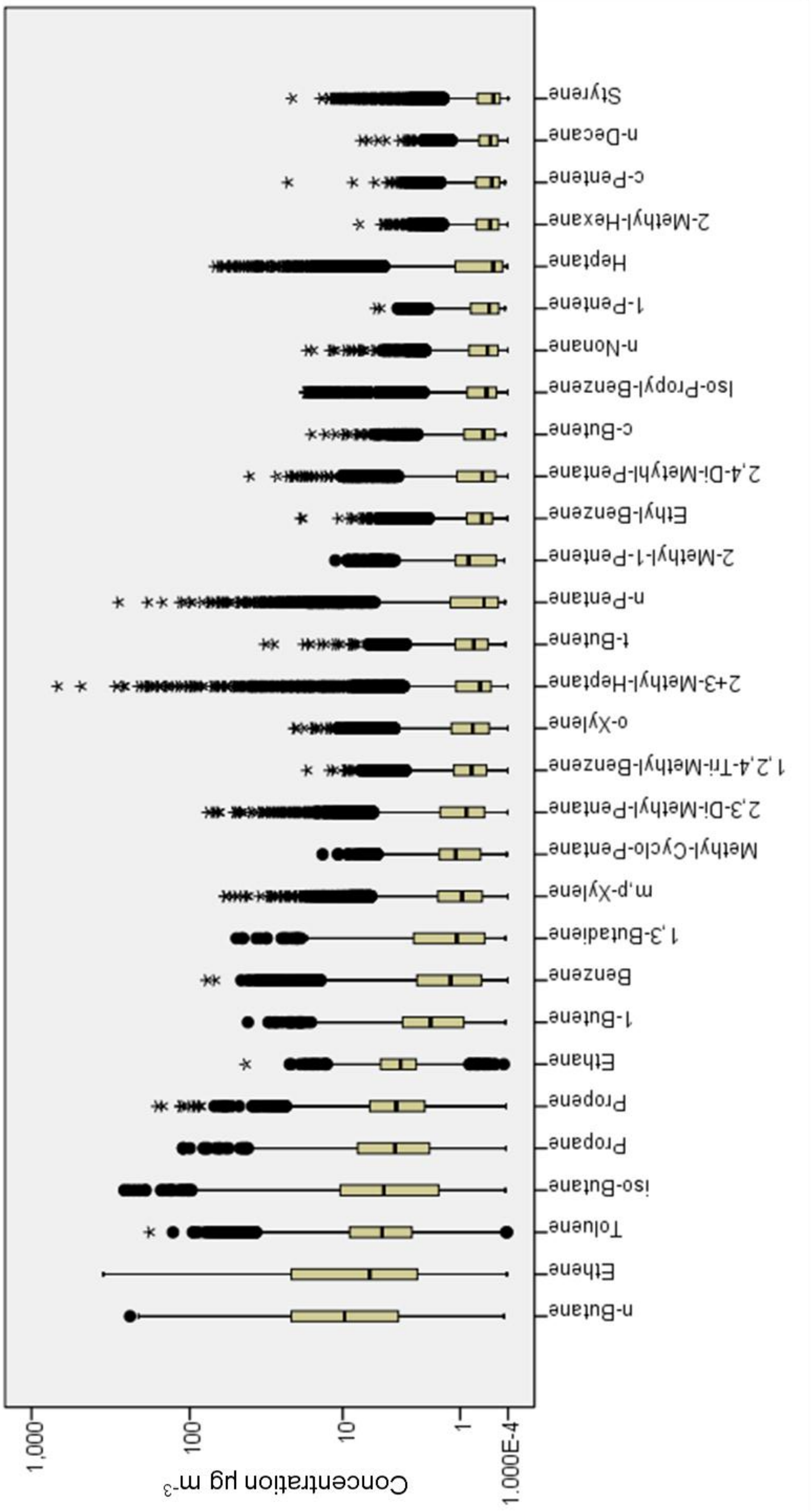


Figure 23 Box-Whisker plot of 30 most abundant VOCs at Aliağa Station

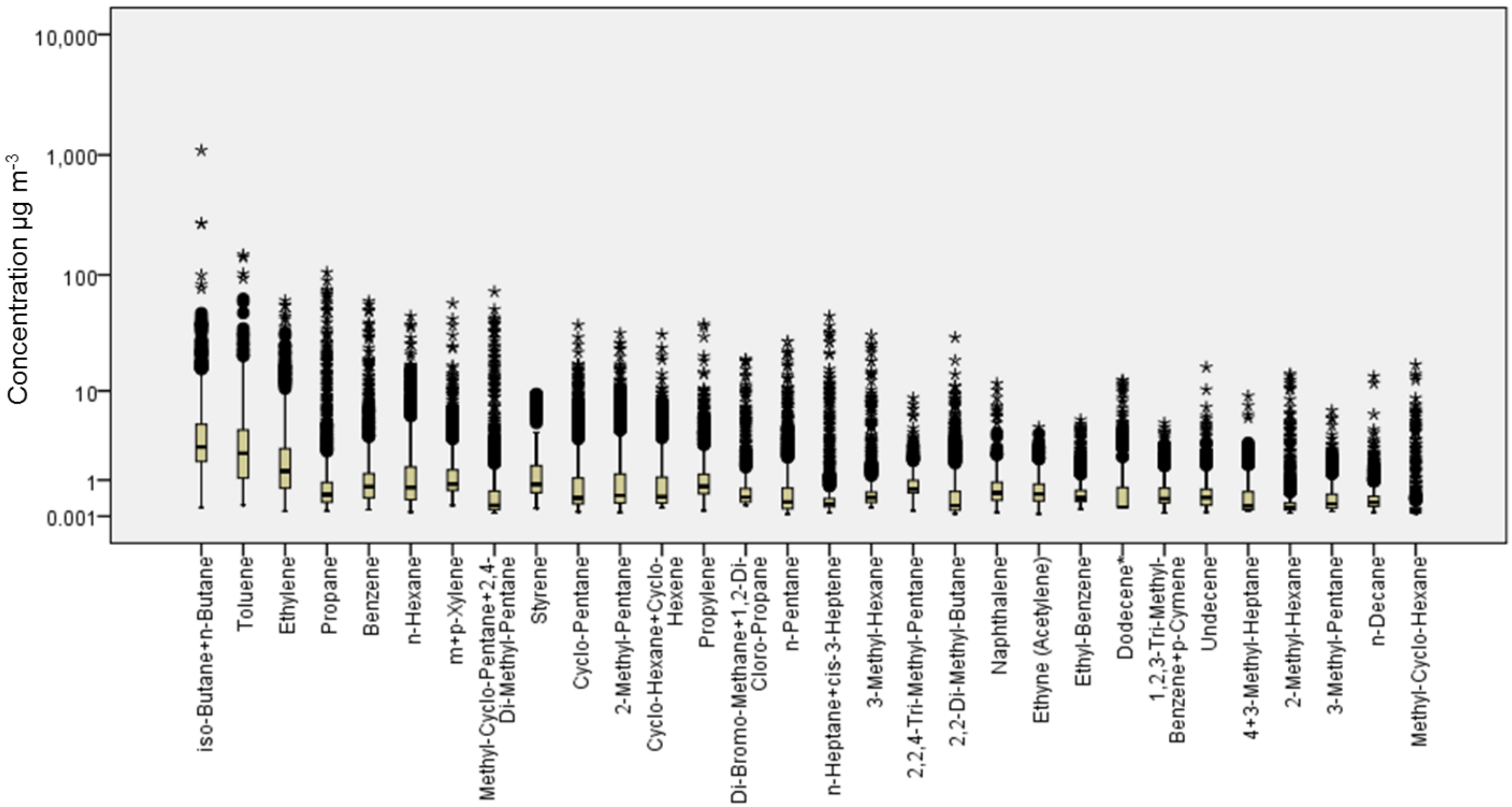


Figure 24 Box-Whisker plot of 30 most abundant VOCs at Horozgediği Station

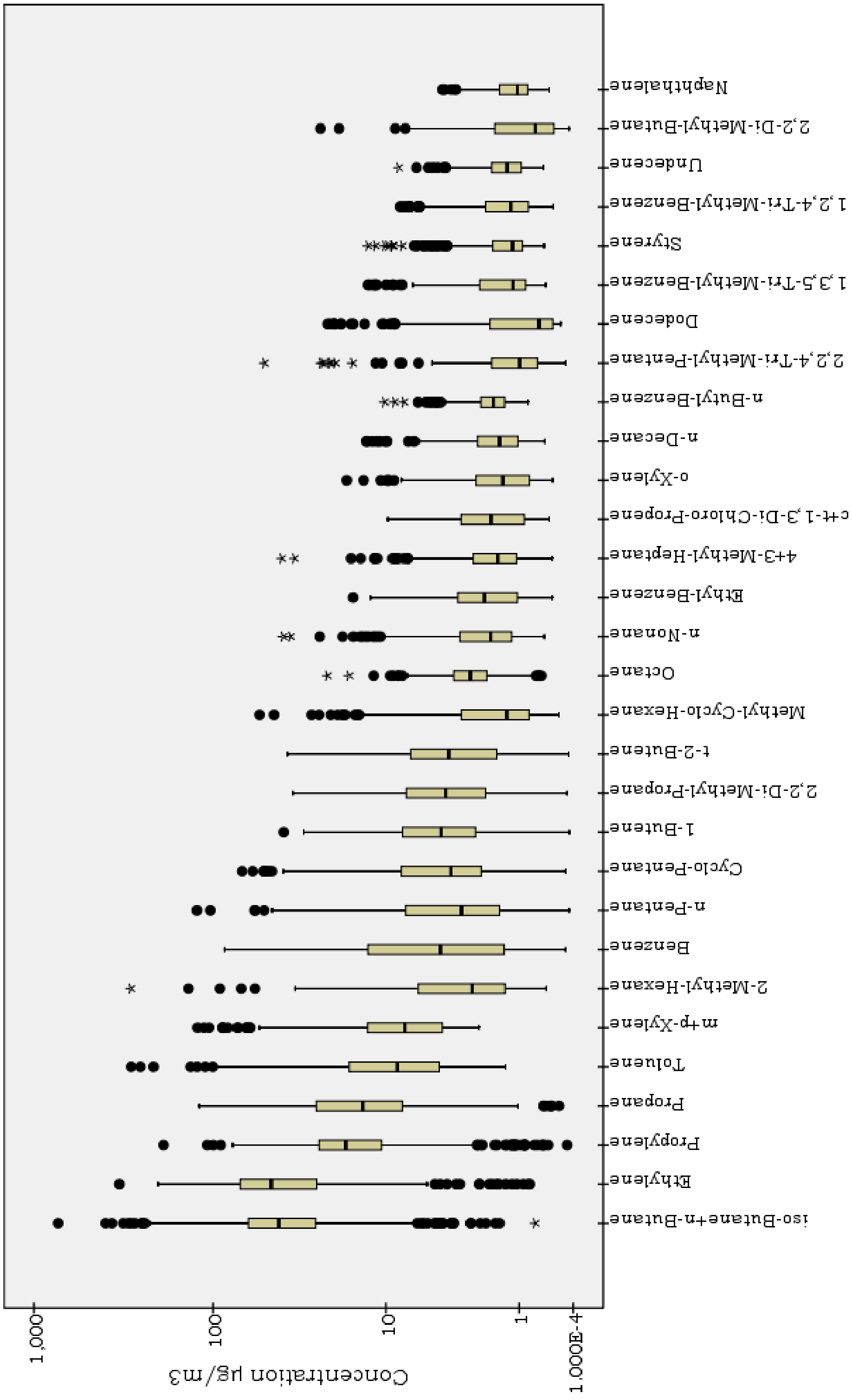


Figure 25 Box-Whisker plot of 30 most abundant VOCs at TÜPRAŞ Station

4.1.3. Frequency Distributions

Frequency distributions of selected VOCs at Aliağa, Horozgediği and TÜPRAŞ stations are given in Figure 26, Figure 27 and Figure 28 respectively. All of these figures clearly demonstrate right-skewed distributions as pointed in previous sections. Chi-square test was used to test how good these histograms fit to a lognormal distribution. The exercise showed that concentrations of 20 VOCs at Aliağa Station, 17 VOCs at Horozgediği station and 5 compounds in TÜPRAŞ station are log normally distributed with 95% statistical confidence.

Rest of the VOCs, although show right-skewed histograms, are not log-normally distributed. Many of them best fited to different right-skewed distributions, such as, Wakebey, log-pearson, log-logistic, Frechet etc. Some examples of less skewed distributions are shown in Figure 29. Although such distributions do exist in all three stations, percentage of measured VOCs that do not show lognormal distribution is higher in TÜPRAŞ station than in other two stations.

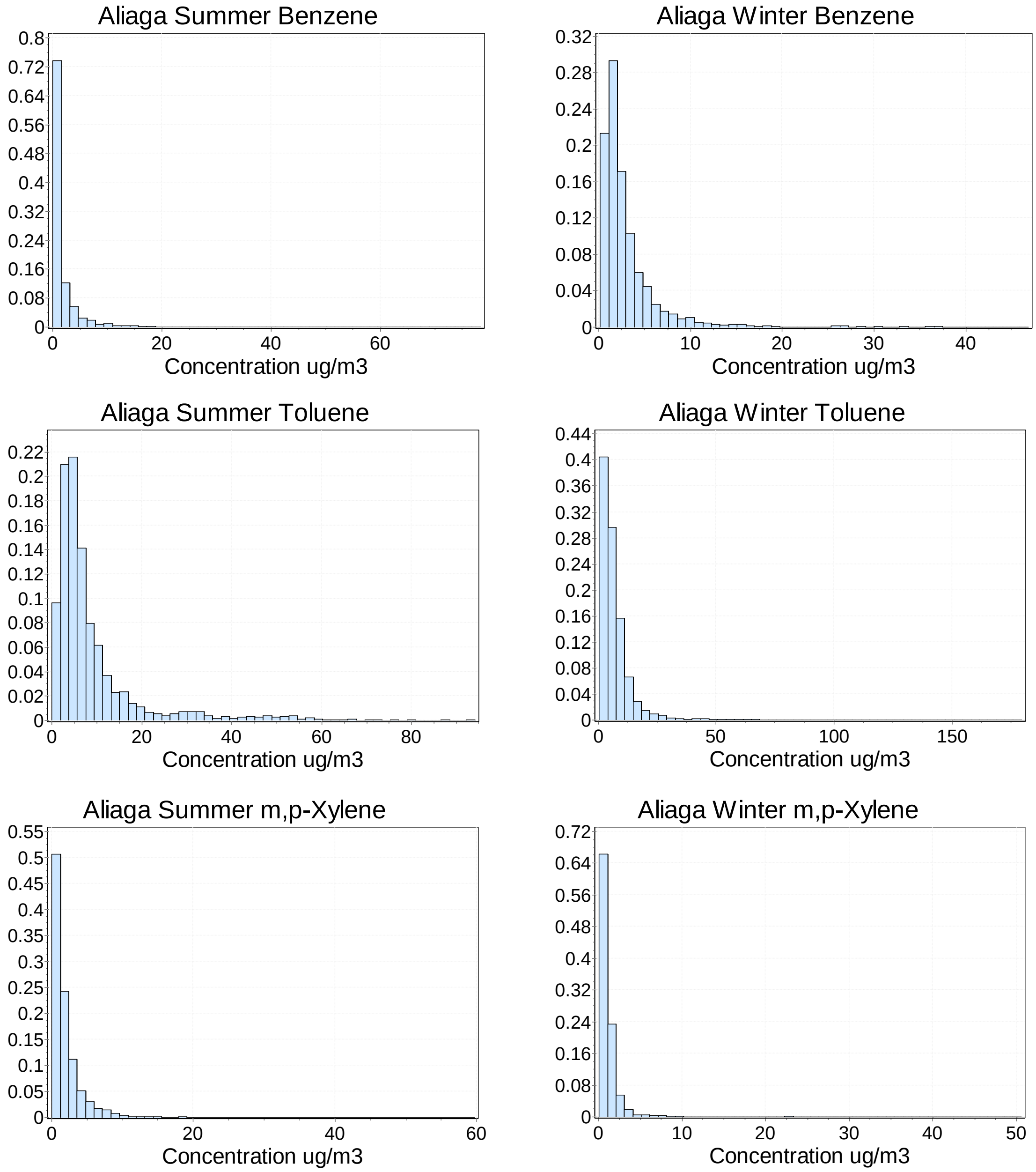


Figure 26 Typical frequency distributions of selected VOCs at Aliağa station

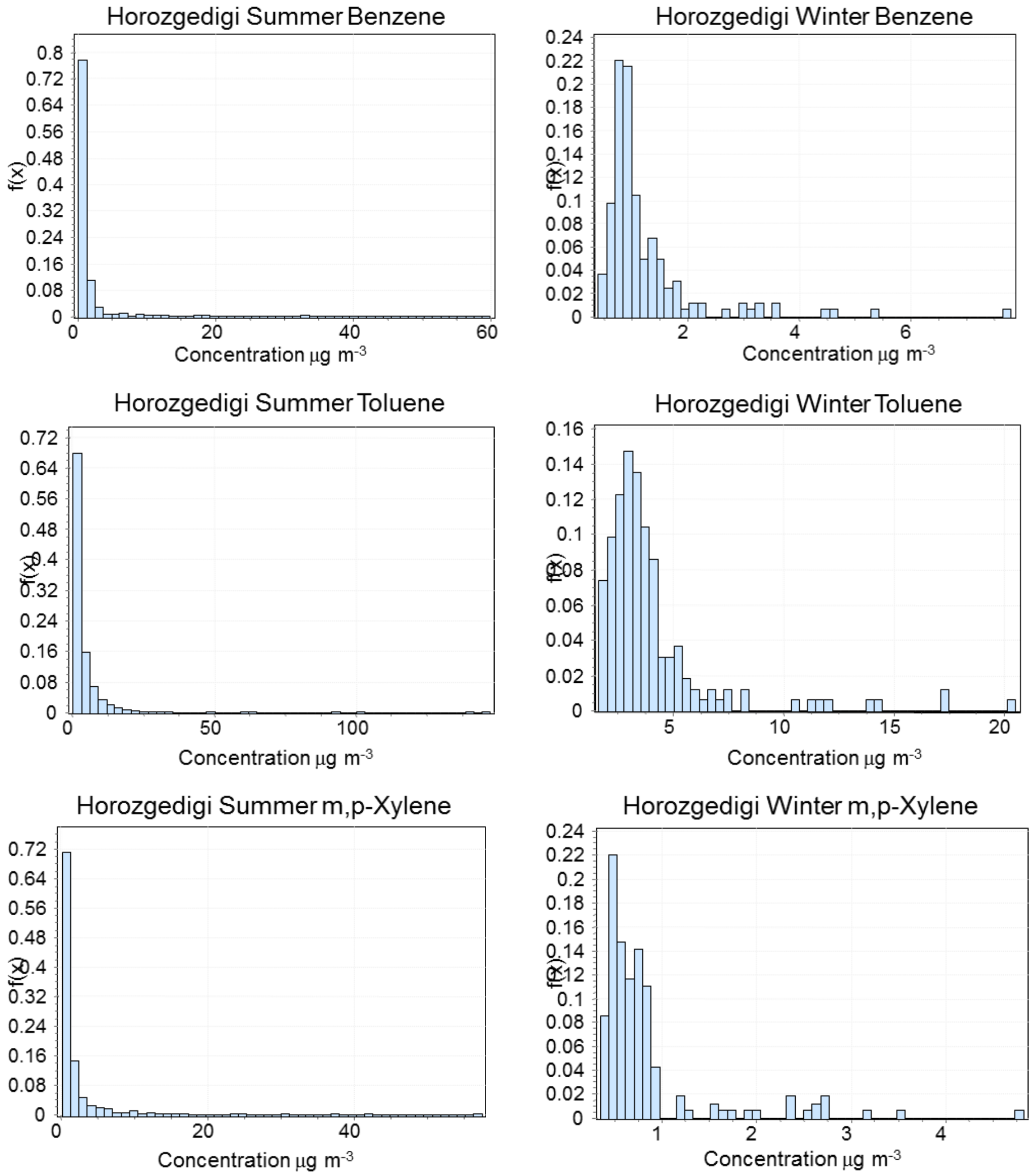


Figure 27 Typical frequency distributions of selected VOCs at Horozgediği station

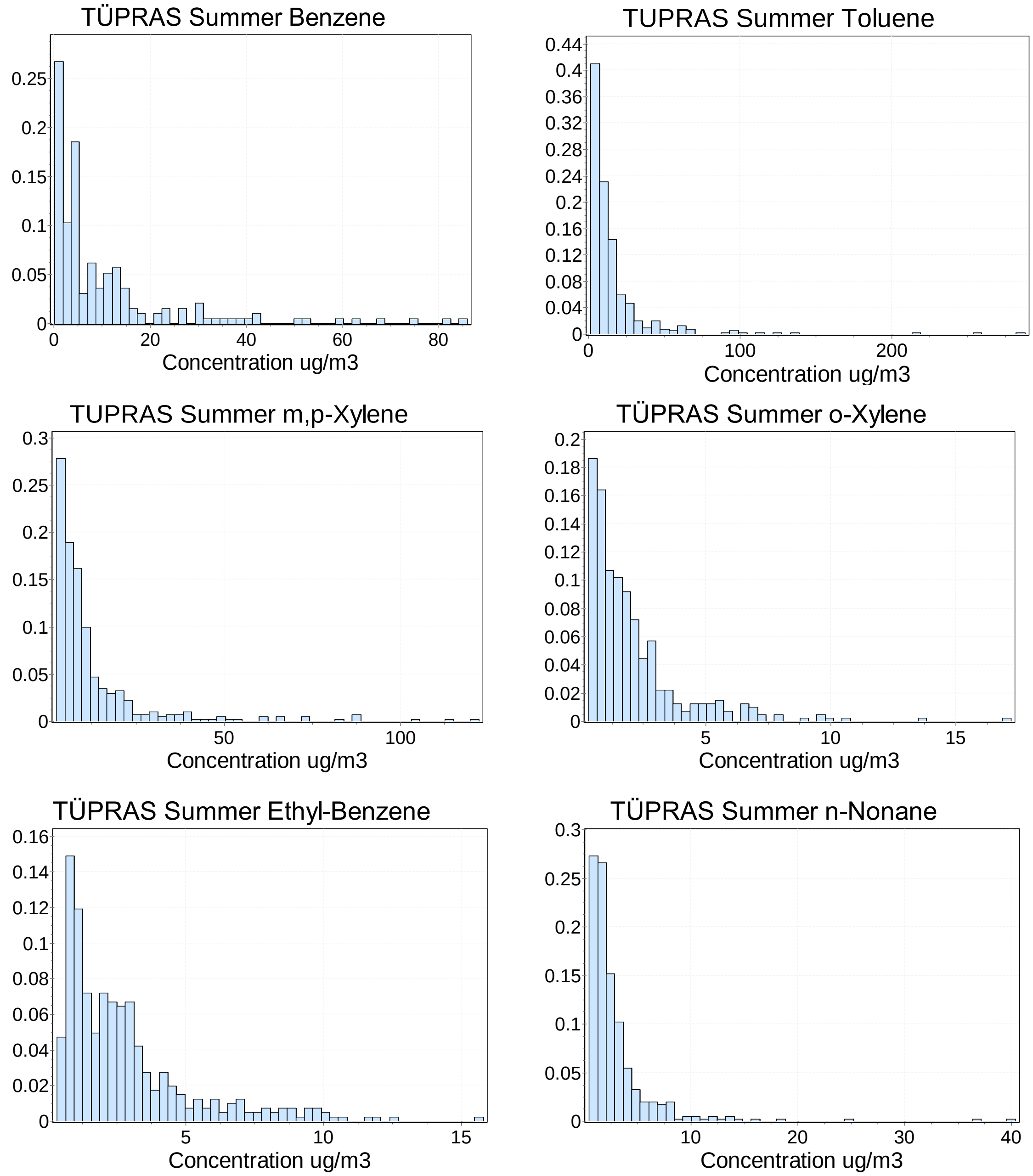


Figure 28 Typical frequency distributions of selected VOCs at TÜPRAŞ station

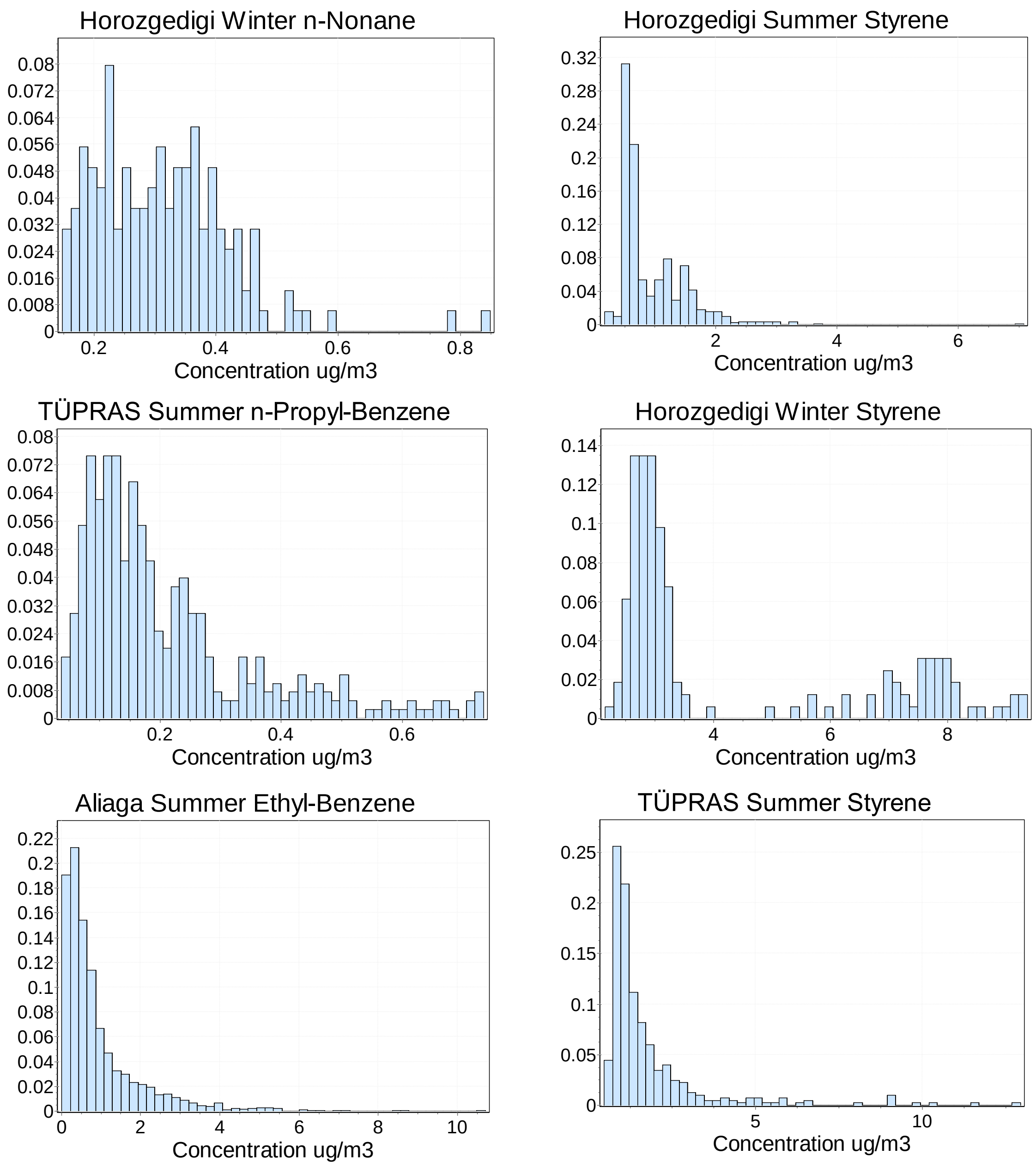


Figure 29 Some examples of less skewed distributions

4.1.4. Comparison of Concentrations between Stations

Concentrations of VOCs measured at the three stations in both summer and winter campaigns, are given in Figure 30. TÜPRAŞ data was generated in November 2006. The same TÜPRAŞ data is used in both summer and winter comparisons to provide a reference point for concentrations of VOCs measured in other two stations.

The VOC concentrations measured at TÜPRAŞ station is higher than both summer and winter concentrations of VOCs measured at other two stations. The only exception to this conclusion is observed in styrene in winter. Styrene has higher concentration at Horozgediği station. Since the location of the TÜPRAŞ station is in the immediate vicinity of very strong sources, namely the petrochemical complex and the refinery, such high concentrations are expected at TÜPRAŞ site.

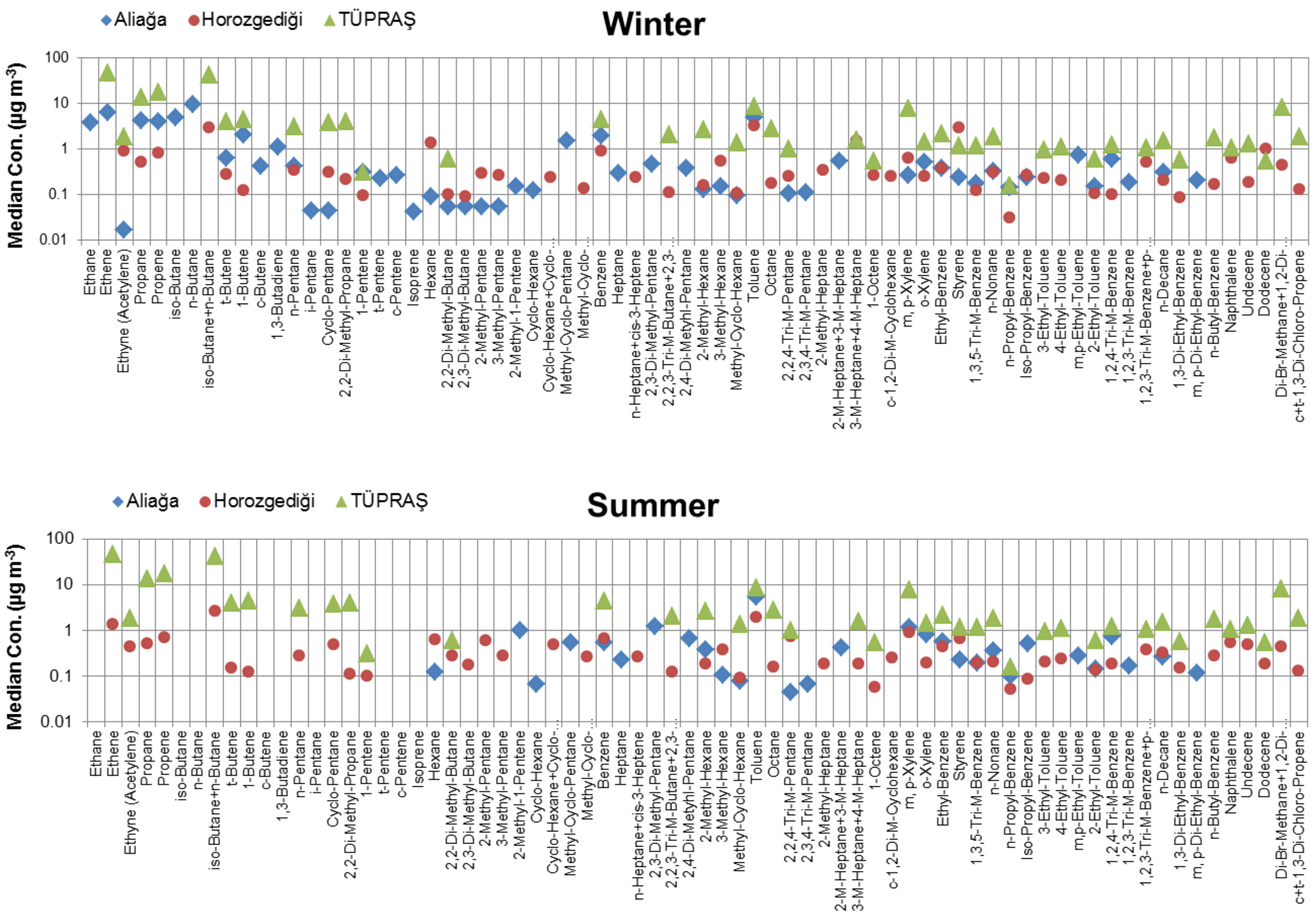


Figure 30 Comparison of VOC concentrations at three stations

Comparison of VOC concentrations measured at Aliağa and Horozgediği showed that both regions are under the influence of different VOC sources during winter season. This is shown in Figure 31, where Horozgediği-to-Aliağa concentration ratios of VOCs are plotted for the VOCs that are measured in both stations. Box and whisker plots of selected VOCs at Aliağa, Horozgediği and TÜPRAŞ stations, which is depicted in Figure 32, also show levels and distributions of these selected species in the three stations.

Winter concentrations of 1-butane, propane, 1,2,4-trimethylbenzene, propene, n-propylbenzene, 1-pentene, t-butene, benzene and o-xylene are higher at the Aliağa site. Among these 1-butene, t-butene, propane, propene, 1-pentene are light VOCs and components of liquefied petroleum gas and natural gas. Trimethylbenzene and propylbenzene are both traffic markers. Since other traffic markers, particularly BTX compounds have also relatively low ratios, then presence of these two compounds at the low end of the Horozgediği-to-Aliağa concentration ratios can be attributed to higher traffic influence on VOC concentrations measured at Aliağa. This is not surprising owing to different distances of these two stations to major roads. Horozgediği station is approximately 500 m to the Aliağa-Yeni Foça road and 4.0 km to the D550 Çanakkale-İzmir highway. However, Aliağa station is in the middle of the city traffic and approximately 300 m to the İzmir-Çanakkale highway. The occurrence of traffic indicators at relatively high concentrations at Aliağa indicates that the traffic influence on measured VOC concentrations is more important at Aliağa station then it is at Horozgediği region, as expected from the locations of the two stations.

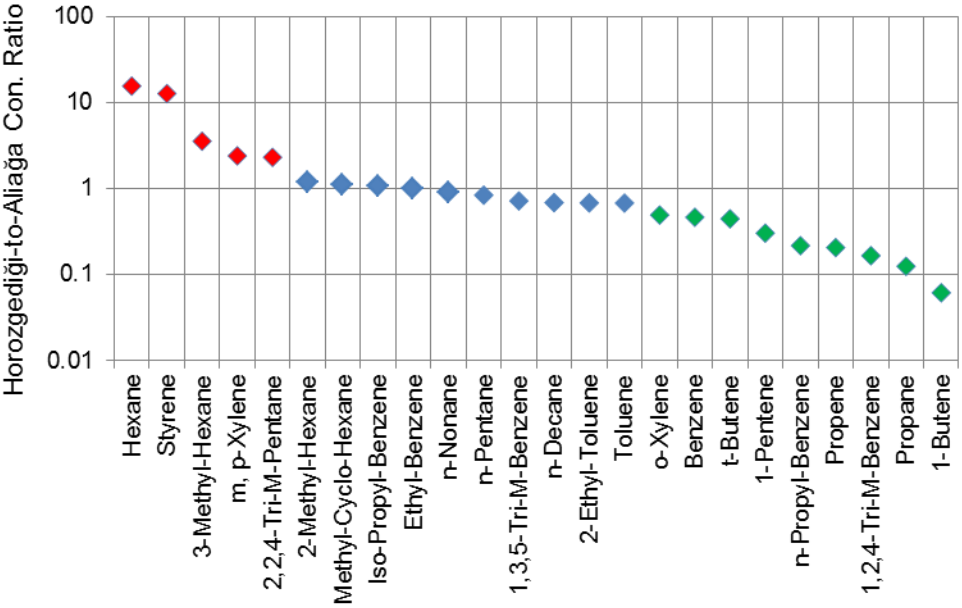


Figure 31 Horozgediği-to-Aliağa winter campaign median concentration ratios of common VOCs

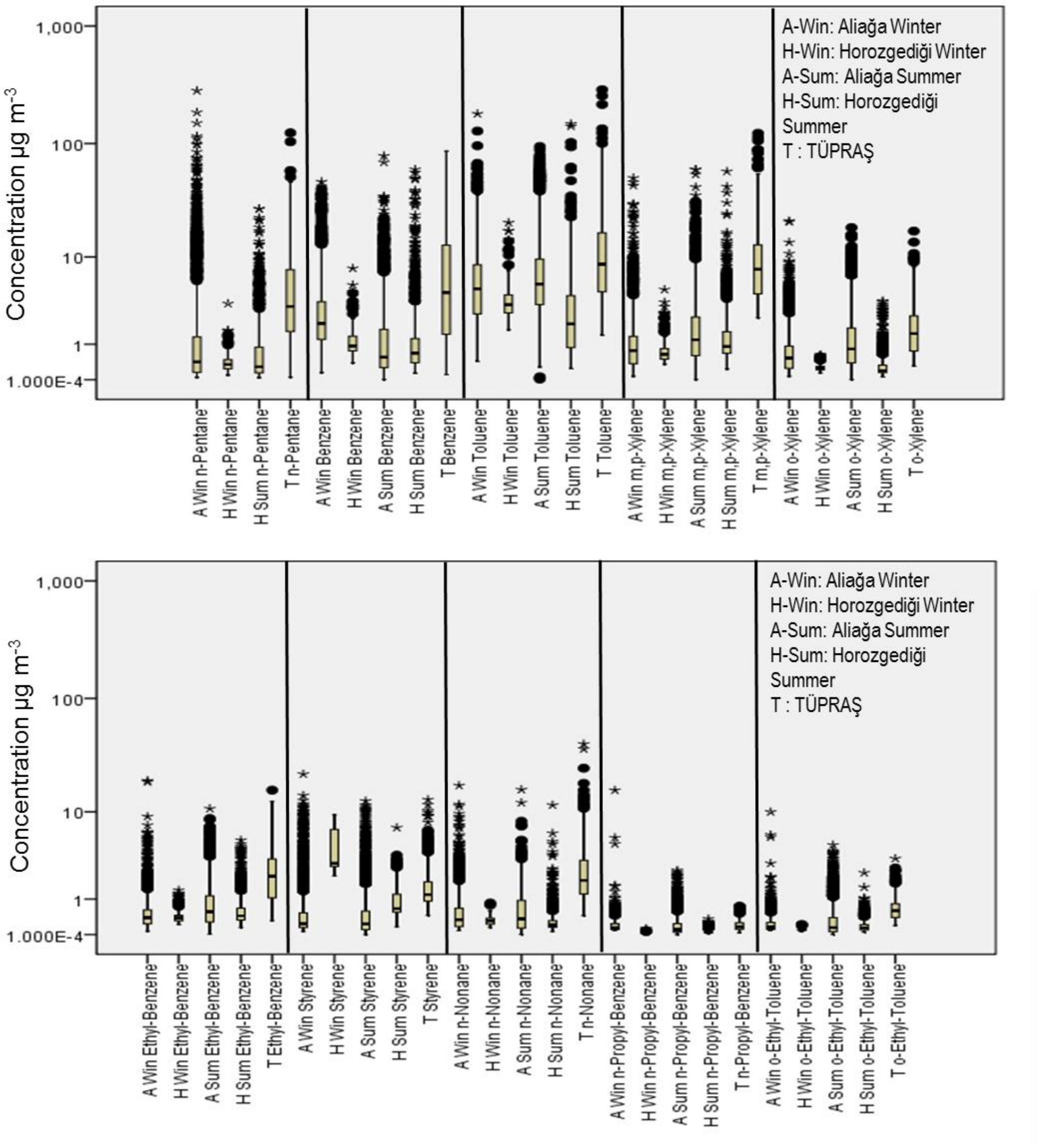


Figure 32 Box and whisker plots of selected VOCs at three stations

4.1.5. VOC profiles

VOC profiles refer to percent contribution of each VOC to total VOC concentration. Profiles can be used as a quick way of understanding important VOCs at a certain location. They can be particularly useful if VOC profiles at more than one site can be compared, because differences can be related to the sources of VOCs.

Since comparison is of VOCs calculated for Aliağa, Horozgediği and TÜPRAŞ stations is the objective in this exercise, profiles are calculated using 17 compounds that are commonly measured in all stations. VOC profiles calculated for the three stations are depicted in Figure 33. Profiles are calculated for summer and winter seasons separately in Aliağa and Horozgediği and for only one campaign for TÜPRAŞ site.

In all stations toluene has the highest contribution to total VOC concentrations. Toluene is followed by the m,p-xylene and benzene. High contribution of BTX compounds to total VOC concentrations is not special to Aliağa airshed, but observed in most ambient VOC studies (Kalabokas et al., 2001; Lai et al., 2004; Chan et al., 2002; Cai et al., 2010). However, there are some clear differences between the profiles calculated for different stations, which can be specific to Aliağa airshed. The most pronounced difference is in toluene contributions to the profiles at three stations. Contribution of toluene to total VOC mass is higher at Aliağa station compared to other two sites. This can be attributed to lack of evaporative sources at Horozgediği station. Evaporative source hypothesis is supported by higher toluene contribution at Aliağa during summer season, when temperature is high and evaporative sources become more significant contribution of toluene is expected to increase.

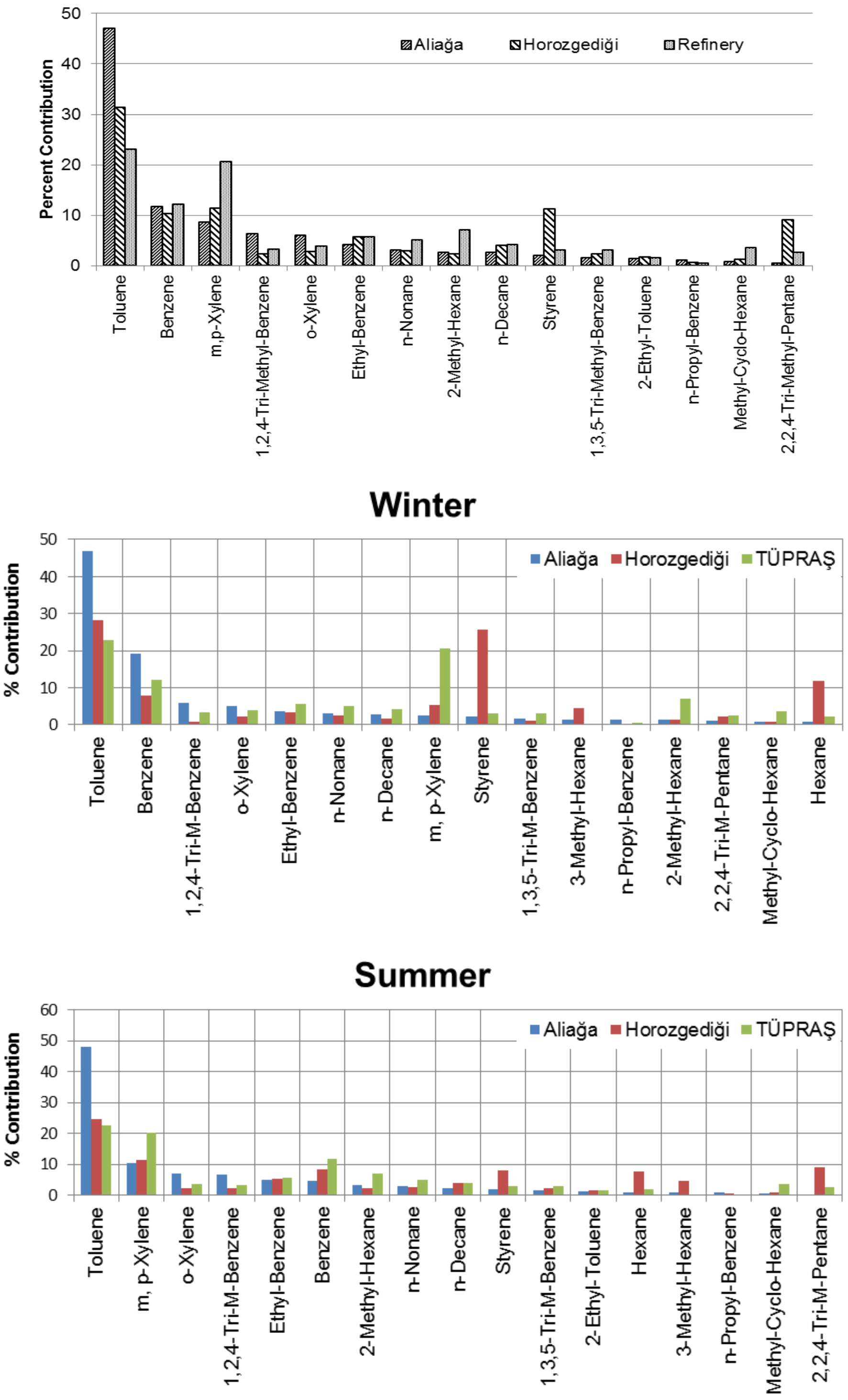


Figure 33 All seasons, winter and summer VOC profiles at Aliağa, Horozgediği and TÜPRAŞ stations with common VOCs

Another significant difference is higher contribution of styrene at Horozgediği station. As will be discussed later in the manuscript, this is an indication of more direct influence of the refinery and petrochemical complex on our Horozgediği station, because there is a styrene factory in PETKİM where styrene emissions are expected to be high. Contribution of the styrene plant is more significant at Horozgediği, because the Horozgediği station is downwind from PETKİM. Contribution of hexane is smaller at Aliağa than TÜPRAŞ and Horozgediği. This observation can also be related to TÜPRAŞ source of the hexane. Although hexane is a commonly used solvent in many applications and is expected to have higher share in the Aliağa profile, as in the case of toluene, its share is higher in Horozgediği and TÜPRAŞ profiles, probably because it is also a distillation product in TÜPRAŞ refinery which affects Horozgediği station located downwind from the refinery.

The data seem to suggest that Aliağa and Horozgediği stations are under the influence of different sources. VOC concentrations at Aliağa station seem to be influenced more from traffic and local evaporative sources (such as evaporation of solvents from paints, or evaporative emissions from inks etc.), whereas VOC concentrations at Horozgediği and TÜPRAŞ are more affected from emissions from the refinery and petrochemical complex as these sources upwind from our Horozgediği station. The contributions of individual VOCs to total VOC concentrations at Aliağa and Horozgediği stations are determined by proportions of the contributions of traffic, solvent evaporation, refinery and PETKİM sources.

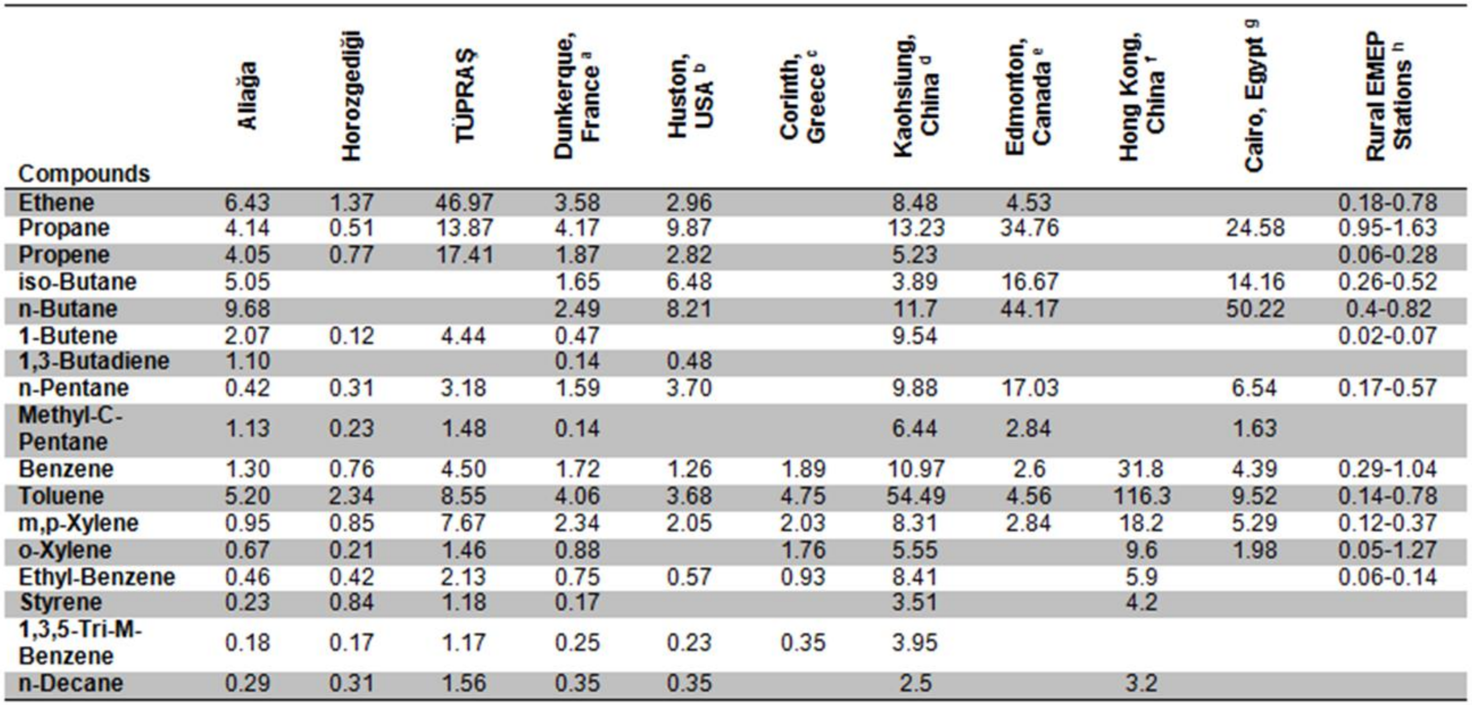
4.2. Comparison of Concentrations Levels with the Literature

Comparison of concentrations of VOCs measured at different sites is a challenging task. There are number of parameters affecting VOC concentrations. Differences in sampling and analytical protocols (including sampling duration, sampler location, sampling period, season and the year of sampling, analytical method and sampling technique) will affect the detected VOCs. Population of city and emission characteristics will have an influence on the VOC concentrations (Kuntasal, 2005). Therefore, in this section, regardless of sampling technique and sampling location, VOC data sets obtained from some industrial sites will be discussed. As the VOCs reported in each site are different, only selected and common VOCs are given in Table 15. The European Monitoring and Evaluation Programme (EMEP) data obtained from 14 rural stations located at different parts of Europe for the year 2005 is also given in the table to compare the obtained results with rural sites in Europe. The median values reported at Table 15 for C_2-C_5 in Aliağa Station are winter campaign results. The rest of the Aliağa and Horozgediği data are the median values of winter and summer campaigns.

In order to make a clear identification of the situation at Aliağa region, it is necessary to describe the characteristics of the other compared stations. Dunkerque, France (Badol et al., 2008) is located in northern France. The population of Dunkerque is 200 000. Approximately 200 factories are located in the region. Chemical and oil industries are the main industrial activities which emits 75% of the total VOC emissions in the Dunkerque region. An online GC system was used for the sampling and analyses. Hourly measurements were conducted for 1 year period. The sampling site is influenced by industrial and urban sources.

Houston, Texas (Kim et al., 2005) is a heavily industrialized area influenced by petroleum refineries and chemical manufacturing facilities. The city had a population of over 2 million people. VOC samples were collected at three locations. The result of Clinton Dr. is used for the comparison. Clinton Drive is located in the Houston Ship Channel area and is subject to extremely high concentrations of VOCs. Hourly integrated VOC samples were collected and analyzed with GC-FID system.

Table 15 Comparison of the median VOC concentrations (µg m^{-3}) with the literature



Compounds	Allağa	Horozgediği	TÜPRAŞ	Dunkerque, France [a]	Huston, USA [b]	Corinth, Greece [c]	Kaohsiung, China [d]	Edmonton, Canada [e]	Hong Kong, China [f]	Cairo, Egypt [g]	Rural EMEP Stations [h]
Ethene	6.43	1.37	46.97	3.58	2.96		8.48	4.53			0.18-0.78
Propane	4.14	0.51	13.87	4.17	9.87		13.23	34.76		24.58	0.95-1.63
Propene	4.05	0.77	17.41	1.87	2.82		5.23				0.06-0.28
iso-Butane	5.05			1.65	6.48		3.89	16.67		14.16	0.26-0.52
n-Butane	9.68			2.49	8.21		11.7	44.17		50.22	0.4-0.82
1-Butene	2.07	0.12	4.44	0.47			9.54				0.02-0.07
1,3-Butadiene	1.10			0.14	0.48						
n-Pentane	0.42	0.31	3.18	1.59	3.70		9.88	17.03		6.54	0.17-0.57
Methyl-C-Pentane	1.13	0.23	1.48	0.14			6.44	2.84		1.63	
Benzene	1.30	0.76	4.50	1.72	1.26	1.89	10.97	2.6	31.8	4.39	0.29-1.04
Toluene	5.20	2.34	8.55	4.06	3.68	4.75	54.49	4.56	116.3	9.52	0.14-0.78
m,p-Xylene	0.95	0.85	7.67	2.34	2.05	2.03	8.31	2.84	18.2	5.29	0.12-0.37
o-Xylene	0.67	0.21	1.46	0.88		1.76	5.55		9.6	1.98	0.05-1.27
Ethyl-Benzene	0.46	0.42	2.13	0.75	0.57	0.93	8.41		5.9		0.06-0.14
Styrene	0.23	0.84	1.18	0.17			3.51		4.2		
1,3,5-Tri-M-Benzene	0.18	0.17	1.17	0.25	0.23	0.35	3.95				
n-Decane	0.29	0.31	1.56	0.35	0.35		2.5		3.2		

[a] Badol et al., 2008; [b] Kim et al., 2005; [c] Kalabokas et al., 2001; [d] Lai et al., 2004; [e] Cheng et al., 1997; [f] Chan et al., 2002; [g] Abu-Allaban et al., 2002; [h] Solberg, 2007.

Corinth, Greece (Kalabokas et al., 2001) is located about 80 km southwest of Athens. The population of the city in 2001 was 30 000. Oil refinery is the main VOC source in the region. Samples were collected actively for 20 min on Tenax-TA adsorption tubes on several sites around oil refinery. The samples were analyzed with GC-FID system. Four sampling campaigns each of 10 days were conducted in 1997.

Volatile organic compounds were measured at two sites in Kaohsiung, Taiwan in the morning, in the afternoon and in the evening on 14 days in spring 2003 (Lai et al., 2004). The samples were collected using multi-bed stainless steel thermal adsorption tubes. The analyses were performed by using GC-FID and ECD systems. There are approximately 1.5 million inhabitant lives in Kaohsiung region. Six industrial sites are present in the region. In Table 15, the results of Hsiung-Kong site are presented.

Edmonton, Alberta Canada is an industrial city with a population of 600 000. The industrial site is located on an open filed with hydrocarbon storage tanks, oil refineries, smelter and chemical and shingle manufacturing plants. The VOC measurements were done at two sites (Cheng et al., 1997). Twenty four hour averaged VOC concentrations were measured every six days. Integrated ambient samples were collected in 6 L canisters. The samples were then analyzed by using GC-FID and GC-MSD systems. One monitoring station was at downtown Edmonton and the other one was near by the industrial site. The results of industrial site are given in Table 15.

Chan et al. (2002) measured VOCs in metropolitan area of Hong Kong. Hong Kong is a densely populated city with over 6.8 million people. The measurements carried out at 16 sites in four districts. The districts are at Tsim Sha Tsui (central business area), Mongkok (urban commercial), Sham Shui Po (old commercial and residential) and Kwai Chung (urban industrial). Sampling was conducted on nine winter days in 1998. Sampling times were at noon non-peak and evening peak hours. Samples were collected by stainless steel multi-sorbent tubes. The samples were collected for 15-30 min depending on the anticipated VOC levels in the air. The samples were then analyzed by thermal desorption GC-MSD system. In Table 15, results of seven measurements conducted at Kwai Chung region are presented.

In Cairo, Egypt (Abu-Allaban et al., 2002), levels of PM_{10}, $PM_{2.5}$ and VOCs were determined. Sampling was conducted in 1999 via two filed campaigns. Measurements were done at six stations on a 24 h basis. VOC sampling was conducted by using stainless steel canisters. Two of the sampling stations were industrial areas: El Massara and Shobra Khemia. The results of El Massara are given in Table 15.

The concentrations of ethene and propene at TÜPRAŞ site are the highest concentrations observed in the literature. This could be due to the location of TÜPRAŞ station as it is surrounded by petrochemical complex and refinery. Propane levels in TÜPRAŞ are comparable with Kaohsiung, China and Huston, USA; and lower than Edmonton, Canada and Cairo, Egypt.

For low molecular weight VOCs (C_2-C_5) observed at Aliağa, concentrations values are lower than the other sites. The only exception is observed at Dunkerque, France where C_4 compounds are observed less than Aliağa. This could be because of site selection. There are lots of vehicular activities around the site and C_4 compounds are generally resulting from evaporation of gasoline, liquefied petroleum gas (LPG) and natural gas (CNG) (Abu-Allaban, 2002; Watson et al., 2001; Lauchner and Rappenglück, 2010).

For low molecular weight compounds, concentrations observed at Horozgediği station are generally low and even as low as rural EMEP stations values, especially for propane and n-pentane. Propane is generally higher at locations which are under influence of refinery emissions and natural gas combustion (Buzcu and Fraser, 2006; Watson et al., 2001). N-pentane is an indicator of gasoline vapor, refinery (Lau et al., 2010; Leuchner and Rappenglück, 2010).

BTX levels at Aliağa and Horozgediği sites are lower than or comparable to the other industrial regions, except for styrene at Horozgediği station. Styrene concentration at Horozgediği site is observed four times that of in Dunkerque, France. Styrene levels observed at Kaohsiung and Hong Kong, China are 3.51 and 4.20, respectively. These levels are higher than the styrene levels in Horozgediği.

Though TÜPRAŞ station is located in between two strong VOC sources, BTX concentrations are not as high in Kaohsiung and Hong Kong, China. Observed BTX levels in TÜPRAŞ are comparable to corresponding concentrations measured in other industrial areas around the world.

4.3. Temporal Variations

Investigation of temporal variations in VOC concentrations is important, because it can provide information on the processes operating and factors affecting measured concentrations of organic compounds in the study area.

In this study temporal variation in VOC concentrations were investigated in three levels. First, time-series plots of concentrations were investigated and possible relations between concentrations and meteorology and emissions are discussed.

In the second level, diurnal variations observed in VOC concentrations are discussed. Presence of a specific diurnal pattern with clear indications of morning and afternoon rush-hours provides an easy way of assessing the contribution of traffic activities on observed VOC concentrations.

Finally in the third level, seasonal variations in VOC concentrations and the role of seasonal variations in meteorology and emissions on these variations are discussed.

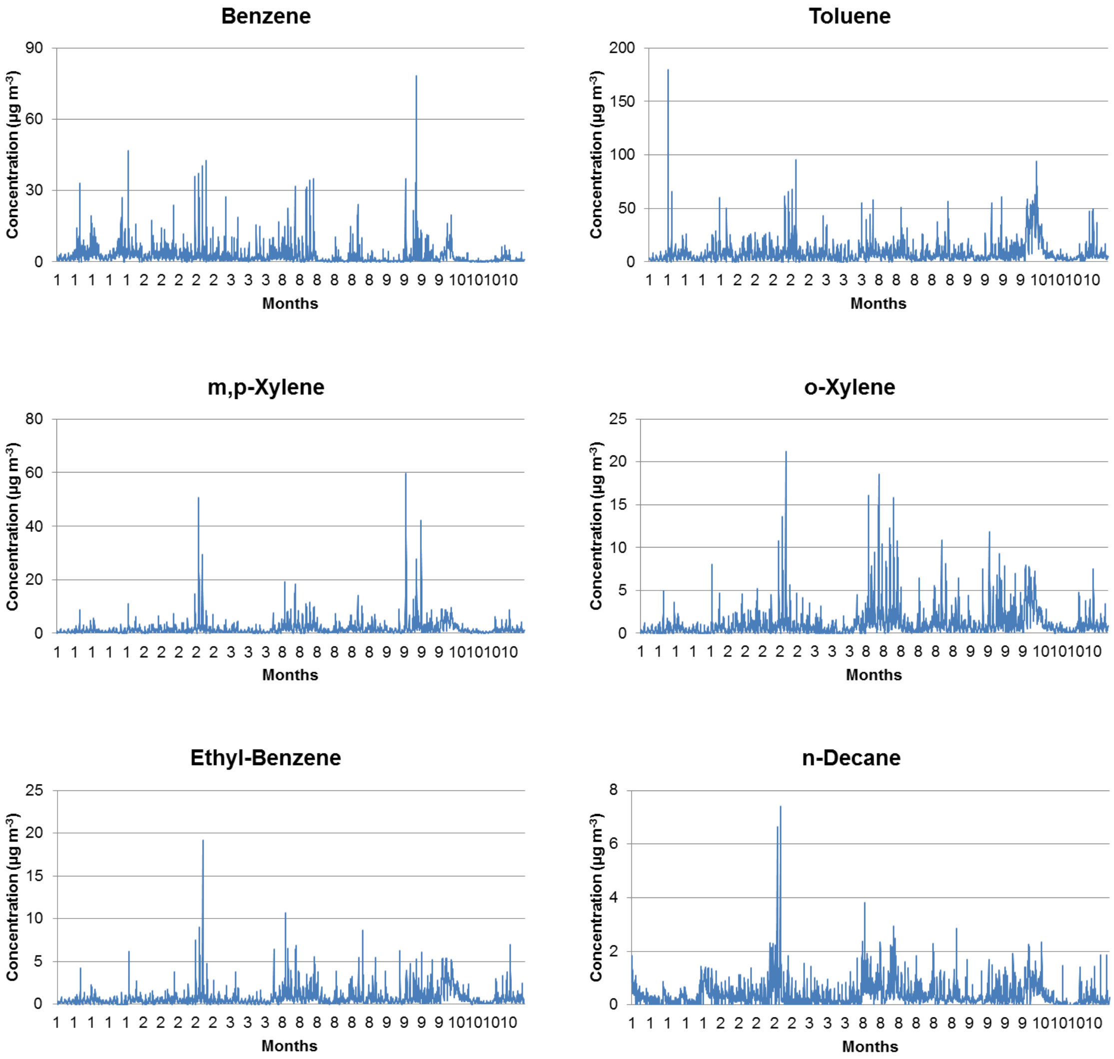
4.3.1. Episodic Variations in VOC Concentrations

Most of the pollutants in the atmosphere depict episodic variations in their atmospheric time series. Such sudden increases and decreases in the concentrations of species can be due to either sudden variations in emission strength or sudden variations in meteorology. Although variations in source strength cannot be completely ruled out, changes in meteorology are more common reason for episodes in concentrations.

The time-series plots of selected VOCs at Aliağa, Horozgediği and TÜPRAŞ stations are given in Figure 34, Figure 35 and Figure 36, respectively. All of these time series plots of VOC concentrations depict sharp and frequent episodes, which are typical for environmental data sets. In regional scale variations of transport patterns is the main source of episodic variations. It is frequently observed that transport of air masses from south of Turkey brings dust which generally reflects as sudden increases in soil-related parameters. The next day when a new air mass arrives from another wind sector, concentrations of the same species decrease quickly, thus generating an episode (Öztürk et al., 2012; Kubilay and Saydam, 1995). However, episodes in urban data sets are generally due to variation in surface wind direction and variation in emission strength. When wind blows from the direction of a strong pollution source, concentrations of all pollutants emitted from that particular source increase and pollutant concentrations rapidly decrease when wind changes direction and start to blow from another sector. Dependence of episodes on wind direction is frequently reported in the literature (Xie and Berkowitz, 2006; Kim et al., 2004; Song et al., 2008).

For VOCs the dominant source in urban and industrial atmosphere is the motor vehicle emissions. This means that high concentrations are observed when winds blow from main arteries in the city or from the direction of busy highways in suburbs, and concentrations rapidly decrease when wind direction shifts and starts to blow from sectors away from main traffic activity (Badol et al., 2008).

As discussed previously in Chapter 2, both of the stations used in this study have a specific distribution of traffic emissions. Aliağa station is in the center of the city, which means that a certain amount of traffic emissions occur all around the station. However, there is a very busy highway connecting city of İzmir to other cities like Balıkesir, Çanakkale.


Benzene

Toluene

m,p-Xylene

o-Xylene

Ethyl-Benzene

n-Decane

Figure 34 Time-series plots of selected VOCs at Aliağa station

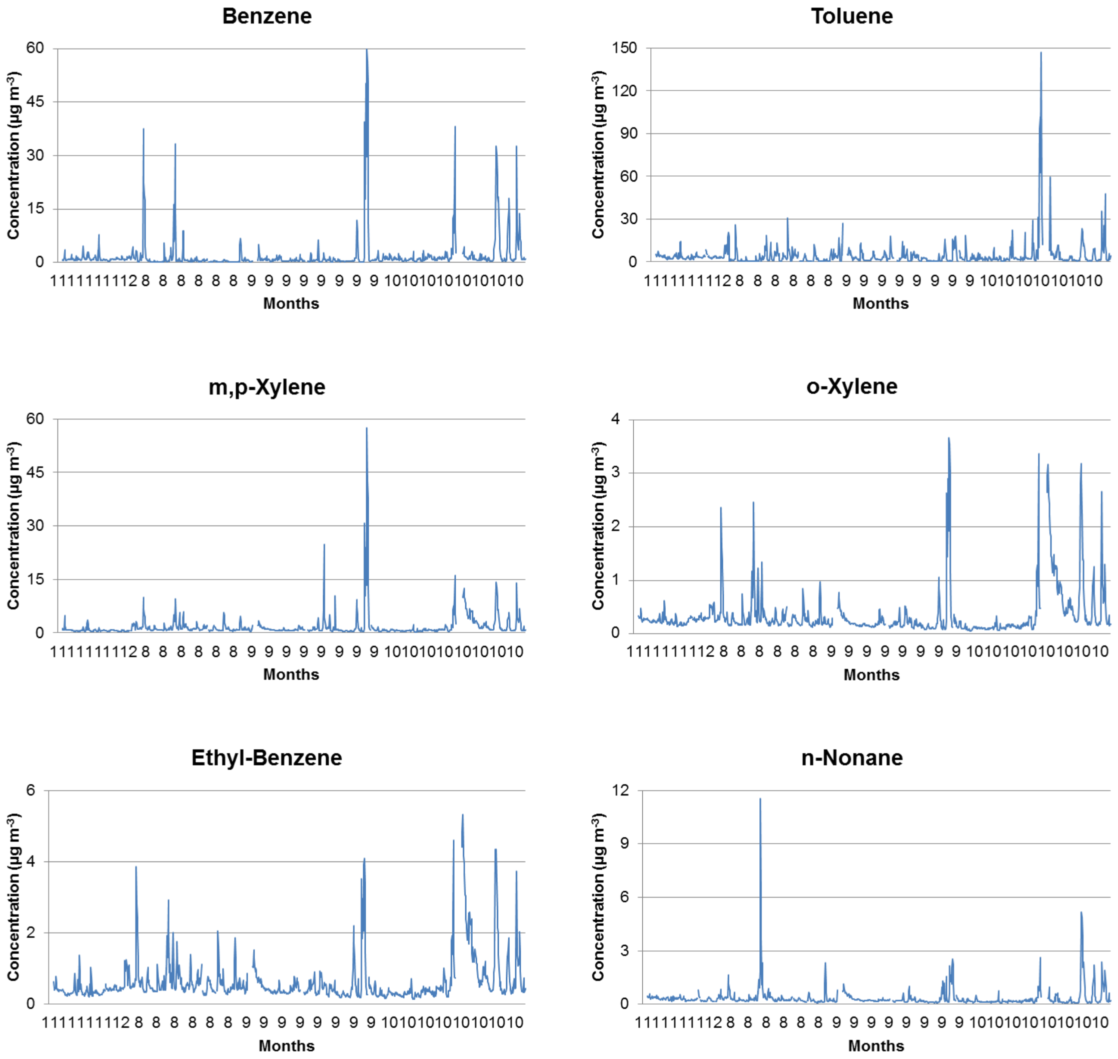


Figure 35 Time-series plots of selected VOCs at Horozgediği station

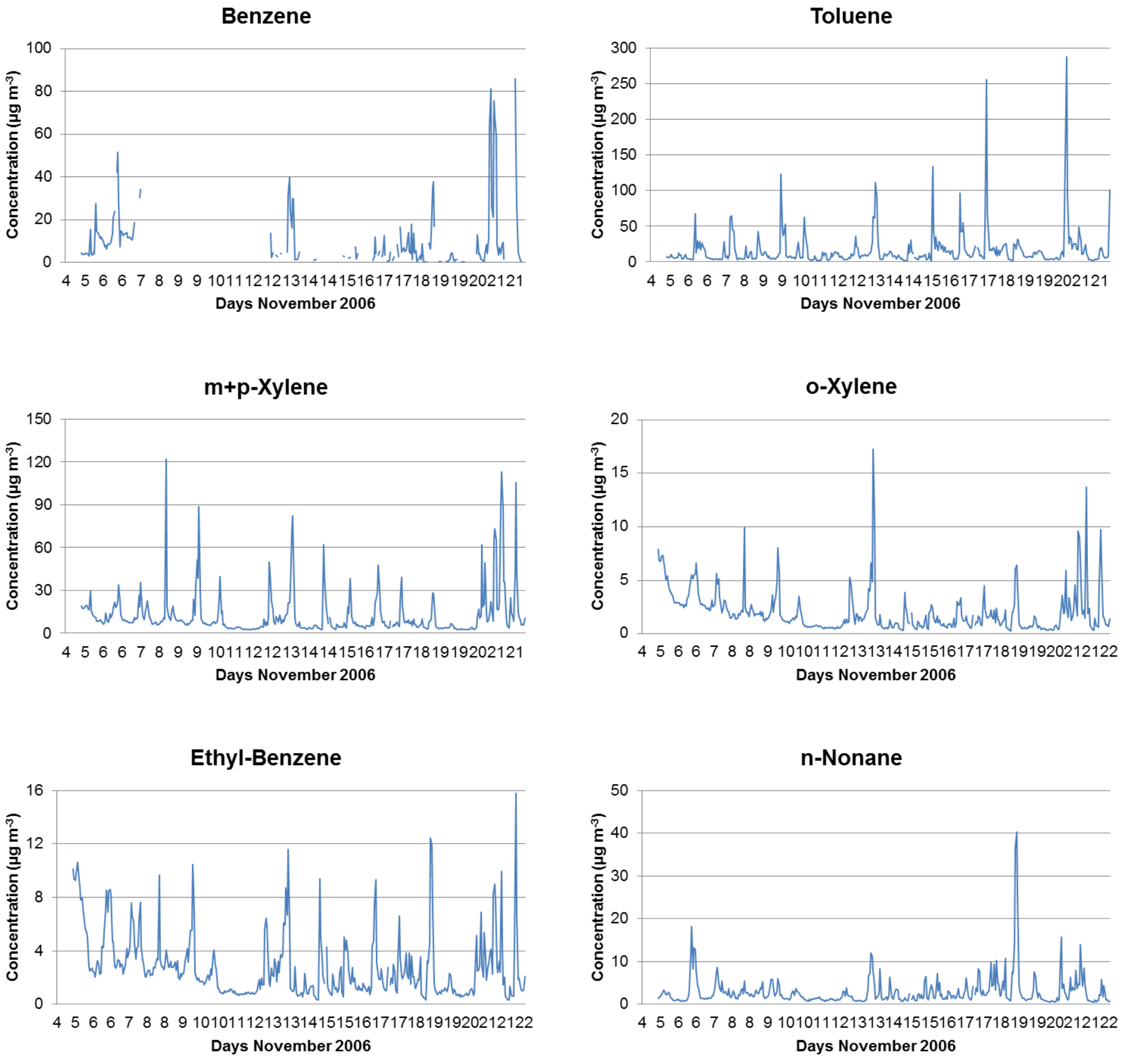


Figure 36 Time-series plots of selected VOCs at TÜPRAŞ station

There is a heavy traffic on this highway, which shows diurnal and seasonal variations, these variations and its effect on VOC concentrations measured in the two stations will be discussed later in Section 4.3.2. Horozgediği station, on the other hand is not under strong influence of very local emissions, but there are two roads with fair traffic which are not very far from the station. One of them is the İzmir-Çanakkale highway which lies approximately 4 km to the east of the station and the other one is the road that connects Aliağa to Yeni Foça village. İzmir-Çanakkale highway has much higher traffic intensity, compared to Aliağa- Yeni Foça road. Unfortunately hourly traffic counts are not available on these roads. However, it should also be noted that most of the discussions in following sections suggest that VOC concentrations measured at our Horozgediği station is strongly influenced from transport of VOCs from PETKİM petrochemical complex and TÜPRAŞ refinery, rather than traffic activity in the roads around the station.

Distribution of traffic emissions around Aliağa station and strong influence of the two very large industrial facilities on VOC concentrations at the Horozgediği stations have strong impact on seasonal and diurnal variations of VOCs measured in these stations. However, such systematic variation in VOC concentrations will be discussed later in Sections 4.3.2 in the manuscript. However, the same distribution of traffic emissions and industrial sources around stations also indirectly affect episodic changes in concentrations of VOCs as well. When winds blow from the direction of these sources high concentrations of different types of VOCs are recorded at the stations. However, when wind direction changes and wind starts to blow from sectors away from these roads, VOC concentrations suddenly decrease, generating an episode.

In addition to roads, which are the main sources of VOCs measured in urban areas, episodic changes observed in VOC levels in Aliağa are also affected by the distribution of industries around stations. High concentrations are expected to be observed in both stations when winds are blowing from the direction of two main industrial VOC sources, namely the refinery and petrochemical complex.

Probably, mixture of all these factors control episodes in VOC concentrations. However, one cannot differentiate these different sources using time-series plots in Figure 34, Figure 35 and Figure 36 alone. A more detailed discussion of source contributions to observed concentrations of measured species will be presented in Section 4.6, using multivariate statistics. However, here a simple wind sector analysis is performed to selected episodes recorded in Aliağa and Horozgediği stations to understand if these episodes can be qualitatively related to industrial and traffic sources around the stations.

The wind sectors used in this part of the study are given in Figure 37. The north sector is between 0 ± 22.5°. All other sectors are similarly positioned around true wind directions. It should also be noted that main industrial sources are included in different sectors in both stations.

There were many episodes during winter and summer sampling periods in both Aliağa and Horozgediği stations. However, few of them were suitable for wind sector analysis. Some were too diffuse and specific hours with well-defined high VOC concentrations were difficult to identify. In some there were missing VOC concentration data and for some there were no meteorological data. Three episodes at Aliağa and two episodes at Horozgediği stations were analyzed as example. These three episodes in Aliağa station are shown in Figure 38. Although only benzene concentrations are shown in the figure, most other VOCs also showed very similar variations in their concentrations. The first episode occurred in August 8, 2006. VOC concentrations started to increase at 18:00 hours, reached to the maximum value of 30 µg m^{-3} at 20:00 and once more at 23:30. Benzene concentration decreased to baseline levels at 05:00 in the next morning. The second episode occurred in August 28, 2006, between 16:00 hours and 24:00. Benzene concentration in this time period reached to 24 µg m^{-3} for one hour, but remained between 15-20 µg m^{-3} for several hours. The third episode analyzed occurred in September 15th between 16:30 and 1:00 in the next morning. Benzene levels in this episode reached to 34 µg m^{-3} for one hour.

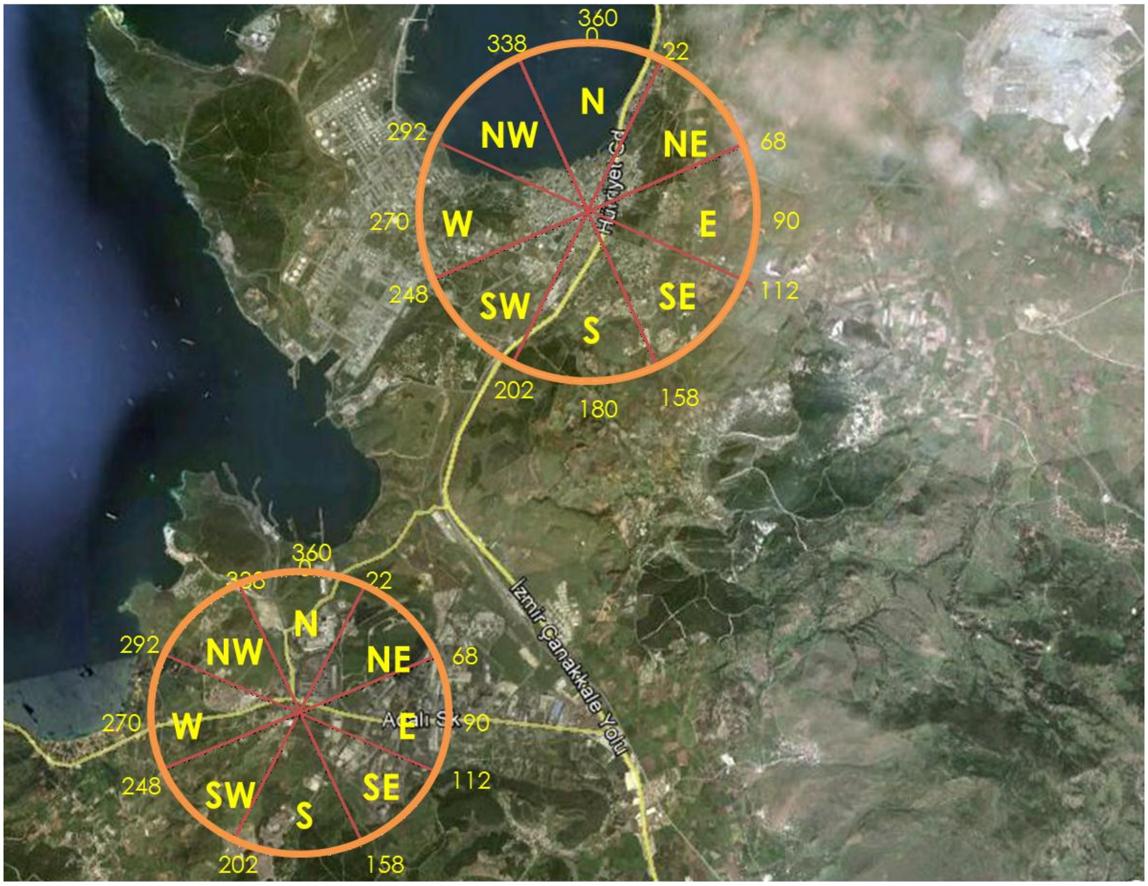


Figure 37 Sectors used in this part of the study and potential sources in these wind sectors

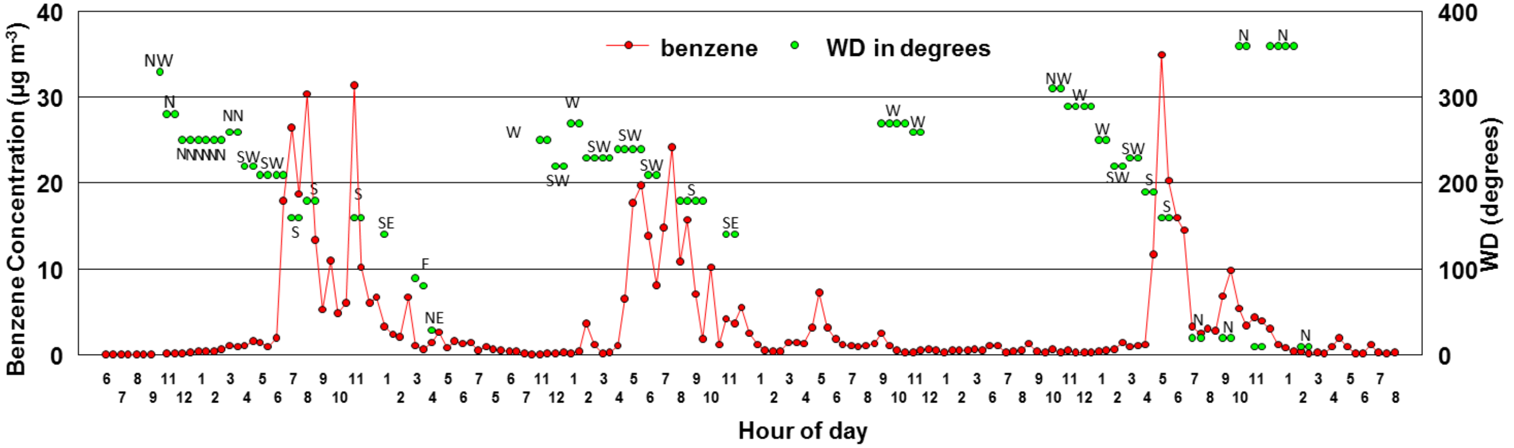


Figure 38 Relation between benzene episodes at Aliağa station with wind direction

There are two interesting points to note in these plots: (1) All three episodes occur in the afternoon and at night. This is not specific to these three episodes and observed very frequently. Hourly average concentrations of VOCs, which will be discussed in Section 4.3.2 also showed high VOC levels in the afternoon and at night. This is explained by a unique diurnal variation in wind direction in Aliağa region, which will be discussed later in Section 4.3.2 and depicted in Figure 43. The wind direction, measured in degrees, at the Aliağa Meteorological station, in the hours corresponding to the three episodes is also depicted Figure 38. (2) All episodes are observed when winds blow from SW and S sectors. In Figure 37, it can be seen that these two sectors include Southern parts of the Aliağa village, part of the İzmir-Çanakkale highway and part of the petrochemical complex. It is not possible to identify one single source for these episodes observed at the Aliağa station, because both the highway and petrochemical complex can be responsible. Obviously one of these two sources or a combination of both are responsible for at least some of the episodes observed in Aliağa village. It should also be noted that, high benzene concentrations were not observed at every time when winds blow from the S and SW sectors. This is probably S and SW sectors cover approximately 2 km distance at the point where industries and highway is located. They bring high concentrations of VOC only when wind blow from a part of that sector where the petrochemical complex and road is located.

The two episodes selected for analysis at the Horozgediği station are given in Figure 39 and Figure 40. The first episode occurred at 10 August 2006. In that day VOC concentrations started to increase 7:00 in the morning, reached to a maximum at 10:00, then, gradually decreased to background levels at 15:00 hours.

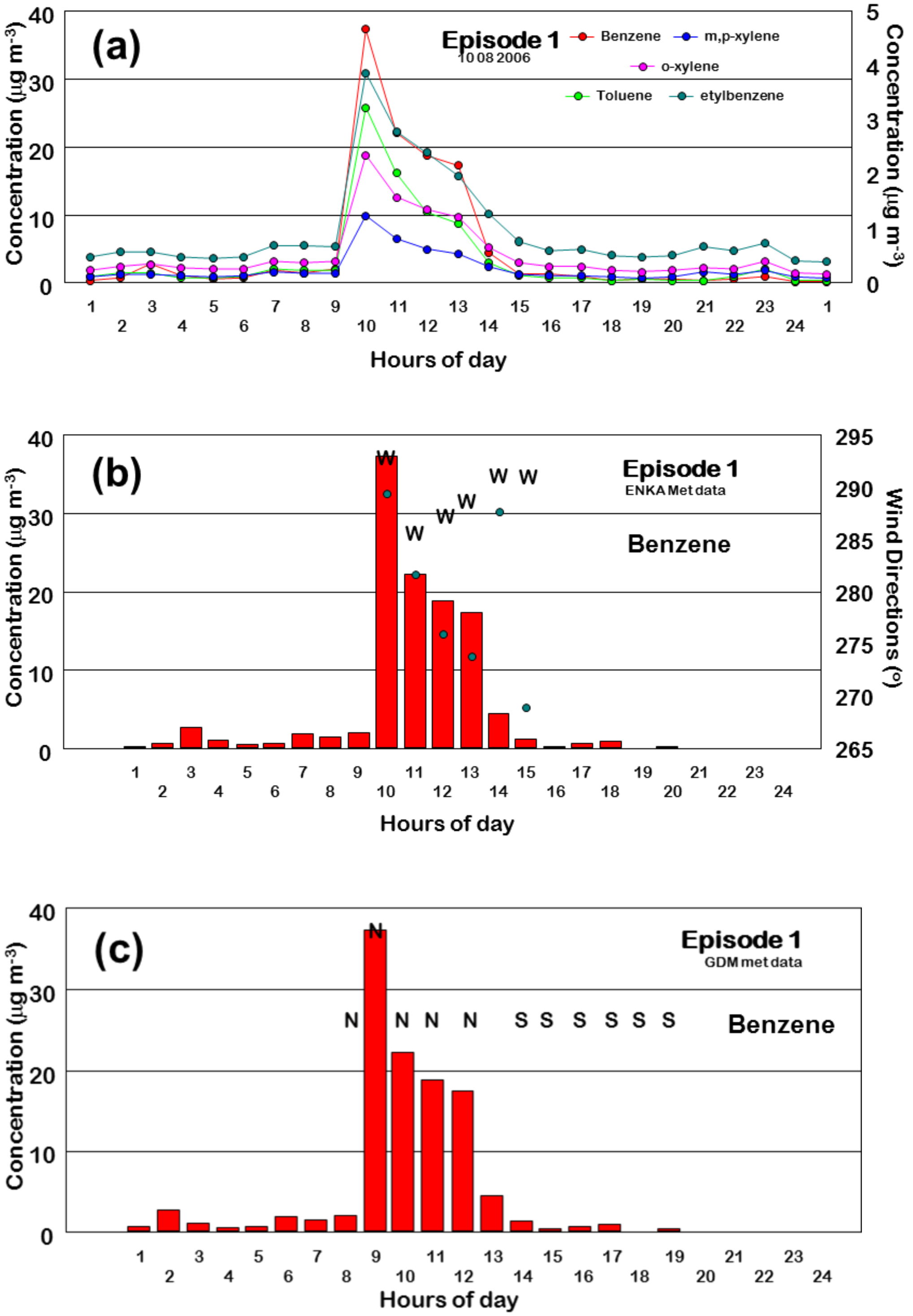


Figure 39 The relation between the BTX episode 1 observed at Horozgediği station and wind direction

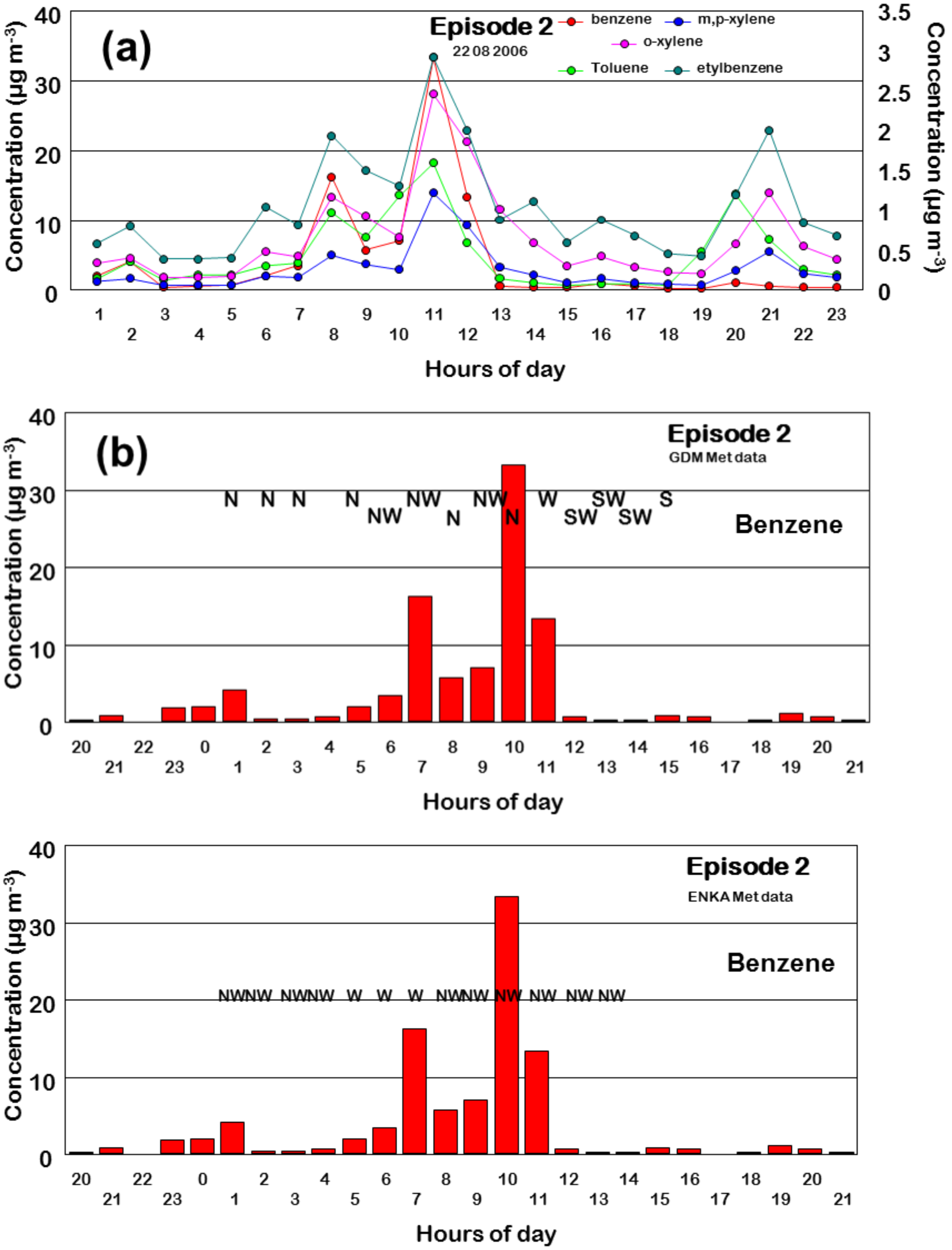


Figure 40 The relation between the BTX episode 2 observed at Horozgediği station and wind direction

The wind direction, which was recorded at the meteorological station in the course of the episode, is given in Figure 39b. Occurrence of the episode coincided with winds from N sector. Concentrations rapidly decreased when winds shifted to S later in the afternoon.

The second episode occurred at 22 August 2006. At this day concentrations of VOCs started to increase at 10:00 in the morning, reached to maximum at 11:00 then gradually decreased to background levels at 15:00. Wind record, measured at Aliağa Meteorological station during the course of the episode is depicted in Figure 40b. Wind record shows that winds were W and NW during episode hours. Initially winds from N did not bring high VOC to the station, but after 5:00 - 6:00 in the morning VOC concentrations started to increase with NW winds and 11:00, winds shifted to SW and VOC concentrations rapidly decreased to background levels.

Both episodes analyzed at the Horozgediği station correspond to N and NW wind sectors. It can be clearly seen from Figure 37 that these wind sectors include the two most important VOC emission sources in the Aliağa region, namely the refinery and the PETKİM, petrochemical complex. This observation clearly demonstrated that the TÜPRAŞ and PETKİM can explain at least some of the episodes observed at the Horozgediği station.

There is one important question related to the above discussion. Sources affecting episodes observed in the two stations do not seem to be the same. At Aliağa station, emissions from part of the village, from the highway and from PETKİM can all account for observed episodes in the city. However, sources affecting episodic increases at Horozgediği are fairly clear and expected, namely the PETKİM and TÜPRAŞ. This conclusion of different sources affecting Aliağa and Horozgediği stations were also supported by diurnal and weekday-weekend variations in VOC concentrations, as will be discussed later in the manuscript.

Another point that should be noted is the small number of episodes included in this discussion. Main reason is the lack of adequate amount of reliable meteorological data. There are two meteorological stations in the area. One of them is situated at the outskirts of the Aliağa village and operated by the General Directorate of Meteorology. The other meteorological station was located at our Horozgediği Station and operated by the ENKA Power Plant. Unfortunately, wind data at these two stations do not agree. We believe in the meteorological data generated by the General Directorate of Meteorology (GDM), but not so much to data generated at the ENKA station (although ENKA station was few meter to our measurement site), because whenever we used meteorological data from GDM station we were able to get consistent and logical results. On the other hand, when meteorological data from ENKA station is used results were generally difficult to interpret. For example, we run a dispersion model using met data from both stations. SO_2 concentrations calculated at the point of our Horozgediği station was reasonable and compared well with measurement results when GDM meteorological data were used, but SO_2 concentrations at the same point were zero at all hours when ENKA meteorology was used. Because of this inconsistency we decided to use only GDM meteorological data in our data interpretation. Unfortunately there were large amount of missing data in GDM data set. This affected our data interpretation whenever, meteorological information is needed. It was also the main reason for small number of episodes analyzed in this section.

4.3.2. Diurnal Variations

Concentrations of VOCs and other pollutants generally depict well-defined diurnal cycles in urban (Qin et al., 2007; Nguyen et al., 2009) and industrial (Ho, et al., 2004; Jorquera and Rappenglück, 2004) atmosphere. The patterns may differ both from one place to another and from one compound to another depending on their sources. Best documented, among these patterns, is the diurnal cycles observed in traffic related pollutants, which consisted of high concentration during morning and afternoon rush hours (Qin et al., 2007). Combustion related pollutants, on the other hand, depict high concentrations during nighttime owing to more extensive heating of houses during cold nights (Sharma et al., 2000). Since the diurnal patterns shown by pollutants depend on their sources, such cycles can be used to obtain information on potential sources affecting concentration of a given pollutant. However, it should also be noted that information obtained from diurnal variations of parameters cannot be considered conclusive, because these patterns can be modified by both short-term and long-term variations in local meteorology.

Daytime-to-nighttime concentration ratios (D/N ratio) of VOCs are shown schematically in Figure 41 and Figure 42, for Aliağa and Horozgediği stations, respectively.

Daytime-to-nighttime concentration ratios of VOCs at Aliağa station, which is shown in Figure 41, have two different patterns in summer and winter seasons. In the winter most of the VOCs measured in this study have higher daytime concentrations than nighttime concentrations. The difference is not dramatic but consistent. The ratio varies between 0.5 for heptanes and 1.8 for 1,2,3-trimethylbenzene with an average value of 1.2 ± 0.3. It should be noted that small standard deviation (σ) value indicates that higher daytime concentration is consistent in most of the VOCs measured.

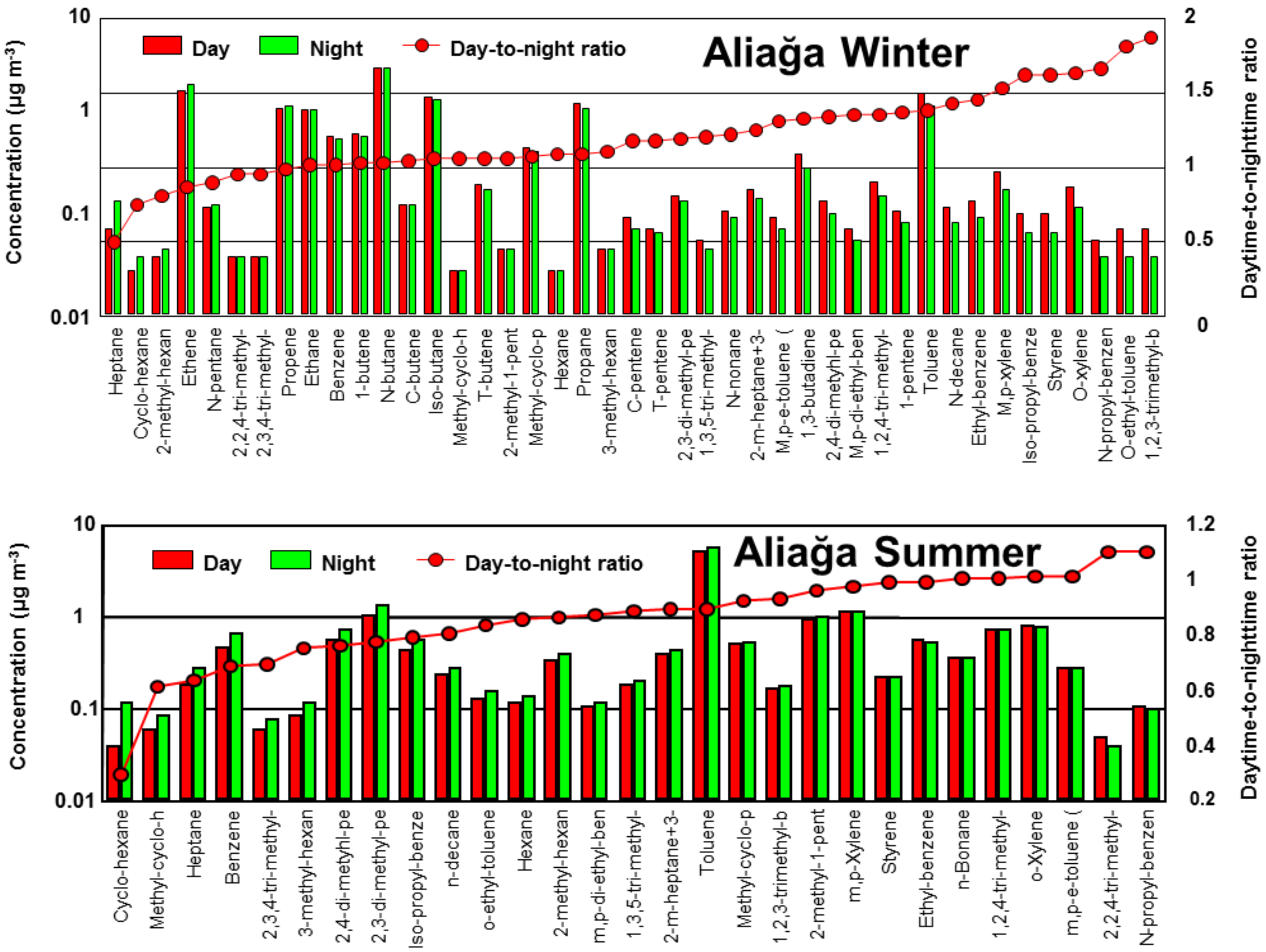


Figure 41 Day-time and night-time concentrations of VOCs at Aliağa station

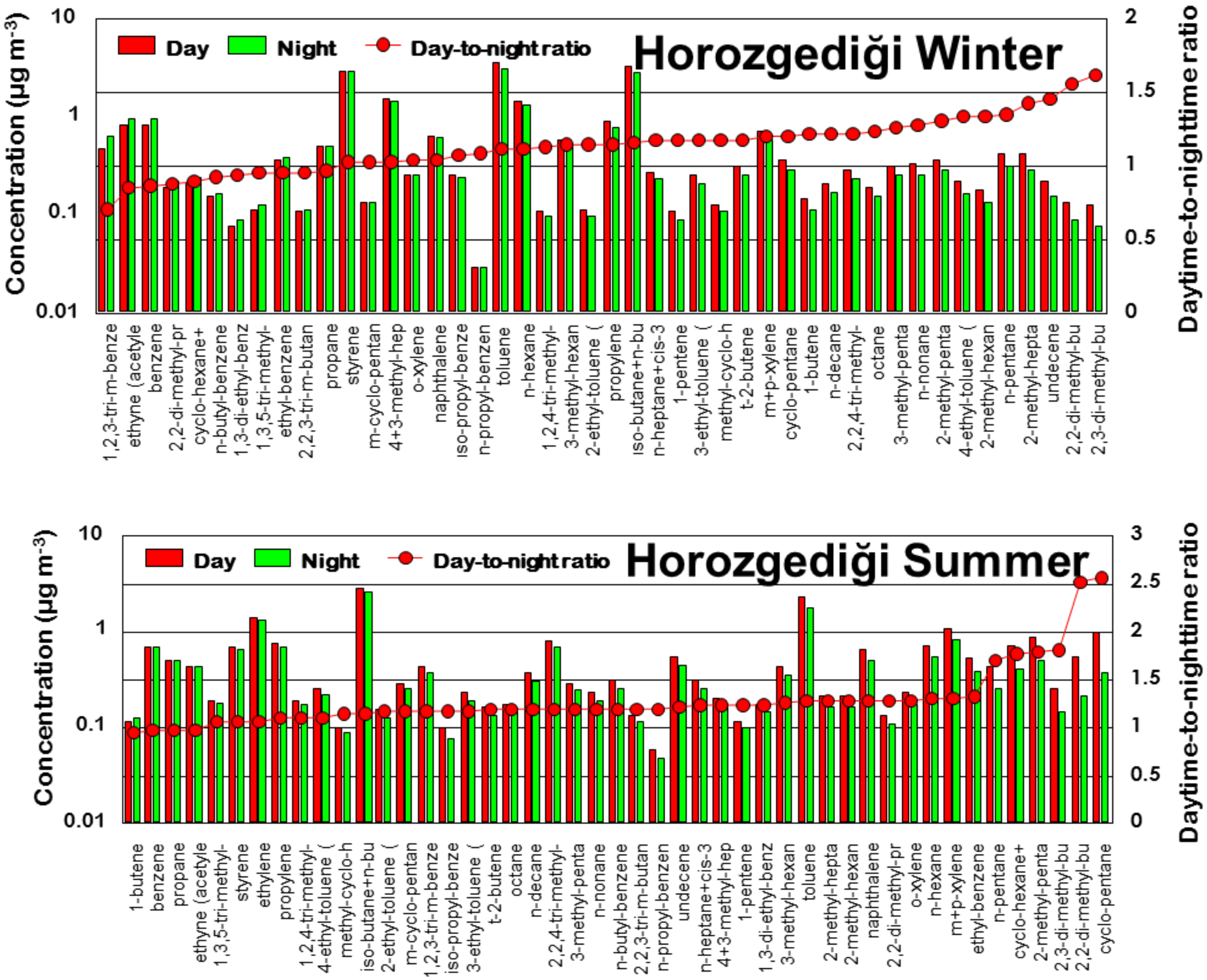


Figure 42 Day-time and night-time concentrations of VOCs at Horozgediği station

In the Aliağa summer data set, which is depicted in Figure 41b however, an opposite trend was observed. Nighttime concentrations of VOCs are higher than their daytime concentrations. The D/N ratios varied between 0.3 for cyclohexane and 1.1 for n-propylbenzene. Average D/N ratio for summer season is 0.86 ± 0.18. Again small standard deviation (σ) value indicates a trend that is consistent in most VOCs.

Hourly average concentrations of selected VOCs (BTX compounds) at Aliağa station, in both seasons are given in Figure 43, for both summer and winter seasons. There is no significant difference in diurnal variation of these VOCs between the two seasons. In both seasons diurnal variation of BTX compounds show influence of traffic emissions on their concentrations in Aliağa atmosphere, which is typical in most urban airshed.

In a typical urban atmosphere, where traffic is the dominating source of VOCs, one expects to see an increase in VOC concentrations between 8:00 and 10:00 in the morning then a decrease in their concentrations during the day and another increase after 17:00 hours in the afternoon, corresponding to increased traffic activity when everybody return to their homes (afternoon rush hour). However in Aliağa, diurnal pattern is slightly modified. VOC concentrations starts to increase at 08:00 in the morning as expected, but they do not decrease after 10:00 hours. Instead, concentrations continue to build-up during the day and reach to a maximum between 17:00 and 18:00 in winter and between 18:00 and 19:00 in summer. In other words afternoon rush hour peak, in VOC concentrations, is clear, but morning rush hour peak is masked by gradual built up of concentrations during the day.

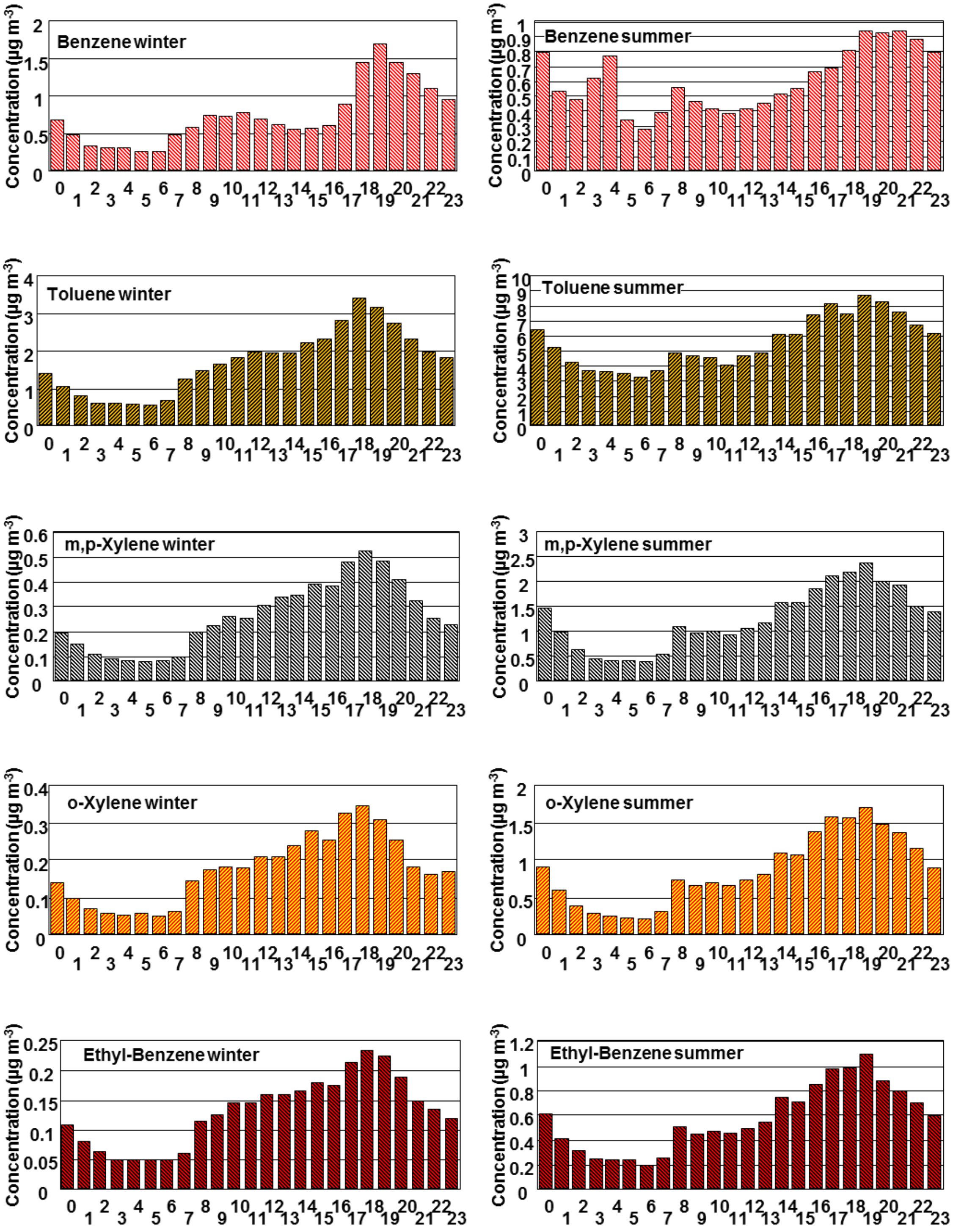


Figure 43 Diurnal variation of BTX Compounds at Aliağa station

Observed gradual buildup of VOCs during the day indicates that traffic is not the only source of VOCs at Aliağa. Observed modification of traffic pattern can be explained by solvent evaporation from various sources, such as paint, photocopying, furniture, carpets etc. for compounds like toluene. However, modification of traffic pattern is observed in concentrations of most of the VOCs and solvent evaporation is not an important source for many of them.

We believe that transport of VOCs from nearby industries, particularly from TÜPRAŞ and PETKİM during daytime is the main reason for observed modification in VOC diurnal patterns. There is a very unique micrometeorological feature in Aliağa region, which will be discussed later in the manuscript. This meteorological feature results in an hourly shift of wind direction throughout the day. This shift is very constant and occurs every day. This meteorological pattern brings pollutants from industries to Aliağa downtown during day time. This transport causes an increase in VOC levels during the day, when traffic activities decreases after the morning rush hour.

Since there is no significant difference between diurnal variations of VOC concentrations in summer and winter seasons higher D/N ratios observed in winter season, which was discussed previously cannot be explained by a difference in the diurnal variations in concentrations. This observed difference in D/N ratios in summer and winter seasons is probably due to variation in traffic patterns due to longer sunlight period in the summer. In calculating day-time concentrations, period between 07:00 in the morning and 18:00 in the afternoon was taken as “day” and period between 19:00 in the afternoon and 06:00 in the morning was taken as “night”. This division was the same in summer and winter campaigns. However, traffic activities shifted to so-called “night” period in the summer when sunlight period was longer. Taking the time 1 hour back in winter and one hour forward in summer also resulted in shifting traffic activities to our “night” period in the summer.

Daytime, nighttime VOC concentrations and D/N ratio for Horozgediği Station is given in Figure 42. Unlike the pattern observed at Aliağa station, summer and winter D/N ratios are not significantly different at summer and winter. Day time concentrations are higher than night time concentrations in both seasons. The D/N concentration ratio varies between 0.7 and 1.7 with an average value of 1.1 ± 0.2 in winter and between 0.9 and 2.6 with an average value of 1.3 ± 0.32 in summer. Again small standard deviation (σ) values both in summer and winter indicates that D/N values vary in a fairly small range.

Hourly average concentrations of selected VOCs (BTX compounds) at Horozgediği station are given in Figure 44. Morning and afternoon rush-hour peaks which were well-defined at Aliağa station do not exist at Horozgediği data. In the winter VOC concentrations are slightly higher during day time, but the difference is not much. That is why average D/N ratio in winter is 1.1. In summer however; although concentrations at each hour is smaller than corresponding concentrations measured in winter, there is an interesting day time increase in VOC concentrations. Concentrations of, not only BTX compounds start to increase at 7:00-8:00 in the morning, reaches a maximum at approximately 09:00 or 10:00, then gradually decrease, reaching to prevent concentrations at 16:00. This pattern is not specific to BTX compounds, but also observed in most of the VOCs.

Observed increase in VOC concentrations during morning hours in summer season cannot be attributed to traffic, because there is no afternoon rush-hour peak in the figure. This is supported with non-traffic behavior depicted by well documented traffic markers, such as NO and NO_2, at Horozgediği station.

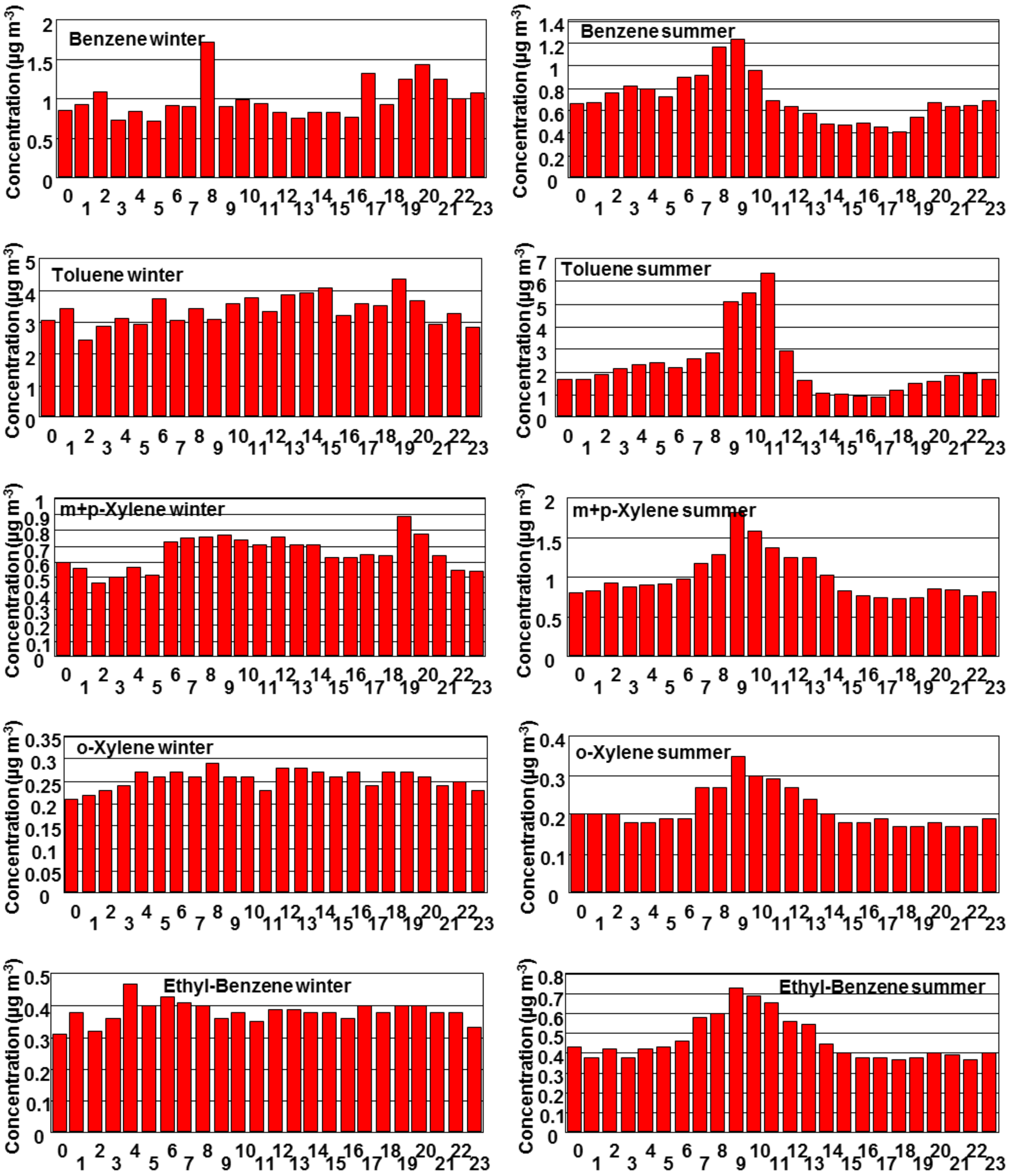


Figure 44 Diurnal variation of BTX compounds at Horozgediği station

Diurnal variation in concentrations of SO_2, NO and NO_2 at Aliağa and Horozgediği stations are depicted in Figure 45. Concentrations of SO_2, NO_2 and NO are measured at our station in the Aliağa. However, data were obtained from ENKA air quality monitoring station at the Horozgediği site. Actually that was the main reason why our Horozgediği station is co-located with ENKA air quality monitoring station. Ozone and PM_{10} concentrations were also measured at both Aliağa and Horozgediği stations. However, discussion of their temporal behavior is beyond the scope of this study.

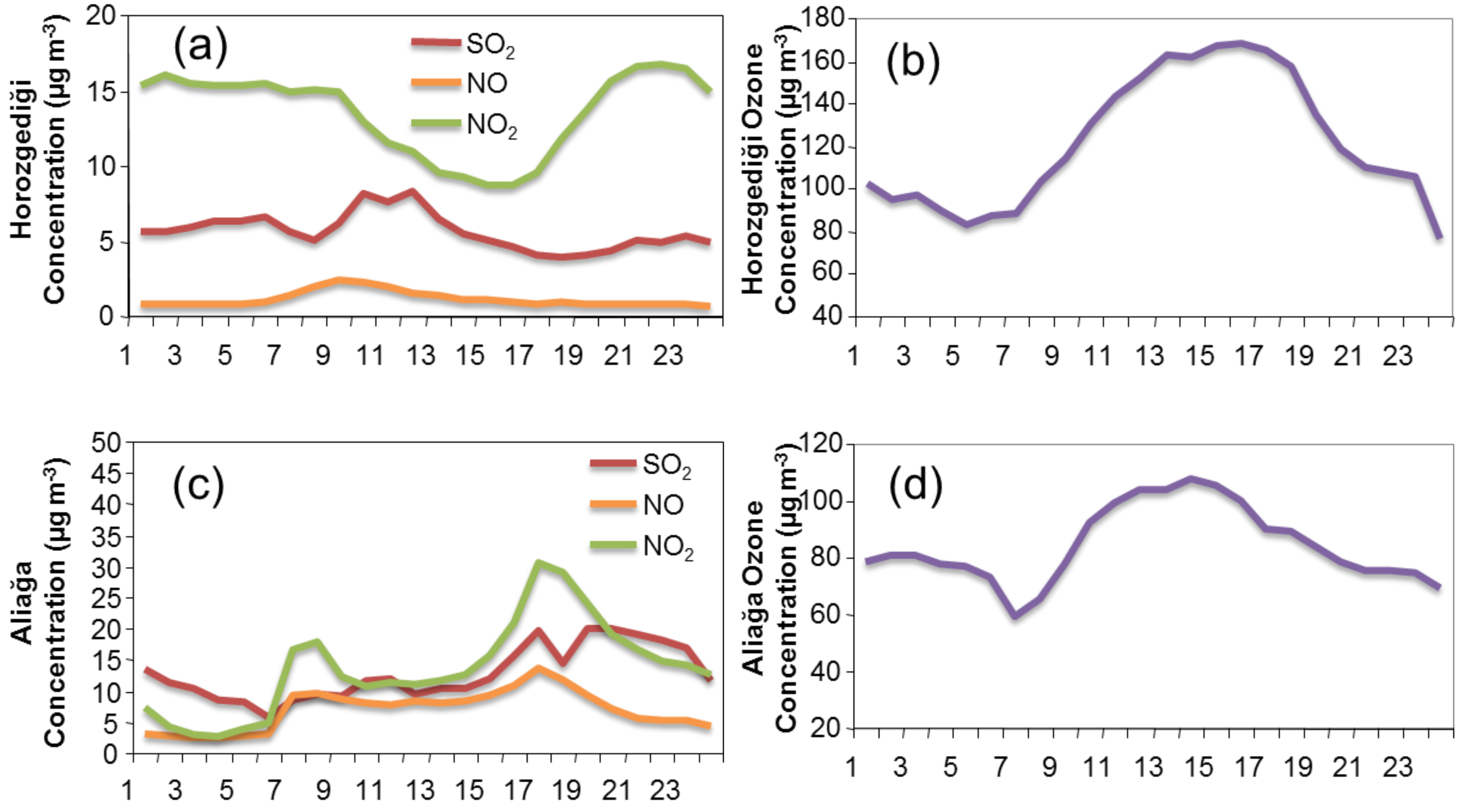


Figure 45 Diurnal variations of NO, NO_2, SO_2 and O_3 concentrations at Aliağa and Horozgediği stations

Both NO and NO_2 concentrations show a well-defined traffic pattern, with clear morning and afternoon rush-hour peaks. Interestingly, SO_2, which is not a good marker for traffic emissions also depict a traffic pattern at the Aliağa station. The traffic pattern observed in SO_2 concentrations is probably due to diesel emissions, because diesel fuel contains 10 – 15 ppm sulfur, both in Turkey and elsewhere (Chen et al., 2012; Jansma et al., 2012). With recent reduction in combustion related SO_2 emissions, owing to the use of natural gas for space heating and industry, diesel emissions became a significant source of SO_2 measured at urban atmosphere (Genç et al., 2010). Industries at the Aliağa region are powered by natural gas and electricity generated at the ENKA Power plant which is gas-fired. This shift resulted in significant reduction in SO_2 concentrations in the region. Hourly SO_2 concentrations were measured for one full year between July 1991 and July 1992, at seven stations distributed in the Aliağa region. One-year-long average SO_2 concentration measured at a station, which is approximately 1.5 km from our Horozgediği station was 60 µg m^{-3} in 1991. Now it is 11±18 µg m^{-3}. Similar reduction in concentrations between 1991 and 2006 was not observed in NO, NO_2 and PM_{10}. Decrease in SO_2 concentrations in 15 year period is obviously due to transition from use coal to natural gas for energy production in the study area. Consequently, traffic pattern observed in VOC concentrations measured at our Aliağa station is not surprising, because combustion-related SO_2 is now very limited in the area.

On the contrary, diurnal variations in NO, NO_2 and SO_2 concentrations measured at Horozgediği station do not show a typical traffic pattern. SO_2 and NO show a diurnal pattern that are very similar to the diurnal pattern observed in VOC concentrations, with a day time maximum at 9:00 and 10:00 in the morning. Concentrations of NO_2 on the other hand showed a very different pattern with higher night time and lower day time concentrations. This peculiar pattern observed in NO_2 concentrations can be explained with more extensive destruction of NO_2 during day time through ozone formation, because conversion of one mole of NO_2 to NO is needed to produce 1 mole of ground level ozone (Seinfeld and Pandis, 1997). Ozone mixing ratios measured at Horozgediği and Aliağa stations are given in Figure 45b and Figure 45d, respectively. Ozone mixing ratios in both sites are high during daytime and low during night. This is consistent with photochemical generation of ozone. Both ozone concentrations and daytime nighttime difference is higher at Horozgediği station. This pattern observed in ozone concentration can explain higher night time NO_2 at Horozgediği, as it is destroyed when ozone is formed. A similar pattern in NO_2 concentrations was not observed at Aliağa station because traffic generated NO and NO_2 produced from this NO is higher at Aliağa. This is supported by a factor-of-two higher NO_2 concentrations measured at Aliağa station than NO_2 concentrations measured at Horozgediği site.

Lack of traffic pattern in diurnal variations of not only VOCs but also in more conventional inorganic traffic markers support the conclusion reached in previous section that, VOCs measured at Aliağa urban atmosphere are controlled by traffic emissions within the city and from the İzmir-Çanakkale highway, whereas VOCs measured at the Horozgediği station is primarily controlled by the transport from industries. The same conclusion is also supported by the weekday - weekend variations of VOC concentrations as will be discussed in the next section.

4.3.3. Weekday-Weekend Variations

Concentrations of VOCs show well defined differences between weekdays and weekends, particularly in an urban atmosphere, due to variations in traffic density and work-hours, between weekdays and weekends. Such variations can be useful to obtain preliminary information on sources of different VOC compounds. Systematic weekday – weekend (WD-WE) differences detected at a rural sampling point can also be used to prove the effect of local anthropogenic sources, or lack of such variations in concentrations of measured species can be used as an indication of lack of local anthropogenic influence on data generated at a rural site, because natural emissions do not show WD-WE differences. Weekday - weekend cycle is not specific to VOC compounds, but generally observed in all atmospheric pollutants that has dominating anthropogenic sources in urban airshed.

Weekday and weekend geometric mean concentrations of VOC and weekday-to-weekend concentration ratios measured at Aliağa, Horozgediği and TÜPRAŞ stations are depicted in Figure 46. Concentrations of VOCs measured at the Aliağa station showed less weekday-weekend differences than we expected initially. Weekday-to-weekend concentration ratios for VOC measured in this station varied between 1.6 for n-pentane and 0.5 for butadiene. Forty-three VOCs were consistently detected at Aliağa station. Thirty-nine of these have WD/WE ratio within 1.0 ± 0.2. The only compounds that have higher concentrations during weekdays are n-pentane and 2-methyl-1-pentane. These are solvents and their higher concentration during weekdays is understandable due to lack of printing, photocopying type of activities during weekends. The only compounds with higher concentrations during weekends, that are statistically significant at 95% confidence level, are 1,3-butadiene and 2,2,4-trimethylpentane.

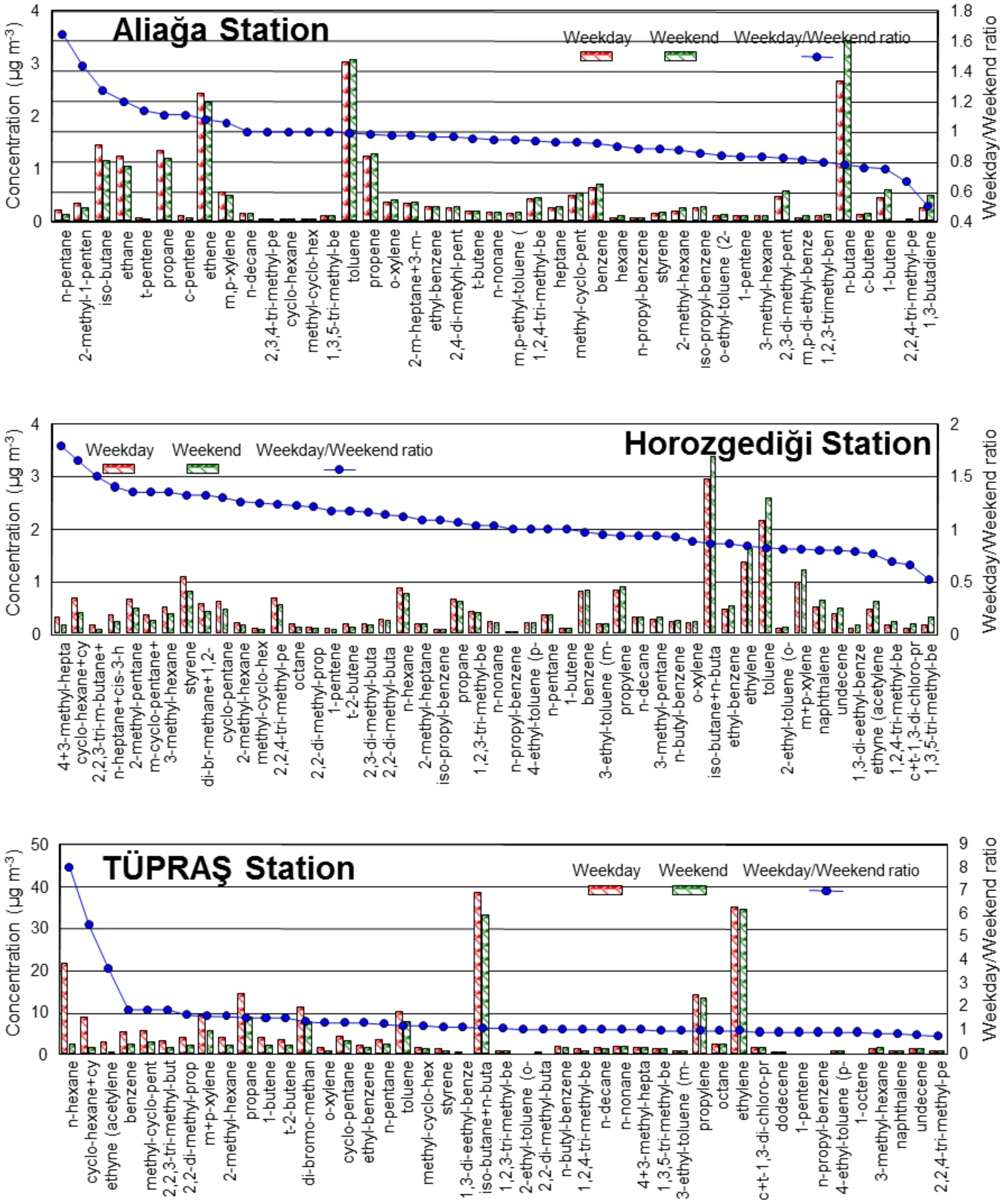


Figure 46 Weekday and weekend concentrations and weekday-to-weekend ratio at all stations

Compounds like isobutene, c-butane, 1-butene and butadiene, which are known to be good markers for LPG use all take place at the low end of the WD/WE ratios. It should be noted that ethane, ethane and propane which are indicators of natural gas, are not among these. Although natural gas was being used since 2003 by the industries in Aliağa region, it was not in use in the city of Aliağa (setting up the infrastructure for natural gas use in the city was underway during our sampling period) and LPG was widely used for cooking and to a certain extend for heating in Aliağa. It is not clear why LPG emissions should be higher in weekends, but apparently they are.

Another interesting point in WD/WE ratios at Aliağa station is the lack of variation in concentrations of traffic-related VOCs between weekends and weekdays. The WD/WE concentration ratios for benzene, toluene, ethyl benzene, m,p-xylene and o-xylene are 1.1, 1.0, 1.0, 1.1 and 1.0, respectively. These BTX group compounds, which are good marker species for traffic emissions have more or less similar concentrations at weekdays and weekends. This is not a typical for traffic-related pollutants. In populated cities concentrations of traffic related VOCs, such BTX compounds decrease during weekends, owing to less mobility of residents at weekends (Qin et al., 2007; Hellen et al., 2003; Brown et al., 2007). One plausible reason for the lack of WD-WE difference at Aliağa can be the increased touristic traffic at the weekends, which can compensate for the reduced daily traffic activity within the city. There are many resort areas around the city of Aliağa, such as Foça, Yeni Foça, Çandarli and Dikili etc. Transport to these areas at weekends increase the weekend traffic. It is not easy to prove this scenario, as there were no hourly or daily traffic counts in and around the city during this study, but surely it can explain observed, unusual, similarity in weekday and weekend concentrations of traffic-related VOC compounds.

Weekday – weekend behaviors of VOCs at TÜPRAŞ station is substantially different from WD - WE behaviors of VOCs at Horozgediği and Aliağa stations. Forty-five VOCs were routinely detected at TÜPRAŞ station. Twenty-seven of these compounds have comparable concentrations in weekdays and weekends (WD/WE ratio 1.0 ± 0.2). This is smaller than number of VOCs at Horozgediği (34/49) and Aliağa (39/43) stations with WD-to-WE ratio of 1.0 ± 0.2.

On the other hand there are 18 VOCs with higher concentrations in weekdays (WD/WE ratio > 1.3, corresponding to 95% statistical significance). Number of compounds with WD/WE ratio > 1.3 is higher than corresponding number of VOC compounds at Horozgediği (12) and Aliağa stations (2).

The VOCs with the highest WD-to-WE ratio at TÜPRAŞ station are hexane, cyclo-hexane+cyclo-hexene, ethyne (acetylene), benzene, m-cyclo-pentane +2,4-di-m-pentane, 2,2,3-tri-m-butane+2,3-di-m-pentane, 2,2-di-methyl-propane. All of these, except for acetylene are light hydrocarbons that can evaporate during loading and unloading operations at the refinery. Acetylene on the other hand is a combustion product and is a good marker specie for traffic exhaust emissions.

Observed high number of VOCs with high WD-to-WE ratio at TÜPRAŞ station can be due to variation of shifts in the refinery and petrochemical plants during weekend. But more likely it is due to reduced number of traffic coming to going from the TÜPRAŞ refinery and PETKİM and reduced loading activity at the refinery during weekends.

Weekday – weekend behavior of VOCs at Horozgediği station is somewhere between patterns observed at Aliağa and TÜPRAŞ stations. There are 12 VOCs with WD/WE ratio > 1.3, the ratio is within 1.0 ± 0.2 for 34 VOCs and <0.8 for 3 VOCs. Interestingly, the VOCs that have higher concentrations at Horozgediği stations are similar to those observed at TÜPRAŞ stations. Since Horozgediği station is far from any strong evaporative sources, observed similarity can only be explained by transport from the refinery and petrochemical complex, and indicates important role of these two plants on the pollution levels observed at the Horozgediği station.

4.3.4. Seasonal Variations

The VOC concentrations measured at Aliağa and Horozgediği stations do not show systematic differences between summer and winter seasons. Summer, winter season median concentrations of VOCs and their summer-to-winter concentration ratios are depicted in Figure 47.

At Aliağa station, there are 29 VOCs that were measured in both seasons. Although 51 compounds were regularly detected during winter campaign, only 29 VOCs were measured in summer due to problems with one of the columns in the online GC system used at the Aliağa station. Average summer-to-winter concentration ratio was 1.37. Seven of the 23 compounds measured in both seasons had ratios within 1.0 ± 0.2. Ten of them have summer-to-winter ratios higher than 1.2 and 12 of them have ratios smaller than 0.8. It is easy to understand higher winter concentrations of VOCs, because even is the emissions are the same in winter and summer, winter concentrations appear higher due to lower mixing height and lower destruction rates in winter season. BTX compounds, except for benzene, have higher concentrations in summer, indicating that lower mixing height and reaction rates in winter is compensated by evaporative or some other industrial emissions in summer.

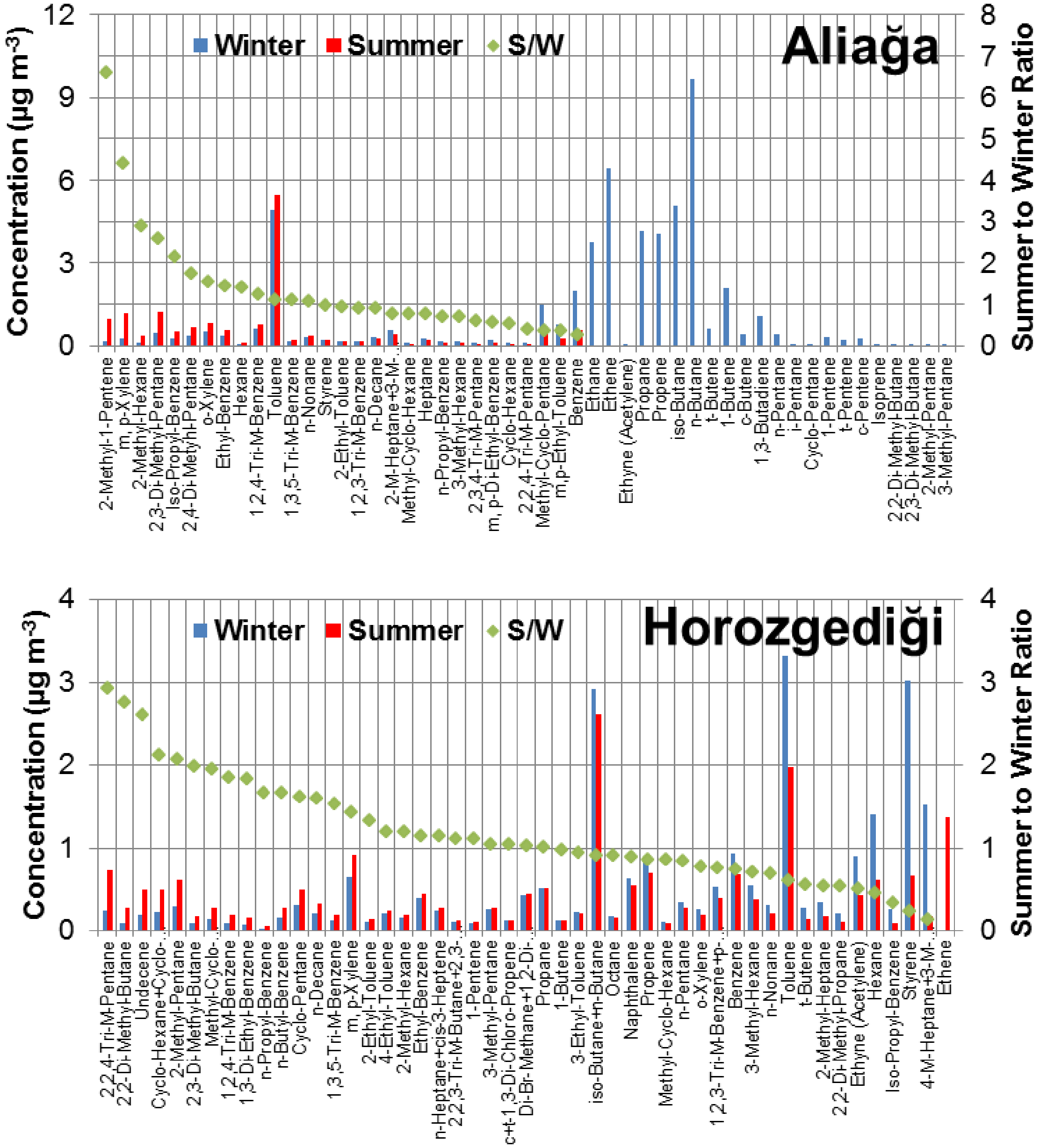


Figure 47 Seasonal variations in Aliağa and Horozgediği

A similar seasonal pattern is also observed at the Horozgediği station. Forty-eight VOCs were detected both in summer and winter campaigns. Eighteen of these have summer-to-winter concentration ratio within 1.0 ± 0.2, 16 had ratios >1.2 and 14 have ratios <0.8. Since, previous discussion on weekday-weekend patterns demonstrated that VOC concentrations at Horozgediği station is strongly influenced from transport of emissions from TÜPRAŞ refinery and PETKİM petrochemical complex, seasonal variations in concentrations of these compounds can be explained by the seasonal variation in VOC emissions at PETKİM and TÜPRAŞ. However, this is only speculation as measurements at the TÜPRAŞ station were performed only during winter campaign, but not in summer.

Eighteen of the VOCs are commonly measured at two stations. Four of the compounds showed similar seasonal variations. In both stations, benzene and 3-methyl-hexane concentrations are observed higher in winter, whereas, m,p-xylene and 1,2,4-trimethylbenzene concentrations are higher in summer season. Benzene and 1,2,4-trimethylbenzene are tracers of both industrial and traffic emissions. Different trends in seasonal variations show that these compounds are emitted from various sources.

4.4. Effect of Meteorological Parameters on Concentrations of Pollutants

4.4.1. Effect of Wind Speed, Mixing Height, Ventilation Coefficient, Temperature and Relative Humidity on VOC Concentrations

Local meteorology is one of the most important factors affecting measured concentrations of not only VOCs but also most of the other air pollutants, particularly at urban and industrial atmospheres. Another important factor is the emissions. Upper atmospheric transport of pollutants from other emission areas can also affect concentrations of pollutants (Kindap, 2006), but this factor, which is important at rural atmosphere, is small and can be neglected in urban and industrial regions, because local emissions are high and can completely mask influence of distant sources.

Meteorological influence on concentrations of species can occur in two forms, horizontal ventilation process, which is caused by winds and vertical ventilation, which refers to convective stability of the atmosphere (Şen, 1998; Yang et al., 2011). Absence of horizontal ventilation is called “calm” and absence of vertical ventilation is called “inversion”. Combination of calm an inversion is referred to as “stagnant”. Stagnant conditions correspond to highest pollution episodes in an urban and industrial airshed, as emitted pollutants are not removed horizontally and vertically from the emission area (Kim et al., 2011; Bustamante et al., 2011; Wallace et al., 2010).

Although there is a close relationship between pollutant concentrations and local meteorology, quantifying that relation is not always straightforward, because atmospheric concentrations of pollutants depend on a number of factors, such as chemical processes they may undergo, different scavenging processes, such as wet removal with rain and dry deposition, in addition to meteorology and emissions. The relation between VOC concentrations measured at Aliağa and Horozgediği stations and prevailing surface meteorology are discussed in this section. Meteorological parameters investigated include wind speed, which is indicator for the effectiveness of horizontal ventilation mechanism in the study area, mixing height, which is an indicator for the vertical ventilation. In addition to these two major parameters the relation between VOC concentrations and ventilation coefficient is also investigated. Ventilation coefficient (VC) is the product of wind speed and the mixing height, thus it combines the influence of horizontal and vertical ventilation mechanisms on measured concentrations of pollutants (Goyal and Chalapati, 2007; Rao et al., 2003). Ventilation coefficient is considered as the assimilative capacity of the atmosphere and it is shown to be better related with measured concentrations of air pollutants than mixing height and wind speed alone (Genç et al., 2010).

The relation between measured VOC concentrations and temperature and relative humidity is also discussed. However, it should be noted that relation between VOC levels and temperature can be indirect, because emissions can change with seasons, which can appear as the influence of temperature on measured concentrations.

Visualization of the relation between VOC concentrations and meteorological parameters is difficult. This is shown in Figure 48 where the scatterplot between BTX concentrations measured at Aliağa station and wind speed is depicted. Although there is a general decreasing trend in concentrations of BTX compounds with increasing wind speed it is difficult to see if the decrease follow a linear or other pattern and it is impossible to see if there are different type of variation for different BTX compounds. To avoid this difficulty, median concentrations of the compounds are calculated for different intervals of meteorological parameters and concentration vs. meteorology plots are prepared for these median values.

Meteorological data used in calculations are the data obtained from General Directorate of Meteorology (GDM). General features of data were discussed in previous sections. VOC data generated at TÜPRAŞ station was not included in this discussion, because, measurements were performed for only 15 days in November, and values of meteorological parameters accumulated in a very narrow range and did not show sufficiently large spectrum, which is necessary for a meaningful regression against VOC concentrations. Plus, the TÜPRAŞ station is in the immediate vicinity of the refinery and petrochemical plant and concentrations measured are expected to be under strong influence of emissions, rather than meteorology. For the further regression analyses, Statgraphics Centurion 16.1 software is used.

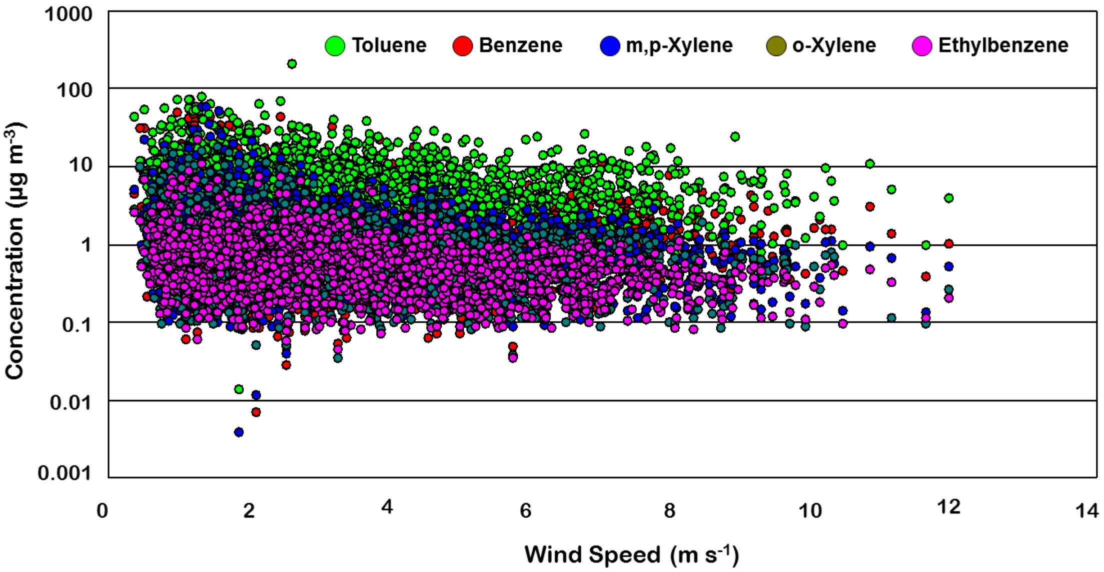


Figure 48 The relation between wind speed and BTX concentrations at Aliağa station, using all available data

The relationship between BTX concentrations with wind speed at Horozgediği and Aliağa stations are depicted in Figure 49. The plot shows the least squares regression line and two sets of limits. The inner limits provide 95% confidence intervals. The outer lines are 95% prediction limits for new observations. Models fitted to BTX data shown in Figure 49 are given in Table 16. Wind is the main horizontal ventilation mechanism for VOCs (and for most of the other pollutants as well). Since pollutants emitted to Aliağa atmosphere will be diluted with increasing wind speed, a decrease in VOC concentrations is expected with increasing wind speed. At Aliağa station concentrations of all five BTX compounds decrease, as expected. The decrease is logarithmic for all five compounds. The “p” values (probability of chance correlation) of the fitted models are 1% or less for all of them, indicating a very good agreement between the model and data. Fitted models explained 84% of the variance in benzene, 85% of the variance in toluene data, 93% of the variance in m,p-xylene data, 91% of the variance in o-xylene data and 93% of the variance in ethylbenzene data. These values clearly demonstrate that VOC concentrations at the town of Aliağa, are strongly dependent on the wind speed as expected. This is an indication that VOC emissions that influence the data at Aliağa station are in the immediate vicinity of the station and horizontal transport of emissions is an important ventilation mechanism in the city.

On the contrary, the relation between wind speed and BTX concentrations at Horozgediği station is not as strong as the relation observed at Aliağa station. Toluene data fitted to log model with 95% confidence. Benzene fitted to a double reciprocal y model. We first attempted to fit data to the simplest models, namely linear and logarithmic. If VOC data fits to both models, the one with higher R^2 is selected. If the VOC data do not fit linear and log models then 27 other models are tested and the one with highest R^2 are used. For example, benzene data at Horozgediği station did not fit to linear and log-x models. Further tests showed that it fits to “double reciprocal-y” model (y = 1/(a + b/x).

Concentrations of the other three compounds, namely m,p-xylene, o-xylene and ethylbenzene did not fit to any of the 27 models with statistical significance > 95%. This clear difference in response of VOC concentrations to WS in the two stations can be explained with more rural nature of the Horozgediği station. The station is not in the immediate vicinity of the VOC emission sources. VOCs are transported to the station from refinery, petrochemical complex and roads. Winds do not transfer the VOCs from the station, but brings them to the station. In such a case, we do not expect to see a categorical decrease in VOC concentrations with increasing wind speed, because high concentrations of VOCs will be measured when winds blow from the direction of the refinery and petrochemical complex, even if the winds are strong. On the other hand, low VOC concentrations can be measured during low wind speeds if that wind is blowing from a clean sector. However, at Aliağa station VOC sources are around the measurement point and winds transport emissions from the station, as well as diluting them. This results in a well-defined decrease in concentrations with increasing wind speed.

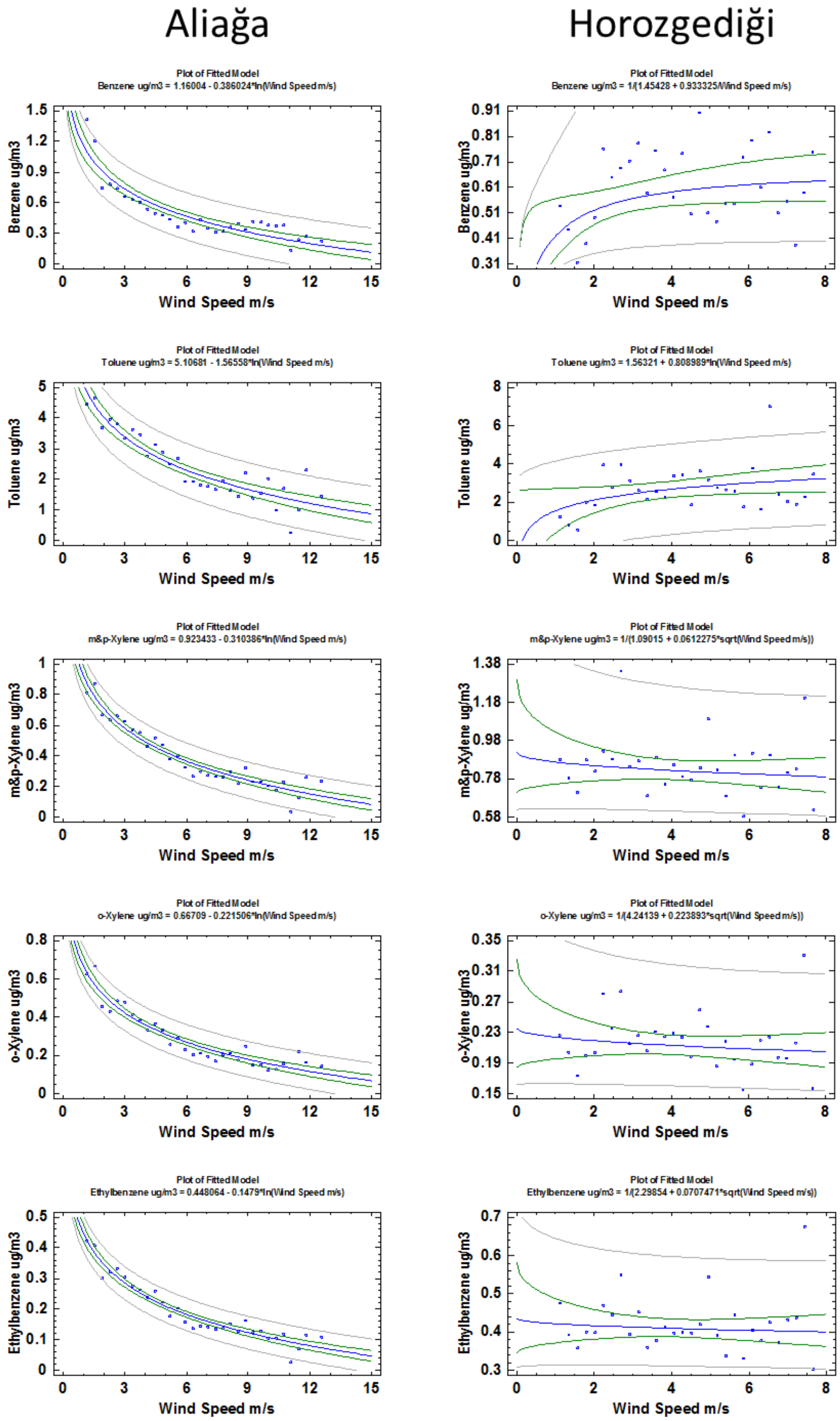


Figure 49 Effect of wind speed on BTX concentrations at Aliağa and Horozgediği stations

Table 16 Regression equations between wind speed and BTX concentrations

Compounds	Fit	Equation	R^2
		Aliağa	
Benzene	Log	Benzene = 1.160-0.386ln(WS)	0.84
Toluene	Log	Toluene = 5.107-1.566ln(WS)	0.85
m,p-Xylene	Log	m,p-Xylene = 0.923-0.310ln(WS)	0.93
o-Xylene	Log	o-Xylene = 0.667-0.222ln(WS)	0.91
Ethylbenzene	Log	Ethylbenzene=0.448-0.148ln(WS)	0.93
		Horozgediği	
Benzene	DR**	Benzene = 1/(1.454 + 0.93/WS)	0.15
Toluene	Log	Toluene = 1/(0.171 + 1.01/WS)	0.13
m,p-Xylene	None	No statistically significant fit	
o-Xylene	None	No statistically significant fit	
Ethylbenzene	None	No statistically significant fit	

*WS: Wind speed, **DR: Double reciprocal: y=1/(a+b/x)

Mixing height is a measure of vertical ventilation of the region. As long as emissions are constant, concentrations of VOCs (and other pollutant as well) are expected to decrease with increasing mixing height. The mixing height calculations were done by using PCRAMMET software. Variation of BTX concentrations with mixing height are shown in Figure 50 and information about fitted models are given in Table 17. Patterns observed in the figure are not substantially different from the patterns observed in relation between concentrations and WS.

Concentrations of all BTX compounds, except for benzene, show poor correlation with mixing height at Aliağa station. Toluene, m,p-xylene, o-xylene and ethylbenzene showed linear correlation. However, the correlation coefficients are lower than wind speed. This indicates that mixing height is not as strong parameter as wind speed at Aliağa.

At Horozgediği data set, concentrations of benzene, toluene and o-xylene decrease with increasing mixing height. The decrease in m,p-xylene and ethylbenzene concentrations observed at the Horozgediği station did not fit to any model with statistical significance better than 95%. Benzene fitted to a reciprocal y squared x, toluene fitted to logarithmic model and o-xylene fitted to a “square-y reciprocal-x” model. Variance explained (R^2) varies between 0.15 for o-xylene and 0.40 for toluene. All these relatively marginal significance of fitted models in both stations indicate that variations of concentrations of VOCs can be partly due to variations in mixing height, but obviously there are other factors which also contribute to temporal variations in their concentrations.

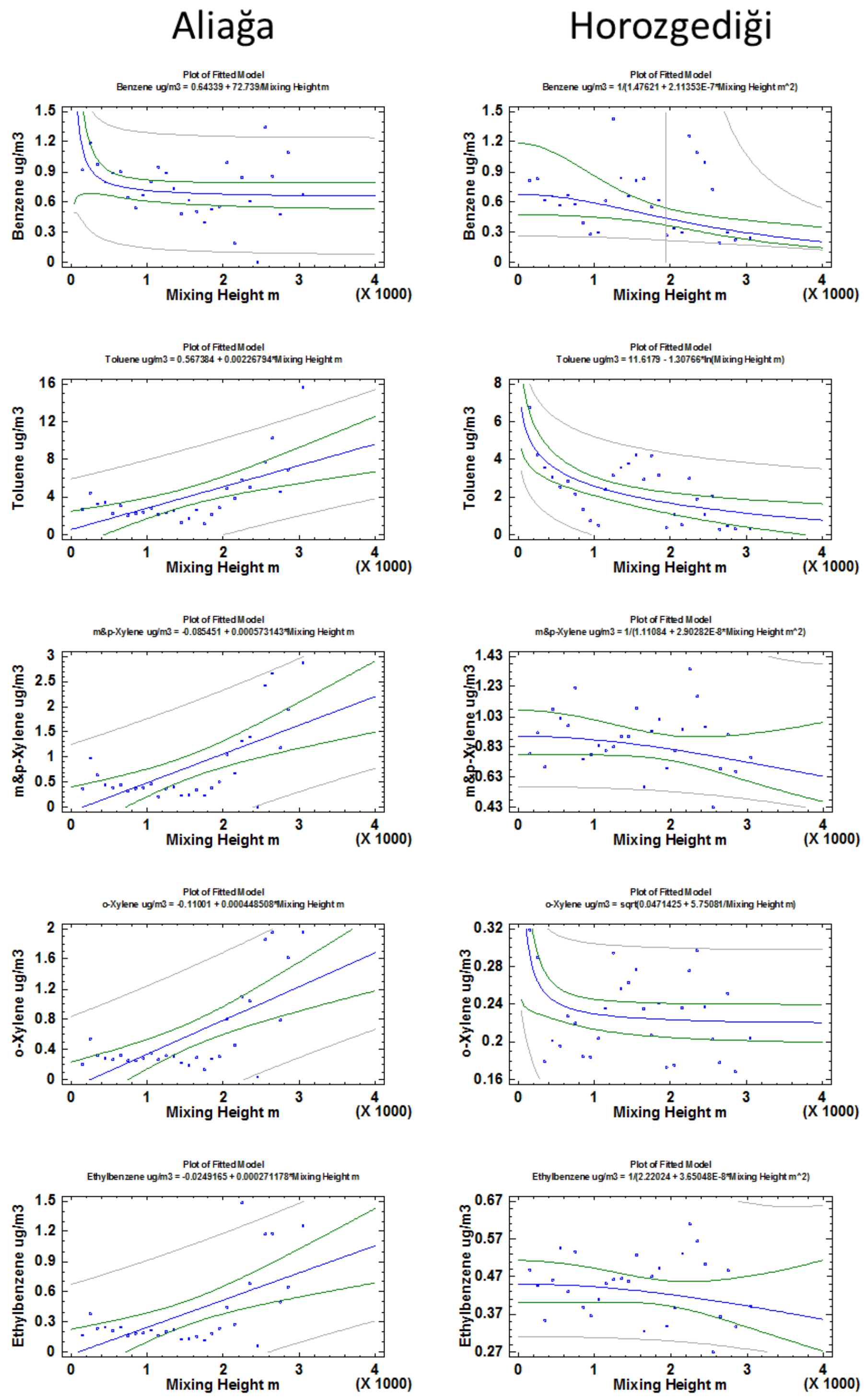


Figure 50 Effect of mixing height on BTX concentrations at Aliağa and Horozgediği stations

Table 17 Regression equations between mixing height and BTX concentrations

Compounds	Fit	Equation	R^2
		Aliağa	
Benzene	None	No statistically significant fit	
Toluene	Linear	Toluene = 0.567+0.0023(MH*)	0.40
m,p-Xylene	Linear	m,p-Xylene = -0.085+0.000573(MH)	0.41
o-Xylene	Linear	o-Xylene = -0.110+0.000448(MH)	0.45
Ethylbenzene	Linear	Ethylbenzene=-0.0249+0.00027(MH)	0.36
		Horozgediği	
Benzene	RySx**	Benzene = $1/(1.476+2.11\times10^{-7}MH^2)$	0.23
Toluene	Log	Toluene = 11.618-1.308ln(MH)	0.40
m,p-Xylene	None	No statistically significant fit	
o-Xylene	SR***	o-Xylene = sqrt(0.047+5.751/MH)	0.15
Ethylbenzene	None	No statistically significant fit	

*MH: Mixing height in meters, **RySx: Reciprocal y squared x: $y=1/(a+bx^2)$ ***SR: Squared y reciprocal x: $y=(a+b/x)^{1/2}$

Ventilation coefficient is the product of mixing height and wind speed. Since it encompasses most important indicators of horizontal and vertical ventilation processes, it is generally believed that it is a better parameter to investigate dependence of pollutant concentrations to local meteorology than wind speed and mixing height alone (Chan et al., 2012; Genç et al., 2010; Ashrafi et al., 2000). The relation between ventilation coefficient and BTX concentrations at Aliağa and Horozgediği stations are depicted in Figure 51. Models fitted to concentrations are given in Table 18. There is fairly strong decreasing trend in concentrations of not only all BTX compounds, but also most of the VOCs measured in this study at Aliağa station. All BTX compounds fit to “log” model indicating that fits are robust. Variances of BTX compounds explained by ventilation coefficient vary between 0.63 for toluene and 0.86 for benzene. Such a strong relation between BTX concentrations and VC is not surprising, because concentrations of VOCs at Aliağa station correlated strongly with both mixing height and wind speed and they are expected to be correlated with the product of these two parameters.

VOCs measured at Horozgediği, on the other hand is not strongly correlated with ventilation coefficient. Benzene, toluene and ethylbenzene fitted to linear model and m,p-xylene fitted to double squared model. O-Xylene did not fit to any of 27 models. Variances of BTX compounds explained by ventilation coefficient vary between 0.16 for m,p-xylene and 0.30 for benzene.

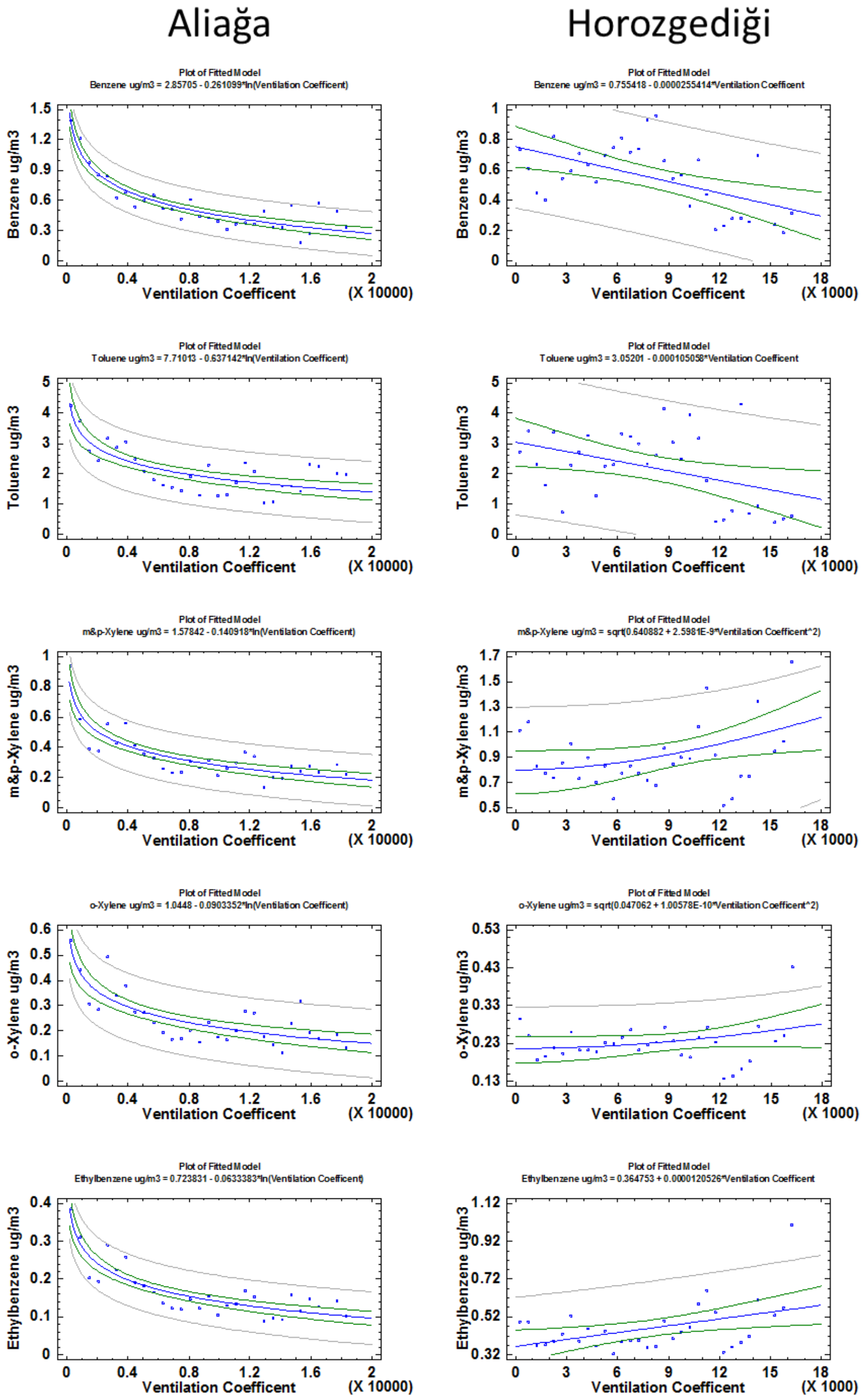


Figure 51 Effect of ventilation coefficient on BTX concentrations at Aliağa and Horozgediği stations

Table 18 Regression equations between ventilation coefficient and BTX concentrations

Compounds	Fit	Equation	R^2
		Aliağa	
Benzene	Log	Benzene = 2.857-0.261ln(VC*)	0.86
Toluene	Log	Toluene = 7.710-0.637ln(VC)	0.63
m,p-Xylene	Log	m,p-Xylene = 1.578-0.141ln(VC)	0.75
o-Xylene	Log	o-Xylene = 1.045-0.090ln(VC)	0.66
Ethylbenzene	Log	Ethylbenzene = 0.724-0.063ln(VC)	0.78
		Horozgediği	
Benzene	Linear	Benzene = 0.755-0.000026(VC)	0.30
Toluene	Linear	Toluene = 3.052-0.00011(VC)	0.17
m,p-Xylene	DS**	m,p-Xylene = sqrt(0.641+2.6x$10^{-9}$$VC^2$)	0.16
o-Xylene	None	No statistically significant fit	
Ethylbenzene	Linear	Ethylbenzene = 0.365+0.00012(VC)	0.19

*VC:Ventilation coeffient, ** DS:Double squared: y=sqrt(a+bx^2)

This lack of strong relation between VOC concentrations and WS, MH and VC clearly demonstrate that it may not be a very good idea to attempt to explain measured concentrations of pollutants with meteorology in rural airshed. In an urban airshed, pollutants are emitted within the city and dispersed by meteorology. Measurement of VOCs and other pollutants in the city is a measure of this dispersion process. Because of this mechanism, pollutant concentrations including VOCs show fairly well-defined and foreseeable variations with met parameters, such as wind speed, mixing height and ventilation coefficient. However, at a rural airshed, relation between pollutant levels and meteorology is much more complicated. First of all rural stations are not located in the immediate vicinity of the emission sources, which means that there is no dispersion or dilution of pollutants from the measurement point, which can be related to meteorology. Furthermore, VOCs and other pollutants can be transported from source regions which are not related to meteorological parameters. The only exception to this is the dependence VOC concentrations on wind direction, which will be discussed later in the manuscript. In addition to these, which are common to all pollutants, VOCs have also chemistry in the atmosphere, which further complicates the relation between concentrations and meteorology. To summarize this discussion it can be said that, at a rural station high VOC concentrations are measured when wind blows from the direction of sources (PEKTİM and TÜPRAŞ in our case), not when mixing height is low or when wind is strong, because that strong wind may be blowing from the direction of PETKİM and TÜPRAŞ, in that case high VOC levels are measured even when the wind is strong.

VOC's depicted interesting dependence to temperature in both Aliağa and Horozgediği stations. The dependence of BTX concentrations on temperature in both stations are schematically shown in Figure 52 and fit parameters are given in Table 19. Concentrations of toluene, m,p-xylene, o-xylene, ethylbenzene at Aliağa station and m,p-xylene at Horozgediği station showed increasing trend with > 0.95 statistical confidence. Concentrations of benzene, toluene and o-xylene at Horozgediği station presented decreasing trend. Benzene at Aliağa station and ethylbenzene at Horozgediği station did not fit to any model.

The increasing trend in VOC concentrations with temperature can be expected in Aliağa satiation, because of several reasons, including increased traffic activity a during summer months, increased evaporation form painted surfaces and from solvents in summer.

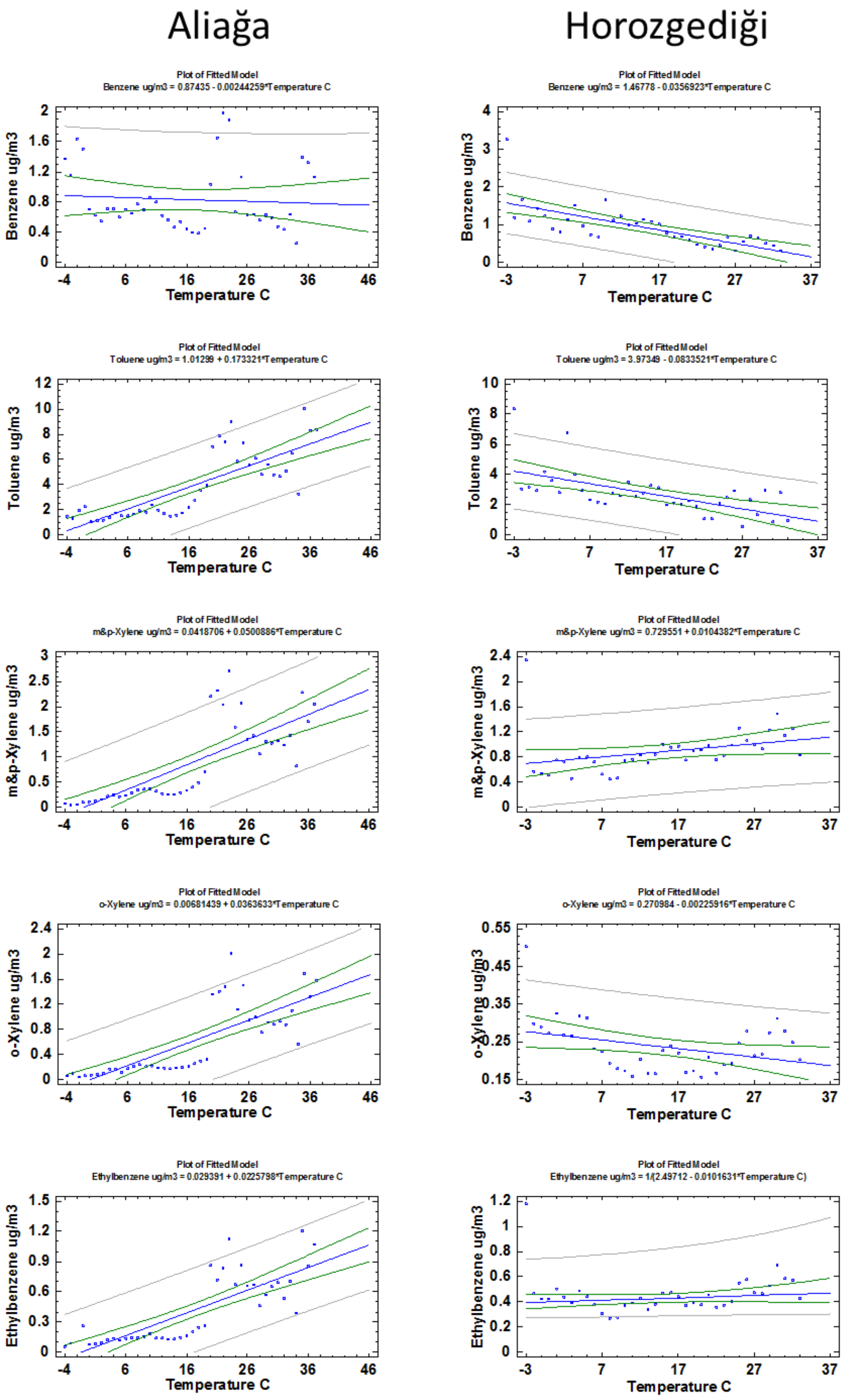


Figure 52 Effect of temperature on BTX concentrations at Aliağa and Horozgediği stations

Table 19 Regression equations between temperature and BTX concentrations

Compounds	Fit	Equation	R^2
		Aliağa	
Benzene	None	No statistically significant fit	
Toluene	Linear	Toluene = 1.013+0.173(T*)	0.64
m,p-Xylene	Linear	m,p-Xylene = 0.0418+0.0501(T)	0.60
o-Xylene	Linear	o-Xylene = 0.0068+0.0364(T)	0.61
Ethylbenzene	Linear	Ethylbenzene = 0.0294+0.0226(T)	0.64
		Horozgediği	
Benzene	Linear	Benzene = 1.468-0.0357(T)	0.51
Toluene	Linear	Toluene = 3.973-0.0834(T)	0.38
m,p-Xylene	Linear	m,p-Xylene = 0.730+0.0104(T)	0.11
o-Xylene	Linear	o-Xylene = 0.271-0.00226(T)	0.13
Ethylbenzene	None	No statistically significant fit	

*T: Temperature (^{o}C)

Variation of VOC concentrations with the relative humidity is depicted in Figure 53 and characteristics of the model fitted to data are given in Table 20. Benzene at Aliağa station and benzene and o-xylene at Horozgediği station showed increasing trend with relative humidity. Toluene, m,p-xylene, o-xylene and ethylbenzene at Aliağa station showed decreasing trend. Toluene, m,p-xylene and ethylbenzene at Horozgediği station did not fit to any model.

Relatively low R^2 values observed in the relations between VOC concentrations, temperature and relative humidity indicates that these two parameters can explain only a small part of the variations in VOC concentrations at the Aliağa region.

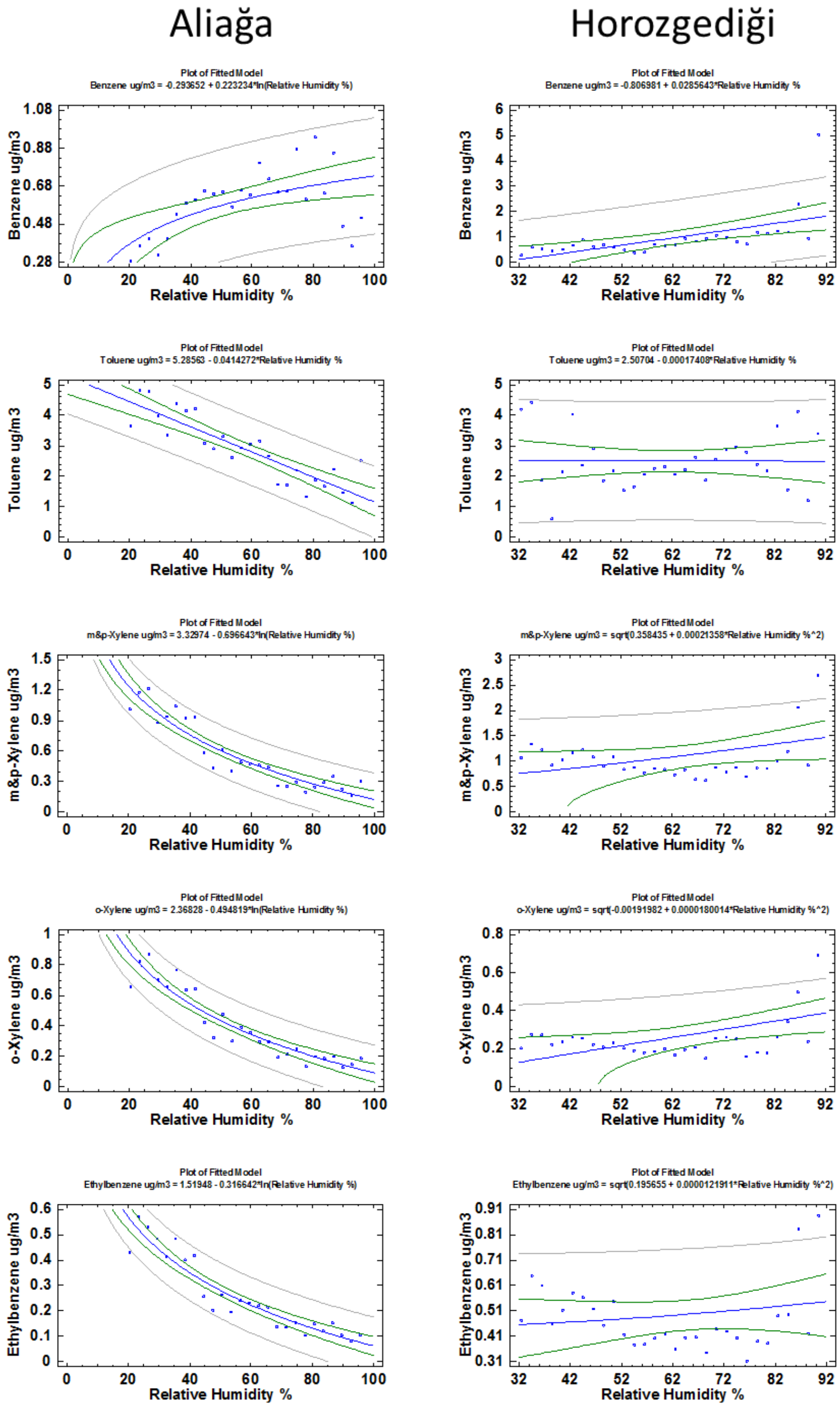


Figure 53 Effect of relative humidity on BTX concentrations at Aliağa and Horozgediği stations

Table 20 Regression equations between relative humidity and BTX concentrations

Compounds	**Fit**	**Equation**	**R^2**
		Aliağa	
Benzene	Log	Benzene = -0.294+0.223ln(RH*)	0.35
Toluene	Linear	Toluene = 5.285-0.0414(RH)	0.77
m,p-Xylene	Log	m,p-Xylene = 3.330-0.697ln(RH)	0.88
o-Xylene	Log	o-Xylene = 2.368-0.495ln(RH)	0.88
Ethylbenzene	Log	Ethylbenzene = 1.519-0.317ln(RH)	0.89
		Horozgediği	
Benzene	Linear	Benzene = -0.807+0.0286(RH)	0.34
Toluene	None	No statistically significant fit	
m,p-Xylene	None	No statistically significant fit	
o-Xylene	DS**	o-Xylene =sqrt(-0.0019+0.000018RH^2)	0.20
Ethylbenzene	None	No statistically significant fit	

*RH: Relative Humidity, **DS: Double squared: $y=\mathrm{sqrt}(a+bx^2)$

4.4.2. Effect of Wind Direction on VOC concentrations: Conditional Probability Function

The influence of wind direction to receptors is particularly important if the receptor is located in close proximity of point emission sources, because depending on wind pattern, the receptor may be strongly affected from emissions or it may not be affected at all. In this study, emission sources, point or mobile, are not homogenously distributed around sampling points. At Aliağa station, mobile source are preferentially located to the East of the station. Although there is traffic activity all around the sampling point main highway that connects İzmir to Çanakkale and İstanbul is located to the east of the Aliağa station. Although residential point source emissions occur fairly homogeneously around the station, large plants, namely TÜPRAŞ and PETKİM are located to the West and Southwest of the sampling point.

At Horozgediği main point VOC sources are located to the north of the station. Iron and steel industry, which is close to the sampling (measurement) point are located to the Northeast of the station. Although iron and steel plants do contribute strongly to PM10 concentrations in the region (Tuncel et al., 2008), their contributions to VOC levels is limited.

Because of explained polarity of sources around sampling stations, we expected to see strong dependence of measured VOC levels to wind direction. The simplest way to investigate the relation between measured pollutant concentrations and wind direction is to use pollution roses, which shows average (or median) concentrations of pollutants at each wind sector. However there is one problem with the use of pollution rose. One or two very high concentrations in a sector with relatively few hourly wind occurrences can result in high sector averages, which can be misleading. In order to avoid this disadvantage of sector averages, we used a different approach to investigate the relation between VOC concentrations and wind direction. The approach used in this study is called “conditional probability function” (CPF). It gives information about probability of sources being in a certain wind sector, rather than concentrations in that sector. Prior information about CPF is given in Section 3.5.2.

The CPF is the simpler version of the “potential source contribution function” (PSCF) which is used frequently in rural studies with upper atmospheric trajectory information. Calculation schemes are the same, except surface wind data and wind sectors are used in CPF instead of upper atmospheric trajectory information and gridded map of whole Europe that are used in PSCF calculations.

In CPF analysis, the threshold level for “high concentration” should be defined beforehand, because hourly wind occurrences that corresponds to higher than threshold concentrations of the test specie are counted separately as polluted wind segments ($m_{\Delta\theta}$). We tested two threshold values as the limit of high concentrations. One of these is the highest 25% of the concentration of test specie is considered as the threshold concentrations and the other one is the highest 40% of the concentrations is considered as high concentrations. In this study highest 40% of the concentrations of test species was considered as threshold concentration and winds corresponding to these concentrations were considered as polluted winds ($m_{\Delta\theta}$). The use of highest 40% of data as threshold concentration was to improve the statistical significance of the results.

Different calculations were performed to data generated at TÜPRAŞ station to see the differences in the results when different approaches were used to investigate the dependence of VOC concentrations on wind direction. For this, sector averages, CPF using the highest 25% of data as polluted and highest 40% of data as polluted, were calculated for selected compounds. The results are depicted in Figure 54. As can be seen from the figure, general shapes of roses are not very different, but there are some minor differences between different calculations schemes. This implies that general picture that will be obtained on dependence of VOC concentrations on wind direction will be similar no matter which approach is used.

Conditional probability functions generated for selected VOCs at the Aliağa station is given in Figure 55. Although CPF calculations were performed for all of the measured VOCs only eight are shown in the figure due to space limitations. The general feature of the CPF distributions among sectors for the Aliağa station is homogenous distribution of sources around the station. Observed homogeneity is typical for the stations in the center of urban areas. In such measurement points, emissions, whether it is residential or from traffic, occur all around stations. In Aliağa, residential areas are generally situated to the NE, E, SE, S, and SW of the station. Sectors between W and NE were toward the sea. There was not much residents in this sector but there were fair amount of commercial activity. Roads surrounded the station in all directions, but Highway D550 which connected İzmir to Çanakkale was the one with particularly heavy traffic activity and it was situated to the east of the station. Two very strong emitters, namely TÜPRAŞ and PETKİM are located in the sectors between SW and NW relative to the station.

For most of the VOCs shown in the figure, distribution of CPF values among wind sectors are consistent with the distribution of emission sources explained in previous paragraphs. CPF values are generally high in all directions, except in sectors that includes sea. However, this is not a general statement that includes all VOCs. There are some compounds, like toluene and n-pentane in the figure which has high CPF values in the sea sector as well. It should be noted that there is no residents in the wind sectors that include sea (between WNW and NNE), but there are commercial activity and traffic. Consequently, higher-than-expected CPF values in these sectors do not mean that there is source in the sea, but may originate from those activities between the sea and the station. For most of the compounds (not all of them), CPF values in SW, SSW and W sectors are higher than CPF values in other factors. The difference is not very high, but consistent. This pattern can be seen in distributions shown for heptanes, toluene, benzene, metylcyclohexane and n-butane. Higher CPF values in some of the west sectors and lower values in the NE sector can be due to presence of TÜPRAŞ and PETKİM in these sectors. However, it should be noted that, this is not a conclusive evidence for the influence of industries, because it may also indicate that the bulk of the residential and evaporative emissions occur in that direction.

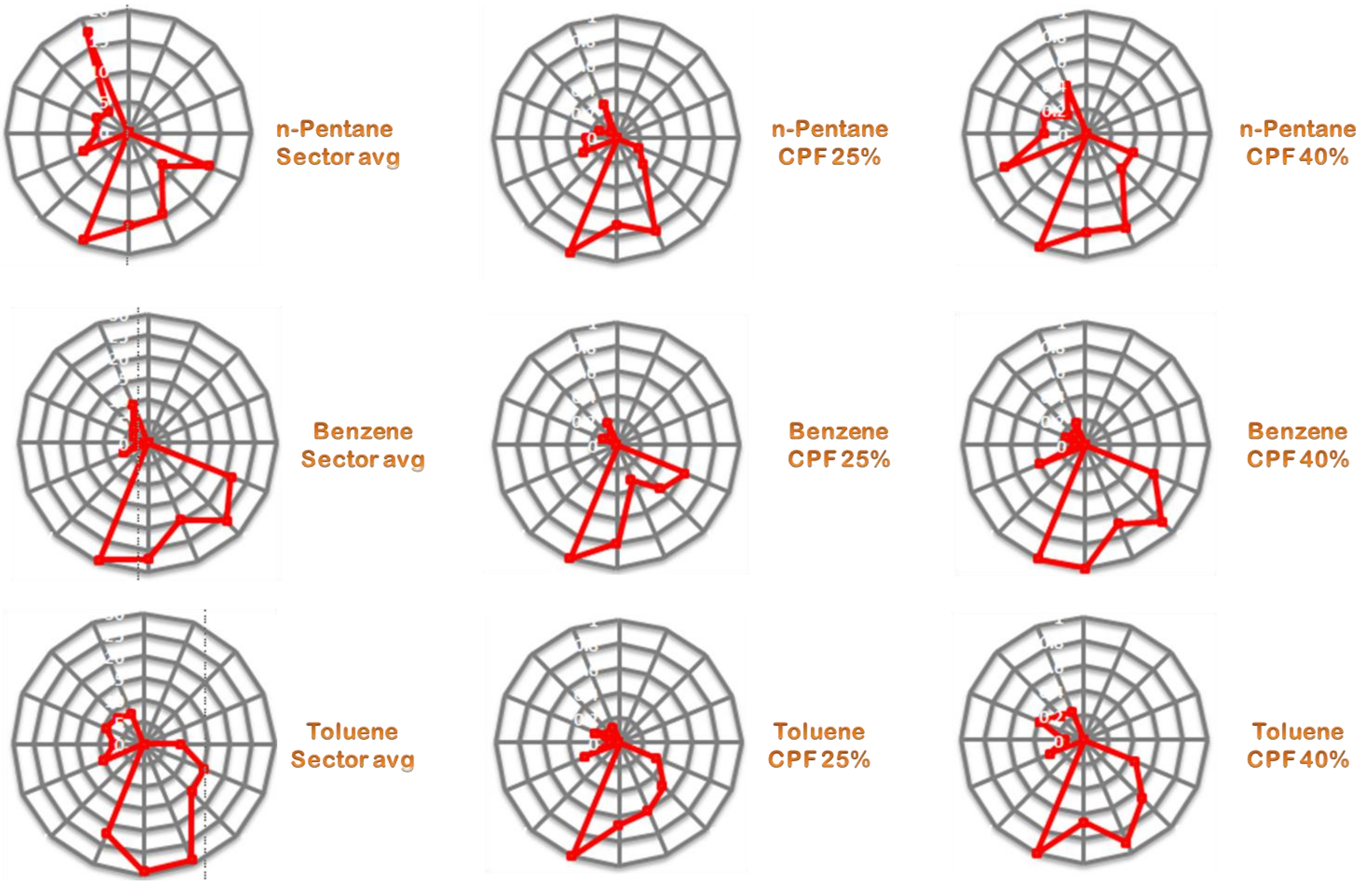


Figure 54 Similarities and differences between sector averages, CPF with highest 25% of data and CPF with the highest 40% of data

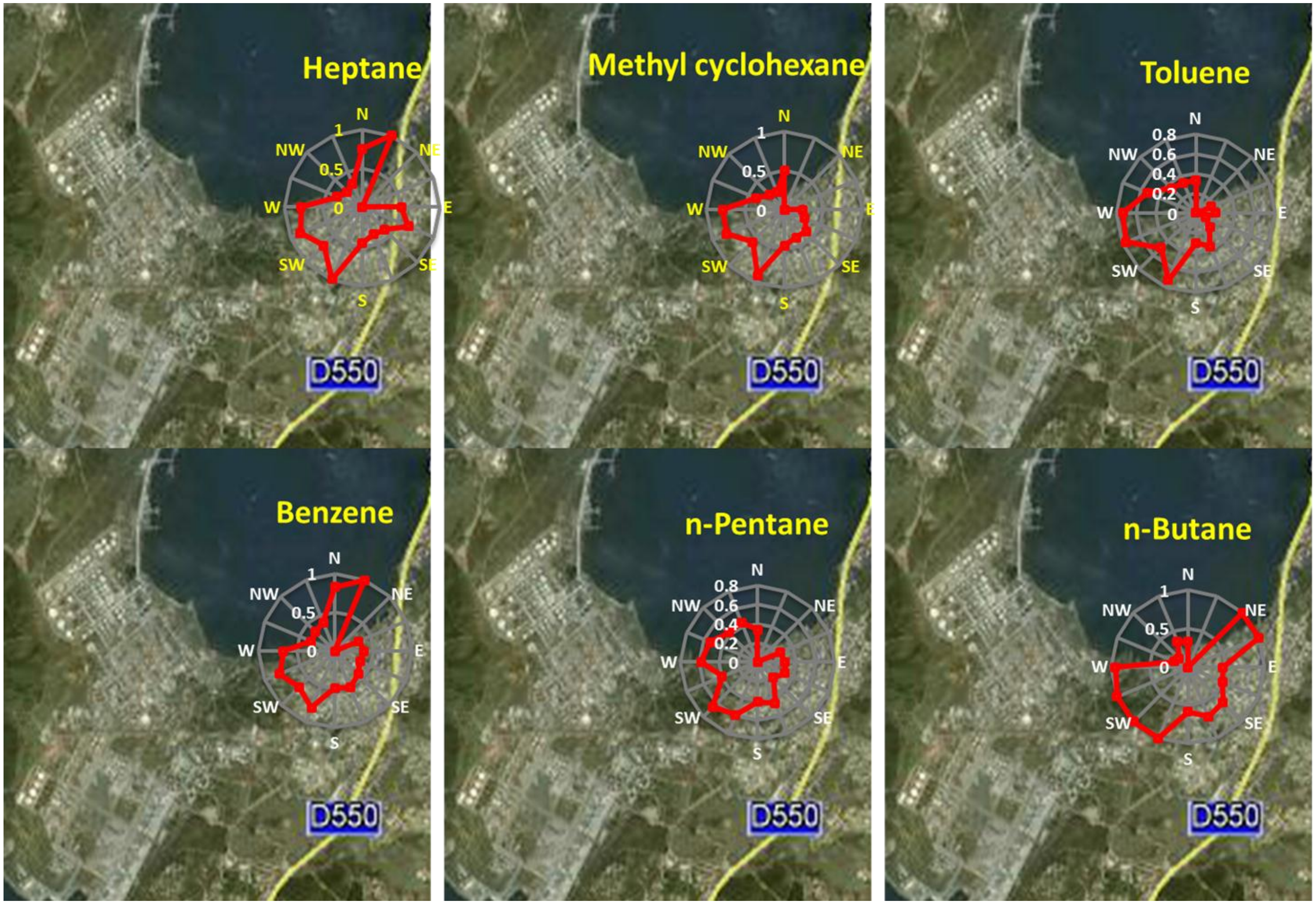


Figure 55 Conditional probability functions calculated for selected VOC s at Aliağa station

Distribution of CPF values among wind sectors at Horozgediği station, for some of the VOCs is depicted in Figure 56. It is clear from the figure that distributions of CPFs in Horozgediği and Aliağa stations are different. Conditional probability function values are not homogeneously distributed among wind sectors as they did at Aliağa station. Values of CPF show strong directional preferences at Horozgediği station. This is the difference between an urban station and a station at the middle of an industrial area. There is no contribution expected from residential emissions at Horozgediği, because there are no major residents around the station. This means that most VOC concentrations measured at Horozgediği station should be explained by emissions from industrial point sources, which are located in certain wind sectors and traffic emissions, which is expected to be the highest in NE and neighboring sectors, which includes İzmir – Çanakkale highway, and sector between W and NNE directions, which includes the local traffic between Aliağa and Yeni Foça. Although traffic count was not performed in this study, traffic activity on İzmir – Çanakkale highway is obviously much higher than the activity on Aliağa – Yeni Foça road. This polarity of sources around our Horozgediği station resulted in strong directional preferences observed in CPF roses for VOCs in Figure 56. There are some sectors in which CPF values are high in almost all VOCs. One and most obvious of these sectors is between N and NW. This sector includes major VOC emitters, including TÜPRAŞ, PETKİM and ship-breaking facilities. In the years 1991-1992 hourly SO_2, NO, NO_2, and PM_{10} concentrations were measured at seven locations in Aliağa region (Ulu, et al., 1994). One of the stations used in that study was located to approximately 1.5 km to the NW relative to our Horozgediği station. SO_2 and PM_{10} roses using data generated in that study are presented in Figure 57. SO_2 pollution rose generated using SO_2 measurements performed during this study are also included to figure to demonstrate the change in SO_2 sources in 15 years. Although interpretation of SO_2 and PM_{10} data is not within the scope of this study, they are included in this discussion, because SO_2 roses calculated 10 years apart very clearly demonstrate the impact of TÜPRAŞ and PETKİM to Horozgediği area, which is approximately 10 km away.

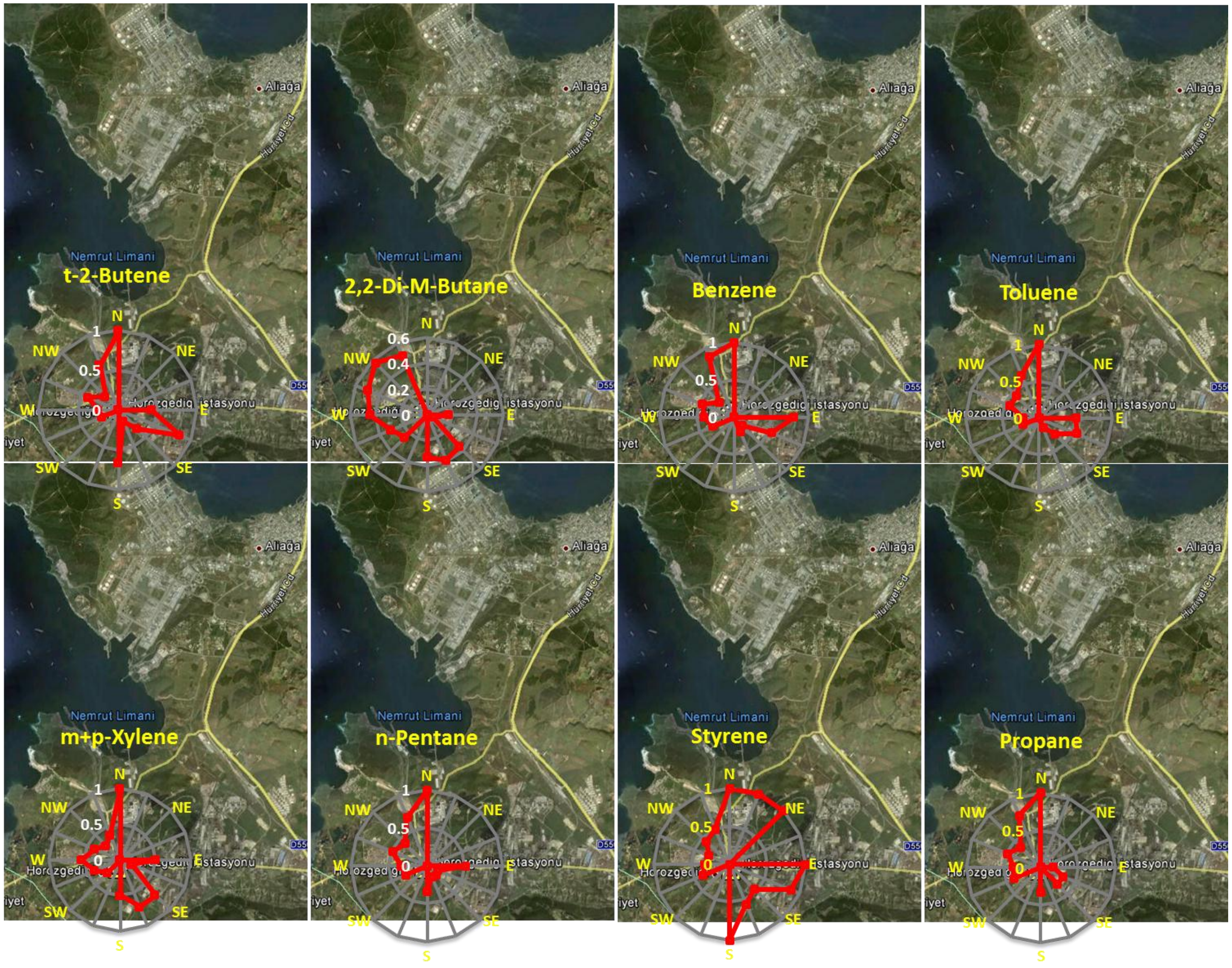


Figure 56 Conditional probability function calculated for selected VOCs at Horozgediği station

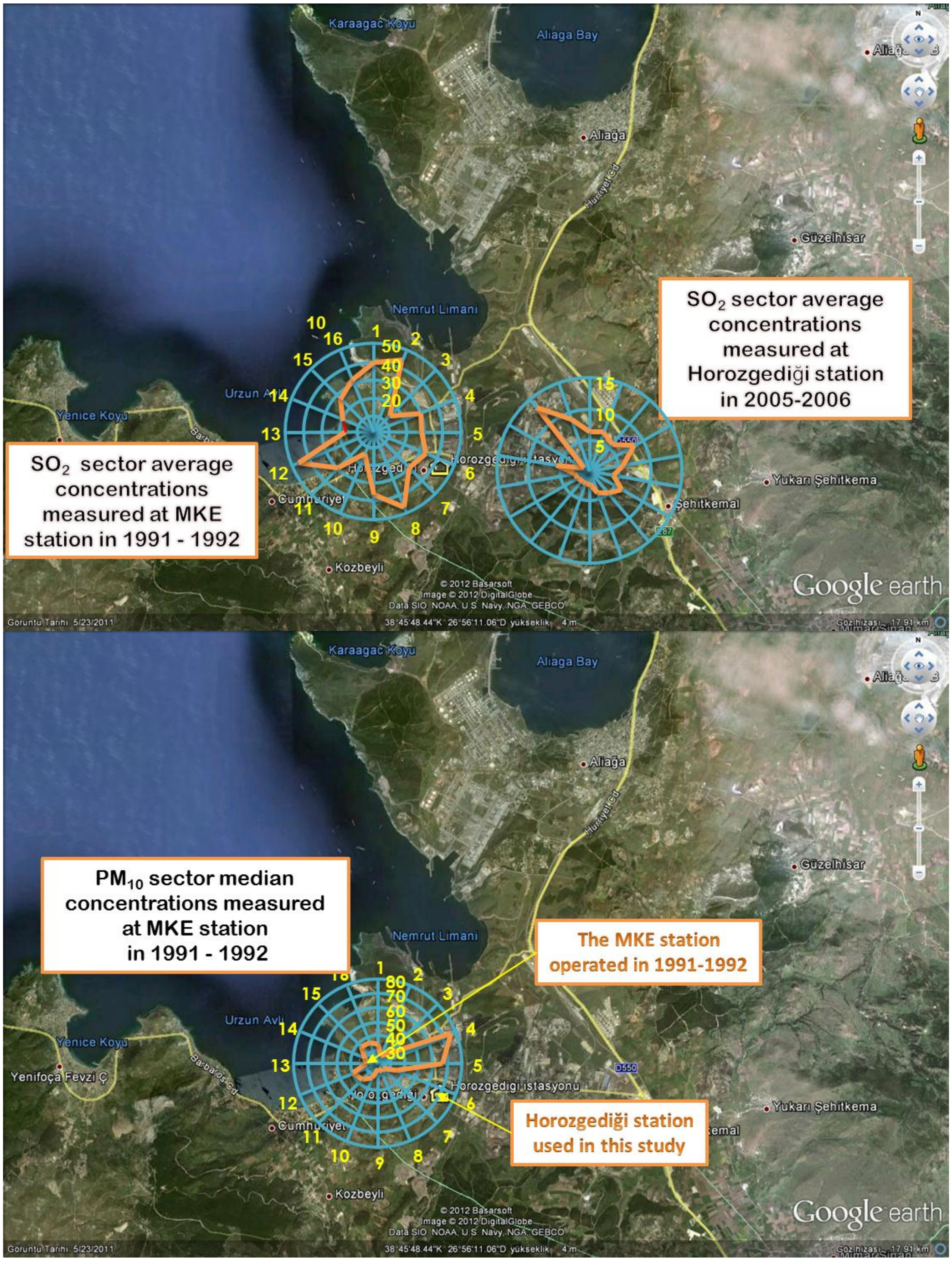


Figure 57 SO_2 and PM_{10} roses calculated with data generated at MKE station in 1991-1992 and at Horozgediği station during this study

There are several points worth noting in Figure 57. First of all SO_2 concentrations decreased significantly in 14 years. Although SO_2 rose is not a proper way to compare concentrations measured in different years, as they are medians of sectors and hourly concentrations can be very different, they still can give an idea about the levels in 1991 and in 2005. Highest sector median value recorded in 1991 was 44 µg m^{-3}. Corresponding value measured at Horozgediği station during this work was less than 15 µg m^{-3}. This dramatic decrease in SO_2 concentrations in the study area is due to change in the mode of energy production in Aliağa region. In 1991 PETKİM and TÜPRAŞ were using liquid and solid fossil fuels as energy source. Now they are using natural gas. This significantly reduced SO_2 levels in the whole air shed. Highest SO_2 concentrations were measured in North sectors (between NNW and NNE) in 1991, but strong sources on the north disappeared in SO_2 rose prepared from data generated in 2005 and 2006. This shows that MKE station and Horozgediği area in general are under strong influence of emissions from PETKİM and TÜPRAŞ.

Another point that should be noted in this figure is the lack of strong contributions from iron and steel plants on SO_2 levels in this area and lack of strong contribution of TÜPRAŞ and PETKİM on PM_{10} levels. There are number of iron and steel plants operating in around Horozgediği station. However, these plants use electricity to melt the scrap iron. Because of this, contribution of these plants on SO_2 levels in Horozgediği area was not high in 1991 and 2005. The situation is the opposite for PM_{10}. Iron and steel plants are very strong sources of PM are their emissions are not properly controlled. PM emissions from iron and steel plants at Aliağa were very poorly controlled in 1991. That is why high PM_{10} concentrations, as high 80 µg m^{-3} was recorded in East sectors, where these plants are located relative to MKE station in 1991. Contribution of N and neighboring sectors on PM_{10} levels was small in 1991. This is important, because it indicates that contribution of PETKİM and TÜPRAŞ on PM_{10} levels in Horozgediği area is significantly smaller than contributions of iron and steel plants. This was because oil was the main fuel used in TÜPRAŞ and PETKİM in those years. Although SO_2 emission from fuel oil can be high depending on its sulfur content, PM emissions are low. This situation probably did not change since then, because these two major emitters are now burning natural gas for energy production and PM emissions from natural gas is even lower. It should also be noted that emissions from iron plants are now much better controlled and their contribution to PM_{10} levels in the area also decreased. This issue will not be elaborated further, because inorganic pollutants are beyond the scope of this thesis.

The SO_2 roses discussed above are directly related to source of VOCs at Horozgediği area, which is measured at the Horozgediği station in this thesis work. As pointed before, SO_2 concentrations in northern sectors decreased by a factor of three between 1991 and 2005. This reduction in SO_2 concentrations in northern sectors, is not because these two important emitters disappeared entirely, but because they are not emitting SO_2 anymore. However, their non-sulfur emissions are continued in last 15 years. This is supported by striking similarity in shapes of the CPF roses prepared for VOCs in Horozgediği station and SO_2 rose prepared 15 years ago. The N and neighboring sectors have high CPF values in all VOCs. This is very similar to high SO_2 sector average in these sectors some 15 years ago and it is clear manifestation of the strong impact of these two VOC emitters to VOC levels in the Horozgediği area. High CPF values are also observed in the E and ESE sectors for most of the VOCs, which probably indicates the effect of İzmir – Çanakkale highway when winds blow from that direction. There is no other potential source in that direction. A third fairly common VOC source sector that appears in CPF roses is the W sector, which is probably due to emissions in Horozgediği village, which is approximately 400 m from the station in W sector. In addition to these common source sectors, different VOCs also showed unique directional preferences in some of the sectors, which may suggest unique sources for those particular VOC. There are many sources around Horozgediği station. One can always assign a source to a particular VOC having high CPF value at any sector, but we confined ourselves to high CPF sectors that are common in many VOCs, because assigning sources based on high CPF alone observed in one or two VOCs would be too speculative.

As summary it can be stated that, directional preferences of measured VOC concentrations are different in Aliağa and Horozgediği stations. Most of the VOCs measured showed typical urban CPF roses. In this typical pattern contribution of sources to measured VOC levels are fairly, if not entirely, homogeneously distributed around the station because, whether they are residential and traffic, these sources exists in most wind sectors around the measurement point. However, there are sectors where CPF values are higher (but not dramatically) then the calculated CPFs in other sectors. In Aliağa, these sectors with relatively high CPF point to the TÜPRAŞ and PETKİM. Considering the short distance between the Aliağa downtown and these two strong VOC emitters (approximately 2500 m from the center of TÜPRAŞ and 3300 m from the center of PETKİM), their contribution is smaller than one expects. Such small contribution is probably due to the fact the town is upwind from the two plants.

Since there are not residents around Horozgediği station, which results in fairly homogeneous distribution of CPF values among sectors, CPF values showed strong dependence on wind direction. Although there are also some other sources affecting concentrations of most of the VOCs measured in this study, such as nearby villages and roads, dominant sources are TÜPRAŞ and PETKİM. This also explains similar concentrations of VOCs in these two stations. Normally, since the station at Aliağa is very close to all sorts of sources, whereas there are no strong VOC emissions in the close proximity of the Horozgediği station, one would expect to see lower VOC levels at the Horozgediği area. However, since this station is downwind from PETKİM and TÜPRAŞ industrial complexes and since these two are very strong VOC emitters, approximately similar VOC levels are measured at both stations.

4.4.3. Dependence of VOC Concentrations Measured at TÜPRAŞ Station on Wind Direction: Source Profiles

The purpose of measuring VOCs at TÜPRAŞ station was to identify specific compounds coming entirely or almost entirely from either one of these plants, in other words to find the marker VOCs for TÜPRAŞ and PETKİM emissions, if there is any of course. These markers can be used in future receptor modeling studies to differentiate between contributions of TÜPRAŞ and PETKİM on surrounding airshed.

With this intention, TÜPRAŞ station was situated on the road that separates PETKİM and TÜPRAŞ and sampling was conducted for only 20 days. In these 20 days chromatograms were generated for 418 hours. Data availability varied between 18 hours and 402 hours, for different VOCs.

Orientation of TÜPRAŞ and PETKİM around sampling station is given in Figure 58. As pointed out before, the station was set up on the road between the PETKİM and TÜPRAŞ to intercept emissions from TÜPRAŞ or from PETKİM depending on wind direction, but not from both of them at the same time. TÜPRAŞ was included in sectors between NNW and ESE when the wind blew from these sectors only TÜPRAŞ emissions are intercepted at the station.

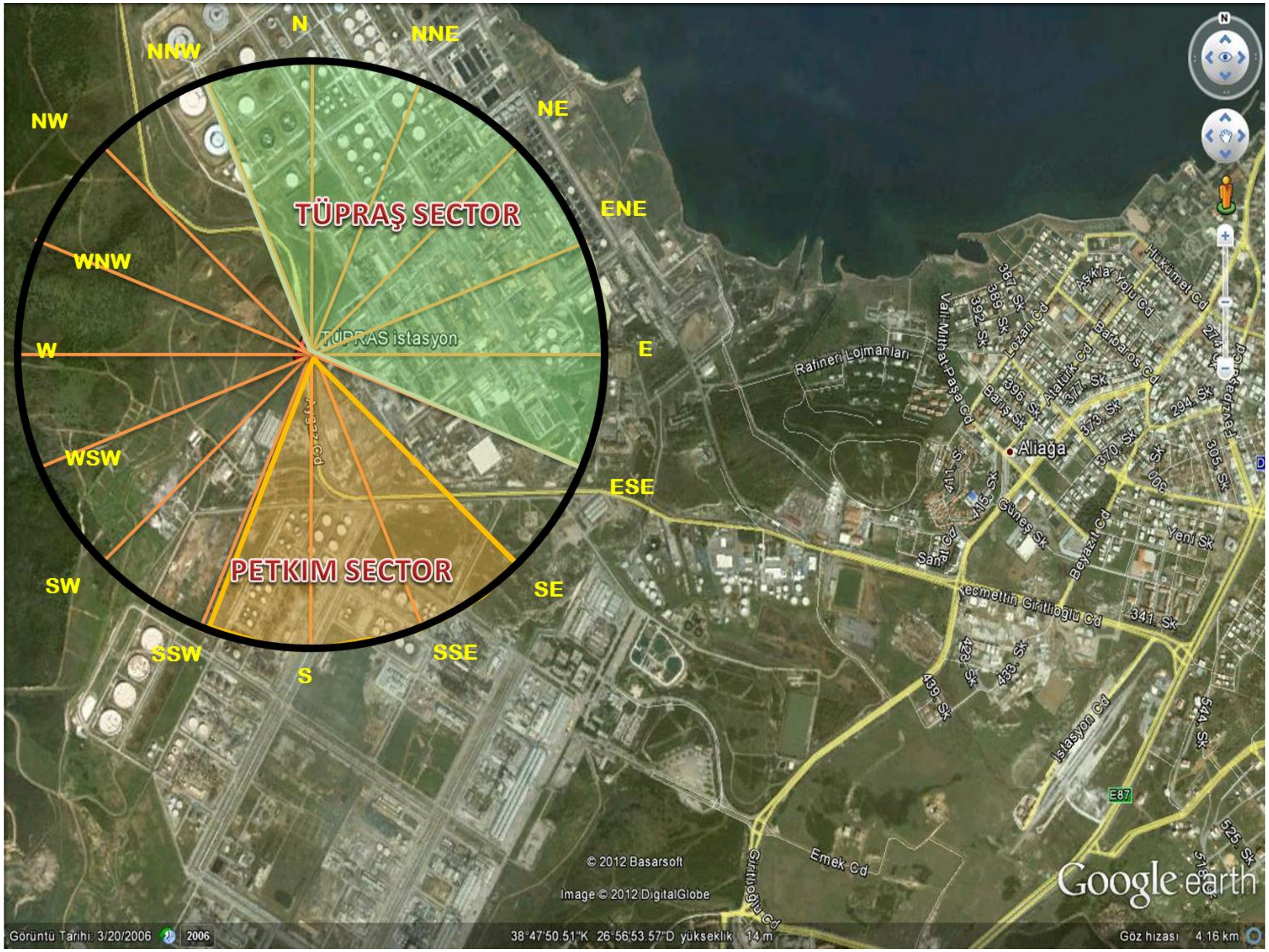


Figure 58 Orientation of PETKİM and TÜPRAŞ around sampling station

PETKİM, on the other hand is included in the sector between SE and SW. Winds from this sector brought PETKİM emissions to the station. Other wind sectors may bring mixed emissions to the site. The sector between SW and NW appears a background sector, but it is not entirely free of emissions from these two industries. There are some storage areas and tanks which are not visible in the figure and which may degrade the background signal due to their close proximity to the sampling point. Because of this we did not use concentrations of VOCs measured when winds blew from this sector as background.

There were a total of 98 hourly wind events from TÜPRAŞ sector and 139 wind occurrences from PETKİM sector. However, these numbers decreased when winds higher than a threshold value was used. The threshold value we used was 1.0 m s^{-1}. Thus winds slower than 1.0 m s^{-1} were not included in sector analysis. We had also investigated possibility of using 2.0 m s^{-1} as the threshold value, but the difference in results that were obtained when 1.0 m s^{-1} and 2.0 m s^{-1} thresholds were used was not large enough to change the conclusions. The only significant difference caused by the 2.0 m s^{-1} threshold value was the reduction in wind occurrences, which increased the uncertainty in the conclusions. Consequently this discussion is entirely based on the winds that were faster than 1.0 m s^{-1}. Number of wind occurrences in TÜPRAŞ sector decreased from 99 to 83 and those in PETKİM sector decreased from 139 to 54. This is interesting, because it implies that the winds from south sector are slower than the winds blowing from north and neighboring sectors.

Distribution of CPF values among wind sectors are given in Figure 59. There are two points that should be noted in this figure. The SW to NW sector which appears as free from contribution of these two industries in Figure 58 cannot be used as background sector, because CPF values in that sector are fairly high for most of the VOCs, which are depicted in the figure. The most significant contribution to measured VOC levels at this station comes from the PETKİM sector. TÜPRAŞ sector have significantly smaller CPF values for most of the species. Average and median concentrations observed when winds blew from PETKİM sector (with a speed > 10 m s^{-1}). The PETKİM-to-TÜPRAŞ median ratios are as high as 15 for some of the VOCs. The only specie for which a factor of two higher concentrations was observed when blew from TÜPRAŞ sector is dimethylcyclohexane. This dominant influence of PETKİM on our station implies that its emissions should be expected to have stronger influence on the surrounding airshed. It is difficult to differentiate emissions from PETKİM and TÜPRAŞ because they are very closely located and they together affect any receptor in Aliağa region. Identification of potential marker VOCs is crucial to quantify contributions of these two industrial complexes using receptor models, particularly CMB. The median concentrations obtained for TÜPRAŞ and PETKİM sectors and their ratios are given in Figure 60. Concentrations of 2-methyl-hexane, n-hexane, cyclo-hexane+cyclo-hexene, benzene, 2,2,3-tri-methyl-butane+2,3-di-methyl-pentane, di-bromo-methane+ 1,2-di-cloro-propane, ethyne (acetylene), 1,3-di-ethyl-benzene, n-pentane, o-xylene, propane, methyl-cyclo-hexane, m+p-xylene, ethylbenzene, methylcyclopentane + 2,4-di-methyl-pentane are higher in PETKİM sector than they are in TÜPRAŞ sector, by a factor of four or more. Among these concentrations of methyl-hexane, n-hexane, cyclo-hexane+cyclo-hexene, benzene, 2,2,3-tri-methyl-butane+ 2,3-di-methyl-pentane are factors of 12 – 15 higher in PETKİM sector. These species are probably good markers for PETKİM emissions. However, there is no good marker to single out TÜPRAŞ emissions.

Even if there is no strong marker for TÜPRAŞ, contributions of these two emitters can be differentiated using least square approaches such as CMB, if their emission profiles are sufficiently different.

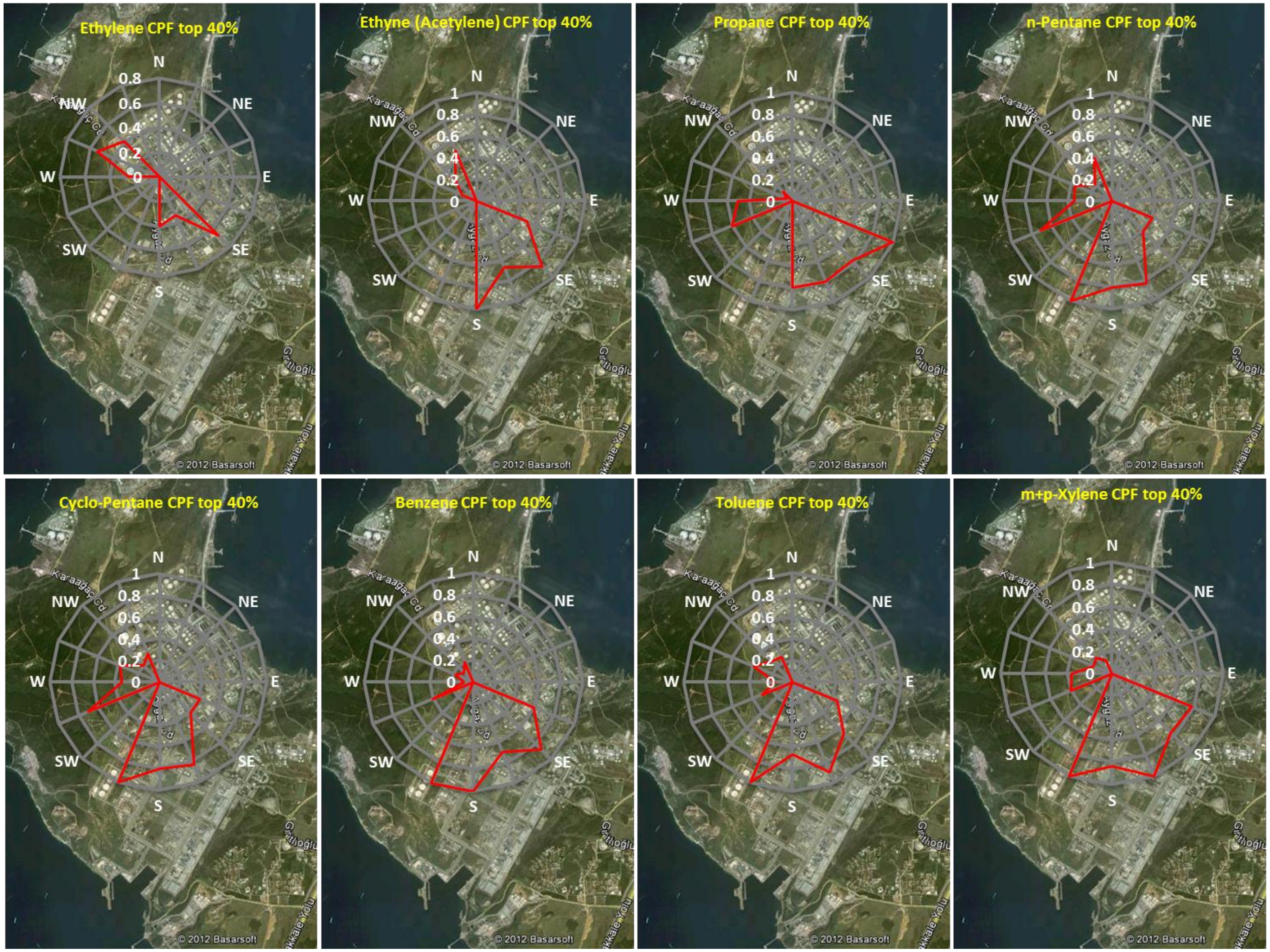


Figure 59 Conditional probability functions calculated for seleceetd VOC s at TÜPRAŞ station

The profiles (% contribution of individual compounds to total VOC) calculated using median concentrations of TÜPRAŞ and PETKİM sectors are given in Figure 61. Only major contributors to profiles are shown in the figure. Each slice in the pie graphs corresponds to percent contributions of a VOC. Names of small slices are not shown in the figure not to make it very crowded. There are some differences between TÜPRAŞ and PETKİM profiles shown in the figure. The most notable difference is the heavier weighting of light hydrocarbons in TÜPRAŞ sector profile. Ethylene, propane, propylene and butanes account for approximately 55% of the ΣVOC mass in TÜPRAŞ sector. Corresponding contributions of the same VOCs to ΣVOC mass in PETKİM sector is 32%. On the other hand, some of the heavier VOCs (not necessarily the heaviest ones) have higher contributions to ΣVOC mass in PETKİM sector. These include, benzene, 2-methylhexane, toluene, m,p-xylene. Contribution of these, except for toluene, was small in TÜPRAŞ sector. Heavier weighting of light VOCs in TÜPRAŞ sector should be expected, because most of the emissions in a refinery are evaporative emissions of hydrocarbons and transformation from one form to another during chemical processing is not expected. Since the vapor pressure of VOCs increase with decreasing carbon number, lighter ones are expected to be the main component in evaporative losses in the refinery. Emissions from PETKİM on the other hand are from chemical processing of organic material. VOCs emitted depend on the chemical process.

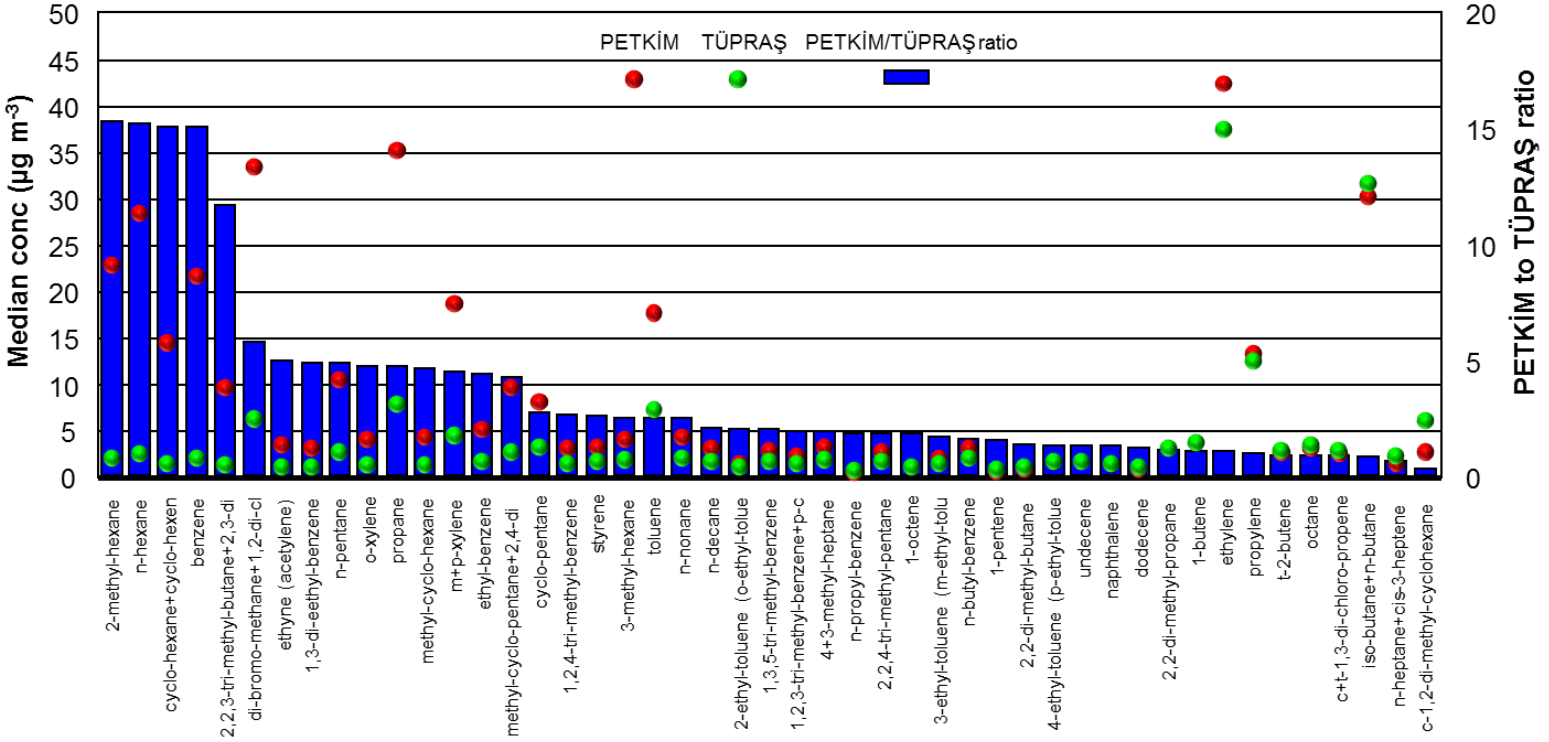


Figure 60 TÜPRAŞ and PETKİM sector median concentrations and PETKİM/TÜPRAŞ concentration ratios

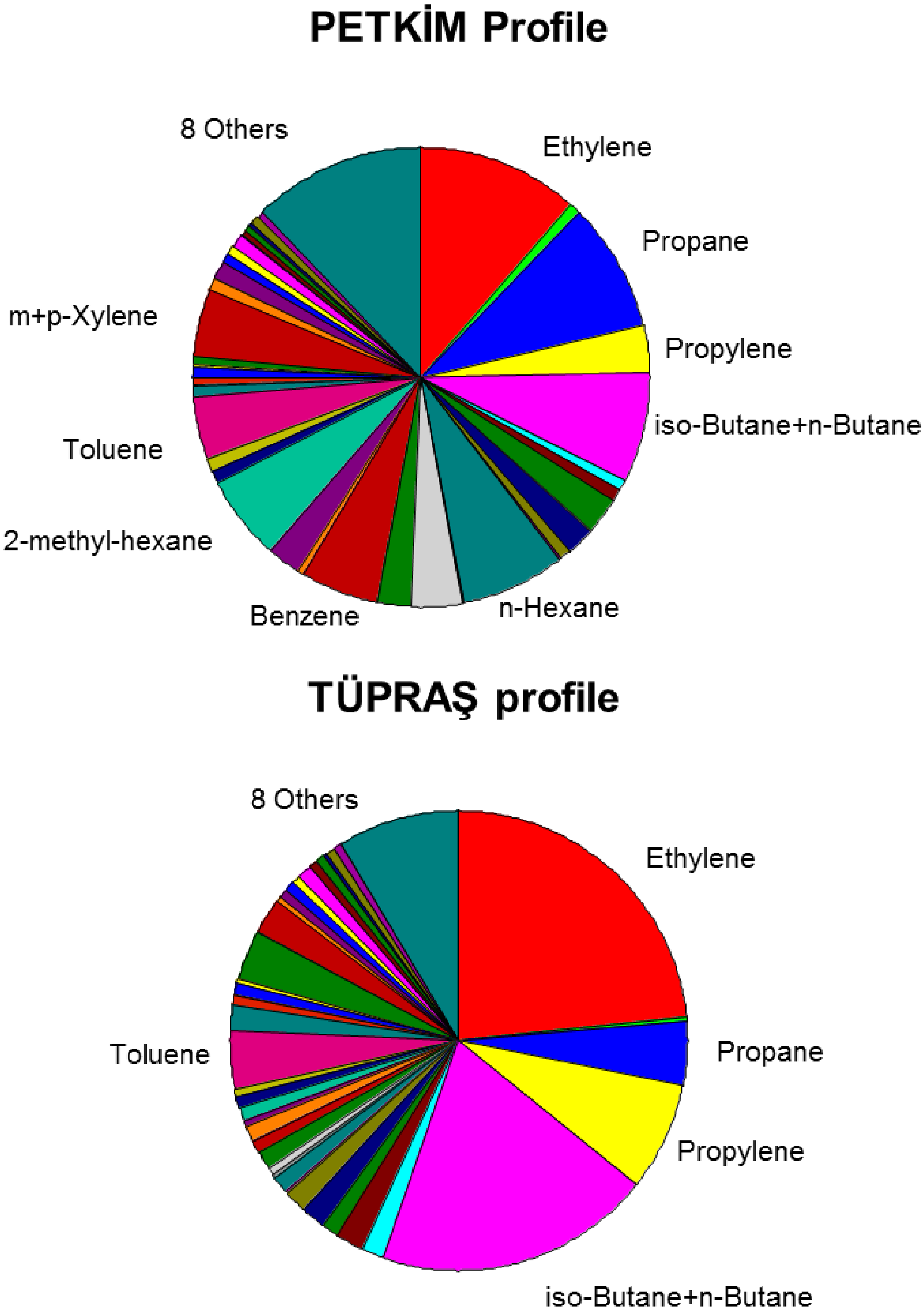


Figure 61 TÜPRAŞ and PETKİM profiles

There were fourteen plants in the PETKİM complex in 2005 when this study was performed. These included; Low density polyethylene plant (AYPE plant), Tubular low density polyethylene plant (AYPE-T plant), High density polyethylene plant (YYPE plant), Polypropylene plant, Ethylene plant, Aromatics plant, chlor-alkali plant, vinyl chloride monomer plant (VCM plant), PVC plant, Acrilonitrilo plant (CAN plant), Ethylene glycol plant, Terephthalic acid plant (PTA plant), Phthalic anhydride plant (PA plant), Plastic processing plant. Various organic compounds such as, ethylene, propylene, propane, LPG etc, are either used as input material or produced in these plants.

Among all plants in the PETKİM Aromatics plant is probably the most important one in terms of affecting the VOC profile in PETKİM sector, because products in this plant includes benzene, toluen, p-xyelene, o-xylene, C_5 hydrocarbons and heavy aromatic compounds. Normally all precautions are taken in this type of plants not to lose the product, because leakage of product to atmosphere means losing money, but yet some of the products may escape to atmosphere either during processing, but more likely during loading or unloading operations. Such losses are clearly seen as enhancement of BTX compounds in the PETKİM sector profile.

4.5. Specie Ratios

Concentrations of species give information about the major sources influencing VOC emissions. There are two commonly calculated ratios used in the literature. These are toluene to benzene (T:B) and m&p-xylene to ethylbenzene (mpX:E) ratio.

Toluene to benzene ratio is used for the identification of motor vehicle and non-motor vehicle sources. In the literature, for motor vehicle emission T:B ratios are reported in the range of 1.5 to 2.3 (Kuntasal, 2005). In case of industrial or solvent intrusion to the air mass, T:B ratio increases. mpX:E ratio is an indicator for the age of the air mass. The ratio of these target species in the emissions is assumed to be constant. However, the atmospheric lifetimes of m&p-xylene and ethylbenzene are 3 hr and 8 hr, respectively. Therefore, as the air mass travel to a distance m&p-xylene react more rapidly in the atmosphere, resulting a decrease in the mpX:E ratio.

The diurnal variation and the rose diagrams of the calculated ratios for Aliağa station are given in Figure 62 and Figure 63, respectively. The diurnal variation of T:B ratio is similar diurnal variation of any industrial related compound measured in Aliağa. The ratio is almost constant through night and starts to increase gradually after 10:00 and then decrease back after 18:00. This variation is due to the shift in the wind direction that has already been discussed in Section 4.1.1.1 and shown in Figure 22. The wind starts to blew from industrial regions after 10:00, leading to increase in the T:B ratio until 18:00. Through 18:00 to 09:00 in the morning, T:B ratio is around 3. This could be due to two reasons. The first reason is fuel composition may differ from point to point and season to season. This could lead to observe higher ratios. Secondly, some solvent intrusions to the air masses might occur due to diffusion. The mpX:E ratio is relatively constant throughout the day. This is expected as the sources are not very far away from the sampling site.

The rose diagram of T:B ratio shows that NW to SW sectors and N sector have high T:B ratios. NW to SW sectors is the industrialized regions where TÜRPAŞ and PETKİM are located. Therefore, such high ratios are expected from these sites. The high contribution from N is not clear. This could be due to some commercial and residential activities such as painting, asphalting, etc. The rose diagram of m&pX:E ratio is constant through the region. This indicates that there is negligible amount of VOCs transported to region.

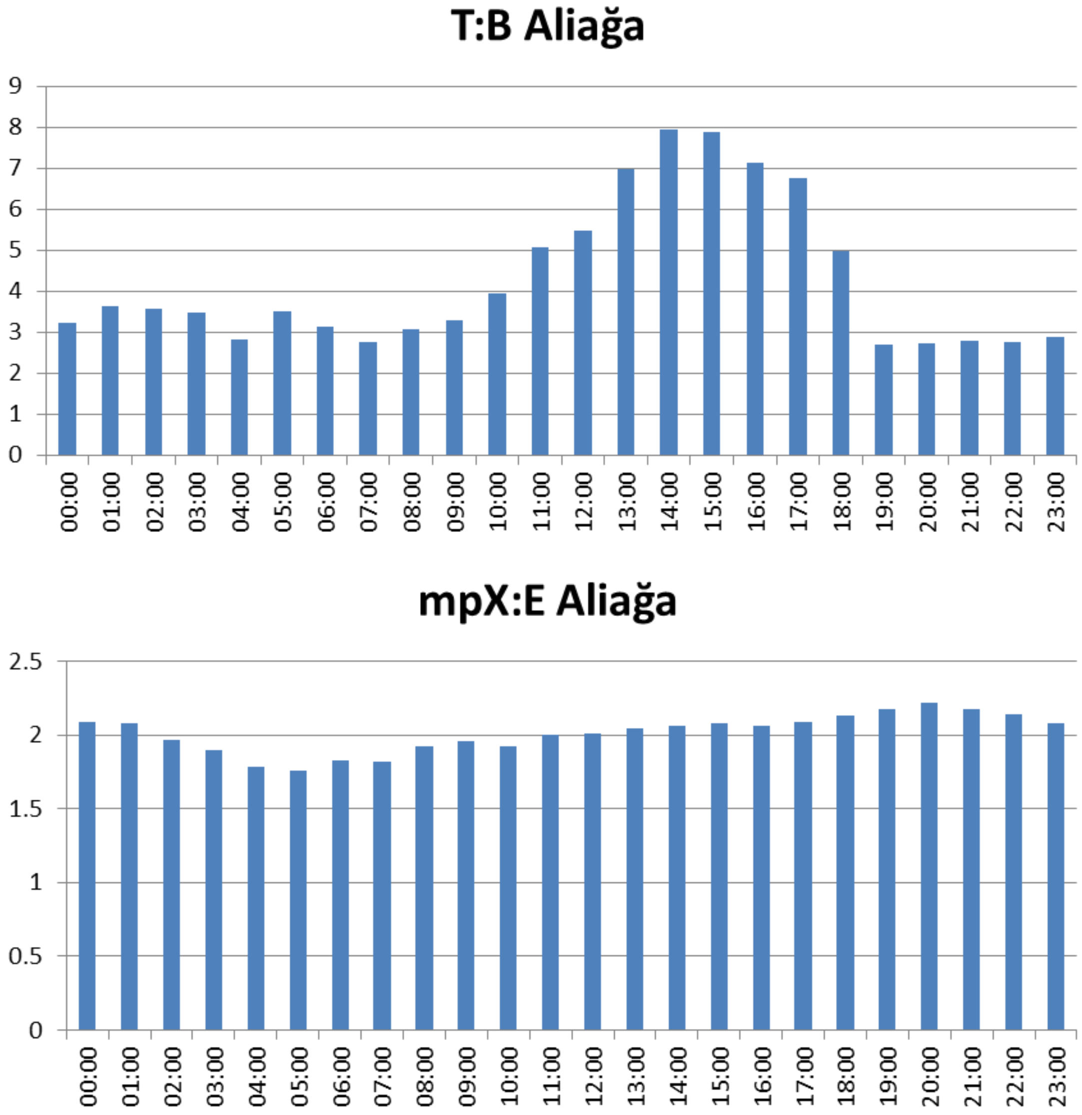


Figure 62 Diurnal variation of T:B and mpX:E ratios at Aliağa station

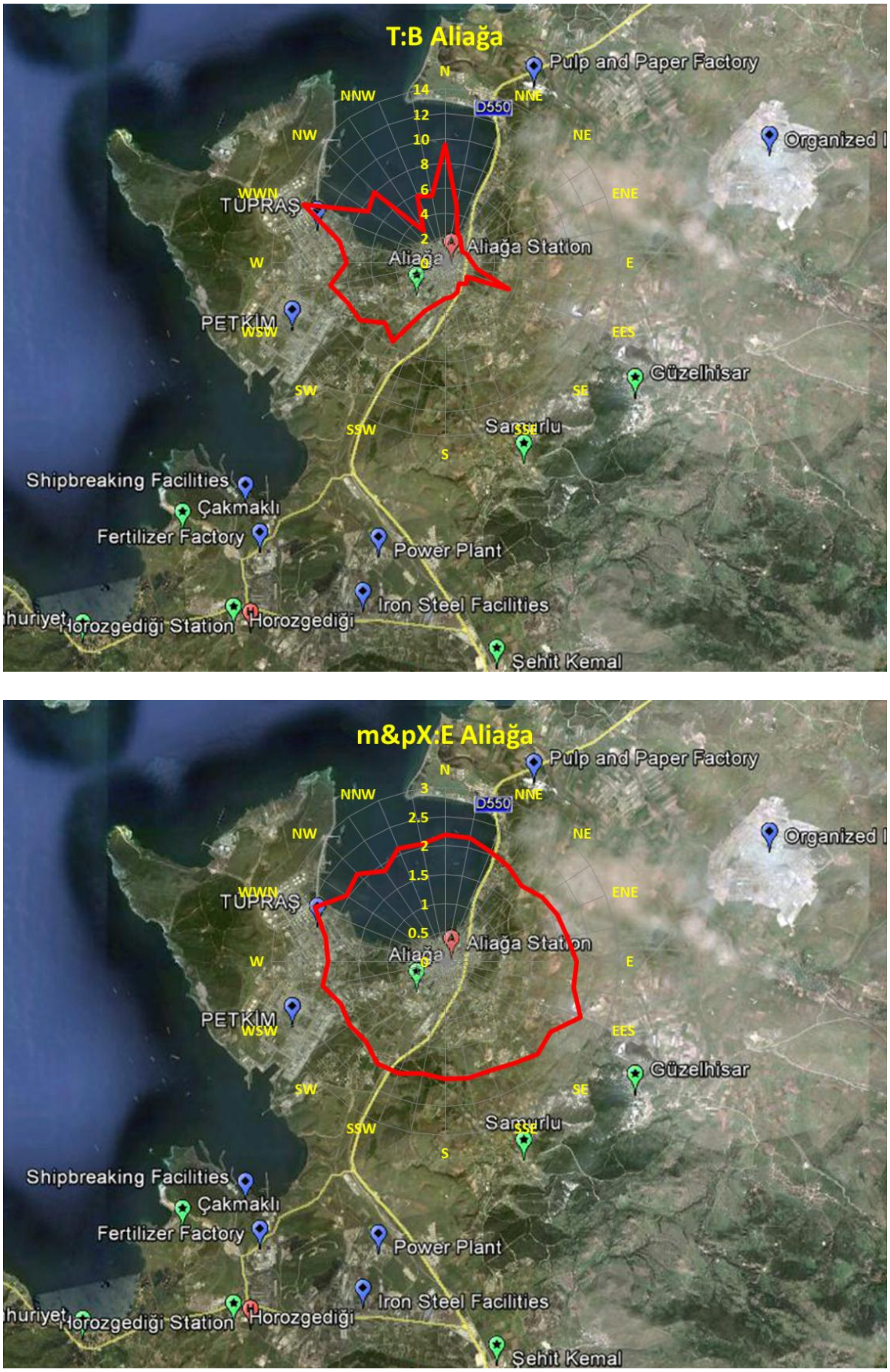
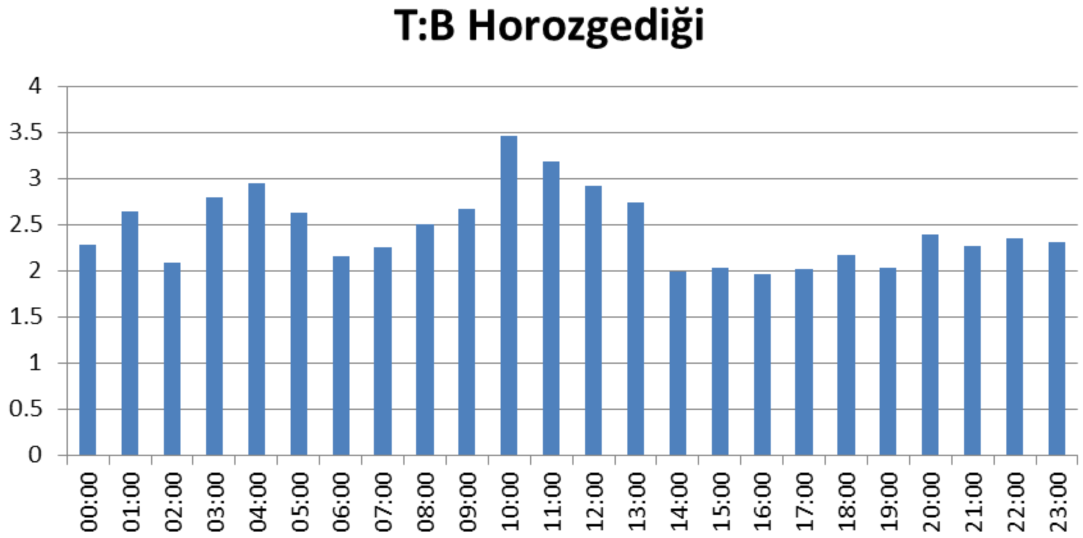


Figure 63 Rose diagrams of T:B and m&pX:E ratios at Aliağa station

The diurnal variation and the rose diagrams of the calculated ratios for Horozgediği station are given in Figure 64 and Figure 65, respectively. The T:B ratio in Horozgediği is not as variable as in the case of Aliağa station. However, there is still an increase in the T:B ratio during day time. As discussed in Section 4.1.1.1, shifts in wind direction also determines the T:B ratio in the region. The rose for T:B ratio at Horozgediği also suggests high contributions of N, NW and SE directions. N and NW of the station, there are industrial areas, ports and villages. The high T:B ratio might be due to industrial emissions, solvent transportation and residential solvent evaporation in the region. High SE T:B ratio might be also due to residential solvent evaporation from Bozköy village.

Similar to Aliağa, m&p-X:E ratio does not show diurnal variation at Horozgediği station. The rose diagram of m&p-X:E ratio shows almost constant ratios through the region only with W exception. On the W of the station, there is no important source region other than the Horozgediği village which is located on the WWN direction. Therefore VOCs transported from the W of the station are slightly aged than the VOCs other wind sectors.



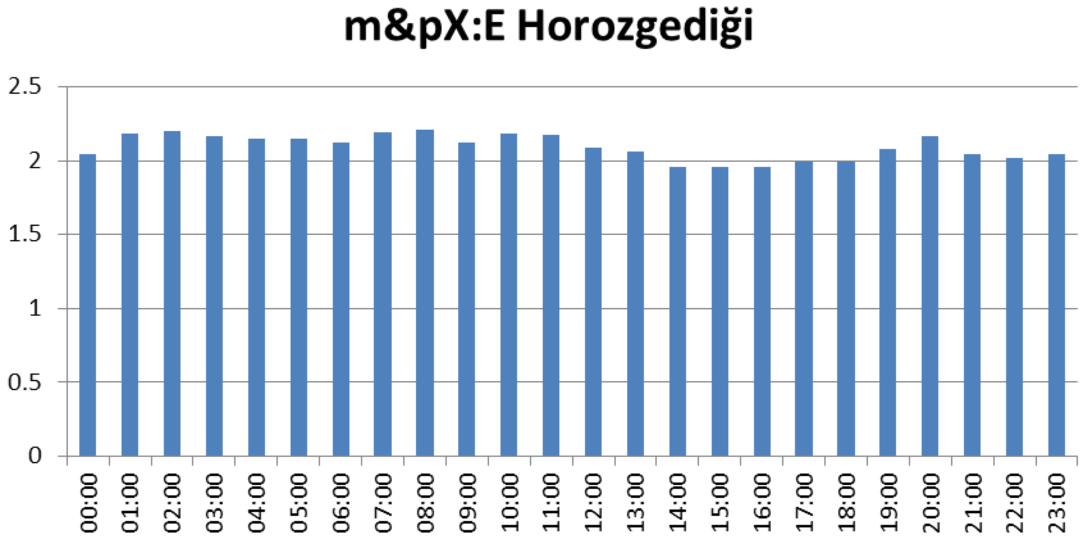


Figure 64 Diurnal variation of T:B and mpX:E ratios at Horozgediği station

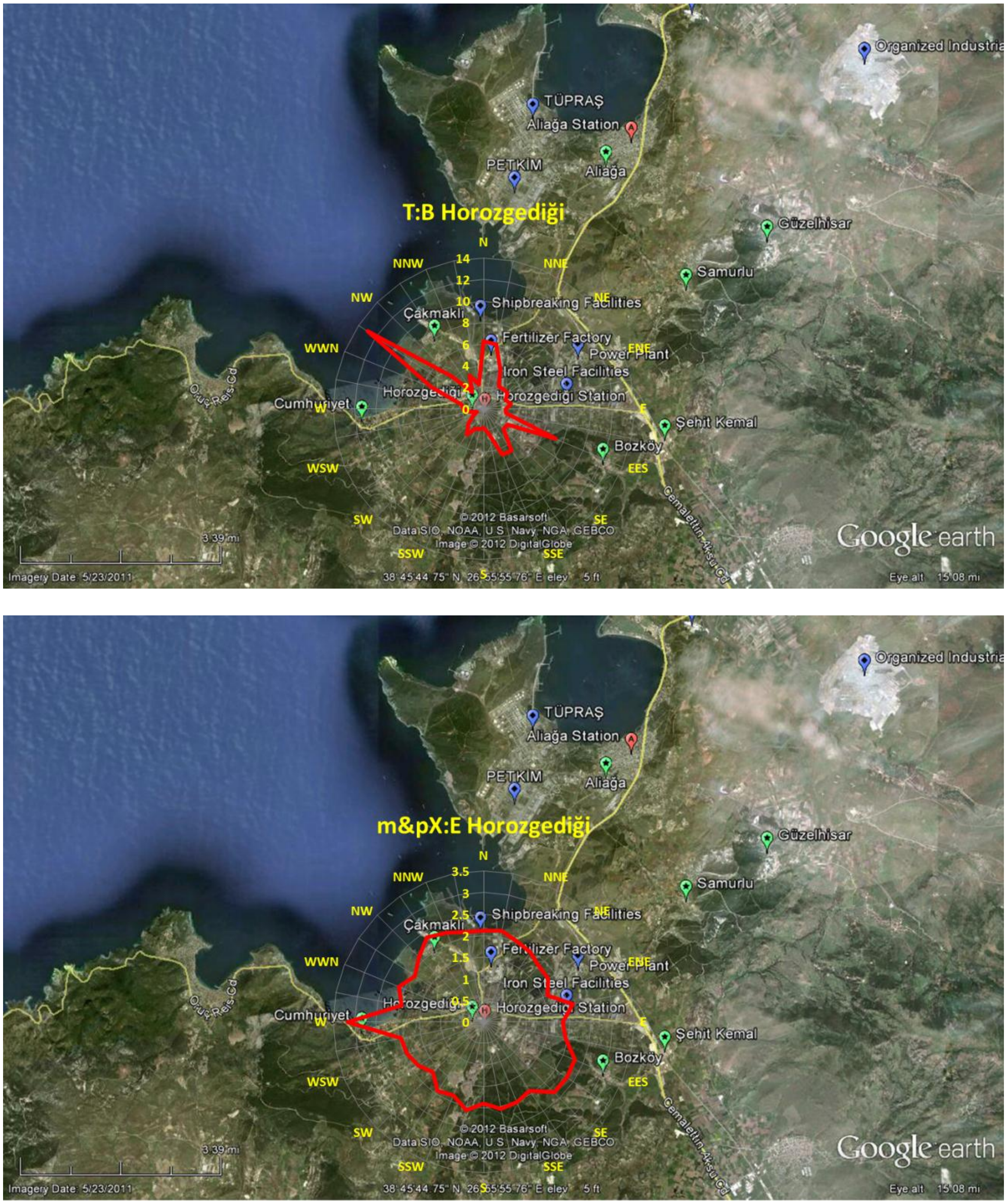


Figure 65 Rose diagrams of T:B and m&pX:E ratios at Horozgediği station

4.6. Receptor Modeling

Positive matrix factorization method developed by Paatero (1997) is used in this study to investigate sources of VOCs and their contributions measured at Aliağa and Horozgediği stations. The description of method and input file preparation steps are discussed in Section 3.4.1. There are some quality control parameters to find out the optimum result with PMF.

As discussed in Section 3.4.1, the main aim and therefore the first quality control parameter of PMF is to minimize the objective function, Q, which is defined in Equation 2. In order to find the result with the lowest Q value, at least 10 runs with different starting point (seed) should be performed. The Q values should be compared and the solution with the minimum Q value is selected. EPA PMF reports two Q values to the user: Q robust and Q true. Q robust is the goodness of fit parameter calculated excluding outliers. A data point is defined as outlier when modeled error to uncertainty ratio is greater than 4 (Paatero, 1997). Q true is also a goodness of fit parameter but it includes all data. Solutions where Q true is greater than 1.5 times Q robust indicate that peak events may be disproportionately influencing the model. The theoretical Q is approximated as:

$$Q_{theor} = n \times m - p \times (n + m) \qquad \text{Equation 4}$$

where n is the number of species, m is the number of samples and p is the number of factors fitted by the model. The optimum final solution Q robust value should be comparable to the Q theoretical value.

The second quality control parameter is to check each species modeling performance. This is done in two ways: (i) by checking predicted concentrations to observed concentration graph and (ii) by checking histograms of scaled residuals for each data point, which is defined as ratio of absolute difference between predicted concentration and observed concentration to uncertainty of that data point. The idea of apportioning sources with PMF is simply grouping compounds with respect to their correlations. If a compound is fitted poorly, then this compounds correlation with other compounds will affect the fit of other compounds resulting false factor profiles. Therefore, poorly fitted specie should be removed from the model input.

An example unwanted predicted concentrations to observed concentration graphs are given in Figure 66, for pentane and butane. The observed-to-predicted plot for pentane is an example of poor performance of a specie. The regression line fitted to predicted concentration to observed concentration is expected to follow one-to-one line as depicted in
Figure 66b, for butane.

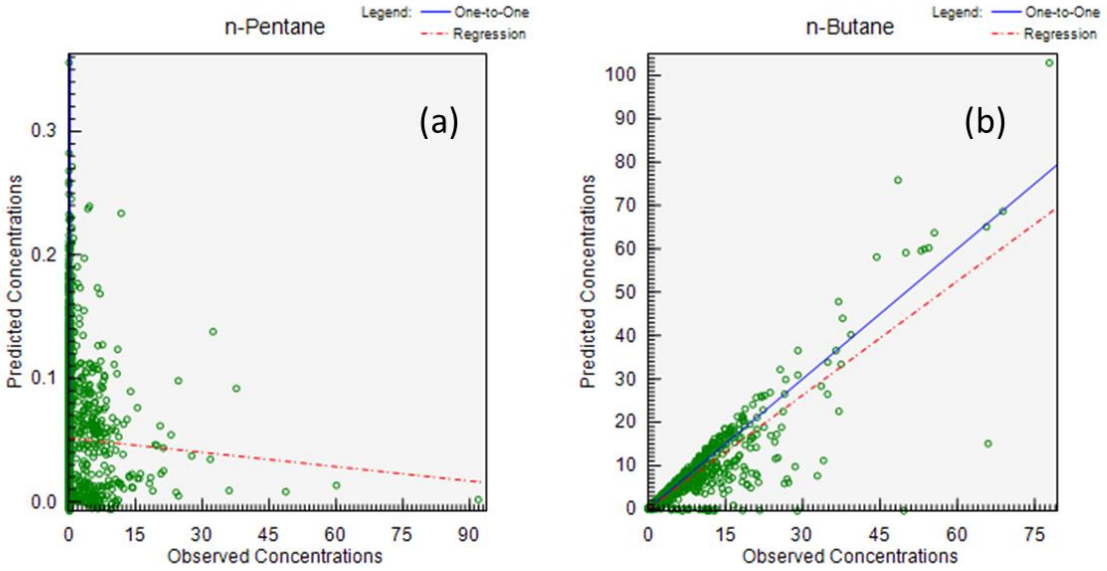


Figure 66 Observed to predicted concentration distributions
(a) a bad example and (b) a good example

Scaled residual distributions of n-pentane and n-butane are given in Figure 67. At an optimum solution, the species scaled residuals should be normally distributed with a median value of 0 and all residuals are expected to be around ±4, as in the case of n-butane. The nonsymmetric distribution with large number of values outside the limits (±4), as can be seen in Figure 66a for n-pentane indicates that model optimization is not yet complete.

The third quality control parameter is to check the source profiles. In the literature, tracers are defined for each source. The user must have priori information about the source profiles and what they might be.

The fourth and one of the most important quality-of-model-fit checks is the correlations between G-scores of different factors. If scores of different factors are strongly correlated with each other, then it can be concluded that a single source emissions is divided into two sources. Correlation between G-scores is not expected. However, in some cases, particularly if the sources emissions are carried to sampling site under the same conditions, there can be a correlation between the G-scores. Such correlations are due to the nature of these statistical tools and have nothing to do with data quality. Most of these multivariate statistical tools, including PMF, FA, PCA and cluster analysis are parametric tools designed for data with Gaussian distribution. Outliers in log-normally distributed data can generate such poor fits to model. Correlation G-scores of different factors can sometimes be solved by the varying F-peak value, or the value of "α", or by increasing uncertainties of outliers causing these correlations. These actions generally merge the two correlated factors into one.

The fifth quality parameter is applying bootstrapping to factors to see if they are robust enough to survive small changes in the data set. Application of bootstrapping to PMF is rather new quality control test implemented to the recent versions of the EPA version of the PMF.

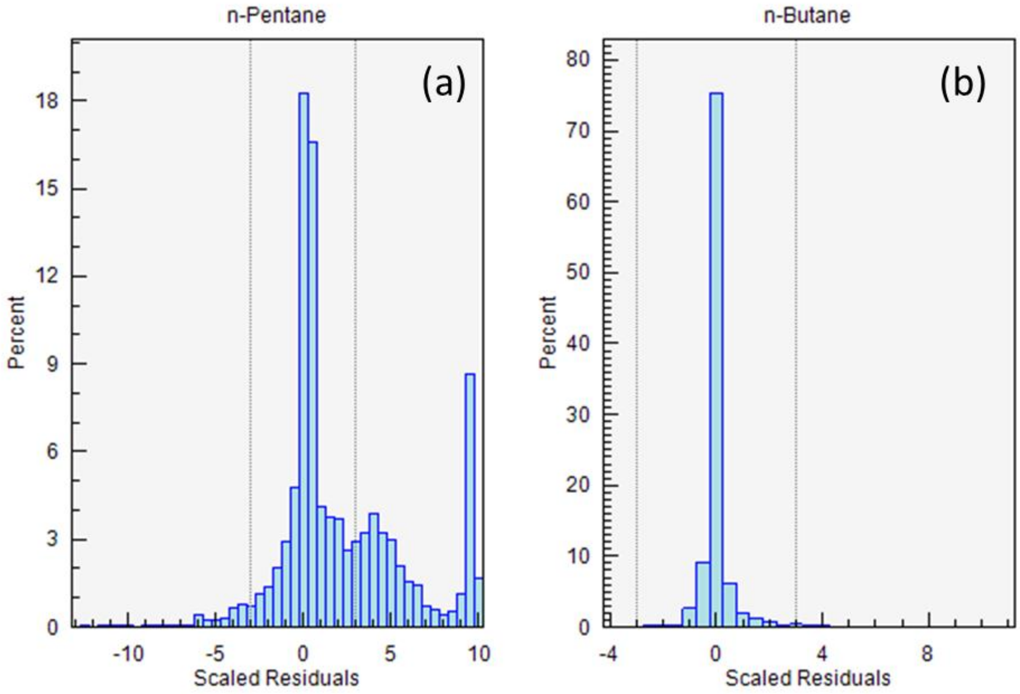


Figure 67 Histograms of scaled residual distributions
(a) a bad example and (b) a good example

The bootstrapping application of EPA PMF is given in the User Guide of PMF3 (EPA, 2008) which is quoted directly below:

> “EPA PMF performs bootstrapping by randomly selecting non-overlapping blocks of samples (consecutive samples) and generating a new input data file of the selected samples, with the same dimensions as the original data set. PMF is then run on the new data set, and each bootstrap factor is mapped to a base run factor by comparing the contributions of each factor. The bootstrap factor is assigned to the base factor with which the bootstrap factor has the highest correlation, above a user-specified threshold. If no base factors have a correlation above the threshold for a given bootstrap factor, that factor is considered “unmapped”. If more than one bootstrap factor from the same run are correlated, best with the same base factor, they will all be mapped to that base factor. This process is repeated for as many bootstrap runs as the user specifies. The user should examine the Q values and factor identifications for stability and the interquartile ranges around the profiles.” (EPA ,2008)

All these tests were performed in PMF runs in this work. Usually composition of factors, variances of species explained by factors and G-scores for each factor is standard outputs of PMF software. It should be noted that no-matter which QC tests are performed, the factors has to be identified. Identification process, which bases on composition of factors alone can be considered as speculation, because some of the VOCs can be emitted from more than one source. Because of this any supplementary information should be used to support the identification of factors. In this study, in addition to standard outputs of the PMF software, diurnal variation of G-scores and distribution of CPF values in wind sectors were also prepared for each factor as supplementary data to confirm proposed identity of factors.

Various sources were identified and quantified in the PMF modeling of Aliağa and Horozgediği data sets. Detection of a TÜPRAŞ or PETKİM factor or a factor associated with any other industry does not necessarily mean that they are polluting Aliağa and Horozgediği area. We used very sensitive measurement techniques and very capable multivariate techniques and detected industrial signatures. These industries can be blamed for a wrongdoing only if concentrations of VOCs are high in the measurement sites. This is not the case. Concentrations of none of the VOCs are high at the Aliağa station and Horozgediği station. This means that industries are contributing to VOC levels at the measurement site, but not high enough to pollute the atmosphere.

4.6.1. Receptor Modeling of Aliağa Station

The number of compounds analyzed with GC system in winter and summer campaigns are 52 and 29, respectively. During summer campaign a part of the GC system was broken and could not fixed through the campaign period.

In order to include as much as compounds possible to source apportionment studies, winter and summer campaign datasets are handled separately.

4.6.1.1. Winter Campaign Receptor Modeling

Several four to seven factor solutions of Winter Campaign data are analyzed. 16 compounds that poorly modeled are deleted from the data set. The deleted compounds are n-pentane, n-hexane, 2-methyl-1-pentene, cyclcohexane, n-heptane, 2-methylhexane, 3-methylhexane, methyl-cyclohexane, 2,2,4-trimethylpentane, 2,3,4-trimethylpentane, 2+3-methyl-heptane, styrene, n-propylbenzene, iso-propylbenzene, o-ethyltoluene and 1,2,3-trimethylbenzene. Remaining 27 compounds are used for the final PMF runs. Five factor solution give the best reasonable solution.

First factor explains 60-80% variances of heavy VOCs, including benzene, 2,3-dimethylpentane, 2,4-dimethylpentane, toluene, m,p-xylene, o-xylene, m,p-ethyltoluene, 1,3,5-trimethylbenzene, n-decane and m,p-diethylbenzene (Figure 68). Also minor contributions of methylcyclopentane, n-nonane and 1,2,4-trimethylbenzene also observed in this factor. Diesel exhust emissions are generally related with heavy VOCs. Benzene, toluene, decane, 1,2,4 trimethylbenzene are commonly observed at diesel vehicle exhaust (Watson et al., 2001; Schauer et al., 1999). The temporal G-score and hourly average G-score variation of Factor 1 are depicted in Figure 69. Even there are some episodic contributions in the G-scores, the contributions follows a diurnal variations. This type of temporal variation is expected at urban monitoring stations. Diesel exhaust profile is expected to have bimodal fluctuations. The G-scores are expected to be higher during rush hours. However, the diesel exhaust G-score profile only has one peak. The contributions increase gradually in between 10:00 to 16:00. After 16:00, the contributions start to increase rapidly peaking in between 18:00-20:00. Then the contributions decrease until the next morning.

The CPF graph of Factor 1 is given in Figure 70a. Emissions from SE, SW, NW and W sectors have an effect on Factor 1. Çanakkale-İzmir highway passes SE and SW of the town. The roads around the sampling station are located on NW and NE of the station. Therefore, the diesel traffic emissions from these roads have an effect on the formation of this profile.

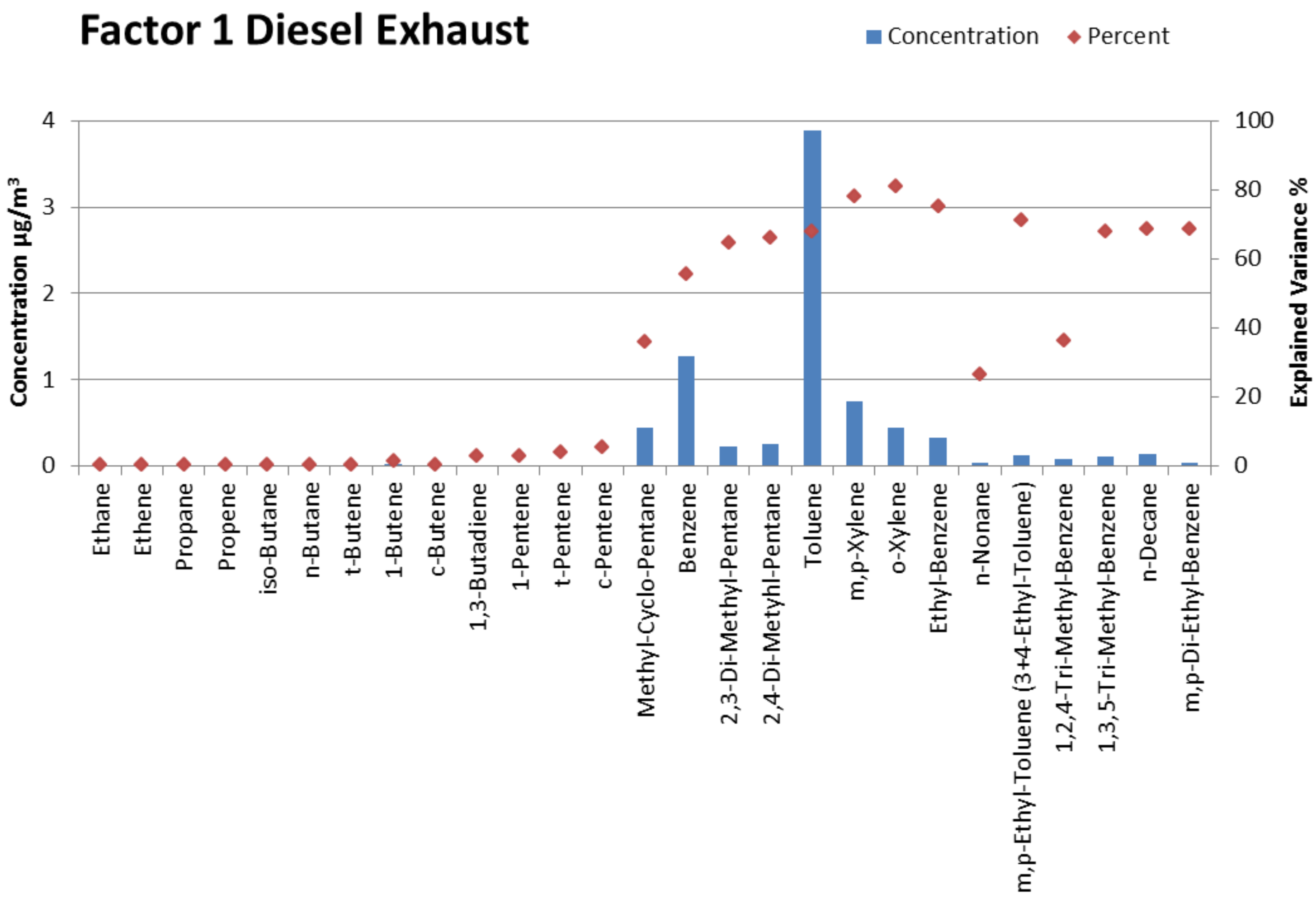
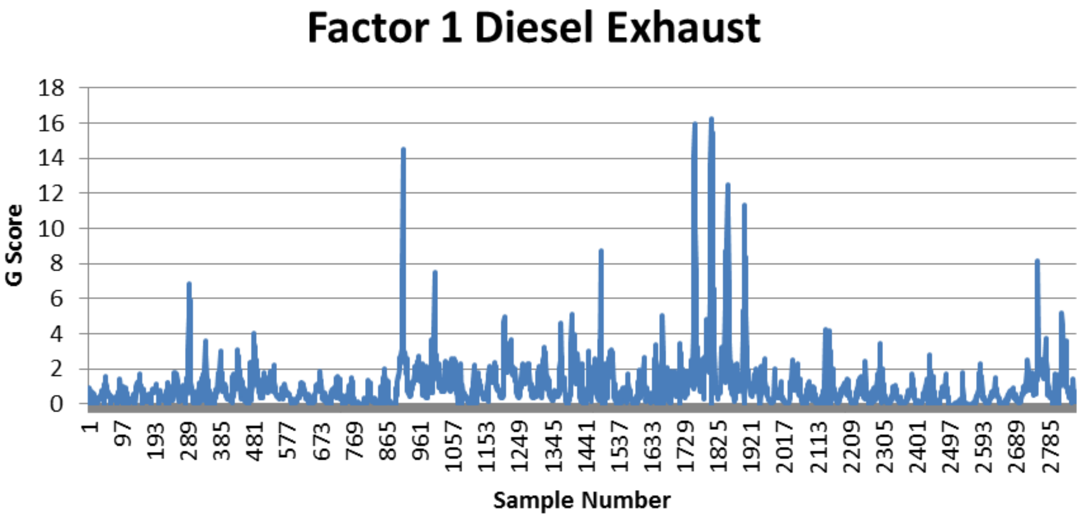


Figure 68 Concentration and percent of species explained in Factor 1 at Aliağa, winter campaign



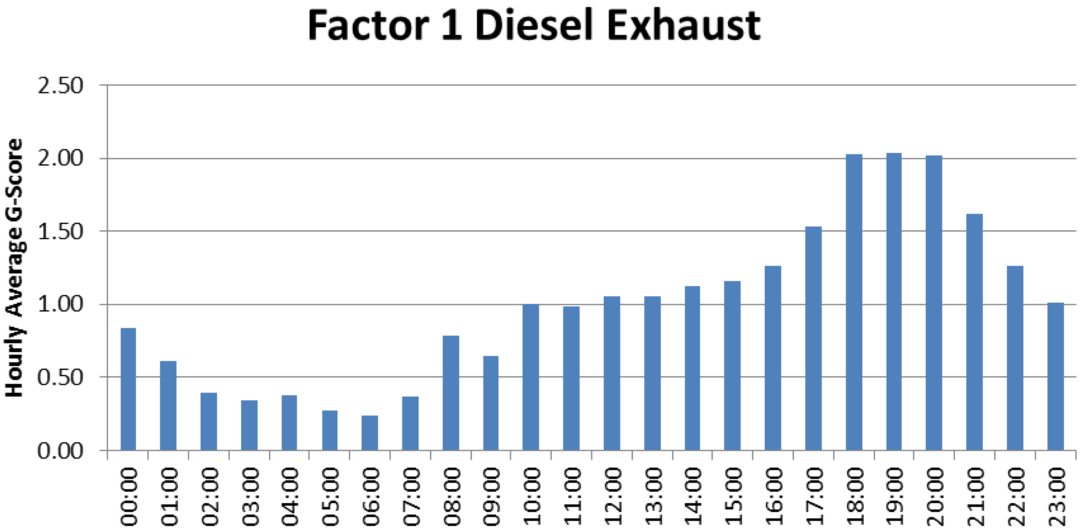


Figure 69 Time series plot of G-scores and diurnal average G-score distributions of Factor 1 at Aliağa, winter campaign

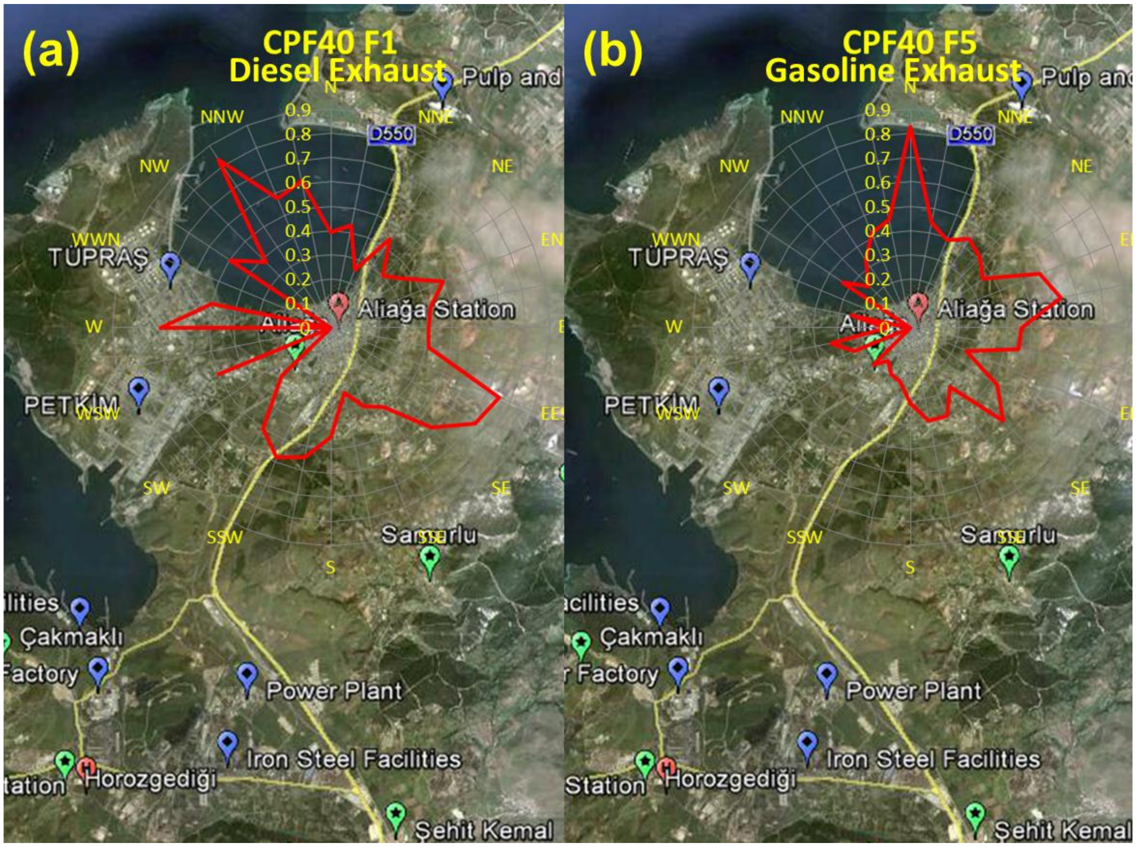


Figure 70 CPF of (a) Factor 1 Diesel Exhaust and (b) Factor 5 Gasoline Exhaust at Aliağa, winter campaign

Factor profiles and variances of VOCs accounted by Factor 2 is depicted in Figure 71. Most of the variances of iso-butane and n-butane are explained in Factor 2. This factor also accounts for approximately 20% of the variances of propane and pentane as well. Iso-butane and n-butane are indicators of gasoline vapor (Leuchner and Rappenglück, 2010; Watson et al., 2001). However, gasoline vapor is also characterized with some of the BTX compounds. Iso-butane and n-butane are also released evaporation from petrochemical processes such as lubricant storage, lubricant refinery, surface treatment and hydrocarbon storage (Conley et al., 2005; Badol et al., 2008).

Temporal variations in Factor 2 scores are given in Figure 72. Time series plot shown in Figure 72a is characterized by very sharp peaks. Such strong episodes can be an indication of nearby point sources. When the wind blew from the direction of source concentrations of pollutants emitted from that source (G-scores in this case) quickly increase. When the wind direction changes, the impact of the source's on the receptor decrease rapidly, resulting in a sharp decrease in the G-score. There are a number of strong episodes in the G-score time series, suggesting that, from time to time, Aliağa station is under strong influence of this source. Diurnal variation in G-scores depicts one peak point, which reaches to a maximum at approximately 20:00 hours.

CPF, which was discussed in previous sections, is good approach to understand spatial distribution of sources around station. In this case CPF was calculated using Factor 2 scores and distribution of CPF values among wind sectors is given in Figure 73a. Strong contribution of industrial area on Factor 2 scores is quite obvious in the figure. Factor 2 was identified as "Industrial Evaporation" based on these arguments.

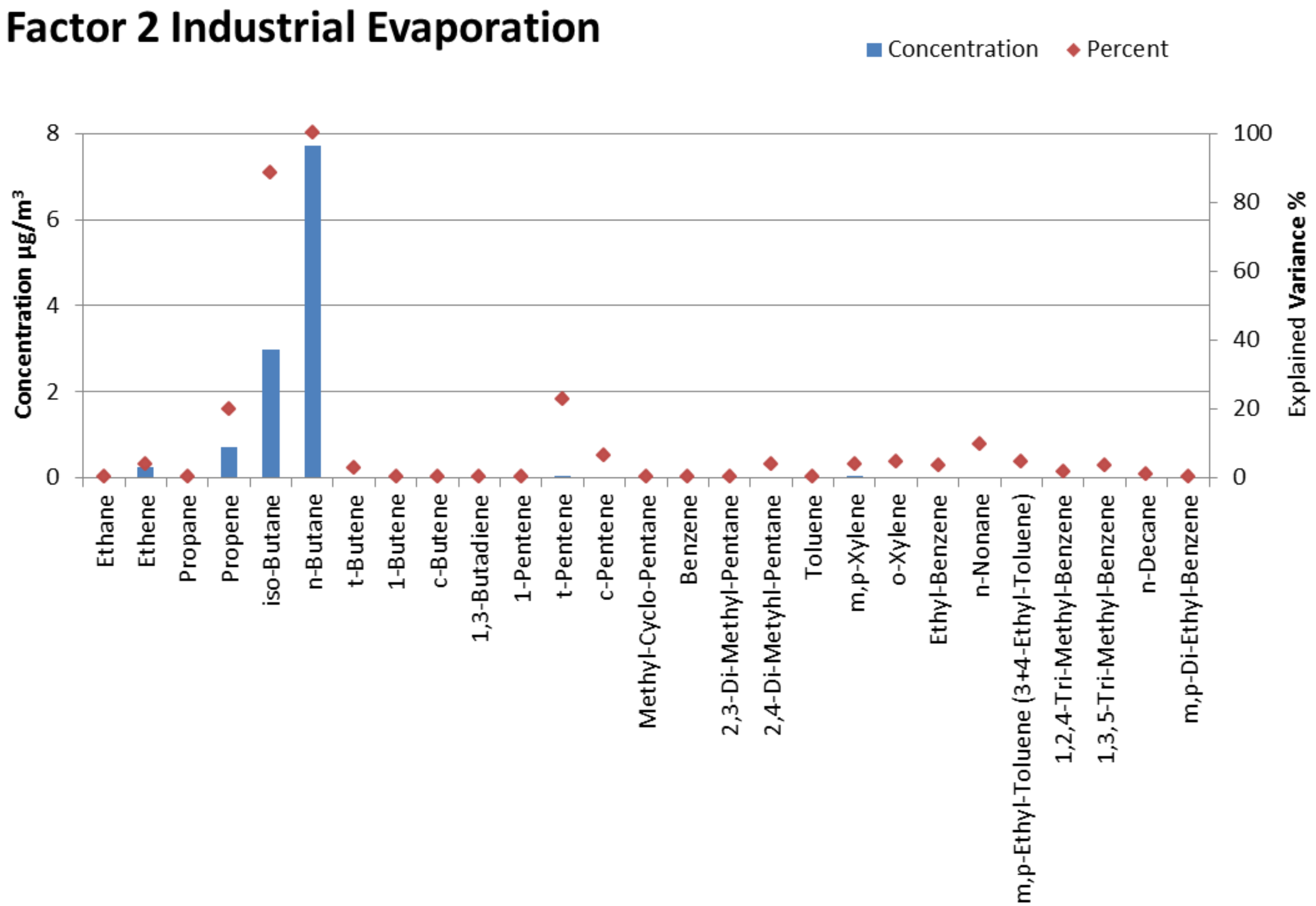
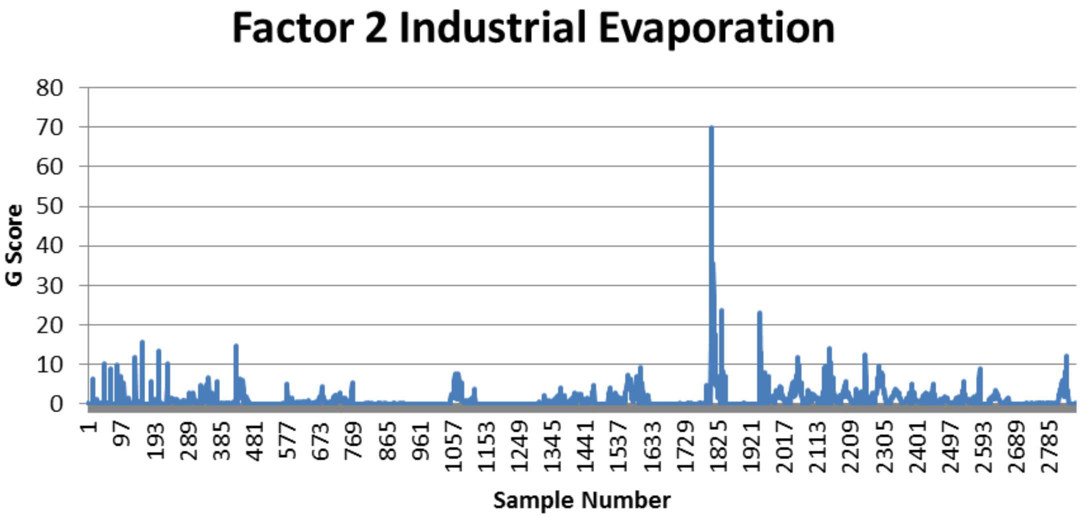


Figure 71 Concentration and percent of species explained in Factor 2 at Aliağa, winter campaign



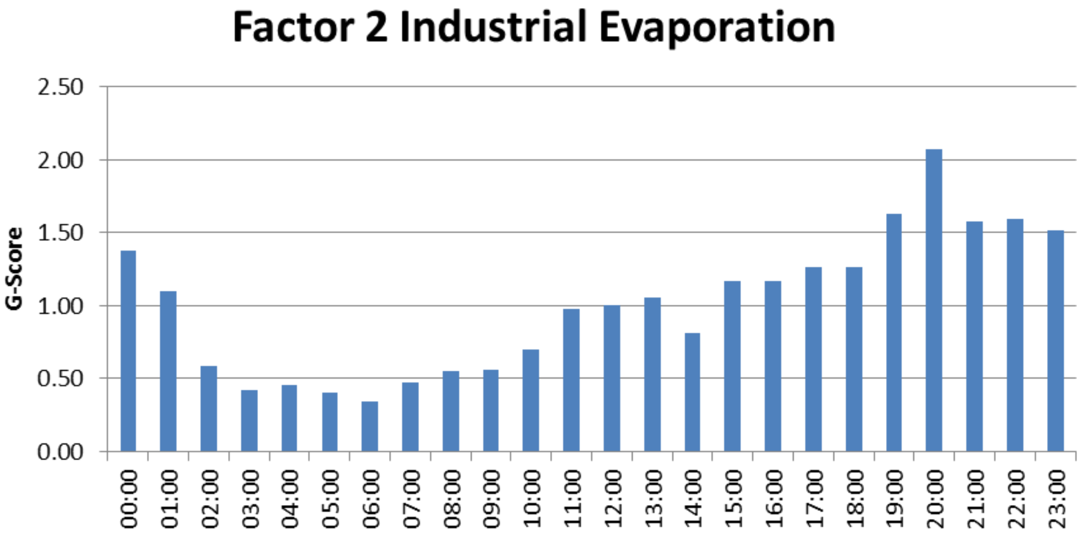


Figure 72 Time series plot of G-scores and diurnal variation of G-score distributions of Factor 2 at Aliağa, winter campaign

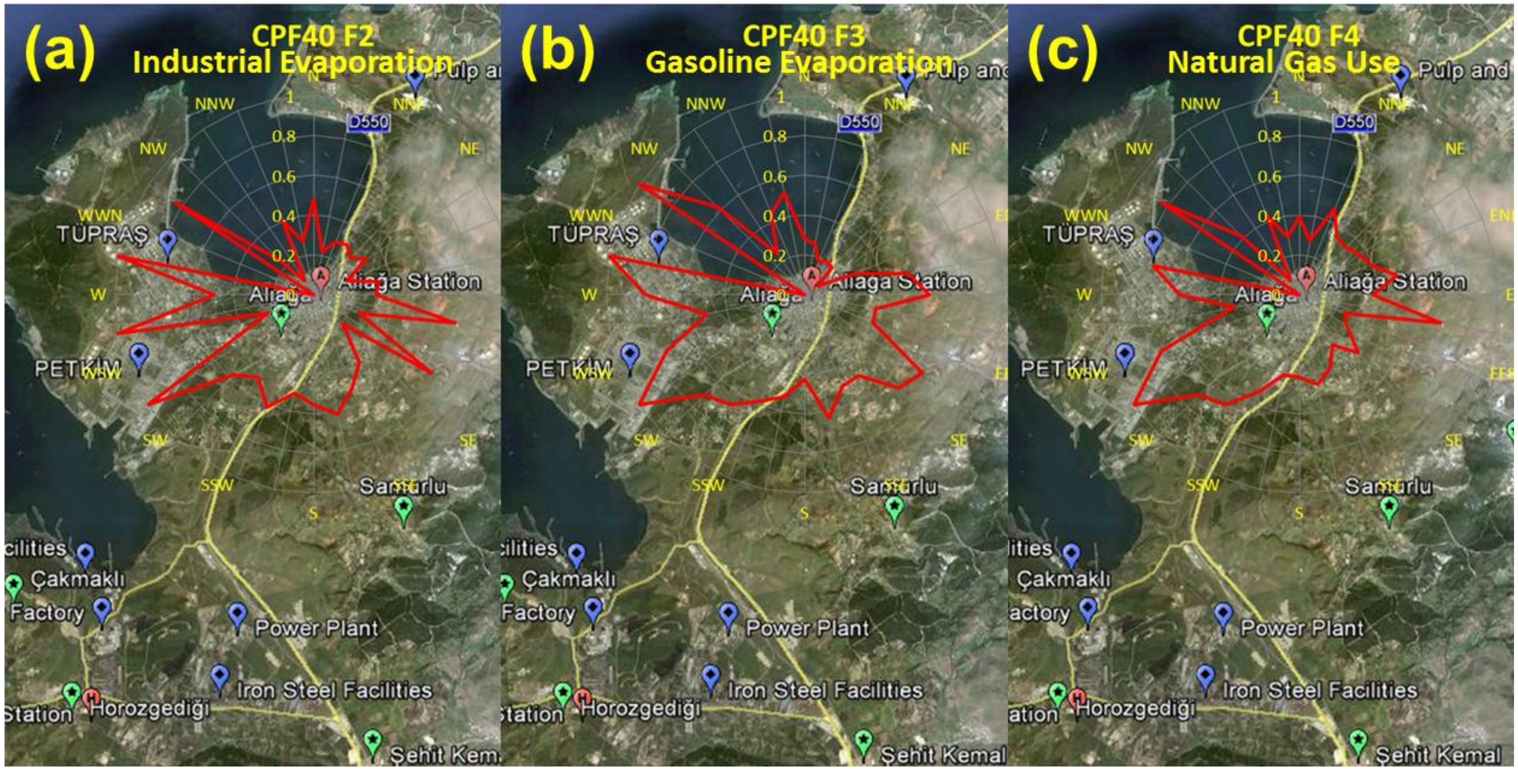


Figure 73 Aliağa winter campaign CPF plot comparison of (a) Factor 2, (b) Factor 3 and (c) Factor 4

Factor 3 profile and fraction of variances of VOCs explained by this factor is given in Figure 74. Approximately 60-80% of the variances of t-butene, 1-butene, 1-pentene and 1,2,4-trimetheylbenzene are explained by this factor. Factor 3 also explains smaller fractions of variances of BTX compounds (except for benzene), 2,3-dimethyl pentane, t-pentene and n-nonane. Since C_4-C_5 VOCs, 1,2,4-trimethylbenzene and BTX compounds are known tracers of gasoline evaporation (Watson et al., 2001; Badol et al., 2008), Factor 3 is identified as "gasoline evaporation".

Diurnal variation of Factor 3 scores are given in Figure 75. The diurnal variation of Factor 3 also starts to increase early in the morning and gradually increase until 20:00 hours. Observed diurnal pattern is interesting and coincides with diurnal variation in wind direction at Aliağa basin. Hourly wind roses for the study area are depicted in Figure 22. Hourly wind roses are not specific to this study, because 6 month long period of the study is not enough to generate hourly roses. They were prepared using two-year-long meteorological data between 2005 and 2006. These hourly wind roses demonstrated a very interesting feature of the local micro meteorology. Dominant wind direction in the study area is from NNE. This is fairly well documented in the literature as well. However, this does not mean that winds blew from NNW and neighboring sectors all the time. Winds only blow from N, NNE and NE sectors throughout the night. It continues like that until 10:00 in the morning. In 10:00 hours a small south component appears, grows in time and also changes direction. At 10:00 there is a small flow from south, but, more importantly there is stronger flow from NW. At 12:00, there is a small south flow, NW component get stronger, while dominant NNE flow prevails. At 13:00 hours, dominant flow from NNE is still there, but now there are fair flow frequency from all sectors between NW and SW. This second wind component got weaker, turns to south, but remains intact until 17:00 hours. After 17:00 hours it gets weaker and completely disappears after 21:00 hours. Between 21:00 hours at night and 10:00 in the morning night pattern, where winds blow only form N, NNE and NE sectors prevail. A very similar hourly wind pattern was also observed in an earlier study conducted in 1991 and 1992 which indicates that such diurnal variation in wind direction is a permanent feature of the study area.

Interestingly, diurnal variation in wind direction coincides with the diurnal variation in Factor 3 scores, given in Figure 75. G-scores for Factor 3 starts to increase at 10:00 and gradually increase until 20:00 hours. This period of increasing factor 3 scores is the time when we have flow from south. After 21:00 hours, winds shift to NNE, south component disappear and Factor scores also start to decrease. This coincidence indicates that sources contributing to Factor 3, which was identified as "gasoline evaporation", are in the southern sectors relative to our station. This is also confirmed by the distribution of CPF values, which is given in Figure 73b. The CPF values do not show a strong directionality which is typical for urban areas, as discussed previously in the manuscript. In general a CPF values are smaller in North and East sectors and higher in SW and W sector. It should be noted that although all indicators suggest that the main source for gasoline evaporation is at SW and W sectors and these sectors include the refinery from where we expect to have gasoline evaporation, particularly from loading operations, it may not be the only source for this factor, bulk of the city is located in that direction relative to our station and evaporative emissions from both the city and the refinery probably generates this factor.

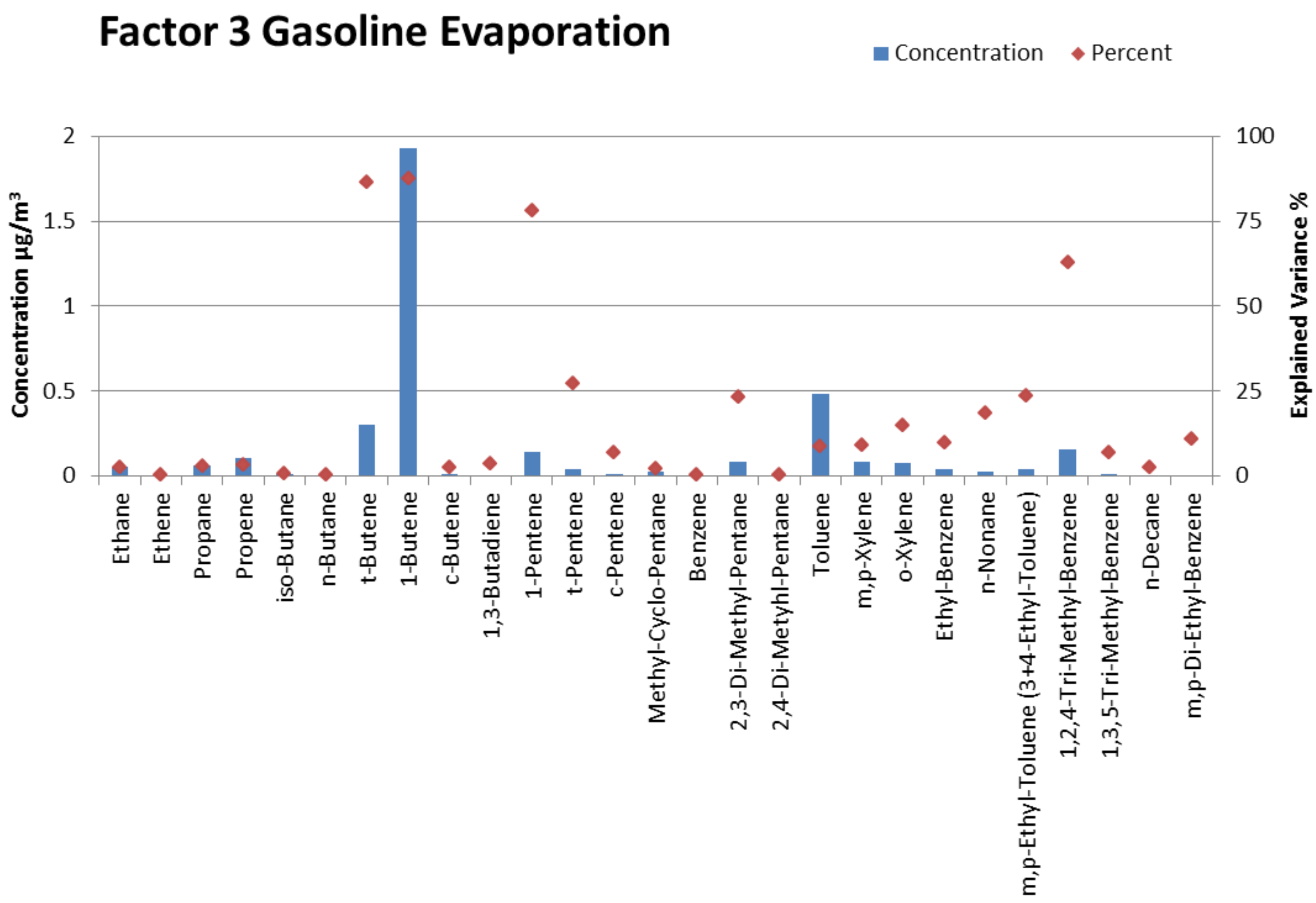


Figure 74 Concentration and percent of species explained in Factor 3 at Aliağa, winter campaign

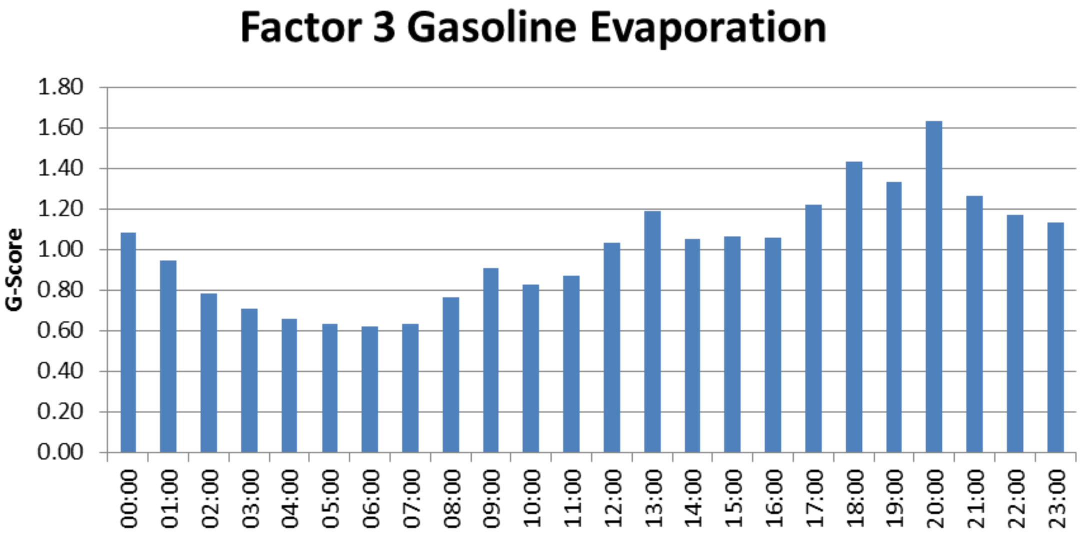


Figure 75 Diurnal average G-score distributions of Factor 3 at Aliağa, winter campaign

Factor 4 profile and fraction of VOCs explained by this factor are given in Figure 76. Ethane and propane are main contributors to Factor 4. Variances of these two compounds are almost entirely explained by this factor. Factor 4 also accounts for 15% - 30% of the variances of propene, c-pentene, methyl-cyclopentane, 2,4-dimethylpentane and toluene. Since ethane and propane are well documented tracers of natural gas emissions (Guo et al., 2007; Abu-Allaban et al., 2002; Brown, 2007) and industrial consumption of natural gas is known in the region. Factor 4 identified as natural gas factor, representing emissions during natural gas use in industries.

Diurnal variation in Factor 4 scores and distribution of CPF values are given in Figure 77 and Figure 73c, respectively. Both diurnal patterns observed in G-scores and distribution of CPF values closely resemble diurnal variation of G-scores and distribution of CPF values calculated for Factor 3. All discussions presented for Factor 3 scores and CPF values can be easily repeated for Factor 4. As in Factor 3, diurnal pattern and CPF distribution for Factor 4 is probably generated by the local micrometeorology of the region.

The source regions of industrial evaporation (Factor 2), gasoline evaporation (Factor 3) and natural gas (Factor 4) factors are very similar. The CPF plots of these three factors are given together in Figure 73. As depicted from the figure, W, SW, S of the sampling site are common source regions in all three factors. One of the important rules in PMF model is that the factors should be independent and scores should not be correlated with each other. To check potential correlations between scores of different factors is one of the first steps in optimization of the model. This was also checked in this PMF exercise as well. However, diurnal patterns in G-scores and distributions of CPF values of these three factors are so similar that we decided to show scatter plots between G-scores of these three factors to show that there is no auto correlation between these three factors. The R^2 for each factor-pair are given in Figure 78. The R^2 values were 0.03, 0.07 and 0.17 for the three pairs. Since R^2 values were very small correlations in between the factor scores are assumed to be negligible. However, since there are approximately 2900 data points are available in the scatter plot, even these small R^2 values can be statistically significant. It is an artifact due to very large number of data and does not mean that these factors are actually not different.

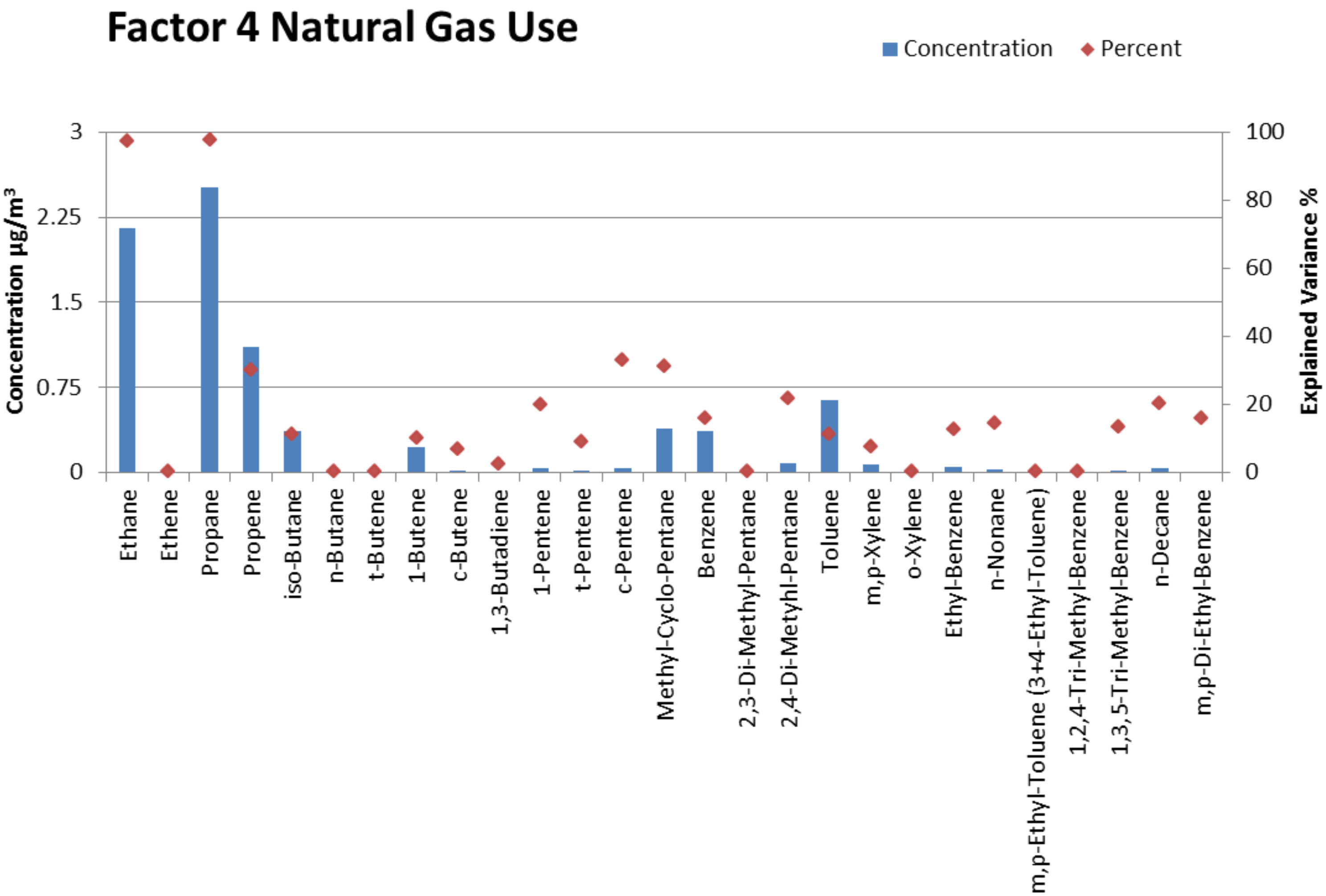


Figure 76 Concentration and percent of species explained in Factor 4 at Aliağa, winter campaign

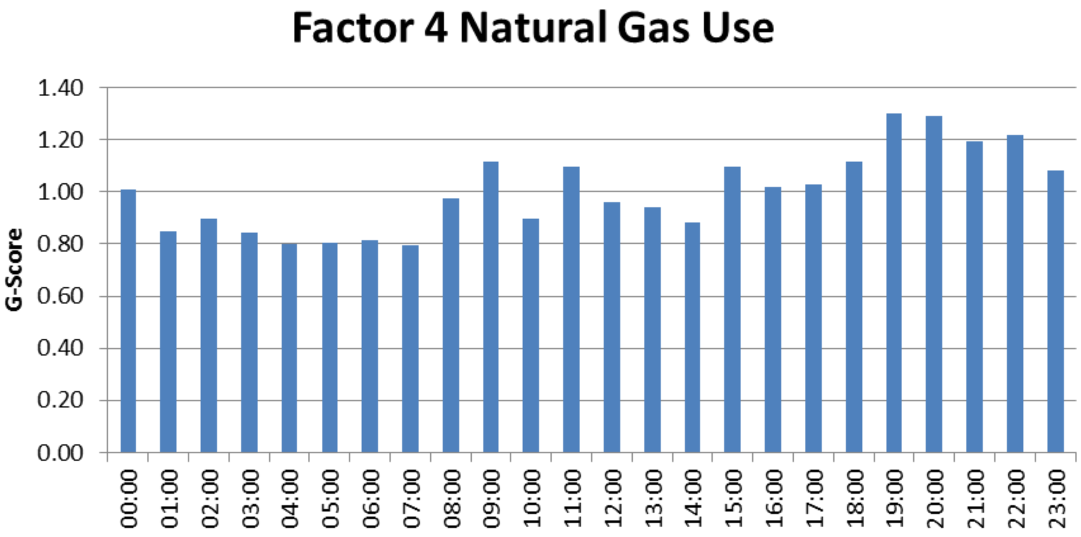


Figure 77 Diurnal average G-score distributions of Factor 4 at Aliağa, winter campaign

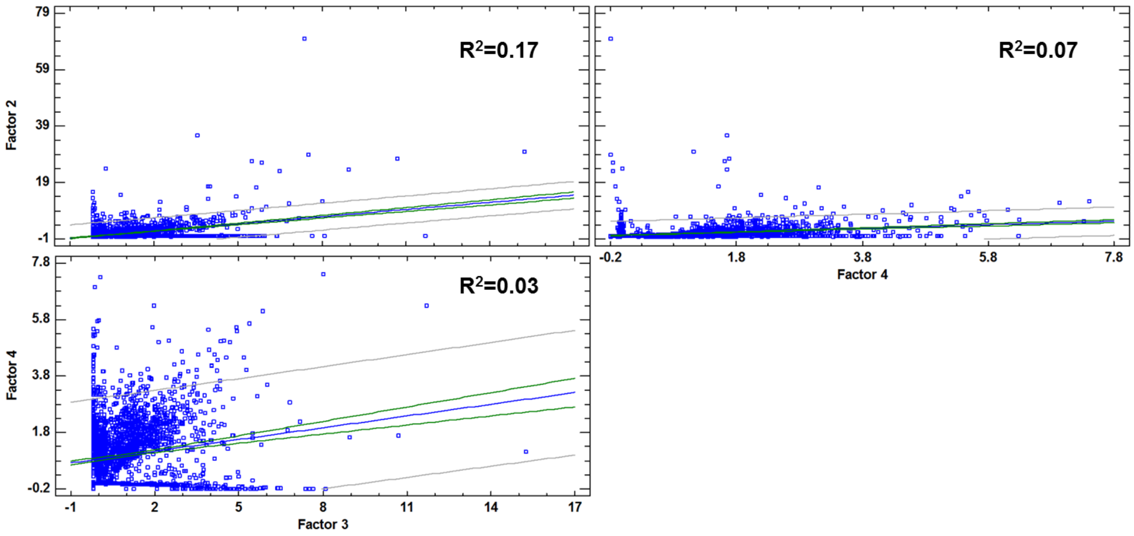


Figure 78 Aliağa winter campaign G-Score correlation comparison of Factor 2, Factor 3 and Factor 4

The concentration profile and explained variance of Factor 5 is shown in Figure 79. Variances in ethylene, c-butene and 1,3-butadiene, are almost entirely explained by this factor. Thirty to 50% of variances of propene, t-pentene, c-pentene, methycyclopentane, benzene and nonane are also explained by Factor 5. The factor also contributes to other VOCs including toluene, but to a lesser extent. Ethylene and propylene are known products of incomplete gasoline combustion (Ling et al., 2011). Ethylene is also reported as characteristic product of internal combustion engines (Barletta et al., 2005). Other VOCs associated with Factor 5, including 1,3-butadiene, c-butene, benzene and toluene are also well documented markers of gasoline exhaust (Ling et al., 2011; Badol et al.,2008). Composition of Factor 5 profile strongly suggests that it is a gasoline exhaust factor. This suggestion is also supported by diurnal variation of factor scores and distribution of CPF values among wind sectors. Diurnal variation of Factor 5 scores is depicted in Figure 80. Diurnal variation in G-scores shows a typical bimodal traffic pattern with higher contributions during morning and afternoon rush hours. It should be noted that a fairly similar diurnal pattern were also generated by diurnal variation in wind direction, as observed in Factor 3 and Factor 4. However, for this diurnal pattern of G-scores to be due to south and west winds, CPF should have higher values at the SW-to-W sectors. Distribution of CPF values among wind sectors, which is shown in Figure 70b, indicates that observed diurnal variation of G-scores cannot be due to meteorology. Contrary to Factors 3 and 4, CPF calculated for Factor 5 have high values between sectors N and SSE, which is the sector that includes Izmir-Çanakkale highway. This sector between N and SSE also include Bankalar Street and İstiklal Street, which are two frequently used roads in the town. The sampling station was located 50 m (NW) and 30 m (NE) from İstiklal Street and Bankalar Street, respectively. This discussion indicates that the wind sectors that have high Factor 5 CPF values are the ones with the highest traffic activity in the village.

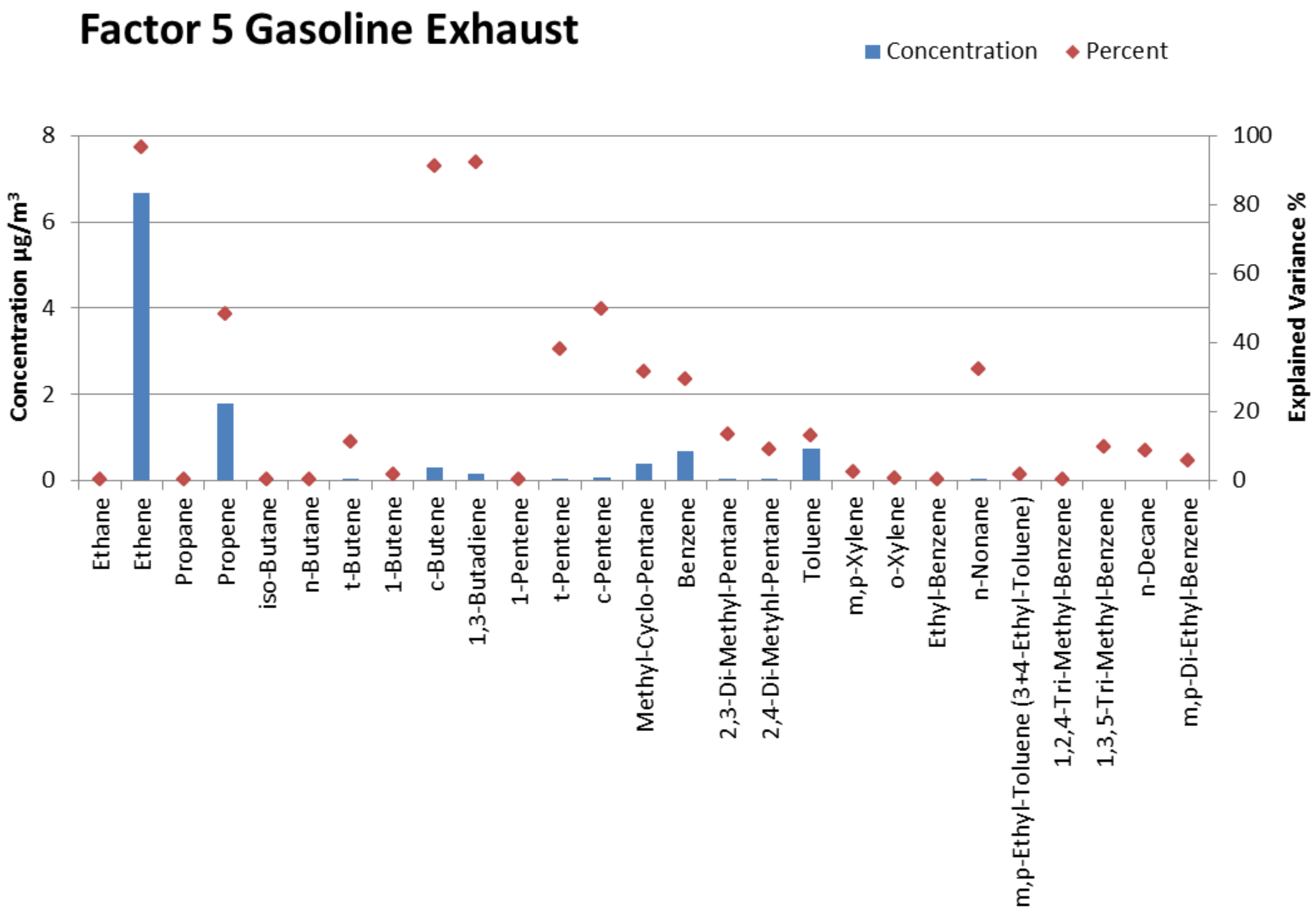


Figure 79 Concentration and percent of species explained in Factor 5 at Aliağa, winter campaign

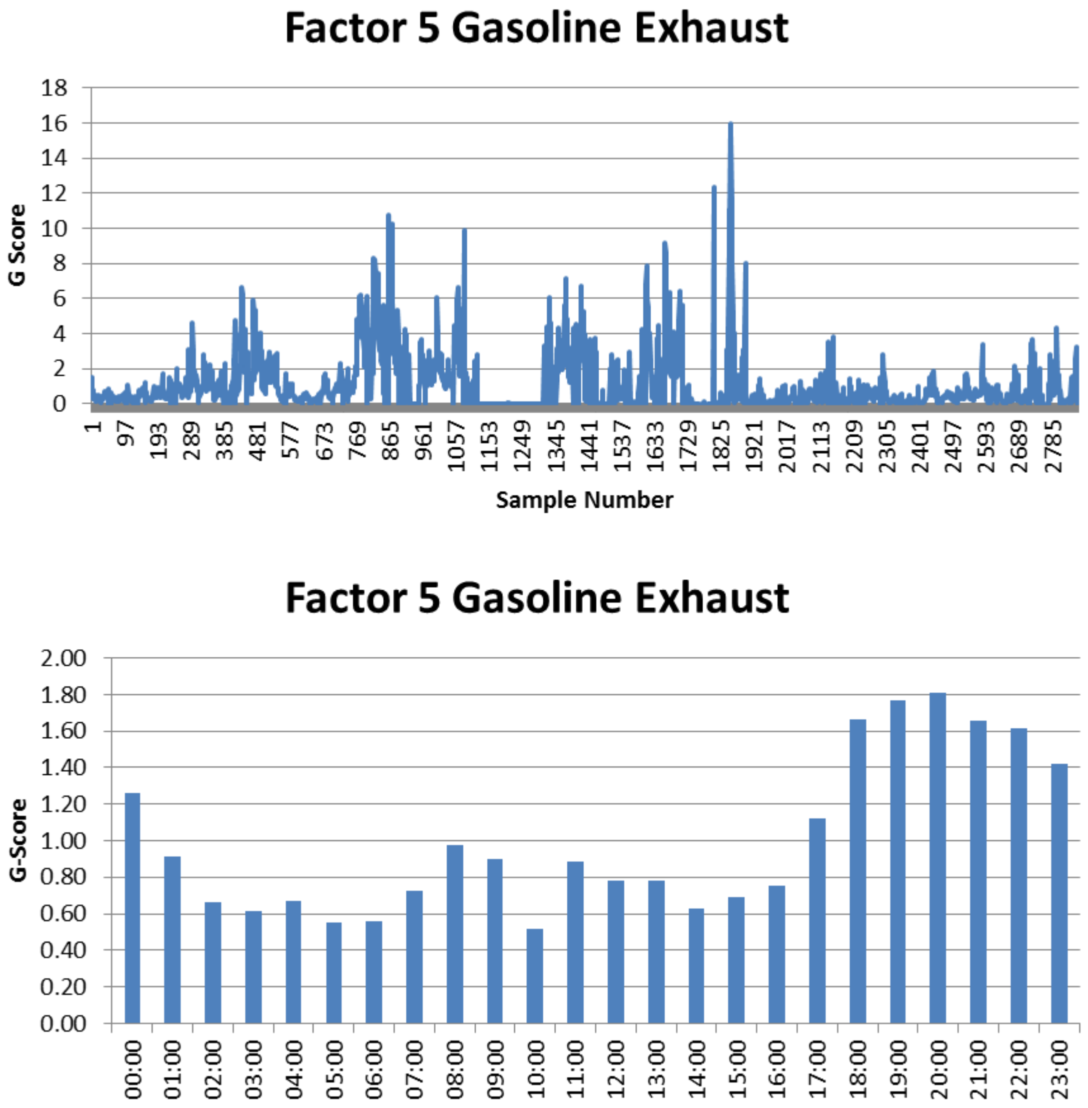


Figure 80 Time series plot of G-scores and diurnal average G-score distributions of Factor 5 at Aliağa, winter campaign

Since Factor 1 was identified as a diesel factor, one expects to see a similar distribution of CPF values for both factor 1 and 5. Although there are similarities in distributions of Factor 1 and Factor 5 CPFs, they are not entirely similar (Figure 70). Both have fairly strong east component showing the importance of İzmir Çanakkale road and/or İstiklal Street, which is also in the same sector, on traffic related pollutants at the Demokrasi Meydanı. On the other hand, CPF values for diesel factor, which is Factor 1, have higher values in SW sector. This is expected because the petrol carrying trucks mainly uses roads located on the south of the town to reach from TÜPRAŞ and PETKİM to Çanakkale-İzmir highway.

Observed vs. predicted plot of total VOC concentrations are given in Figure 81. The R^2 of the regression is 0.81. Figure demonstrate that 5 factor solution used in PMF adequately reconstructed VOC levels observed at Aliağa in winter season.

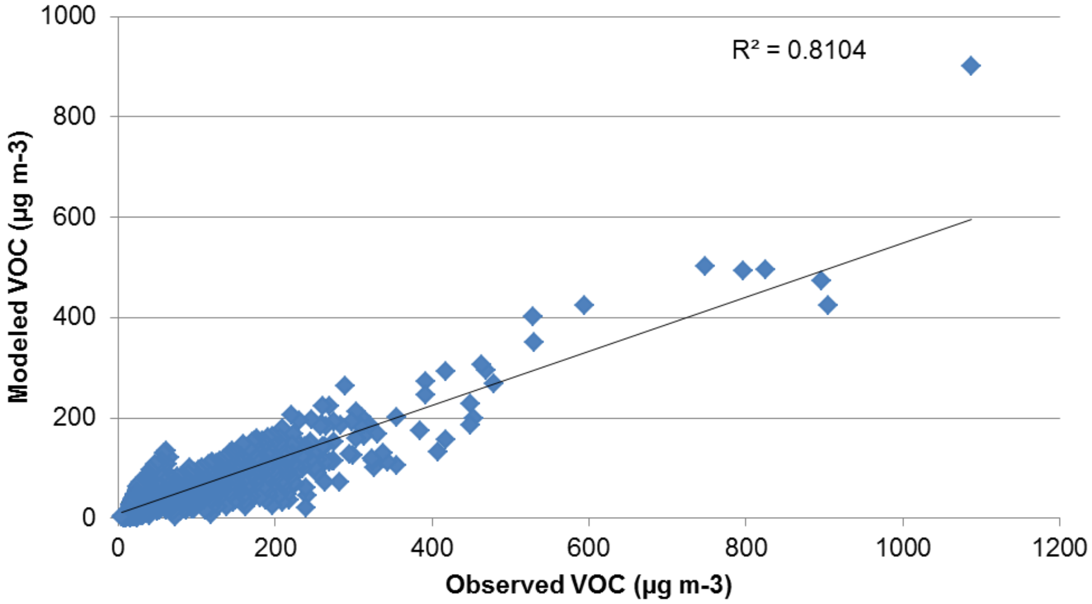


Figure 81 Modeled vs observed VOC concentrations at Aliağa, winter campaign

Contribution of each source (Factor) to ΣVOC mass is given in Figure 82. The most important VOC source is industrial evaporation, which accounted for approximately 28% of ΣVOC mass. Industrial evaporation closely followed by gasoline exhaust, which accounted for 25% and diesel exhaust, which accounted for 19% of ΣVOC mass. Evaporative sources together accounts for 55% and traffic sources account for the remaining 45% of the ΣVOC mass at Aliağa during our winter campaign.

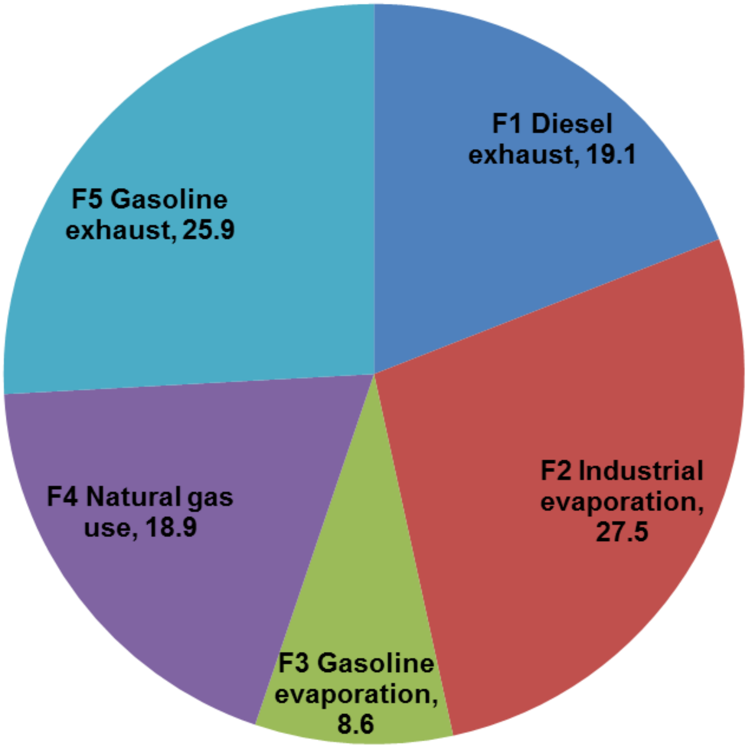


Figure 82 Sources and percent contribution sources of VOC at Aliağa, winter campaign

4.6.1.2. Summer Campaign Receptor Modeling

During summer campaign light VOCs were not measured since part of GC system was not working properly. Only 29 VOCs in the C_6-C_{10} range were analyzed. Several four to seven factor solutions of Aliağa summer campaign are investigated. Depending on the residual distributions of compounds, three of the compounds, namely 2,3-dimethylpentane, 2-methyl-1-pentene and n-nonane, are removed from the dataset. Among the twenty six compound included solutions, five factor solution is selected as the optimum model.

Factor profile and explained variance of VOCs in Factor 1 is depicted in Figure 83. 60-80% variances of methylcyclopentane, 2,4-dimethylpentane, toluene and iso-propylbenzene are explained in this factor. The factor also explained approximately 20% of variances of benzene, xylenes, ethylbenzene and hexane.

The temporal G-score and diurnal average G-score variation of Factor 1 are shown in Figure 84. As can be seen in the time series plot, anomalously high values of factor-1 scores was observed for a period, which lasted approximately one week, at the beginning of October, 2006. Investigation of logbooks showed that in that week, natural gas maintenance activities were carried at Bankalar Street which is located 30 m from the sampling site. We think that this factor is a result of all activities for natural gas maintenance including solvents and chemicals used for replacing and fixing pipes and asphalting process. The diurnal variation of G-scores shows high contributions during night hours. There is no explanation that can relate natural gas maintenance with high nighttime concentrations, because most of these activities occurred during day-time. However, there may be an indirect relation through meteorology. High night-time concentration of any pollutant is at least partly contributed by lowering of the mixing height during night hours. Inverse resemblance between diurnal variations of Factor 1 scores and mixing height, which are given in Figure 85, also supports this hypothesis. However, inverse relation between G-scores and the mixing height may be casual, on hourly basis. Because of this, a correlation analysis was performed using hourly score and mixing height data. Result is given in Figure 85, in this exercise hourly mixing heights calculated by PCRAMMET software was used. As can be seen from the figure, these two parameters are correlated. Statistical significance of correlation was better than 95%. The correlation analysis demonstrated that observed inverse diurnal patterns of Factor 1 scores and mixing height, may be real and higher night-time scores can be due to lower mixing height at night. It should be noted that this factor has nothing to do with natural gas factor, because the line shut down for natural gas during maintenance operations. The emissions that generated this factor comes from the solvents used or any other material used during maintenance process. Since everything is laid in the open solvent emissions continued during night time as well. When day time and night time emissions or concentrations is similar, night-time concentrations of that specie appears higher due to the influence of mixing height lowering.

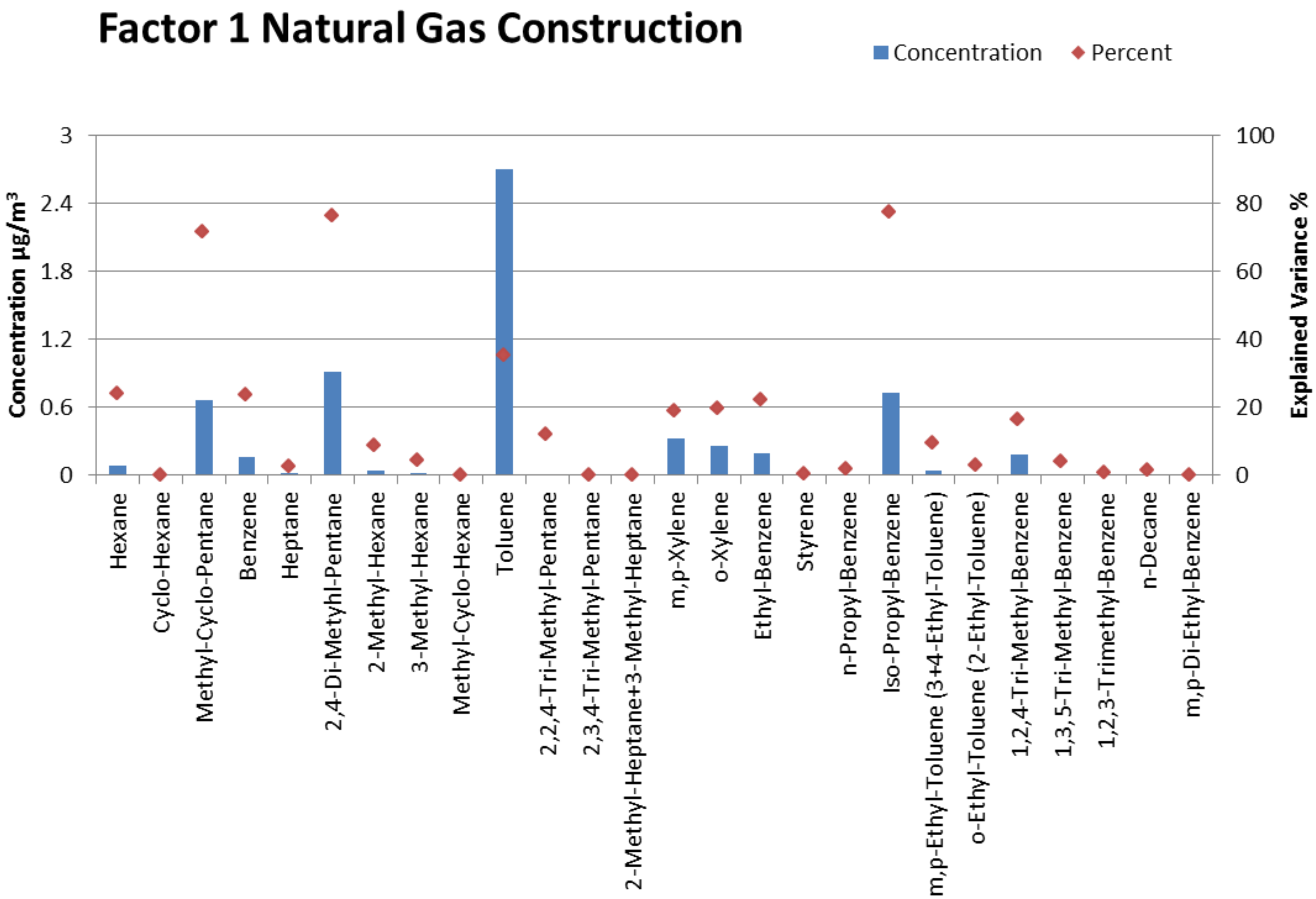


Figure 83 Concentration and percent of species explained in Factor 1 at Aliağa, summer campaign

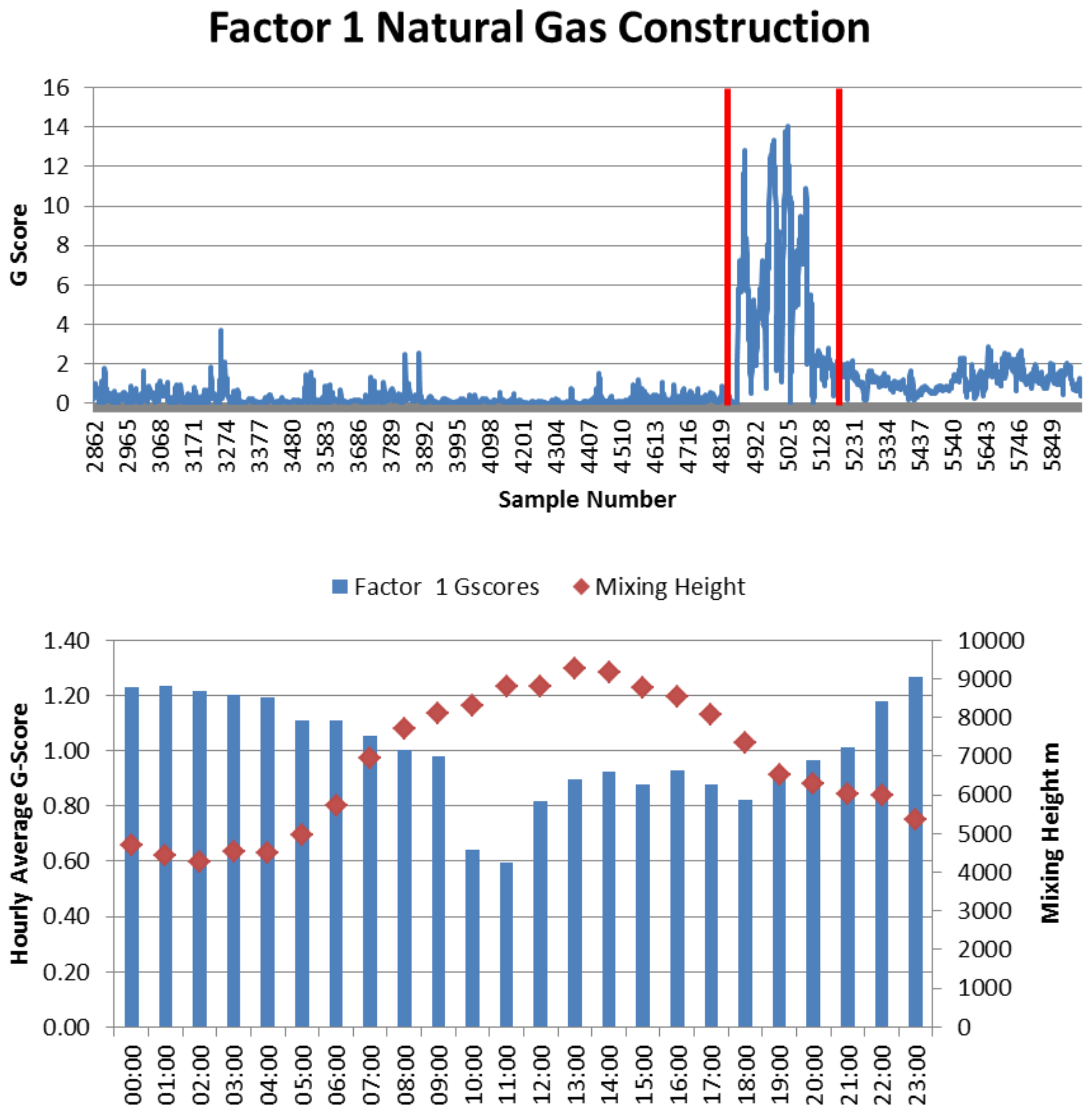


Figure 84 Time series plot of G-scores and diurnal average G-score distributions with mixing height of Factor 1 at Aliağa, summer campaign

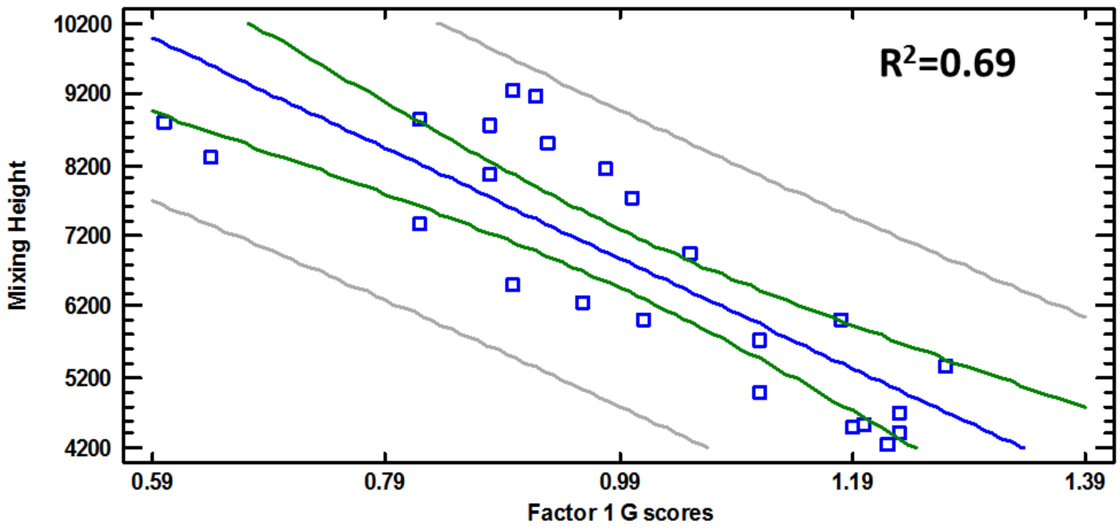


Figure 85 Effect of mixing height on Factor 1 G-scores at Aliağa, summer campaign

Factor 2 profile and variances of species explained by this factor is given in Figure 86. Large fractions of the variances of heavy VOCs, such as diethylbenzene, decane, trimethylbenzene, ethyltoluene and propylbenzene are explained by this factor. Since these VOCs are well documented tracers of diesel combustion, Factor 2 was identified as “diesel exhaust”. Diurnal variation of Factor 2 scores is given Figure 87. Diurnal variations of scores very closely resemble the diurnal variations of Factor 1, Factor 3 and Factor 4 scores in winter PMF. Those temporal patterns were explained by diurnal variation in wind direction in Aliağa basin. Consequently this factor too is generated by variation in wind direction throughout the day and strongly contributed by the sources at the south. Heaviest heavy duty vehicle traffic in the area occurs to the SW and W of the Aliağa town. This hypothesis is also supported by the distribution of CPF values calculated using Factor 2 scores, which is shown in Figure 88. Higher CPF values are found for SW W sectors which include very heavy diesel engine activity as trucks go to an from PETKİM and particularly TÜPRAŞ, and E and SE sectors, which includes İzmir – Çanakkale highway. Actually distribution of CPFs for this factor is very similar to the distribution of CPF values for diesel exhaust factor found in winter PMF exercise.

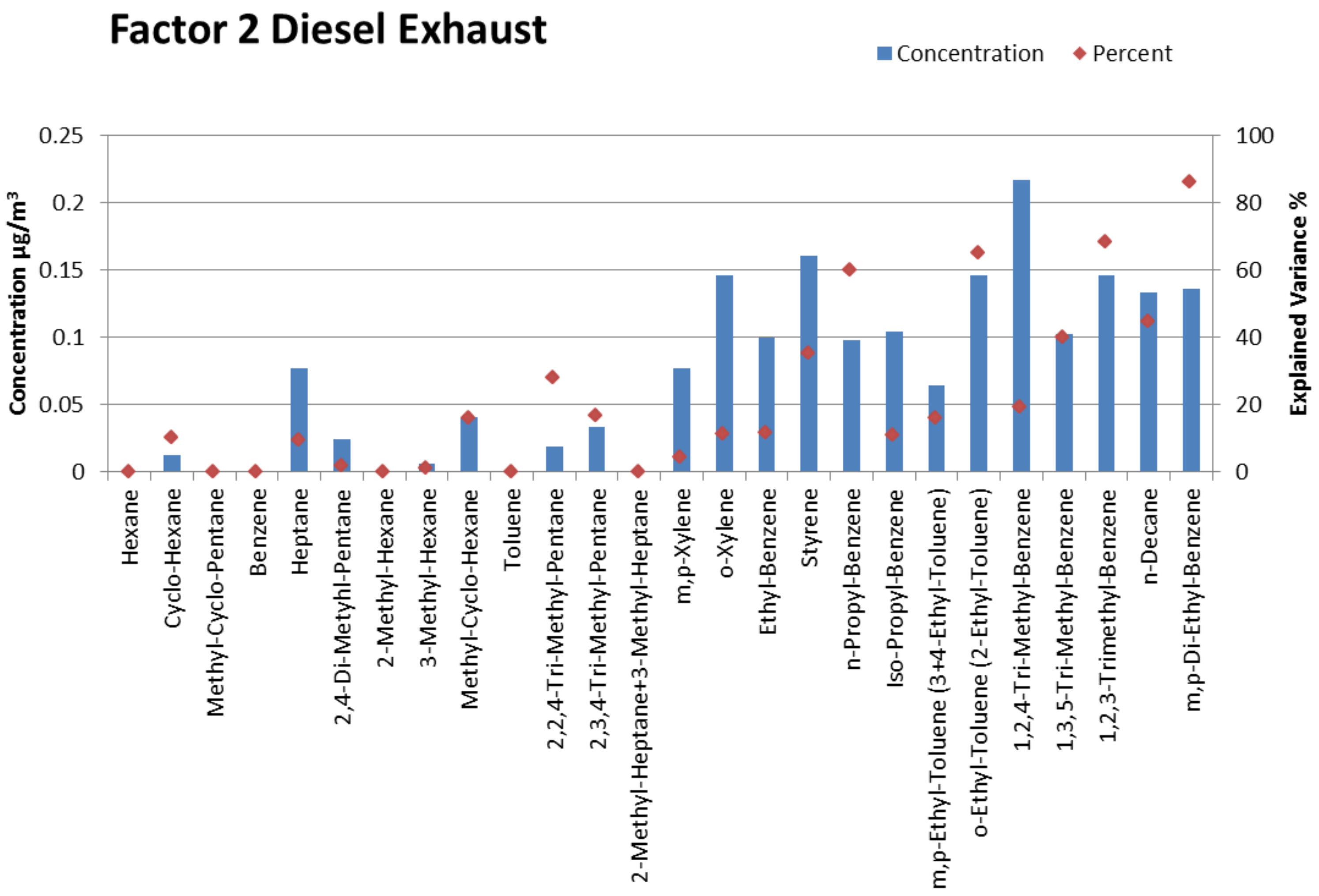
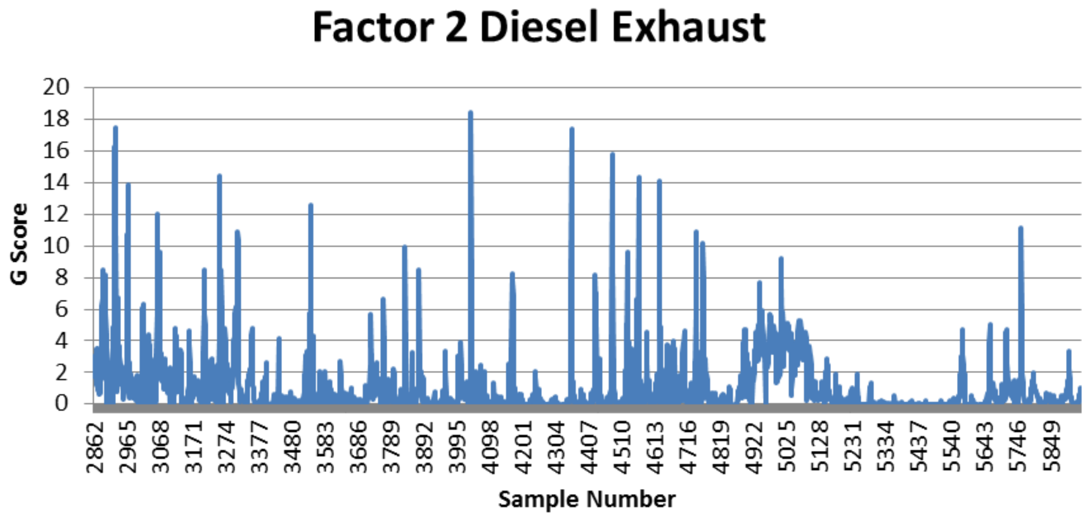


Figure 86 Concentration and percent of species explained in Factor 2 at Aliağa, summer campaign



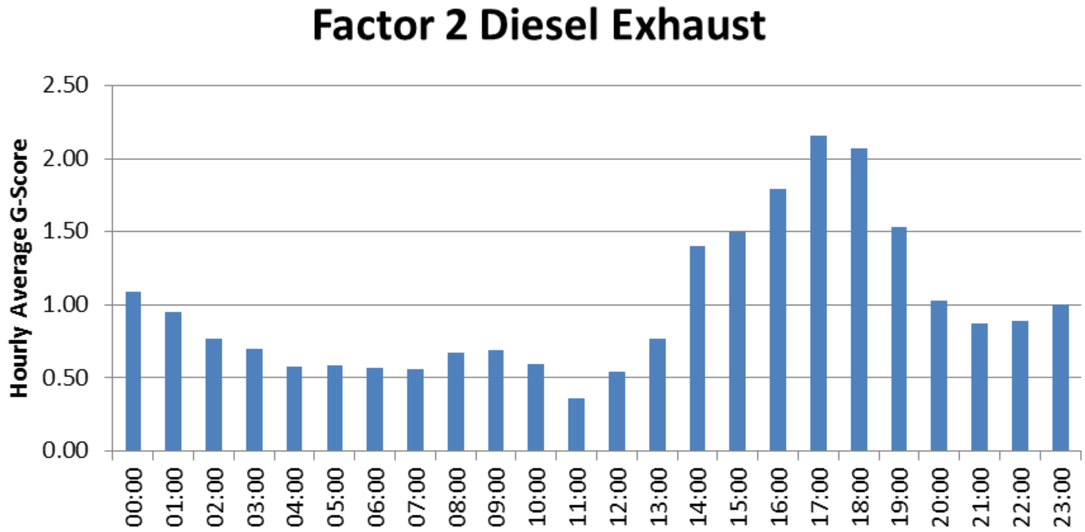


Figure 87 Time series plot of G-scores and diurnal average G-score distributions of Factor 2 at Aliağa, summer campaign

Figure 88 CPF of Factor 2 at Aliağa, summer campaign

Third factor is composed of BTX, m,p-ethyl-toluene, 1,2,4-trimethyl benzene,1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene and n-propylbenzene (Figure 89). BTX, 1,2,4-trimethylbenzene, 1,3,5-trimethyl benzene are commonly observed at gasoline exhaust profiles (Civan et al., 2011; Chin and Batterman; 2012).

Diurnal variation in Factor 3 scores and distribution of CPF values among wind sectors are given in Figure 90 and Figure 91, respectively. G-scores shows a typical traffic pattern with two modes matching with morning and afternoon rush hours, confirming the traffic source assigned to this factor. Distribution of CPF values is similar to the pattern observed for Factor 2 (diesel exhaust), with higher contributions from a sector between NE and S, which includes İzmir – Çanakkale highway. Interestingly, CPF pattern observed for this factor do not exactly match with the pattern observed for the gasoline exhaust profile in winter PMF (Factor 5). The reason is not very clear.

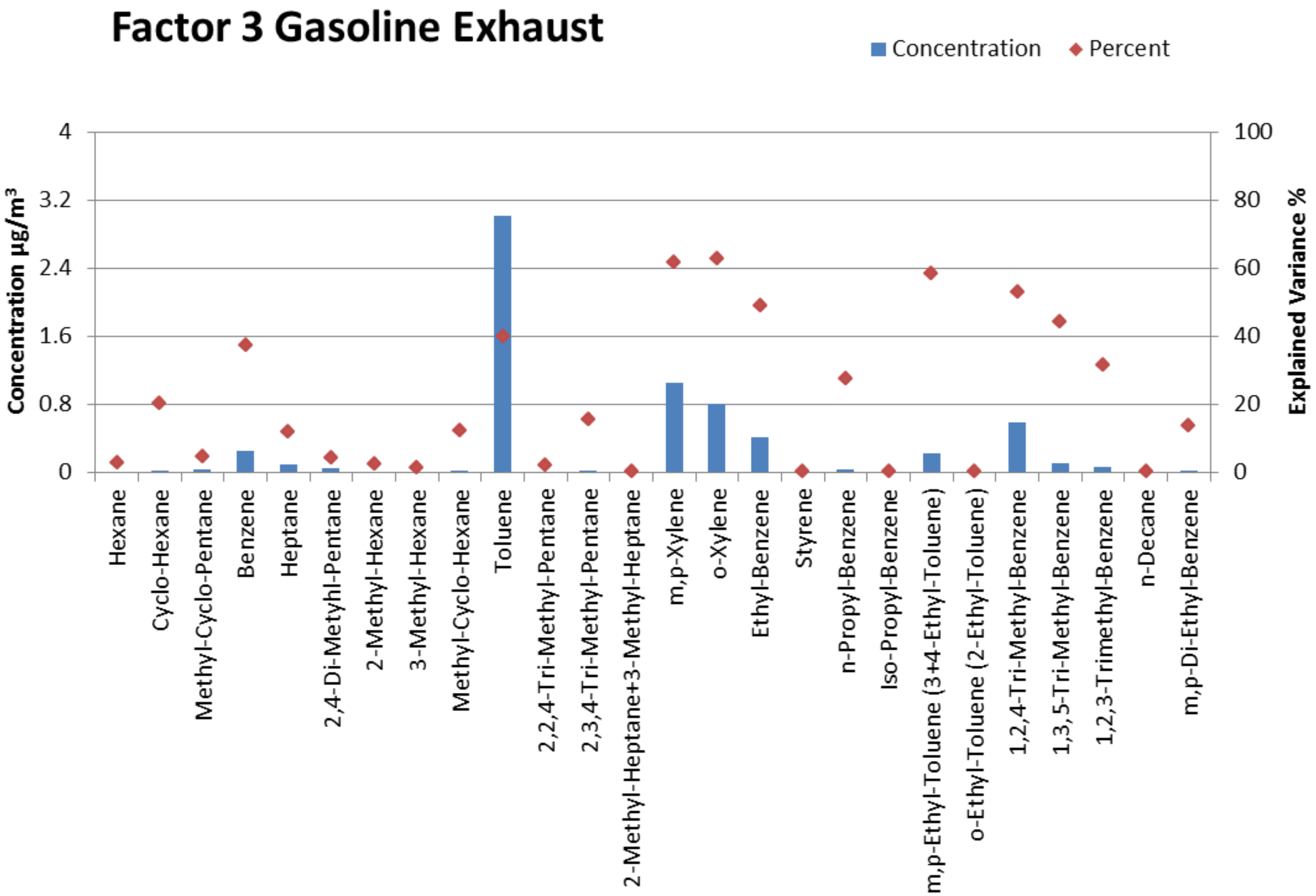
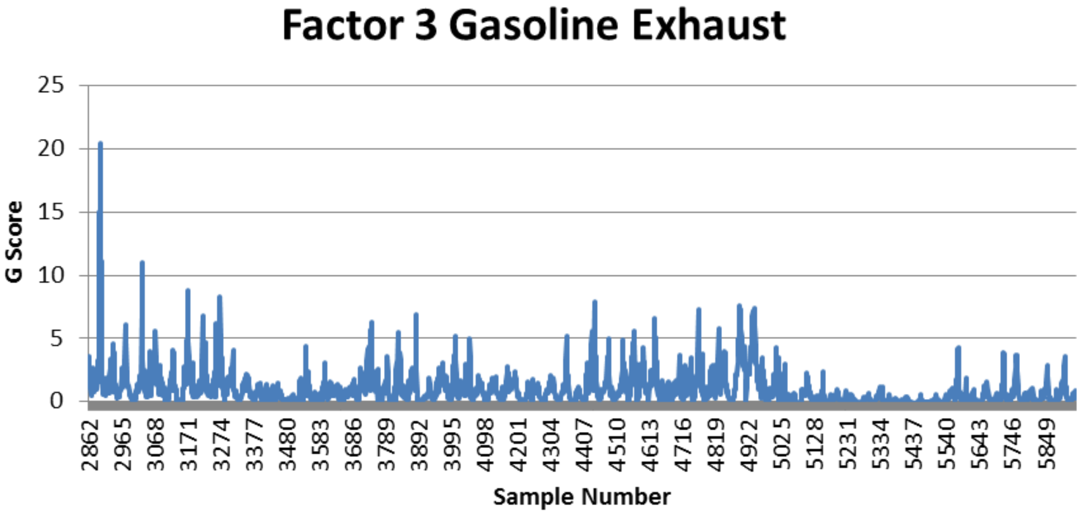


Figure 89 Concentration and percent of species explained in Factor 3 at Aliağa, summer campaign



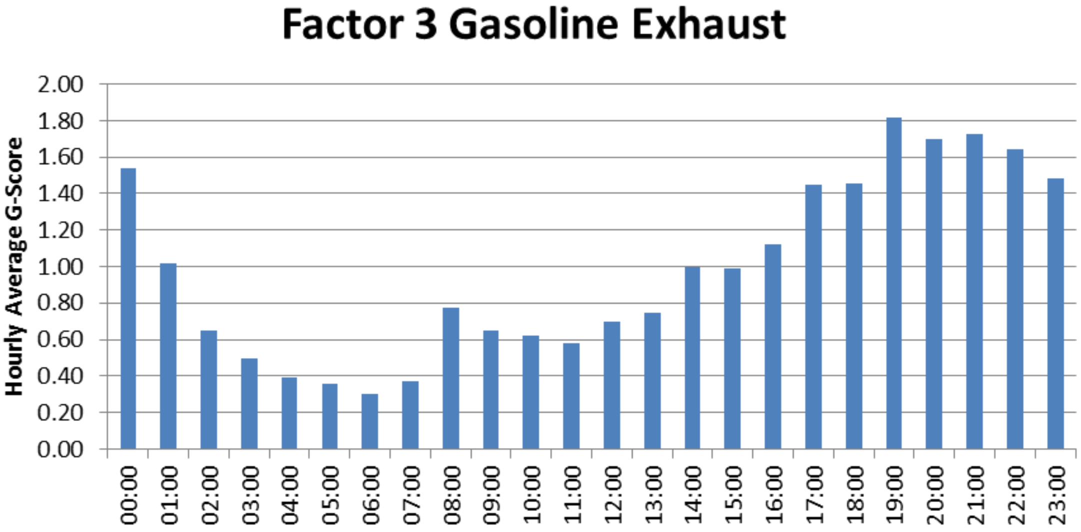


Figure 90 Time series plot of G-scores and diurnal average G-score distributions of Factor 3 at Aliağa, summer campaign

Figure 91 CPF of Factor 3 at Aliağa, summer campaign

Factor 4 profile and variances of VOCs explained by this factor is given in Figure 92. Large fractions of the variances of 2-methylhexane, n-decane, 2+3-methylheptane, toluene, benzene, 2,2,4-trimethylpentane,styrene and 2-ethyltoluene. Toluene, benzene are tracers of solvent use. However, the formation mechanism of this factor is not understood. The G-score plots, depicted in Figure 93, suggests that this source is almost emitted all the time. The diurnal variation of G-scores indicated that mixing height is an important parameter controlling the contribution of this factor at the sampling site. The relation of diurnal average G-score with mixing height is statistically significant. As mixing height increase, the contribution decrease.

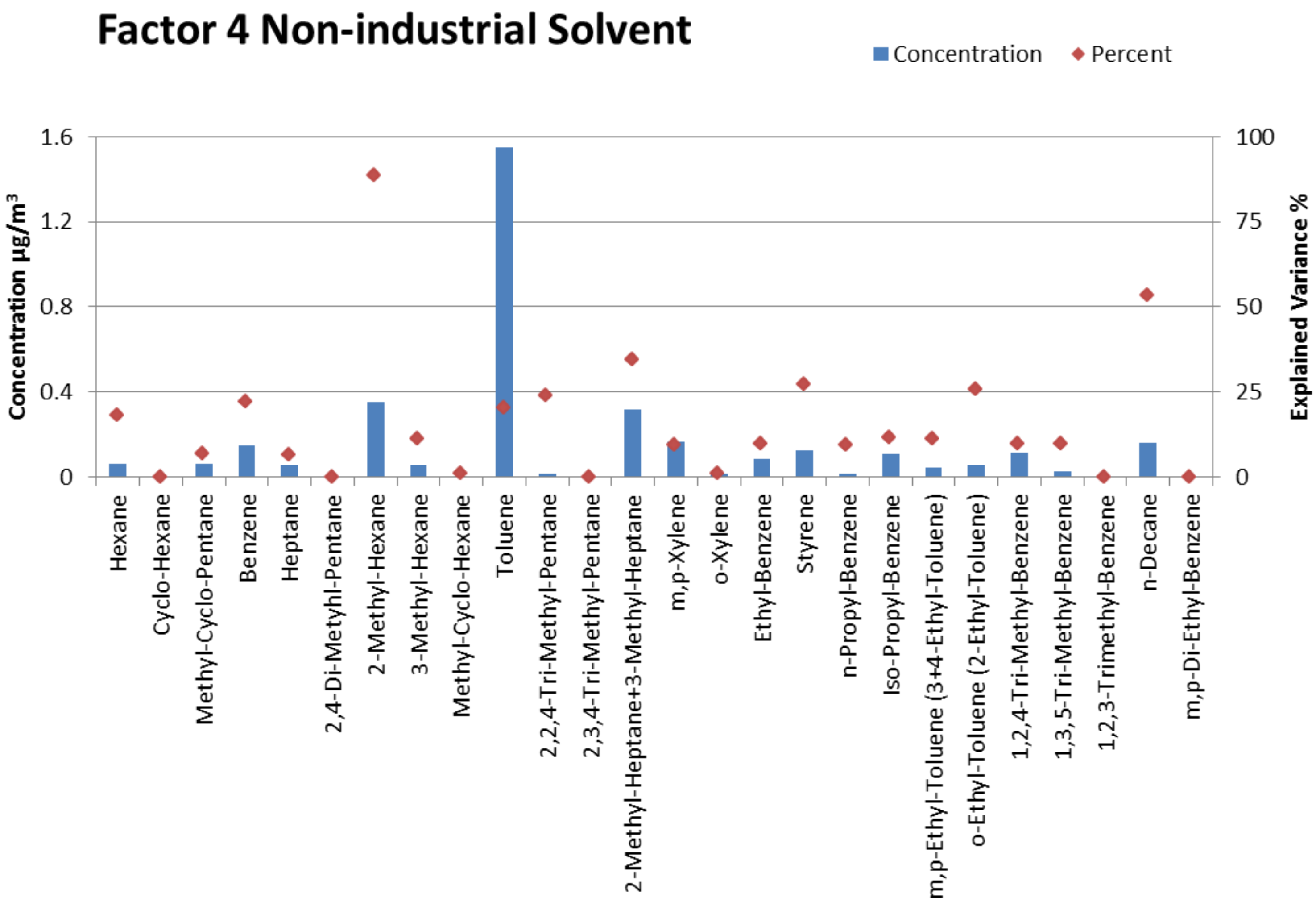


Figure 92 Concentration and percent of species explained in Factor 4 at Aliağa, summer campaign

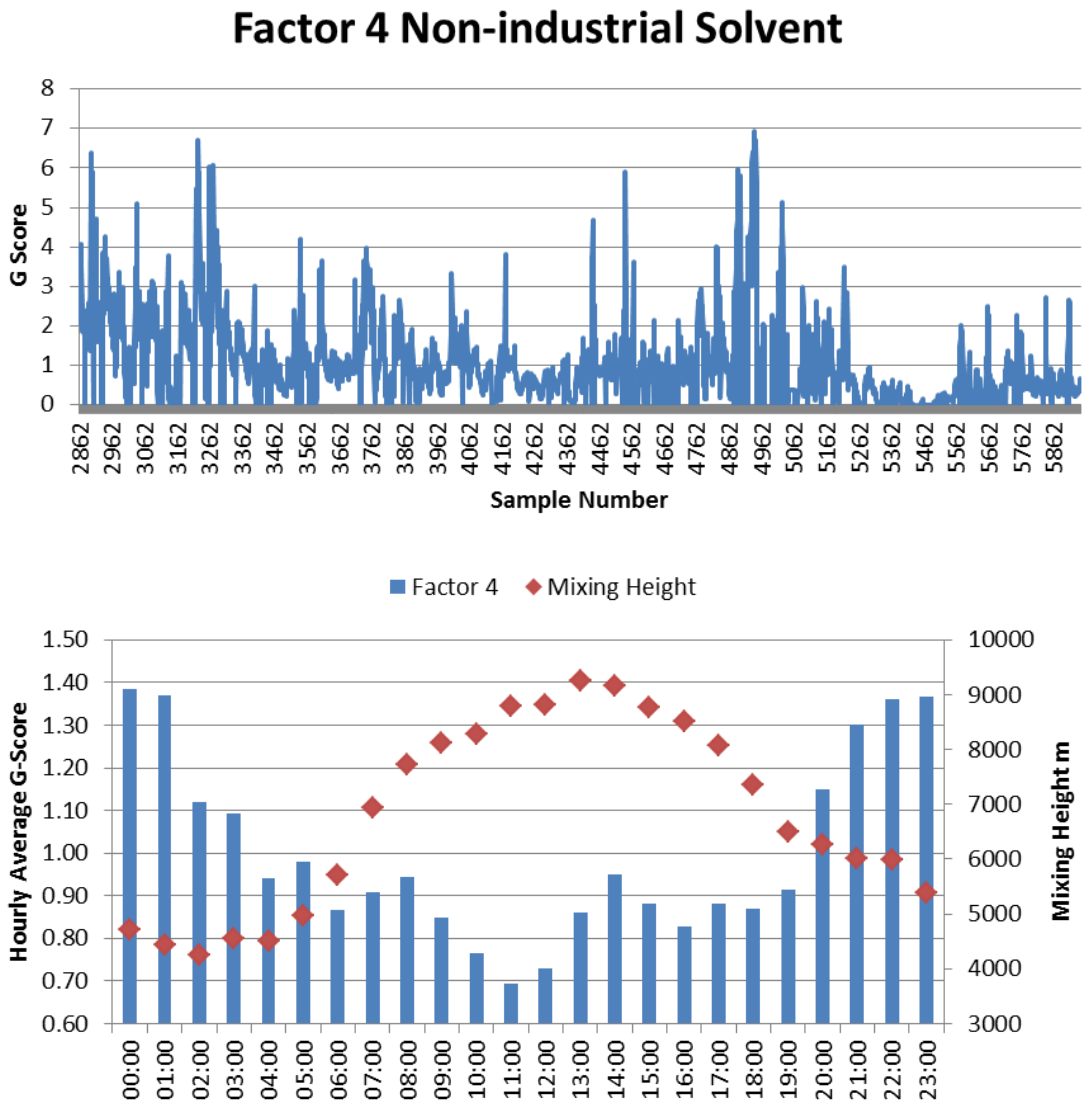


Figure 93 Time series plot of G-scores and diurnal average G-score distributions with mixing height of Factor 4 at Aliağa, summer campaign

The CPF plot of Factor 4 is shown in Figure 94. All of the town, especially, NW and SE sectors contribute to this factor. The source regions are well separated over the town. It is clear that this source is not from industrial emissions. Therefore, this source is named as non-industrial solvent evaporation.

Figure 94 CPF of Factor 4 at Aliağa, summer campaign

The factor profiles and explained variances of Factor 5 is given in Figure 95. Most of the variances of n-hexane, cyclohexane, heptane, 3-methylhexane, methyl-cyclohexane, toluene, 2+3methylheptane and 2,3,4-trimethylpentane are explained in this factor. Styrene, 2,2,4-trimethyl pentane, benzene, xylenes, ethylbenzene, 2,4-dimehtylpentane and methylcylcopentane are the other compounds in this factor. An important point to note in this factor is that it is heavily weighted by relatively light hydrocarbons. This gives the impression that it can represent some sort of evaporative emissions, rather than traffic related emissions. Diurnal variation of factor 5 scores and distribution of CPF values among wind sectors are given in Figure 96 and Figure 97. Diurnal variation of G-scores is characterized with a well-defined peak, which is centered at 18:00 hours. This diurnal pattern closely resembles the diurnal pattern of factors generated due to variations in wind direction (Factors 2, 3, and 4 in winter PMF). However, there are some differences as well. This pattern is sharper, G-scores start to increase later in the day, maximum is earlier (it was 20:00 hours in winter PMF and 18:00 in this one). Distribution of CPF values support the wind induced factor hypothesis, because sources are heavily in the sector between SE and NW, which includes TÜPRAŞ and PETKİM. Based on these evidences, the factor is identified as “mixed industrial” factor representing evaporative emissions from TÜPRAŞ and PETKİM and also from the part of the town that lies to the south and west relative to the station.

It should be one important point, about identification of evaporative sources in Summer PMF exercise. Since light VOCs were not measured in summer campaign, identification of evaporative sources cannot be with sufficiently high resolution and prone uncertainties, because best marker species for evaporative emissions and natural gas are among those light VOCs. In winter campaign we identified three evaporative emission factors (Factor 2, industrial evaporation, Factor 5 gasoline evaporation and Factor 4 natural gas). Light hydrocarbons, such as ethane, ethylene, propylene propane, butanes etc. proved to be very useful to resolve these factors with low uncertainty. Lack of these light VOCs in the Summer data set, increased uncertainties in our identification process and reduced the resolution. We were able to identify two factors that represent evaporative emissions; Factor 4 non- industrial evaporative and Factor 5, which was named as industrial evaporative. We are quite sure that they represent some sort of evaporation, but resolution as non-industrial and industrial evaporation is highly uncertain. For example one of the identified evaporative sources contributing to VOC levels at Aliağa is gasoline evaporation. Gasoline evaporation is expected to be much more pronounced in summer, due temperatures that were around 40°C during measurements. One of the evaporation related factors found in Summer PMF can easily be misidentified gasoline evaporation factor. It is very to resolve evaporative sources without light VOCs.

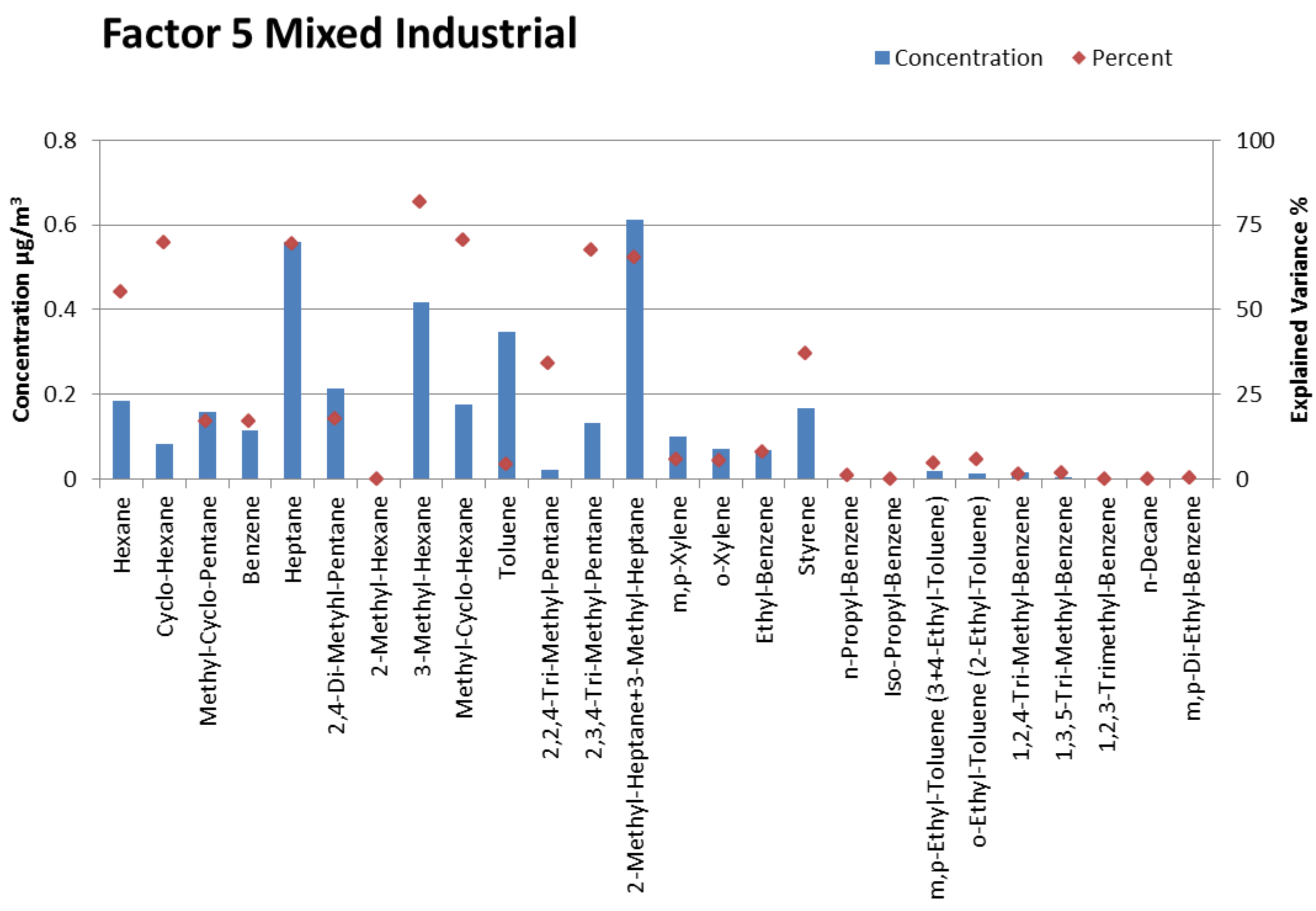
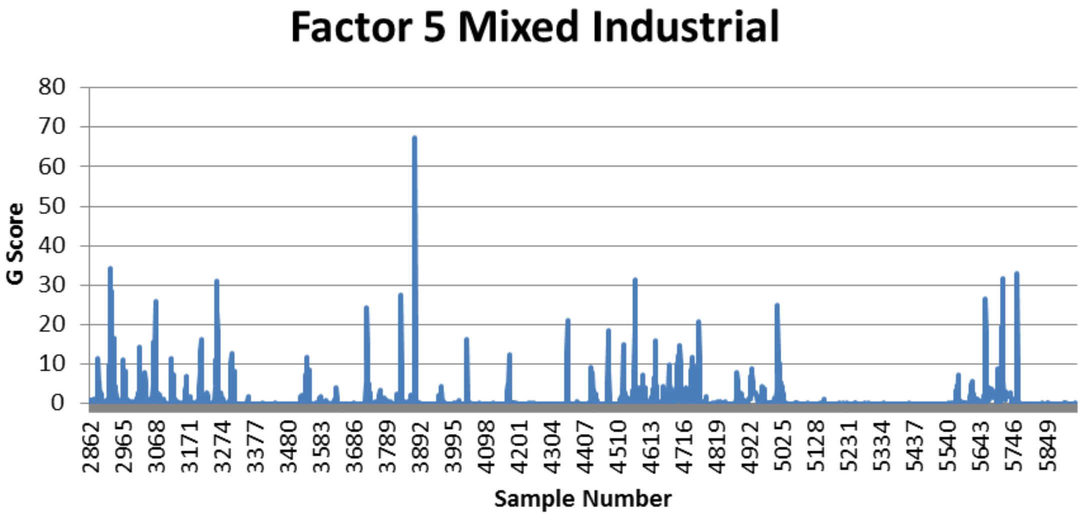


Figure 95 Concentration and percent of species explained in Factor 5 at Aliağa, summer campaign



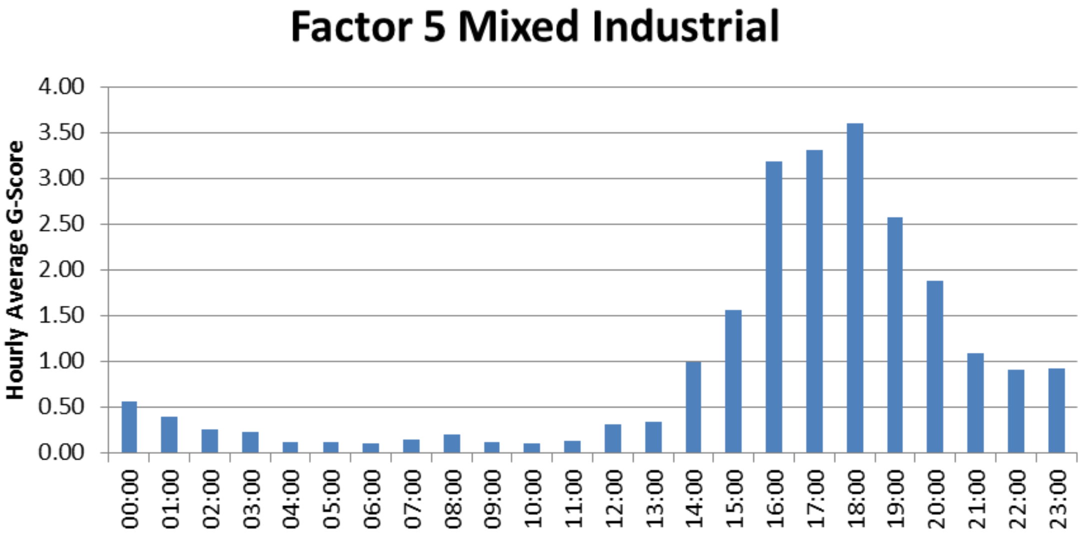


Figure 96 Time series plot of G-scores and diurnal average G-score distributions of Factor 5 at Aliağa, summer campaign

Figure 97 CPF of Factor 5 at Aliağa, summer campaign

The scatterplot between modeled mass and observed total VOC masses is depicted in Figure 98. As expected observed ΣVOC agrees very nicely with predicted ΣVOC mass. Since there is approximately 300 data in the graph, statistical significance is almost 100% level. Such good agreement demonstrates the adequacy of 5 factor solution for the data set.

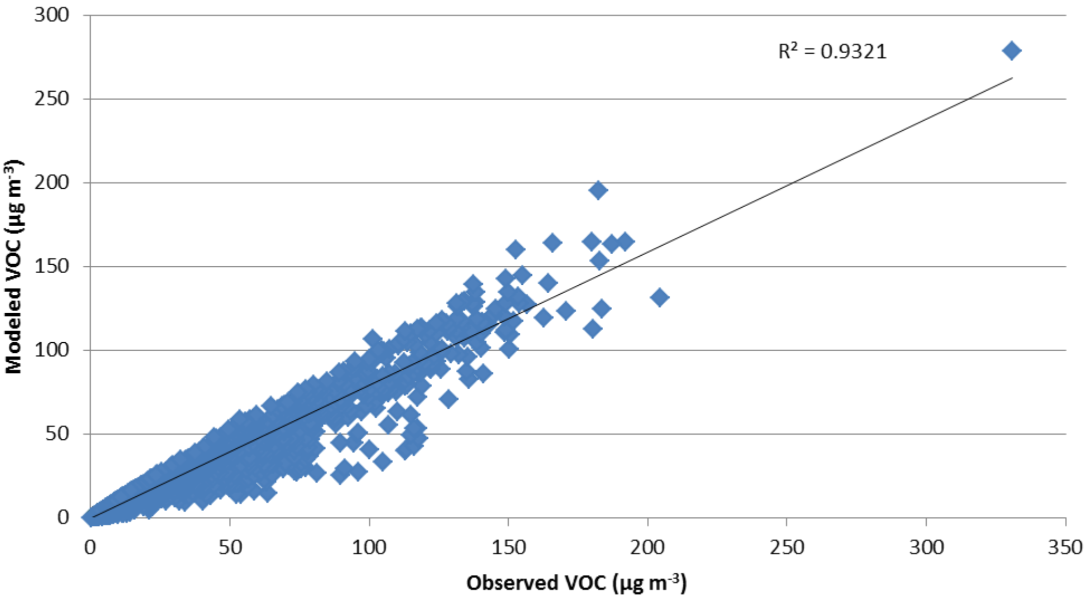


Figure 98 Modeled vs observed VOC concentrations at Aliağa, summer campaign

Contribution of each factor (source) on ΣVOC mass is given in Figure 99. Gasoline exhaust, which accounted for approximately 31% of the VOC mass, has the highest contribution VOC levels at Aliağa. Contribution of Natural gas maintenance factor, which accounted for 28% of VOC mass, was the second highest contributor after gasoline exhaust. High contribution of this source is probably due to its close proximity to the measurement point. The maintenance took place within 30 m from the station and activities lasted for a week. Two evaporative sources totally accounted for 30% of the ΣVOC mass at Aliağa and the diesel exhaust accounted for 8.3% of the total VOC mass. The gasoline exhaust contribution was higher in summer than it was in winter and diesel exhaust contribution is lower that diesel contribution found for winter. This may be due to higher light-duty traffic activity between İzmir and summer houses around Aliağa in the summer season.

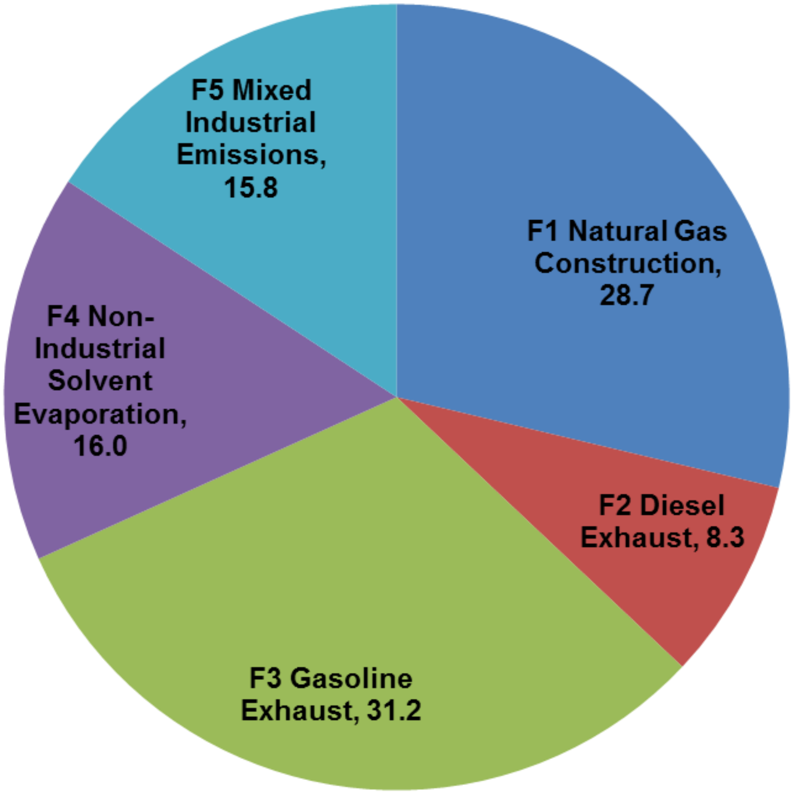


Figure 99 Sources and percent contribution sources of VOC at Aliağa, summer campaign

4.6.2. Receptor Modeling of Horozgediği Station

PMF was also applied to data set generated at the Horozgediği station. However, PMF was applied only to summer data, because of the insufficient coverage of the winter data set as discussed previously in the manuscript.

All of the compounds quantified during summer sampling were used in the PMF exercise. Four to seven factor solutions were performed and optimized. Among them, solution with 5 factors was found to be the optimum for the Horozgediği VOC dataset. Definition of "optimum" was given in previous sections in the manuscript.

The factor profile and explained variances of Factor 1 is presented in Figure 100. In the first factor, propylene, iso-butane+n-butane, t-2-butene, 1-butene, n-pentane, cyclo-pentane, 2,2-dimethylpropane, 2,2-dimethylbutane, 2,3-dimethylbutane contributions are observed. Also moderate loading of toluene is also seen in this factor. Iso-butane, n-butane and n-pentane are well known tracers of liquefied gasoline evaporation (Watson et al., 2001; Buzcu and Fraser, 2006). This source is identified as gasoline evaporation factor.

Diurnal variations in Factor 1 scores is given in Figure 101. Factor scores show a very well defined monomodal distribution that reaches to a maximum between 08:00 to 11:00 in the morning. This pattern does not agree with gasoline evaporation source suggested for Factor 1, because the highest evaporation is expected to occur during warmer periods in the day, not 8:00 in the morning. There are two sources of gasoline evaporation in this area. First and the most important source is the refinery. Tons of gasoline is loaded to trucks every day. Although all possible precautions are taken to minimize gasoline loss to the atmosphere (because any loss of gasoline to atmosphere means loss of product and thus money for the refinery), some leaks are inevitable in such a large scale operation. The second, and much smaller, evaporative gasoline source is the gas stations in the area. Since neither of these sources operates only in the morning hours, this distribution of scores cannot be explained by variations in emissions. The observed pattern can probably be explained by diurnal variation in wind direction as in the Aliağa PMF. Aliağa station is located to the E – SE of the Refinery and PETKİM, so winds from SW to W can bring their emission to the town. Horozgediği station, on the other hand, is located to the S – SSW of the industries. Winds from N and NNE can bring emissions from refinery and PETKİM to the Horozgediği area. Hourly wind roses, which were discussed in previous section, demonstrated that dominant wind direction is from NNE sector which is very close to the refinery and PETKİM. Throughout the night when winds blow from NNE sector (also to a lesser extend from N and NE sectors) scores are high, but not the highest. After 6:00, frequencies of N and NNW component start to increase. This is the time when Factor 1 scores start to increase. Winds from N and NNW (also from NW) continue to blow with high frequency throughout the morning hours, then winds shift to more southern sectors and N, NNW and NW component disappears. This is the time when Factor 1 scores drop to their low levels. These interesting coincidences suggests that dominant NNE flow do not bring emissions from Refinery to the station site, During high frequency of N, NNW and NW flow, Horozgediği area receives emissions from refinery and when frequency of flow from these sectors decrease early in the afternoon emissions from the refinery no longer reaches to our station.

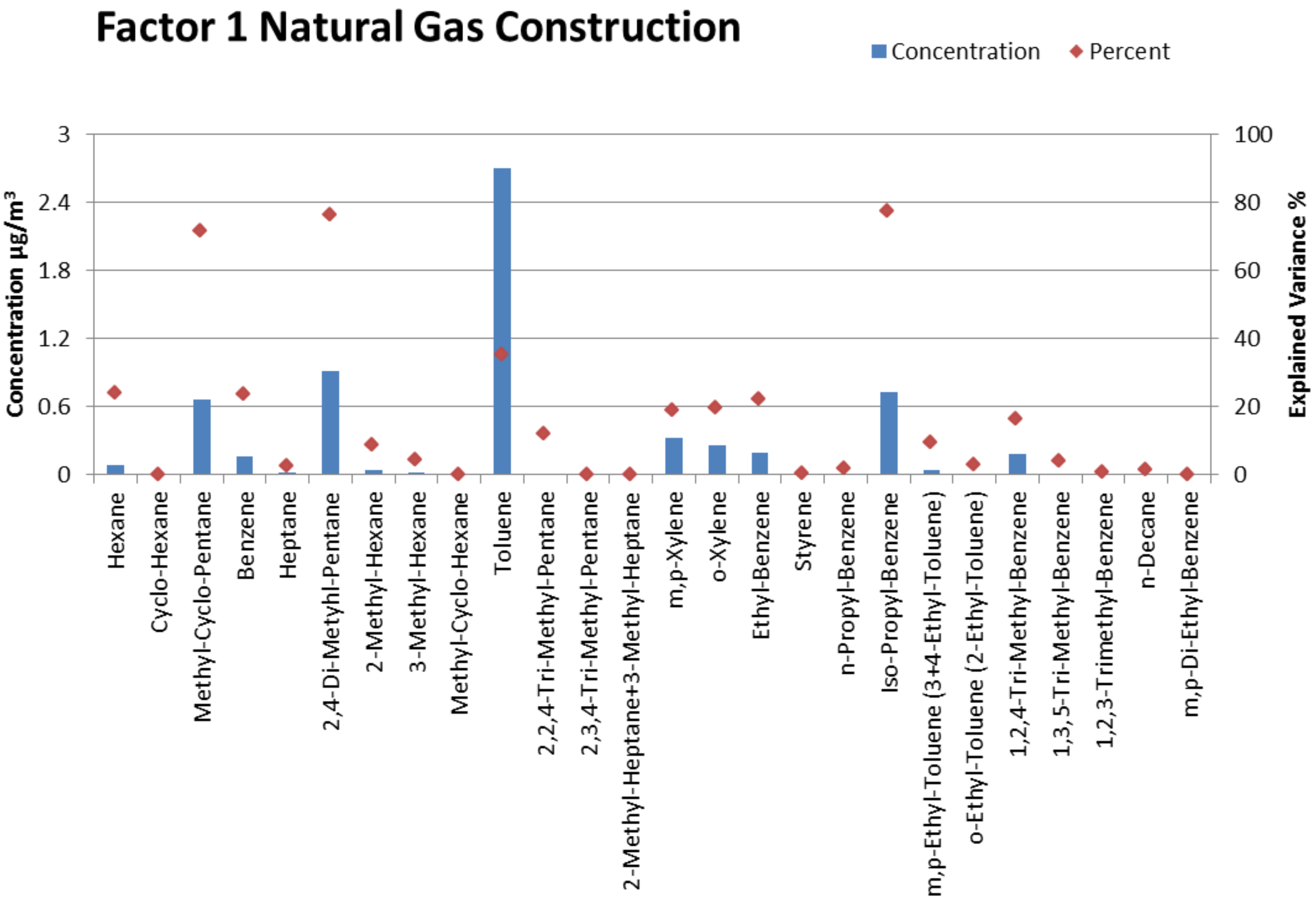


Figure 100 Concentration and percent of species explained in Factor 1 at Horozgediği station

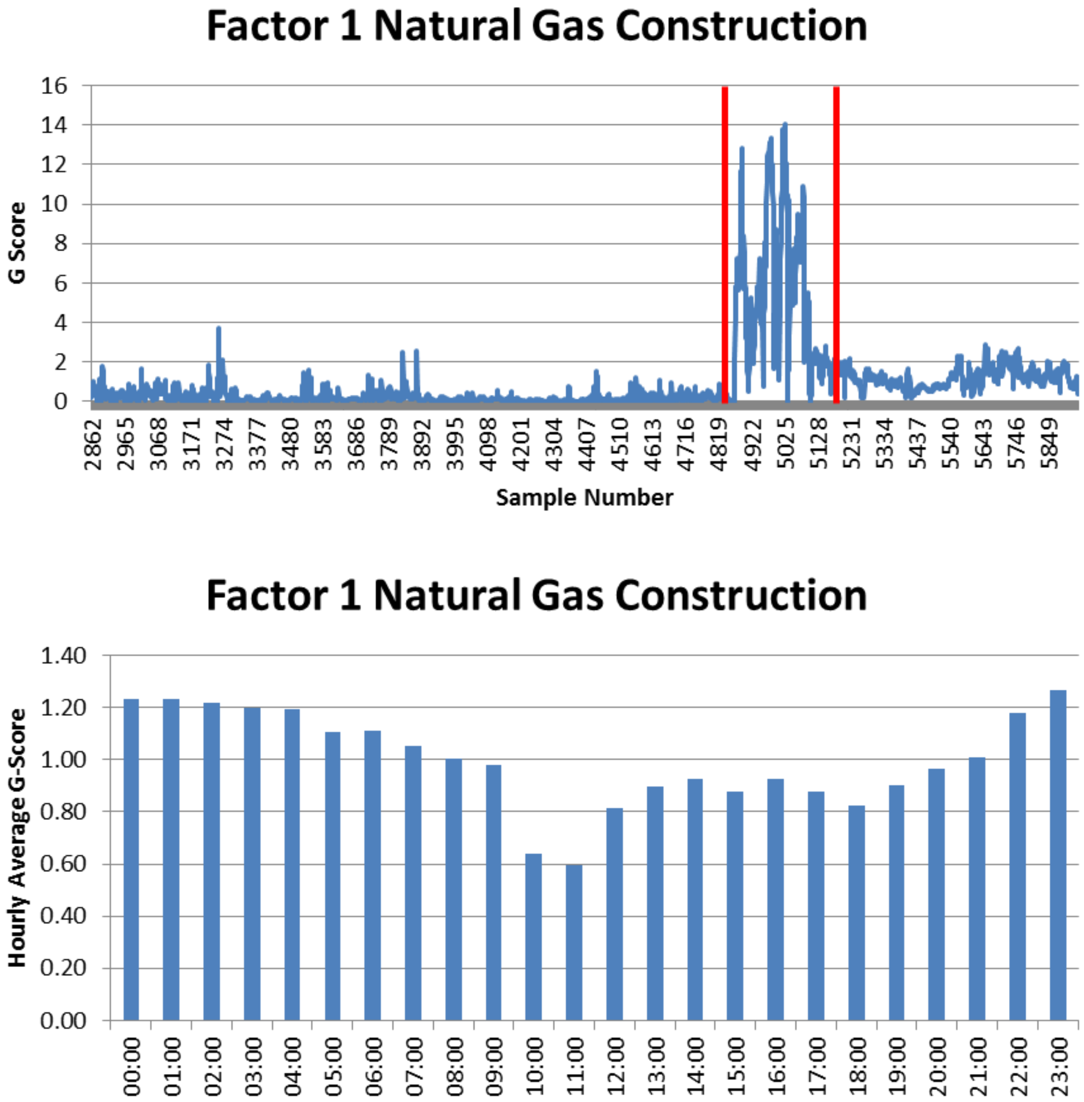


Figure 101 Time series plot of G-scores and diurnal average G-score distributions of Factor 1 at Horozgediği station

The CPF graphs constructed from G-scores and wind data is shown in Figure 102. Distribution of CPF values also supports the wind direction hypothesis. As depicted from the figure, the major source region of the factor is located on N of the station. This factor is most probably due to emissions of TÜPRAŞ during gasoline filling operations. There are also some contributions from SW of the station which seem to be a strong source. There are three hourly wind data from SW direction, Horozgediği village. In all three hour, contribution to this factor is high. In the village there is a truck park located 100 meters from the sampling station. This truck park might have an influence on such contribution.

Figure 102 CPF of Factor 1 at Horozgediği station

There is one interesting point here that should be highlighted. TÜPRAŞ and PETKİM are in the same general direction relative to Horozgediği station. They are very closely located. Because of this separating these two sectors with wind sectoring is an important accomplishment. Diurnal variations in Factor 1 scores pointed to refinery as an important source for gasoline evaporation, CPF analysis confirmed this. One last test was also performed to see if the refinery or PETKİM are important contributor to this “gasoline evaporation” factor. In this test Factor 1 profile is compared with the TÜPRAŞ and PETKİM profiles derived from data generated at TÜPRAŞ station. Since generation of operational profiles for TÜPRAŞ and PETKİM and similarities and differences between them were discussed in detail in the previous sections. It will not be repeated here. For this comparison, composition of Factor 1, which was generated by PMF are normalized to $\sum$VOC in that factor. Operational TÜPRAŞ and PETKİM profiles that were discussed in previous sections are slightly modified, because there 3 VOCs that existed in TÜPRAŞ and PETKİM profiles, but was not included in the PMF. The change in VOC contributions in TÜPRAŞ and PETKİM profiles by this modification was insignificant. Nevertheless, modified profiles were used in the following comparison.

Scatter-plots between Factor 1 profile vs. TÜPRAŞ and PETKİM profiles are given in Figure 103. The p = 0.004 shows that there is a statistically significant correlation between these two species with a probability > 99%. The R^2 = 0.29 indicating that approximately 30% of the variance in Factor 1 scores can be explained by emissions from TÜPRAŞ. On the other hand, correlation between Factor 1 profile with PETKİM profile is not statistically significant. Generally probability values that indicates <95% confidence are not considered statistically significant. For this reason, $p<0.05$ is considered as the requirement for statistical significance in this study. The p value between Factor 1 profile and PETKİM profile is 0.07 and that is why we considered that there is not a statistically significant relationship between these two parameters.

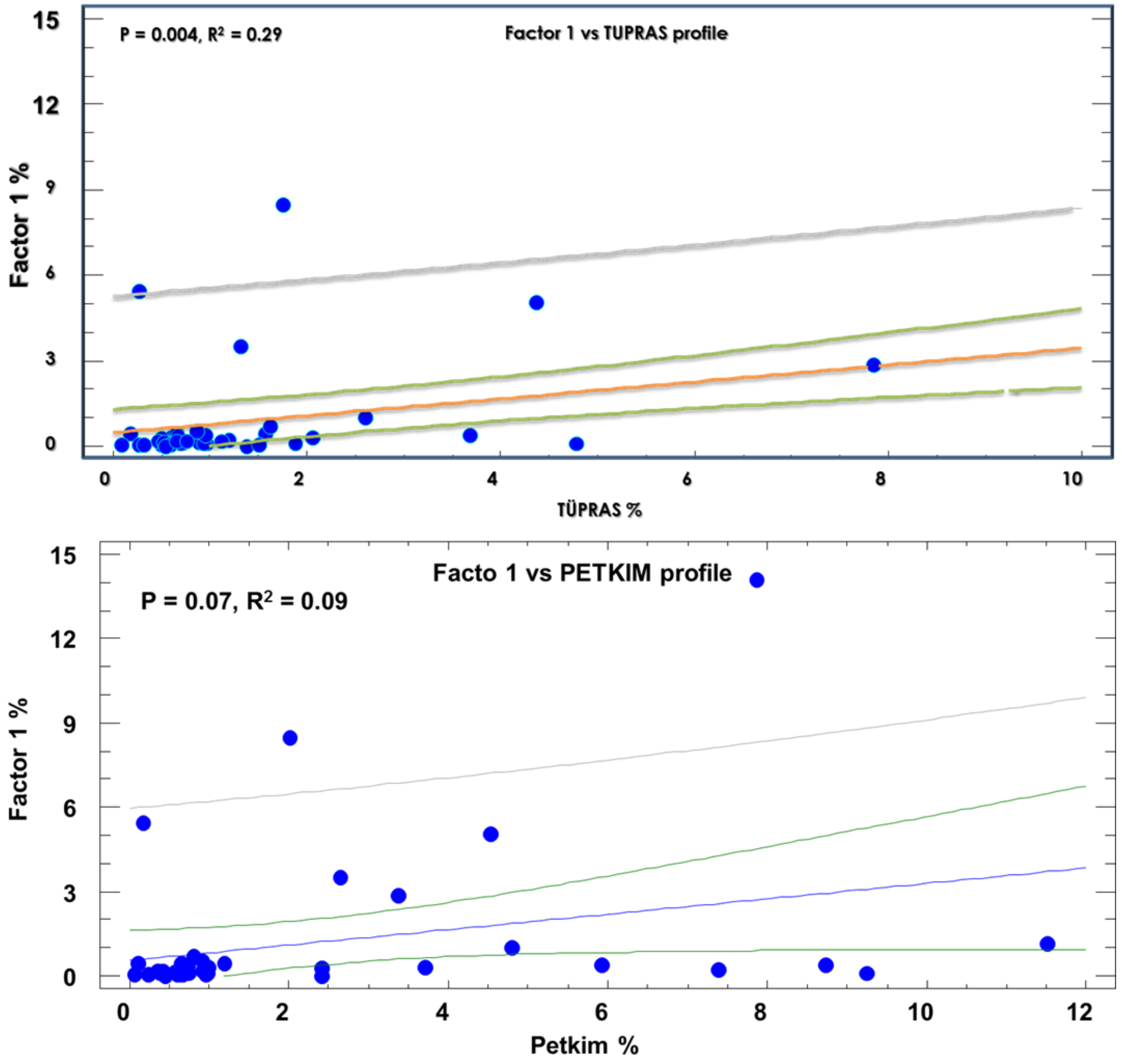


Figure 103 Correlations of TÜPRAŞ and PETKİM profiles with Factor 1 profile

Obviously comparison Factor 1 profiles with TÜPRAŞ and PETKİM operational profiles also supported that Factor 1 is correctly identified as gasoline evaporation, evaporative emissions from TÜPRAŞ, but not from PETKİM is a strong component of this factor and the diurnal variation of wind direction hypothesis seems to be correct. It is really interesting to see that the impact of two sources, which are very closely spaced, can be separated at a receptor 7 kms away by wind analysis. TÜPRAŞ emissions account for approximately 30% of the variance in Factor 1 scores. This means that Factor 1 is not entirely refinery emissions, or in receptor modeling jargon; Factor 1 is not a "refinery factor". Refinery accounts for approximately 30% of this VOC component, but there are also other sources. Factor 1 is gasoline evaporation factor and probably there are gasoline stations, particularly in the summer, should be an important source for it.

The concentrations and fractions of explained variances of VOCs in Factor 2 is given in is depicted in Figure 104. High fractions (40 – 90%) of variances of heavy VOCs, including 2,2,4-trimethyl-pentane, 2-methyl-heptane, 4+3-methyl-heptane, styrene, 1,3,5-trimethylbenzene, n-propyl-benzene, iso-propyl-benzene, ethyl-toluenes, 1,3-diethyl benzene, n-butylbenzene, naphthalene, undecane and c+t-1,3-dichloro-propene, are explained by Factor 2. Heavy hydrocarbons, and particularly, undecane, n-decane and 1,2,4-trimethylpentane are indicators of diesel emissions (Watson et al., 2001). This factor is assigned as diesel exhaust factor.

Diurnal variation of Factor 2 scores, which is given in Figure 105, are higher at night. This diurnal pattern is very similar to those observed in Aliağa PMF (Factors 3 and 4), where such pattern was attributed to diurnal variation in wind speed. If the diurnal variation of wind speed is also valid in generating Factor 2 at Horozgediği then sources of this factor should be in a sector between S and W relative to Horozgediği Station. The reason for high contribution expected between S and W sectors were discussed extensively previously, when Factor 3 in Aliağa PMF was interpreted.

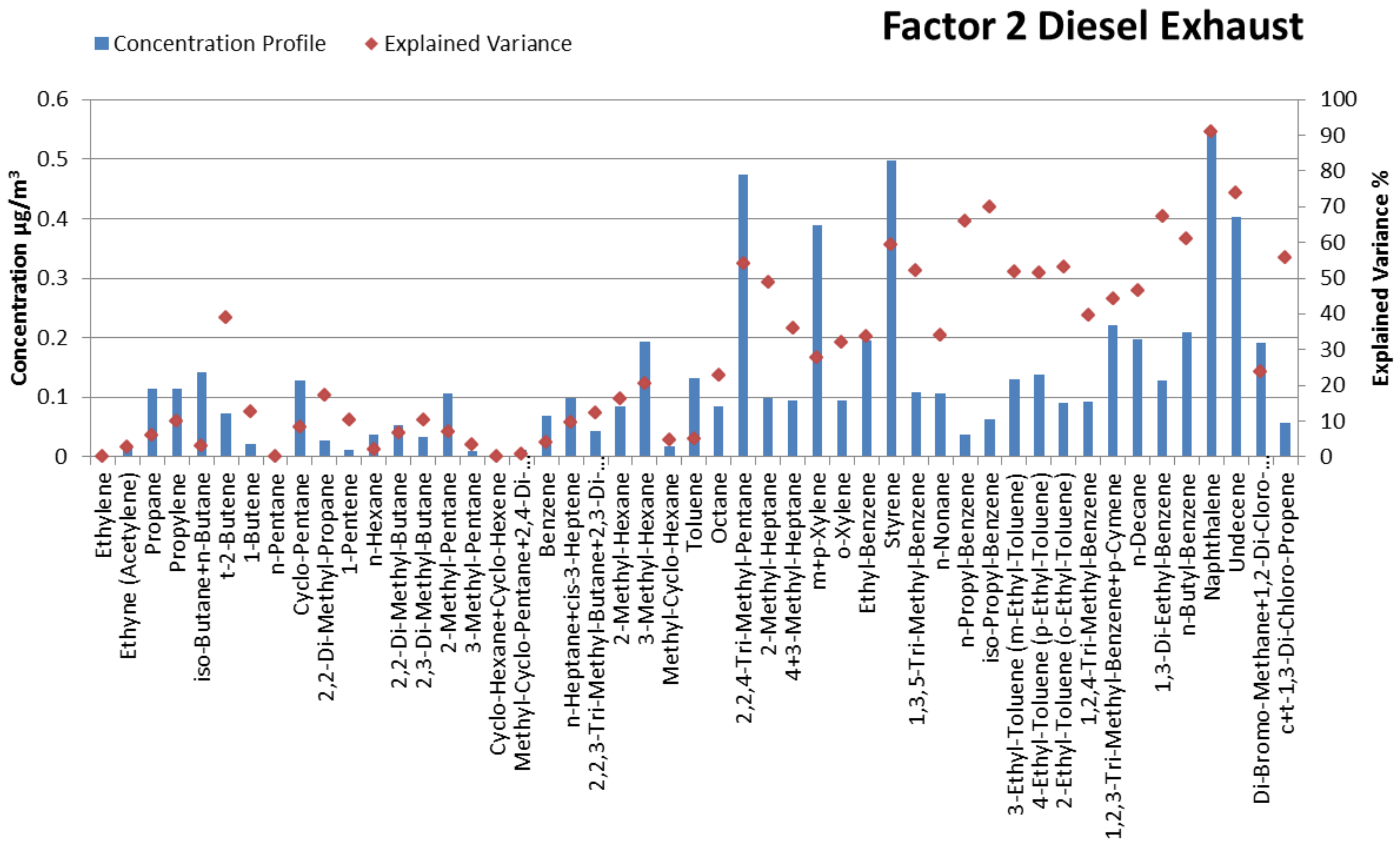


Figure 104 Concentration and percent of species explained in Factor 2 at Horozgediği station

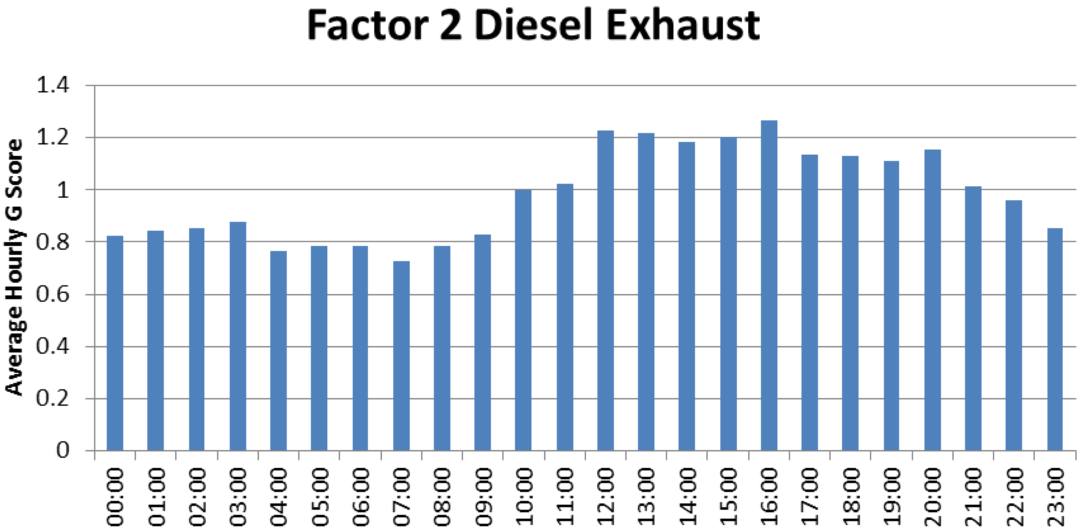


Figure 105 Diurnal average G-score distributions of Factor 2 at Horozgediği station

Distribution of CPF among wind sectors, which were calculated using Factor 2 scores, is depicted in Figure 106. CPF rose clearly demonstrate a sector between S and NW as expected from wind hypothesis. Furthermore, p values for the correlation of Factor 2 profile with TÜPRAŞ and PETKİM profiles are 1.0 and 0.6, respectively, indicating that here is no statistically significant correlation between Factor 2 and PETKİM or TÜPRAŞ emissions. All these suggest that Factor 2 is generated by wind flows between S and W sectors; it has no bearing with refinery and PETKİM. Sources responsible from this factor are between S and W sectors. Their emissions are intercepted in our Horozgediği station when winds blow from that sector which occurred between 10:00 hours in the morning and 21:00 hours at night. Two likely sources in this sector are the Kozbeyli and Horozgediği villages, which are in the immediate vicinity of the station. Heavy duty vehicles (both agricultural and transportation) in those villages are probably responsible for the enrichment of heavy VOCs in this factor. Although these are not strong diesel emission sources, they are very close to the station (Horozgediği is approximately 400 m away, and Kozbeyli is approximately 3 km away) which can make them important sources of heavy VOCs.

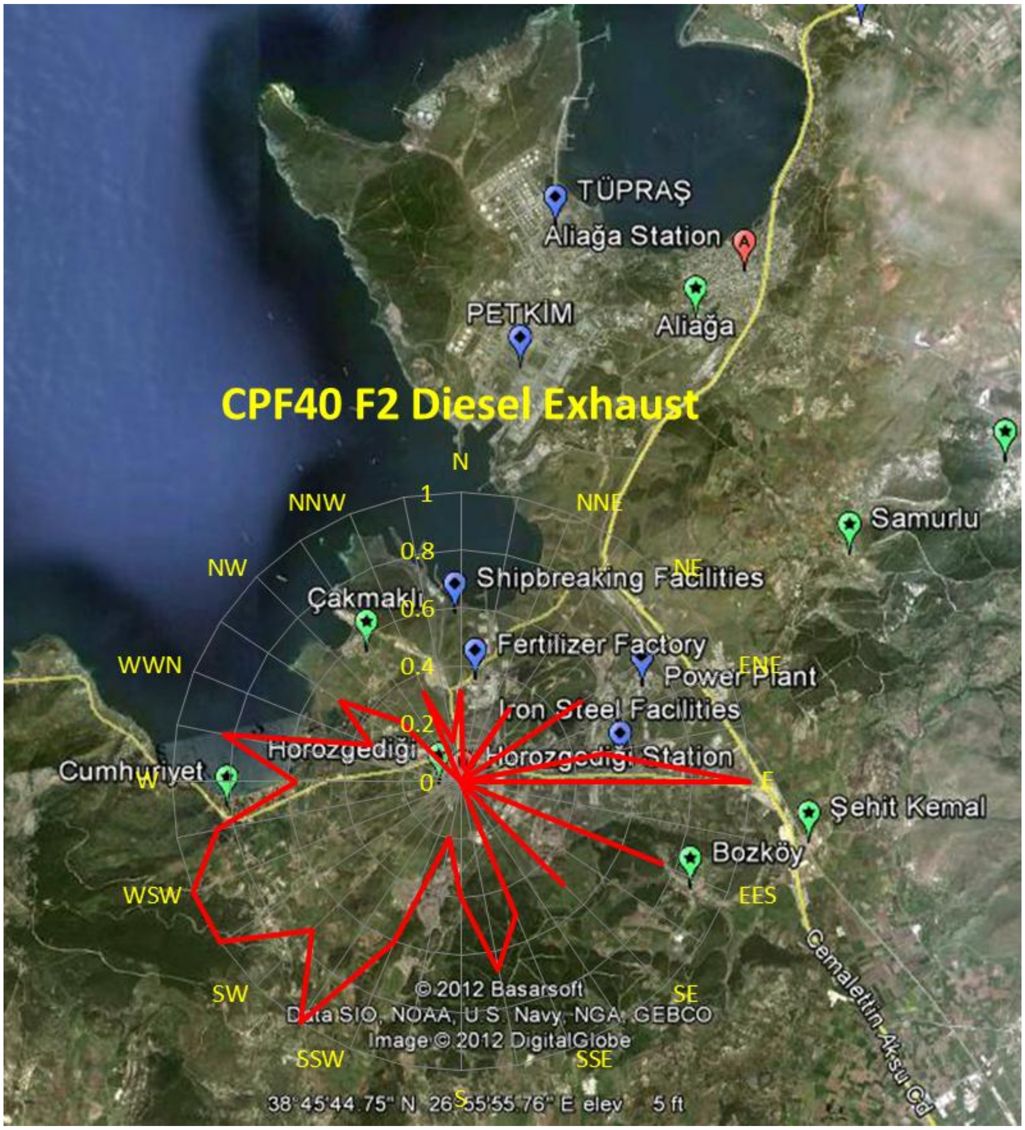


Figure 106 CPF of Factor 2 at Horozgediği station

Scatter plot between Factor 2 scores and temperature is depicted in Figure 107. There is a statistically significant correlation between scores and temperature ($p<0.05$), indicating that some of the VOCs in Factor 2 can be there due to evaporation of diesel fuel. Although vapor pressure of diesel fuel is fairly low (it is 0.0009 atm at 25°C; for comparison, vapor pressure of benzene at the same temperature is 0.12 atm), in summer temperatures in Aliağa, evaporation diesel fuel can contribute to the observed factor. There is a truck parking area very close to the station (approximately 200 m away), which is a likely source of both evaporative and exhaust emissions.

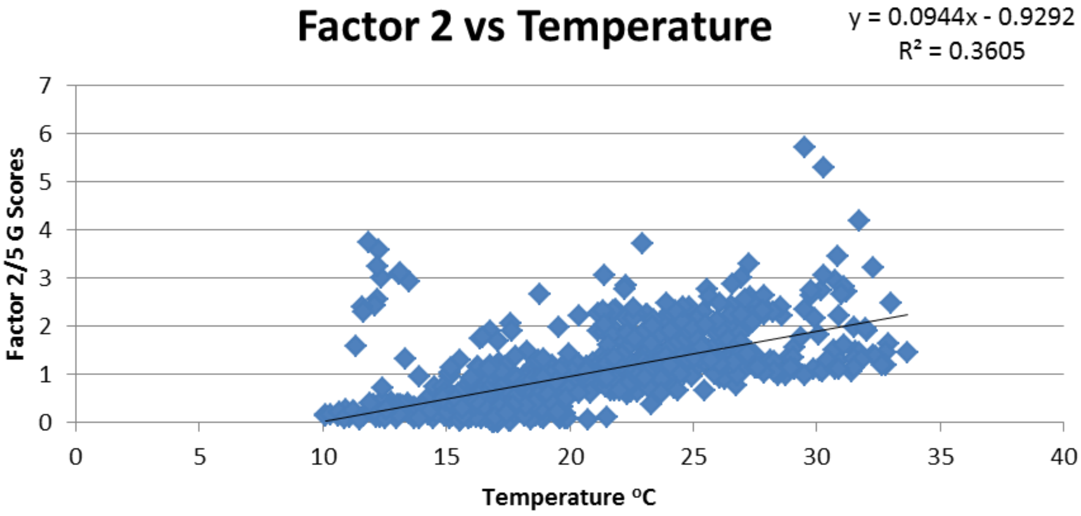


Figure 107 Factor 2 G-scores at Horozgediği station versus ambient temperature

Concentrations and explained variances of VOCs in Factor 3 is given in Figure 108. Most of the variances of ethyelene, propane, n-pentane, C_5-C_8 VOCs and di-bromo-methane+1,2-dichloropropane explained in Factor 3. Some variances of xylenes and isobutane+n-butane are also observed in this factor. Ethylene, benzene, toluene and xylenes are an indicator for motor vehicle emissions (Watson et al., 2001). However these do not occur together with propane, n-hexane, di-bromo-methane+1,2 dichloro propane in motor vehicle exhaust. They can also be associated with emissions from petrochemical complex and refinery (Buzcu et al., 2006; Badol et al., 2008). The presence of aromatic factory in PETKİM was discussed in previous sections. Strong association of BTX compounds with this factor can be attributed to the emissions from aromatic factory. Ethylene is also an input material in a number of plants in the PETKİM. This plant appears to be associated with emissions from PETKİM and TURAS and identified as PETKİM and TÜPRAŞ operational emissions.

Diurnal variations of scores and CPF rose for Factor 3 are given in Figure 109 and Figure 110, respectively. The contributions to this factor start to increase at 03:00, reaches to a maximum at approximately 11:00 in the morning, then decrease gradually in the afternoon. This is the period when winds exclusively blow from between N and NE sectors. Distribution of CPF shows that sources contributing to Factor 3 are in the sector between NNW and NE. This sector defined by the CPF rose includes TÜPRAŞ and PETKİM.

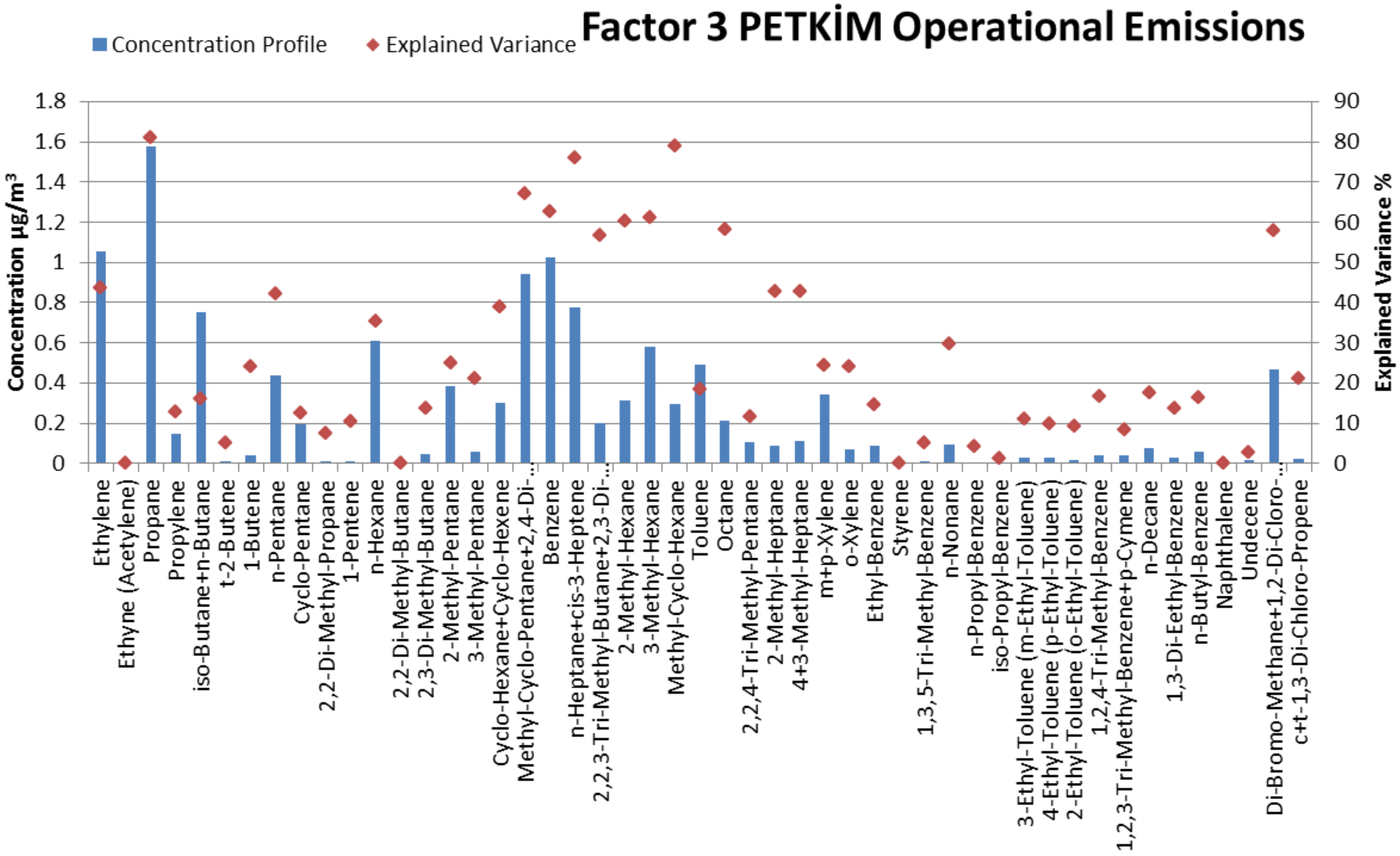
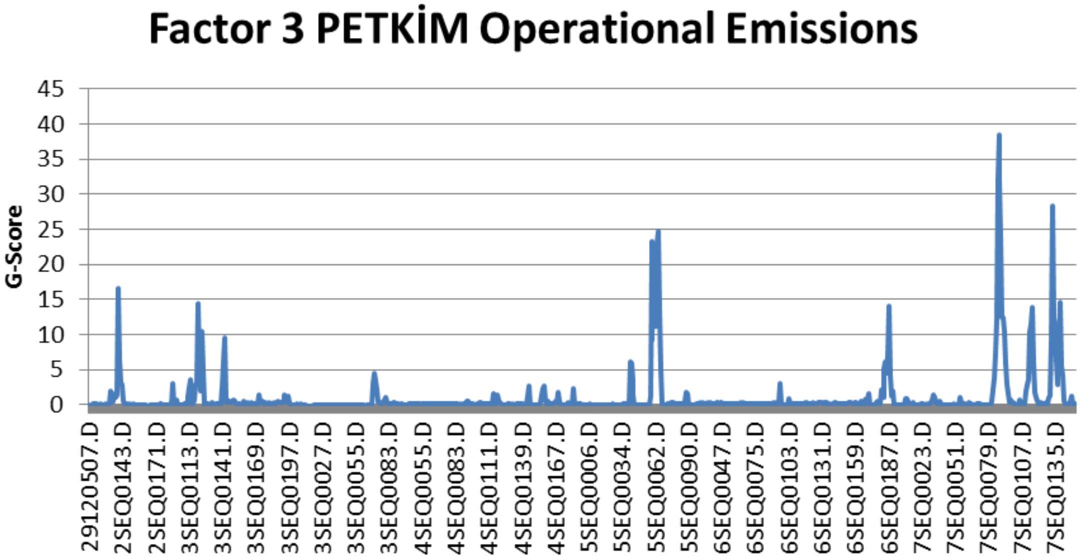


Figure 108 Concentration and percent of species explained in Factor 3 at Horozgediği station



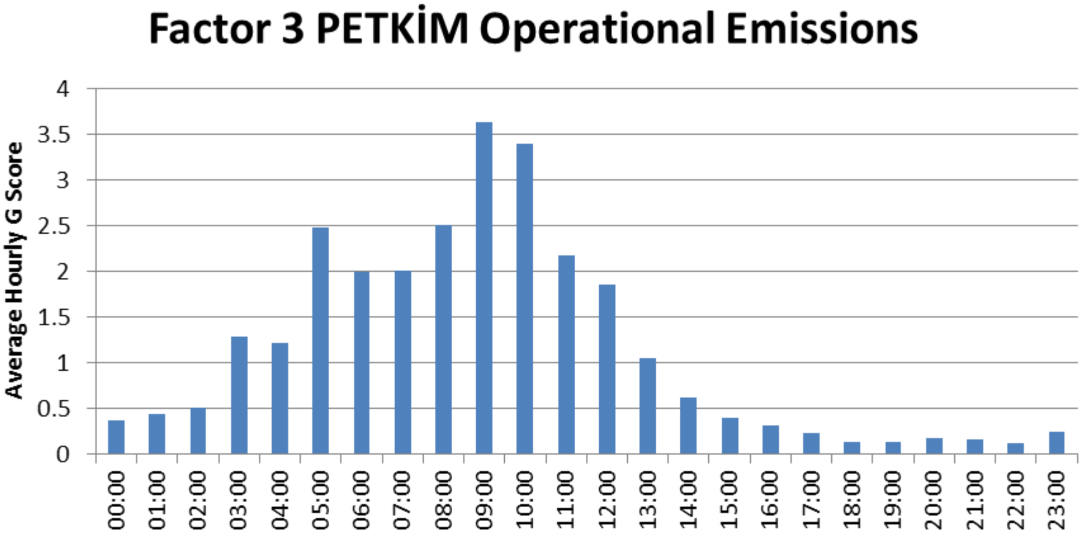


Figure 109 Time series plot of G-scores and diurnal average G-score distributions of Factor 3 at Horozgediği station

Figure 110 CPF of Factor 3 at Horozgediği station

Chemical composition of factor, fraction of variances of VOCs explained by Factor 3, diurnal variation of factor scores and CPF rose all point to the refinery and petrochemical complex as potential sources generating Factor 3. But these evidence is not enough to differentiate between TÜPRAŞ and REFINERY as the main contributor to Factor 3. Chemical composition seems to suggest PETKİM as the main source of this factor. But since these two sources are very close to each other, neither diurnal variation of G-scores, nor distribution of CPF can provide conclusive support for primarily PETKİM source.

Factor 3 profile is compared with TÜPRAŞ and PETKİM operational profile to differentiate between these two industries as the main source of VOCs in Factor 3. Scatter plots and regression information for the linear regression between Factor 3 profile and profiles of TÜPRAŞ and PETKİM are given in Figure 111. Both TÜPRAŞ and PETKİM profiles show statistically significant correlations with Factor 3 profiles. However, regression information revealed that association of PETKİM with Factor 3 is much stronger than association of TÜPRAŞ. The "p" values, which indicate probability of chance correlation are <0.00001 for PETKİM and 0.002 for TÜPRAŞ, demonstrating that correlation between PETKİM and Factor 3 profiles is stronger than the correlation between TÜPRAŞ and Factor 3 profiles. R^2 values for regressions between PETKİM vs Factor 3 and TÜPRAŞ vs Factor 3 are 0.57 and 0.22, respectively, indicating that approximately 60% of the variance of Factor 3 scores is explained by PETKİM emissions and 20% of the variance is due to TÜPRAŞ emissions. Comparison of PETKİM and TÜPRAŞ profiles with Factor 3 profile shows that Factor 3 is a PETKİM factor, with minor contribution from the refinery. The original name assigned to this factor, which was "PETKİM and TÜPRAŞ operational emissions" is changed to "PETKİM operational emissions"

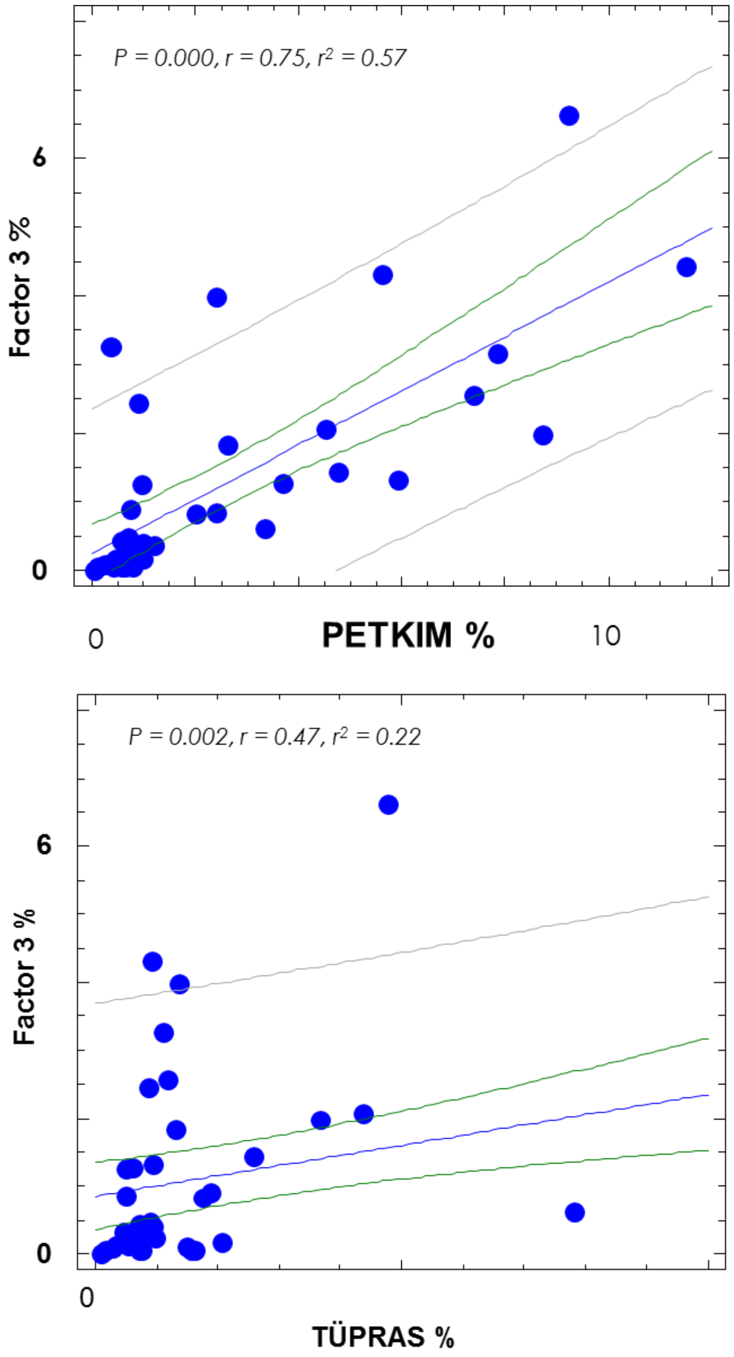


Figure 111 Correlations of TÜPRAŞ and PETKİM profiles with Factor 3 profile

Composition of Factor 4 and variances of VOCs explained are shown in Figure 112. Approximately 30% - 90% of variances of ethylene, ethyne, propylene, iso-butane+n-butane, benzene, toluene variances are explained by Factor 4. These compounds are indicators of motor vehicle exhaust (Watson et al., 2001). Among these, acetylene (ethyne) is an important gasoline exhaust marker and frequently used to differentiate between exhaust emissions and evaporative gasoline emissions, because it is a combustion product and occurs in exhaust emissions, but does not exist in gasoline evaporation. Presence of ethyne in Factor 4 is a good signal that it is gasoline exhaust factor. This gasoline exhaust source for factor 4 is also supported by diurnal variation of Factor 4 scores, which is given in Figure 113. Diurnal variation of factor scores display a typical bimodal traffic pattern, with two maxima corresponding to morning and afternoon rush hours.

Distribution of CPF values among wind sectors is depicted in Figure 114. The CPF of Factor 4 shows the major source regions as the Yeni Foça-Aliağa road and İzmir-Çanakkale highway. Weekend contribution to this factor is higher than weekday contribution. Such kind of behavior is expected as the region is also tourism area. Motor vehicle emissions accounts for 20.3% percent of the modeled mass. Neither CPF calculations, nor diurnal variation of factor scores suggest that the refinery is a source of this factor. However, factor profile is strongly correlated with TÜPRAŞ profile ($p < 0.0001$, $r = 0.78$ and $r^2 = 0.62$). We believe that this is an artifact and due to inadequacy of the PMF model to differentiate between whole gasoline and exhaust emissions. It is normal to expect that most of the gasoline used in Aliağa, and actually in İzmir region is the one produced in TÜPRAŞ.

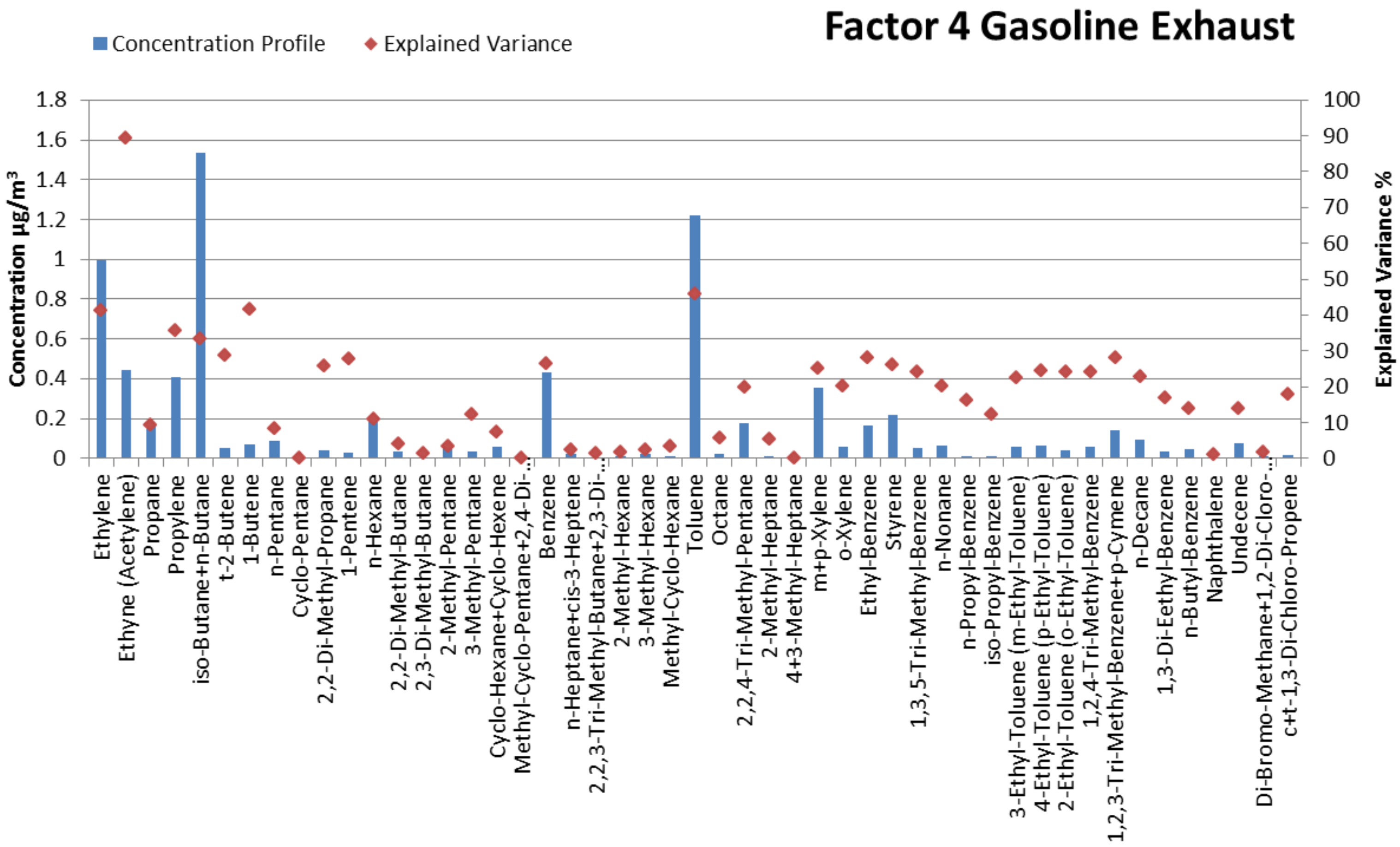


Figure 112 Concentration and percent of species explained in Factor 4 at Horozgediği station

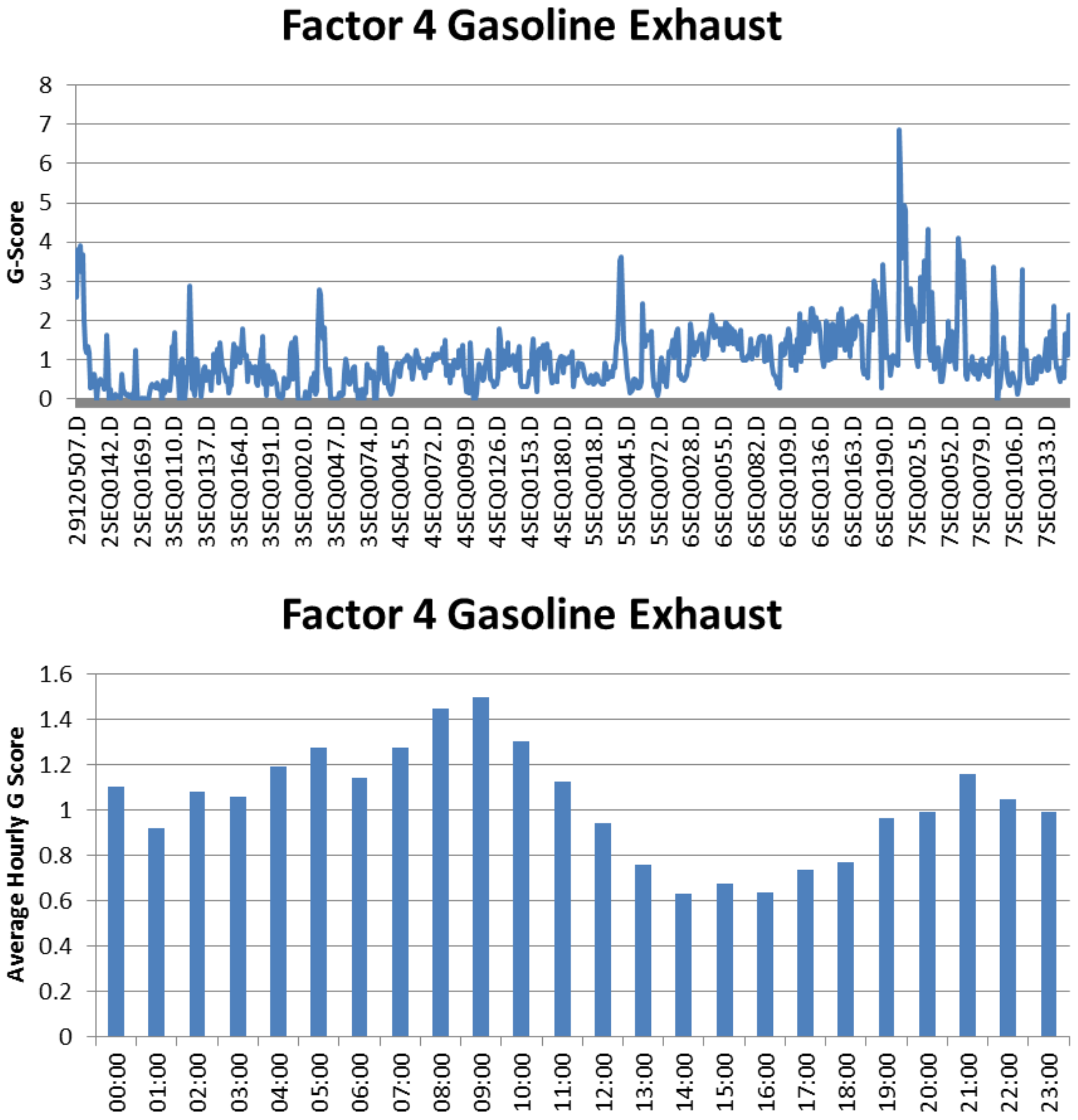


Figure 113 Time series plot of G-scores and diurnal average G-score distributions of Factor 4 at Horozgediği station

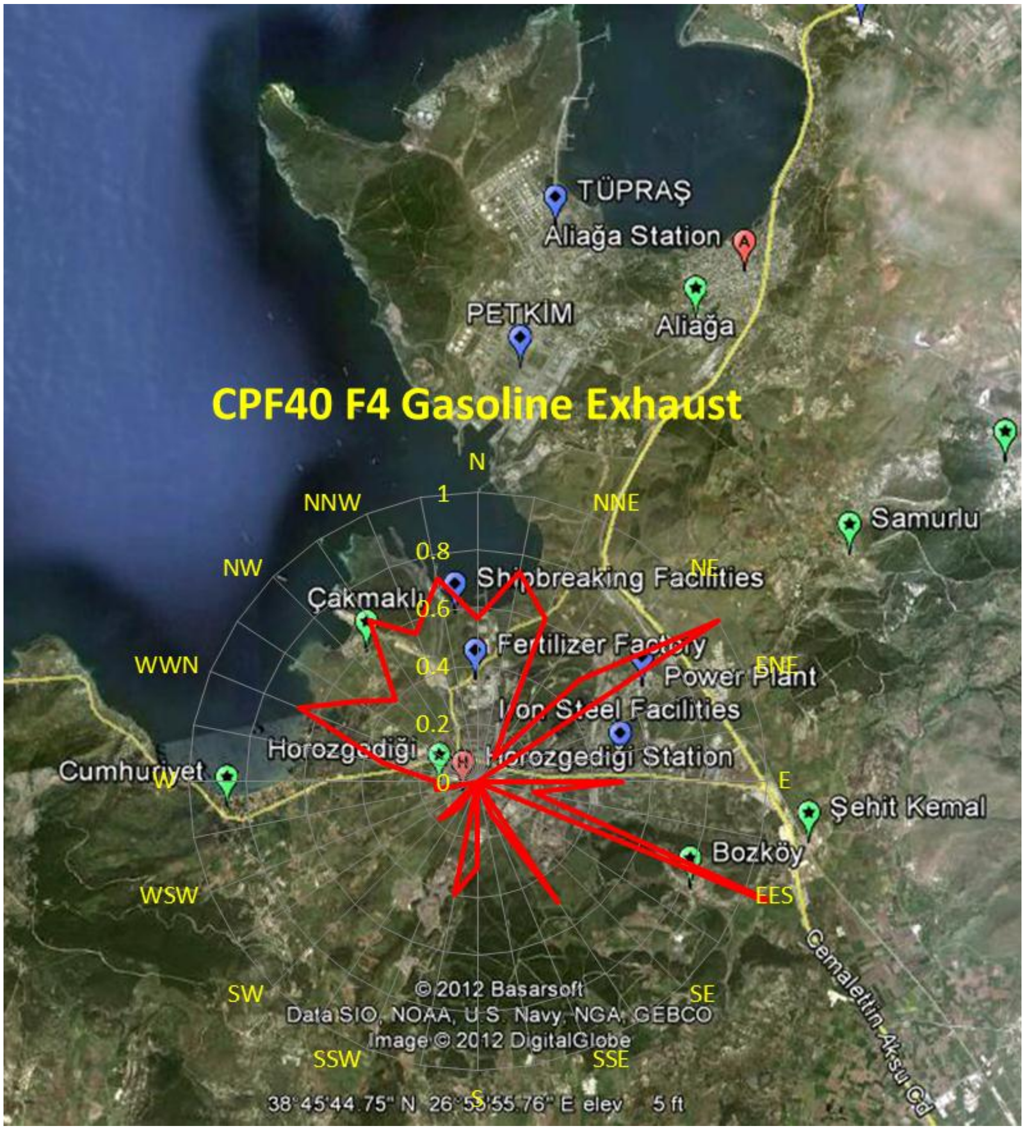


Figure 114 CPF of Factor 4 at Horozgediği station

Difficulty of differentiating gasoline exhaust, gasoline evaporation and whole gasoline from each other using multivariate techniques is also well documented (Watson et al., 2001; Kuntasal, 2005). This is probably what happened in Factor 4. PMF was not able to separate gasoline exhaust and evaporative components due to their very similar compositions, and assigned some of the refinery contribution to total VOC mass into this gasoline exhaust factor.

Factor composition and explained variances of Factor 5 is given in Figure 115. Factor 5 explains large fractions of variances of C_4–C_5 hydrocarbons, including, n-hexane, 2-3-dimethylbutane, 2-methyl-pentane and 3-methyl-pentane, cyclo-hexane+cyclo-hexene and methyl-cyclo-pentane+2,4-di-methyl-pentane. Smaller fractions of variances of heavier VOCs are also explained by Factor 5. Compounds associated with this factor are the solvents used in PETKİM and produced in TÜPRAŞ. Diurnal variation of factor 5 scores, which is given in Figure 116 show one well-defined maximum which occurred at 10:00 in the morning. This pattern is very similar to the pattern observed for Factor 3, which was attributed to northerly flow during night and early morning, which brings TÜPRAŞ and PETKİM emissions to the Horozgediği station. This also confirms the PETKİM and TÜRPRAS, particularly PETKİM, which are associated with Factor 5 based on chemical composition of this factor. Although chemical composition and diurnal variation of factor scores suggest PETKİM and TÜPRAŞ as likely sources of Factor 5, CPF rose, which is given in Figure 117 do not point these two industries directly, as it did in Factor 3. There is a northerly component in CPF rose, but main directions for location of Factor 5 sources are between SW and N. Horozgediği village, which is located to the west of the station, ship dismantling facilities, which are located between W and N wind sectors relative to station are potential sources in the directions where there is high values of CPF is found.

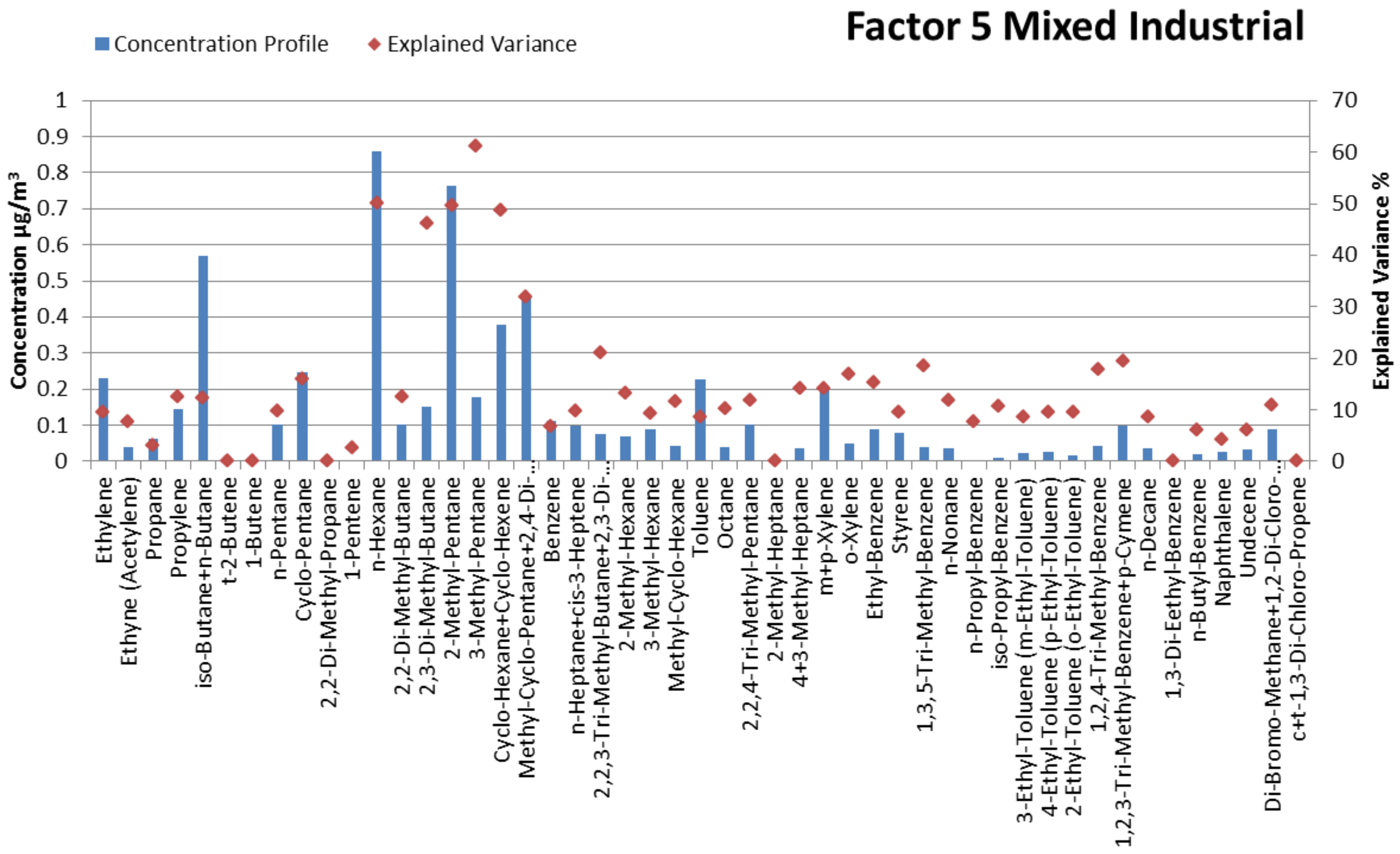
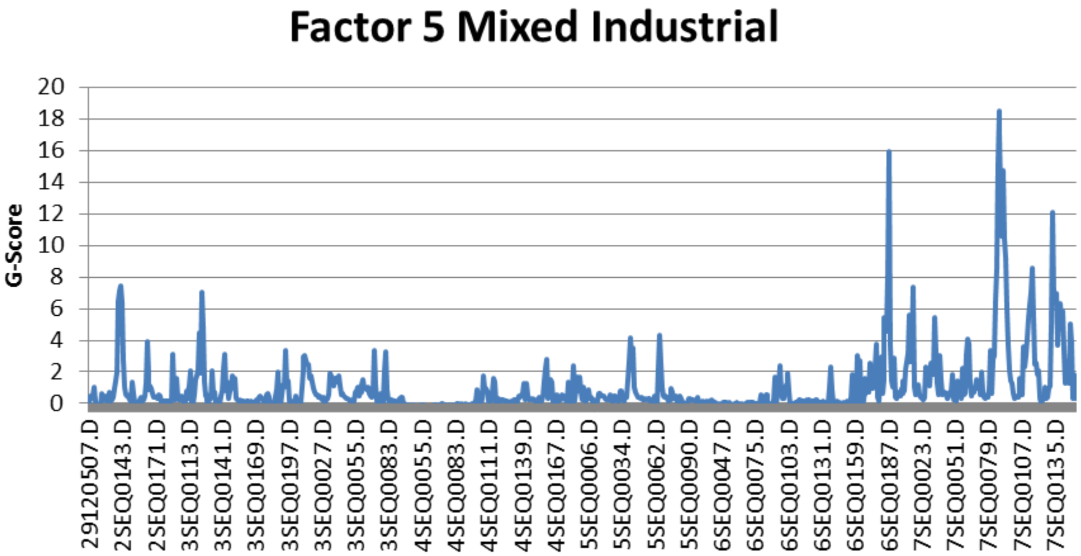


Figure 115 Concentration and percent of species explained in Factor 5 at Horozgediği station



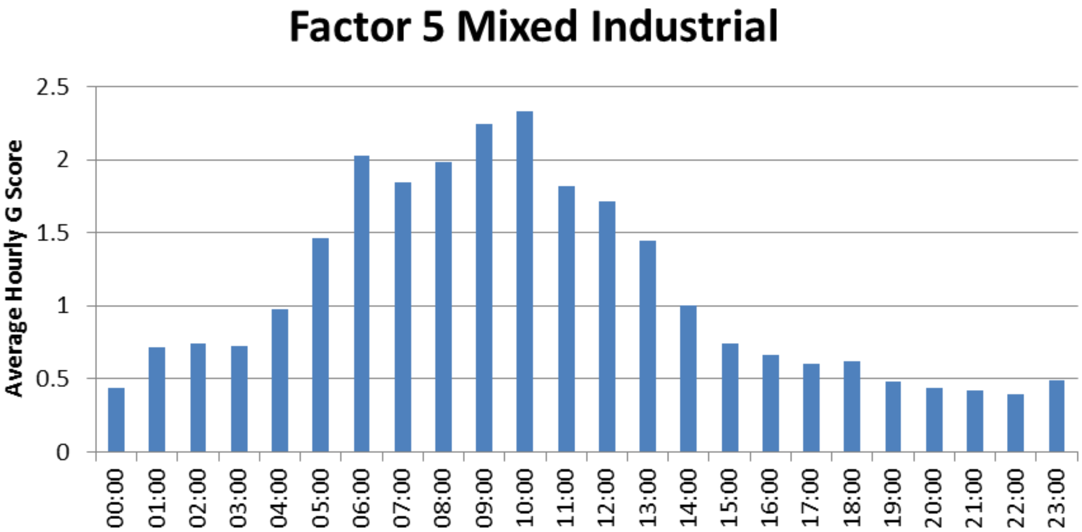


Figure 116 Time series plot of G-scores and diurnal average G-score distributions of Factor 4 at Horozgediği station

Figure 117 CPF of Factor 5 at Horozgediği station

To clarify this uncertainty in assigning sources to Factor 5, Factor 5 profile is compared with profiles of PETKİM and TÜPRAŞ. Scatter plots between Factor 5 profile and profiles of industries are given in Figure 118. Factor 5 profile correlates with the profiles of the two industries with statistical significance better than 95% confidence level. Association of TÜPRAŞ with the factor is marginal (p = 0.02). However, association of PETKİM with the profile is fairly strong (p = 0.0007). 27% of the variance in Factor 5 scores can be explained by PETKİM emissions (TÜPRAŞ on the other hand explains only 14% of the variance in Factor 5 profile), which is significantly smaller than fraction of variance explained in PETKİM factor (Factor 3). This discussion seem to suggest that Factor 5 is a mixed factor, contributed PETKİM, ship dismantling facilities and possibly emissions from some of the villages, particularly Horozgediği village.

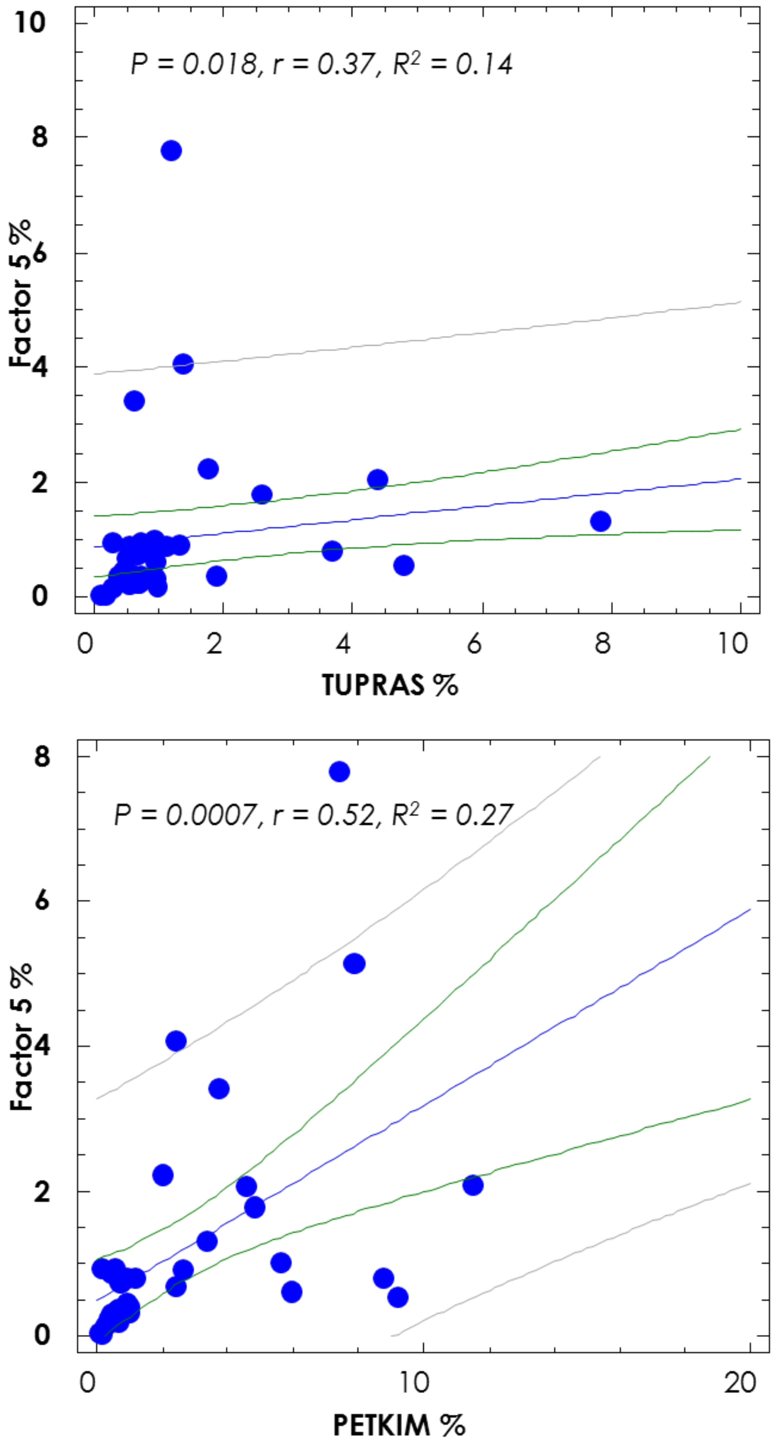


Figure 118 Correlations of TÜPRAŞ and PETKİM profiles with Factor 5 profile

Observed VOC mass is correlated with modeled mass in order to check the performance of the five factor solution. Results are given in Figure 119. Very good correlation between observed and predicted ΣVOC concentrations suggest that the optimized 5 factor PMF solution adequately explained 96% of the variance in measured ΣVOC concentrations.

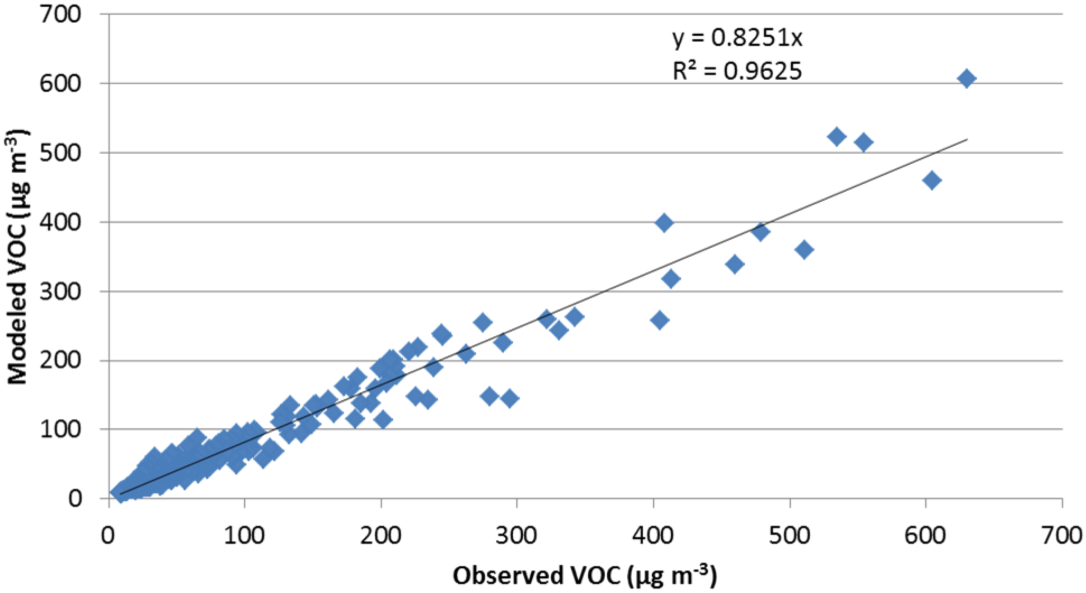


Figure 119 Modeled vs observed VOC concentrations at Horozgediği station

Contribution of each factor (source) on ΣVOC mass is given in Figure 120. PETKİM operational emissions, which accounted for approximately 32% of the VOC mass, has the highest contribution VOC levels at Horozgediği. Contribution of gasoline exhaust factor, which accounted for 20.3% of VOC mass, was the second highest contributor. Diesel exhaust factor is accounted for 16.2% of the VOC mass. Gasoline evaporation factor is another motor vehicle related source and account for 15.6% of the VOC mass. The mixed factor, contributed PETKİM, ship dismantling facilities and possibly emissions from some of the villages accounted for 16.0% of the VOC mass.

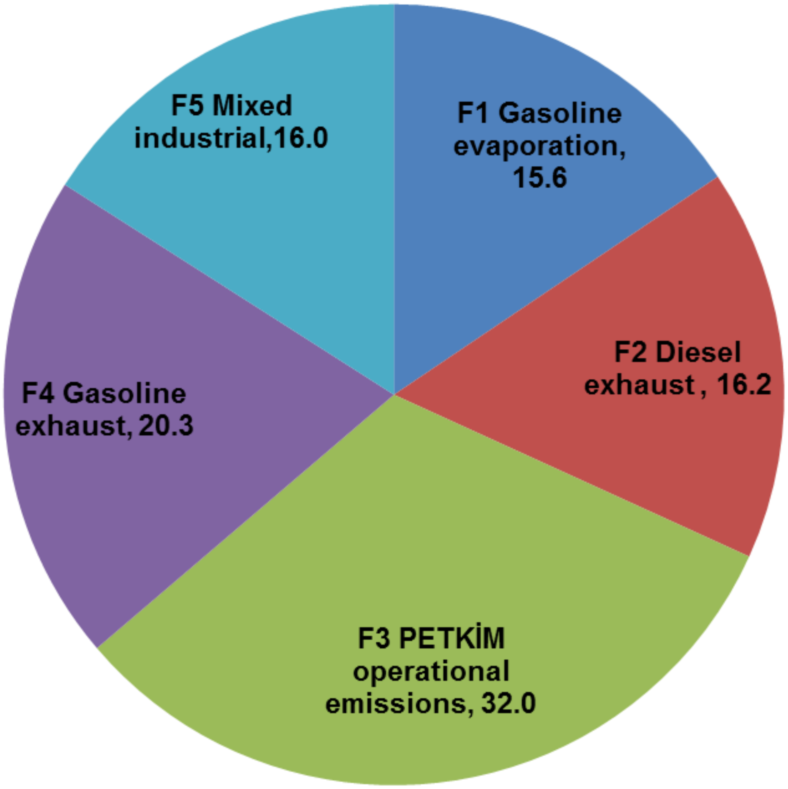


Figure 120 Sources and percent contribution sources of VOC at Horozgediği

4.6.3. Comparison of PMF Results

The sources of VOCs and their contributions to each dataset in Aliağa region is given in Table 21. A total of 10 different factors are identified. Gasoline exhaust and diesel exhaust profiles are the two common profiles observed in three PMF studies. The percent contributions of gasoline exhaust at Aliağa summer, Aliağa winter and Horozgediği studies are 31.2%, 25.9% and 20.3%, respectively. The percent contributions of gasoline exhaust at Aliağa is observed higher than Horozgediği. Higher mass contribution of gasoline exhaust is expected to be higher at Aliağa because Aliağa station is closer to the Çanakkale İzmir highway and there are some busy downtown roads around the sampling station.

Table 21 Comparison of VOC sources

	Aliağa Summer		**Aliağa Winter**		**Horozgediği**	
Sources	(%)	(µg m^{-3})	(%)	(µg m^{-3})	(%)	(µg m^{-3})
Gasoline Exhaust	31.2	6.9	25.9	11.1	20.3	7.7
Diesel Exhaust	8.3	1.8	19.1	8.2	16.2	6.2
Gasoline Evaporation			8.6	3.7	15.6	5.9
Industrial						
Mixed Industrial	15.8	3.5				
Industrial Evaporation			27.5	11.9		
PETKİM Operational					32.0	12.1
Natural Gas Use			18.9	8.2		
Mixed Industrial and Village					16.0	6.1
Natural Gas Construction	28.7	6.4				
Non-Industrial						
Solvent Evaporation	16.0	3.5				

Contributions of diesel exhaust on modeled VOC are 8.3%, 19.1% and 16.2% for Aliağa summer, Aliağa winter and Horozgediği, respectively. The contribution of Aliağa summer season diesel emissions is approximately a factor two smaller than the winter contribution. This is at least partly due to higher gasoline exhaust contribution in summer campaign owing to more extensive touristic mobility in summer. Comparable contributions are observed in between Aliağa winter and Horozgediği studies. The contribution of diesel exhaust at Horozgediği is expected to be less. However, due to nearby truck park higher than expected diesel contribution was found.

Another traffic related factor observed both at Horozgediği and Aliağa stations was gasoline evaporation. This factor is not observed at Aliağa summer PMF as the tracer of gasoline evaporation (C_4-C_5 compounds) are not measured during summer campaign. The percent contributions of gasoline evaporation at Aliağa winter and Horozgediği are 8.6% and 15.6%, respectively. Gasoline evaporation can arise from both gasoline stations and TÜPRAŞ where gasoline vapors may leak during loading operations. Unfortunately, PMF were not able to differentiate these two sources. Higher contribution of gasoline evaporation factor to $\sum$VOC mass at Horozgediği station is due to higher contribution of refinery to Horozgediği area, as this area is downwind from the industries. Traffic related sources together accounted for approximately 50% of the $\sum$VOC mass in both stations.

Three different types of industrial sources are identified from three PMF studies, including industrial evaporation, mixed industrial and PETKİM operational factors. In addition to these, contribution of refinery to various factors, particularly gasoline and gasoline evaporation was observed, but the refinery did not stand out as a separate factor. These sources accounted for approximately 40% and 32% of ∑VOC mass at Aliağa and Horozgediği sites, respectively. However, it should be noted that, PMF was not able to separate gasoline evaporation from TÜPRAŞ and from other sources, a greater portion of this factor should be from TÜPRAŞ. Contribution of industries on VOC mass at Horozgediği is lower than expected, because gasoline evaporation is included among traffic related sources in this estimation.

Natural gas construction factor is a unique factor identified at Aliağa summer study. This factor represents emissions during the maintenance of natural gas lines near the Aliağa sampling station. Natural gas use factor is also another unique factor observed at Aliağa winter campaign. A similar profile is also expected to observe at Horozgediği site because PETKİM and TÜPRAŞ are the two major natural gas consumers in the area and their emissions are affecting Horozgediği sampling station. The PMF model was not able to identify this profile. Ethane and propane are the tracers of natural gas. Only propane is measured at Horozgediği station. Most of the propane variance is explained in the PETKİM operational process factor. PMF could not identify signature difference in between the other operational process in the PETKİM and the use of natural gas at PETKİM and TÜPRAŞ.

There are two non-industrial factors found at Aliağa summer and Horozgediği. Both of the sources explain 16% of the modeled VOC mass. Even though the compositions of the factors are different, both of the factors are as a result of anthropogenic urban activities around the sampling sites.

The applied PMF model is useful for identification of industrial sources. The PETKİM and TÜPRAŞ profiles obtained from the TÜPRAŞ station dataset are used for the characterization of the factors at Horozgediği station profiles. The PMF model also showed good performance for differentiating the sources affecting the VOC compositions at Aliağa and Horozgediği stations. The additional analyses of G-scores by CPF rose analyses and diurnal pattern analyses are important for the identifying the sources and their characteristics.

Unfortunately, major disappointing result of PMF analyses is that TÜPRAŞ emissions are not differentiated from other evaporative sources in the region.

CHAPTER 5

CONCLUSION

5.1. Conclusions

The main purpose of this study was to investigate concentrations and sources of ambient VOC levels at the Aliağa industrial region. Two monitoring stations were installed and operated in order to evaluate VOC contributions of industrial facilities to Aliağa atmosphere. One of the stations was located at downtown Aliağa and the other one was situated at 500 m southeast of the Horozgediği village, which is downwind of industrial facilities. VOC measurements were conducted using online GC-FID/PID systems. Samples were collected through two campaigns, one in summer and the other one in winter of 2005 and 2006. After summer campaign, online GC at Horozgediği station was transported to TÜPRAŞ station for 15 days of sampling.

This study is the most extensive study in terms of number of data points generated and number of stations for VOC determination in ambient atmosphere ever produced in Turkey. This unique dataset is useful for the determination of sources and for factors leading their diurnal and seasonal variation.

The key conclusions of the study in terms of the observed levels can be summarized in the following points:

- Among the common VOC species measured in all three stations, toluene has the highest concentration. m,p-Xylene and benzene are two other common higher concentrated compounds in the region.
- The only VOC that needed to be followed according to Air Quality Assessment and Management Regulation (AQAMR) is benzene with an annual limit of 5 μg m^{-3}. The benzene concentrations find in the Aliağa, Horozgediği and TÜPRAŞ stations are 1.3 μg m^{-3}, 0.76 μg m^{-3} and 4.5 μg m^{-3}, respectively. In all of the stations, the observed benzene concentrations are below the level defined in AQAMR.
- The concentration values obtained at TÜPRAŞ station are higher than the other two stations. This is expected because TÜPRAŞ station is located in between two major VOC sources, namely PETKİM and TÜPRAŞ.
- Traffic related VOCs are observed higher at Aliağa station whereas solvent and industrial process related VOCs are higher at Horozgediği station.
- The VOC levels of Horozgediği and Aliağa stations are found to be comparable with the literature. The VOCs which are as a result of incomplete combustion are the highest observed values for TÜPRAŞ station.
- The analyses of episodic events and diurnal variations at Horozgediği and Aliağa stations showed that PETKİM and TÜRPAŞ emissions do affect VOC concentrations measured in our two stations.
- The CPF roses also demonstrated that high VOC concentrations are observed at Horozgediği and Aliağa stations when the wind is blowing from TÜPRAŞ and PETKİM sectors.

- Source profiles of PETKİM and TÜPRAŞ are constructed by using data from TÜPRAŞ station. The markers for PETKİM emissions are found to be methylhexane, n-hexane, cyclo-hexane+ cyclo-hexene, benzene and 2,2,3-tri-methyl-butane+2,3-di-methyl-pentane. Although there is no unique VOC specie, which is a good tracer of TÜPRAŞ refinery, its profile is characterized by higher contributions of light VOCs.
- Positive matrix factorization was applied to summer data sets generated at Aliağa and Horozgediği stations and winter data set generated at the Aliağa station. Diesel exhaust and gasoline exhaust profiles are commonly observed sources in all PMF studies. Gasoline evaporation factors are observed at both Horozgediği and Aliağa winter campaign results.
- Though the profiles are different, for each source apportionment study, a different industrial factor was identified.
- Source profiles generated from TÜPRAŞ station and CPF plots are used to characterize the sources. With the use of generated source profiles, it is verified that industrial factor found at Horozgediği is due to emissions of PETKİM. CPF plots are useful for the identification and reasoning of the sources.
- The application of PMF to the data set generated at Horozgediği was particularly challenging to test (1) if the model can differentiate between two strong emissions sources that are approximately 10 km away and very closely spaced and (2) if the model can differentiate between sources that have very similar chemical signatures. Results showed that PMF model is able to separate two closely spaced sources if supplementary information is available, such as CPF distributions, or profiles of these two sources. However, the model could not differentiate different sources with very similar chemical signatures. The best example of this is observed in diesel exhaust factor at the Horozgediği PMF study. PMF isolated a typical diesel exhaust factor, which explained variances of most of the heavy VOCs. However, scores of this factor show a statistically significant increasing trend with increasing temperatures, which is probably due to mixing of diesel exhaust with diesel fuel evaporation in the same factor. A similar mixing was also observed in gasoline evaporation and gasoline exhaust factors, again in Horozgediği PMF exercise. This time gasoline evaporation and gasoline exhaust sources were separated from each other, but PMF was not able to differentiate contributions of TÜPRAŞ and non-TÜPRAŞ sources on these factors.

5.2. Future Recommendations

Following suggestions are provided for future research:

- This study showed that PETKİM and TÜPRAŞ are very important sources for Aliağa airshed. Therefore continuous measurement of VOCs together with other inorganic gases and PM at downtown Aliağa, TÜPRAŞ and PETKİM is essential for the region.
- This study was an extensive study in terms of number of VOCs included in the analyses. Less number of VOCs should be determined with higher averaging time (more than an hour) to understand the source and easily respond against it.
- Secondary organic particles (SOP) are the hot topic of the recent years. SOP are important as they generate health problems. Aliağa is an important source region for VOCs, PAHs and particles. The interactions of these pollutant groups are not clearly known. SOP sampling and analyses should be conducted in the region.
- In this study inadequacy of PMF under certain circumstances is demonstrated. In order to separate diesel exhaust and diesel fuel evaporation sources from each other, and to differentiate contributions of TÜPRAŞ and non-TÜPRAŞ sources on gasoline evaporation and gasoline exhaust, a CMB study can be recommended. In order to be able to use CMB approach source measurements should also be performed. Profiles generated for TÜPRAŞ and PETKİM proved very useful to separate their contributions

to ΣVOC levels, but other source profiles will also be needed for a potential CMB study. There is fair amount of source measurements performed by the Dokuz Eylül University. These measurements can be very helpful to establish all available source profiles.

- Researches on secondary pollutants generated from VOCs, PAHs and PCBs must be handled in the region. These could are important tracers of primary pollutants and their sources. The accumulation of secondary pollutants in the region must also be investigated.
- Halogenated VOCs cause major environmental problems. There are certain factories in the region which produces halogenated VOCs. In this study, FID and PID detectors were attached to GC systems. These detectors are not suitable for the characterization of wide range of halogenated VOCs. It is recommended to use a suitable GC system for the determination of halogenated VOCs in the region.
- In this study, the sampling was carried out for two campaign periods. Samples were collected on summer and winter seasons. However, there were no samples collected during spring and fall. There need to be at least one year continuous VOC measurement in the region in order to understand the effect of seasonal changes in the region.
- Throughout the study, industries were very helpful to us. However, since the sampling was done on campaign basis, the major aim was to collect samples without considering any change in the emissions from the industries. In order to quantify the effect of change of industrial emissions, there has to be coordination between the scientist and the industries in the region about the changes in the industrial emissions.
- The traffic count in the region was on yearly basis. Motor vehicles are important VOC source. Even though the VOC dataset generated in the region was on hourly basis, the results were not correlated with the traffic counts in the region. It is recommended to count motor vehicles using the nearby roads at least on hourly basis for a significant correlation analysis.
- Every year, new investments are made in the region. The effect of these investments on urban and rural atmosphere and biota are not clearly known. There has to be measurements on daily or weekly basis in the region for the characterization of effects of the new investments.

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CURRICULUM VITAE

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EDUCATION:

- Middle East Technical University, Ankara

PhD. in Environmental Engineering, January 2005 to present.

Thesis title: Apportionment of sources affecting concentrations of volatile organic compounds at Aliağa industrial area.

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Master of Science in Environmental Engineering, September 2002 to January 2005.

Thesis title: Comparison of the rural atmosphere aerosol compositions at different parts of Turkey

- Middle East Technical University, Ankara

Bachelor of Science in Environmental Engineering, September 1997 to July 2002.

Graduation Project: Investigation of effects of mono- and bi-modal distribution assumptions on dry deposition fluxes of trace elements to the Eastern Mediterranean

- Middle East Technical University, Ankara

Geographic Information Systems and Remote Sensing Minor Program, September 1999 to July 2002

EMPLOYMENT:

- Middle East Technical University, Ankara

Teaching Assistant, April 2004-....

- Carlton University, Ottawa, Ontario Canada

Visiting Researcher, March 2009-October 2009

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MEMBERSHIPS:

- Air and Waste Management Association, Member
- ODTÜ'lü Malatyalılar Derneği, Board Member
- Union of Chambers of Turkish Engineers and Architects, Chamber of Environmental Engineers, Member
- Middle East Technical University Alumni Association, Member

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SKILLS and INTERESTS:

- Knowledge of C Programming Language, SQL, MatLab.
- Working knowledge in MapInfo, S-Plus, Stat-graphics, Surfer, Lotus, ChemStation.
- Dancing- LA Salsa, Table Tennis, Football, Bağlama.

COOPERATIVE RESEARCH

- September 2011-March 2012 Source Apportionment Study of Speciated $PM_{2.5}$ and Volatile Organic Compound Measurements for Quesnel, British Columbia, Canada. Contractor-Güray Doğan
- March 2010-March 2013 Determination of Domestic and International Source Contributions to Upper Atmosphere Air Mass Compositions During Their Trip Over Turkey. Contractor-Prof. Dr. Gürdal Tuncel
- December 2010- June 2011 Determination of Ozone Levels Inside and Surrounding of a Washing Machine under Different Working Conditions.
  Contractor- Prof. Dr. Gürdal Tuncel
- March 2009- October 2009 Source Apportionment of PAHs at Ontario Sites Using Receptor Modeling Techniques. Contractor- Prof. Dr. Deniz Karman
- 2008-2011 Determination of compositional changes of air masses during their travel over Turkey and contributions of national and trans-boundary emissions to the air pollutants. Contractor- Prof. Dr. Gürdal Tuncel
- 2005-2008 Determination of levels of indoor and outdoor levels of volatile organic compounds, heavy metals and inorganic gases in different micro climates in Kocaeli. Contractor- Asst. Dr. Hakan Pekey
- 2005-2008 Determination of levels and health effects of organic and inorganic pollutants causing air pollution in Izmir Aliağa Industrial Site.
  Contractor- Prof. Dr. Gürdal Tuncel
- 2005-2007 Accreditation of Environmental Engineering Laboratories of Middle East Technical University according to TS ISO/IEC 17025:2005 General requirements for the competence of testing and calibration laboratories.

LIST OF PUBLICATIONS:

Full paper published in a peer reviewed journal covered by SCI, SSCI or AHCI core list

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Doğan, G. and Tuncel, G., 2003. Comparison of aerosol compositions at different parts of Turkey. 4th National Symposium on Combustion and Air Pollution Control, İzmir.

Kuloğlu, E., ***Doğan, G.*** and Tuncel, G., 2003. Investigation of effects of mono- and bi-modal distribution assumptions on dry deposition fluxes of trace elements to the eastern Mediterranean. 2nd National Symposium on Environmental Pollution Control, Ankara, 112.