TEMPORAL VARIATION OF VOLATILE ORGANIC COMPOUND CONCENTRATIONS IN BURSA ATMOSPHERE

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ABSTRACT

TEMPORAL VARIATION OF VOLATILE ORGANIC COMPOUND CONCENTRATIONS IN BURSA ATMOSPHERE

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Volatile organic compounds (VOC's) attracted attention as air pollutants due to their health effects, particularly with their potential to induce cancer. The levels and sources of VOCs in Bursa atmosphere, which is one of the most heavily industrialize cities in Turkey, were investigated by measuring C_2 – C_{12} VOCs in two campaigns. Concentrations of 148 VOCs were measured with 60 minute intervals using an on-line gas chromatograph. Data generated in this study is the first extensive and high-resolution data set generated in Turkey. VOC concentrations measured in this study are generally low compared to similar concentrations reported for cities with similar population with Bursa.

VOCs showed well defined short- and long-term temporal variations. The most pronounced short-term variation was diurnal pattern with a morning and afternoon maxima. In addition to diurnal variations, concentrations of VOCs also showed consistent weekend-weekday differences and differences between the two sampling campaigns.

One of the important outcomes of this study is the asphalt profile developed from the data generated. Volatile organic compounds, including 1-octene, 1-nonene, 1-undecene, n-nonane, n-decane, 1,2,3-trimethylbenzene, undecane and dodecane were shown to be good tracers for asphalting operations. Emissions from asphalt do not significantly affect concentrations of light hydrocarbons ($< C_5$).

Positive Matrix Factorization (PMF) applied to data yielded eight sources for both campaigns, including Light Duty-Vehicle (LDV), Vehicles operating with LPG, paint, gasoline evaporation, asphalting operations, industrial processes, solvent evaporation form small scale commercial activities and industrial solvent evaporation contributing to total VOC concentrations.

Key words: VOC, BTEX, PMF, Temporal variation, Source apportionment, Active sampling

ÖZ

BURSA ATMOSFERINDEKİ UÇUCU ORGANİK BİLEŞİK KONSANTRASYONLARININ ZAMANSAL DEĞİŞİMİ

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Uçucu organic bileşikler (UOBler) sağlık etkilerinden dolayı özelikle kansere yol açma potansiyellerinden ötürü hava kirleticileri arasında dikkat çekmektedirler. Türkiye'nin en ağır sanayileşmiş şehirlerinden biri olan Bursa atmosferindeki UOBlerin seviyeleri ve kaynakları, karbon sayıları iki ve oniki arasında değişen UOBlerin iki kampanya halinde ölçülmesiyle incelenmiştir. 148 UOB nin konsanstrasyonu 60 dakikalık aralıklarla on-line olarak gaz kromotragrafi ile ölçülmüştür. Bu çalışmada elde edilen veri seti Türkiye'de elde edilen en kapsamlı ve yüksek çözünürlüğe sahip ilk veri setidir. Bu çalışmada ölçülen UOB konsantrasyonları Bursa ile yakın nüfusa sahip şehirler için bildirilen benzer konsantrasyonlar ile karşılaştırıldığında genellikle düşük olarak bulunmuştur.

UOB konsantrasyonları gün içi, haftaiçi/haftasonu ve mevsimsel olarak belirgin değişimler göstermiştir. En belirgin kısa vadeli değişim, gün işerisinde sabah ve öğleden sonra maksimum değerlerin gözlendiği değişimlerdir. Gün içerisindeki değişimlere ilaveten, ölçülen OUB konsantrasyonları iki örnekleme dönemi ve hafta içi/hafta sonu arasında da belirgin farklar göstermiştir.

Elde edilen veri setiyle oluşturulan asfalt profili bu çalışmanın önemli sonuçlarından biridir. 1-okten,1-nonan, n-dekan, 1,2,3-trimetilbenzen, undekan ve dodekanı kapsayan uçucu organik bileşiklerin asfaltlama çalışmaları için iyi birer izleyici oldukları gösterilmiştir. Asfaltlamadan kaynaklanan emisyonlar hafif hidrokarbon konsantrasyonlarını (<C_5) belirgin derecede etkilememiştir.

Çalışmada her iki örnekleme döneminde elde edilen veri setine uygulanan Pozitif Matriks Faktörizasyonu (PMF) ile Hafif-Hizmet Taşıtı (HHT), LPGli taşıtlar, boya, benzin buharlaşması, asfaltlama, endüstriyel prosesler, küçük ölçekli işletmeler ve endüstri kaynaklı solvent buharlaşması olmak üzere sekiz adet kaynak elde edilmiştir.

Anahtar Kelimeler: UOB, BTEX, PMF, Zamansal değişim, Kaynaklar arasında dağılım, Aktif örnekleme

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LIST OF ABBREVIATIONS

ANOVA: Analysis of Variance

BDL: Below Detection Limit

BTEX: Benzene, Toluene, Ethylbenzene, and Xylene

CMB: Chemical Mass Balance

CO. Carbon Monoxide

EV: Explained Variation

FA: Factor Analysis

GC-FID: Gas Chromatography-Flame Ionization Detector

LDV: Light Duty Vehicle

LPG: Liquid Petroleum Gas

MH: Mixing Height

MIR: Maximum Incremental Reactivity

NAEI: UK National Atmospheric Emission Inventory

NMHC: Non-methane hydrocarbons

NOx: Nitrous oxide

PAN: Peroxyacyl Nitrates

PCA: Principle Component Analysis

PMF: Positive Matrix Factorization

QA/QC: Quality Assurance/Quality Control

T/B: Toluene to Benzene ratio

TEX: Toluene, Ethylbenzene, Xylene

US EPA: United Stated Environmental Protection Agency

VOC: Volatile Organic Compound

VC: Ventilation Coefficient

WD/WE: Weekdays to Weekend ratio

X/E: Xylene to Ethylbenzene ratio

CHAPTER 1

INTRODUCTION

1.1 Background Information

Volatile organic compounds (VOCs) are considered to be one of the most significant groups of air pollutants due to their toxic and carcinogenic effects on human health and vegetation (Khoder, 2007; Parra et. al, 2006). In addition to their adverse effects on humans, VOCs also contribute to the formation of secondary pollutants such as photochemical oxidants, smog and fine particles (Hoshi et al., 20008; Khoder, 2007). When NO_X emissions are present in the atmosphere, VOCs react with OH radicals, leading to the production of tropospheric ozone (Parra et al., 2006). Decreasing tropospheric ozone concentrations and controlling VOC concentrations are very important issues in air pollution problem world-wide (Yang et al., 2005). Towards this aim, VOC measurements in the ambient atmosphere are essential in big cities (Parra et al., 2006). Studies on the determination of VOC concentrations in urban atmospheres provide a valuable tool in the fight against smog and ozone problems (Khoder 2007).

Significant amounts of VOCs are emitted to atmosphere from different anthropogenic and natural sources. Traffic is the main source of organic compounds in the urban atmosphere. In addition to traffic, VOCs are also emitted from different industrial activities such as coating operations, solvent usage and industrial processes (Khoder 2007; Barletta 2005; Parra et al., 2006). Recently, VOCs have become an important topic because of their widespread usage for the different types of industrial activities (Bayil et al., 2008). Textile and automotive industry are at the top of the list because volatile organic solvents are commonly used in these sectors. Textile finishing, dyeing, drying, fabric printing processes, vehicle body painting processes and undertook activities are assumed as a significant sources of VOC emissions.

Bursa is the fourth largest city of Turkey with a population of about 2.5 million. Bursa, covering an area of 10,819 km^2, is located in the northwestern part of Anatolia. Bursa is an industrial city. There is approximately 8000 business working with textiles in Bursa. Cotton weaving, artificial and synthetic yarn production, woven fabric and home textile are leading sub sectors of Bursa textile industry. More than 75% of the yarn is produced in Bursa. In addition to textile industry, motor, motor parts, hydraulic and pneumatic components, rubber and rubber components motor oils and additives are major sub-industry products of Bursa. Bursa is the automotive center of Turkey. Globally well-known automotive manufacturers were located in Bursa and 60% of the automotive production of Turkey was performed in Bursa. The number of motor vehicles is about 500,000 in Bursa, (TSI, 2009). Therefore, this automobile traffic contributes to Bursa's already serious industrial air pollution problem. Although Bursa is the textile and automotive center of Turkey, there are few studies on levels and sources of organic pollutants in Bursa atmosphere. Civan (2010) was investigated the levels, sources and spatial distributions of VOCs in Bursa urban atmosphere. The cancer and non-cancer risks of the measured VOCs were also calculated in the study. A total of seven weekly passive sampling campaigns were performed across the Bursa city center from 2005 to 2007 and spatial distribution of the organic compounds was also examined. Factor Analysis (FA) was used for the identification of organic compounds and motor vehicle emissions (63%) and industrial solvent usage (20%) were found to be main VOC sources in Bursa atmosphere. Moreover, vehicle emissions and industrial activities were also identified as significant sources health risk related with VOC exposure.

1.2 Purpose of the Study

The purposes of this study are to determine;

- VOC concentrations,
- VOC temporal variations,
- The factors affecting VOC temporal variations,

- The sources of VOCs and the contribution of these sources on measured VOC concentrations in the Bursa atmosphere.

1.3 Scope of the Study

The scope of the study can be described under three general headings, namely measurements, quality assurance/control and interpretation of results. Details of the activities that were performed under these general headings are given below.

1) Measurements; throughout this study, two sampling campaigns were performed in Bursa and about 3400 chromatograms were generated as a result of these hourly measurements. After campaigns, integration of chromatograms was done and raw data set was generated.

2) Quality Assurance and Quality Control (QA/QC) of data set; since huge number of peaks were fitted in >3000 chromatograms, there is always a possibility of errors during the integration process. Therefore, a QA/QC procedure was applied to raw data set to detect erroneous results. After QA/QC process, generated data set was used for the further statistical processes.

3) Interpretation of the produced data set; to understand level of VOCs pollution, obtained values were compared with the literature. Furthermore, effect of the different meteorological parameters on measured VOC concentrations and temporal variation of the data set were investigated. By using Positive Matrix Factorization (PMF), sources of the VOCs were determined and their contributions to the VOC pollution in Bursa atmosphere were identified.

1.4 Layout of the Study

VOC pollution in big cities has gained much importance due to adverse health effects and contributions to the formation of tropospheric ozone. Tropospheric ozone chemistry, sources of VOCs, applied sampling methods and studies by performed by other researchers focusing on VOCs are given in Chapter 2. The sampling location, applied methodology for the collection of samples, Quality Assurance (QA) and Quality Control (QC) procedures applied during sampling, analysis of samples and data processing are explained in Chapter 3. Interpretation of the findings, which includes the effect of the meteorology on measured VOC concentrations, statistical descriptive results and temporal variation of the measured VOC concentrations, inter correlations between measured organic compounds, ozone formation potentials of the measured VOCs in Bursa atmosphere and comparison of the results with literature are given in Chapter 4. Receptor modeling results from PMF model is presented in Chapter 5. Chapter 6 concludes all the results which were obtained at the end of this study.

CHAPTER 2

THEORETICAL BACKGROUND

As non-methane hydrocarbons (NMHCs) (VOCs) modulate the concentration of OH radicals in the atmosphere, they are assumed to be one of the important components of tropospheric chemistry. VOCs control most of the reactions which are observed in troposphere (Jacob, 1991). VOCs react with nitrogen oxides (NO_x), ozone (O_3), peroxyacyl nitrates (PAN), carbon monoxide (CO) and secondary aerosols produced as decomposition products from non-methane hydrocarbons (NMHCs) (Field et al, 1992). Moreover, many of these decomposition products or byproducts are considered health hazards (Jacob, 1991; Field et al, 1992).

2.1 Tropospheric Ozone Formation

VOCs in the atmosphere are removed by different physical processes (wet and dry deposition). In addition to these removal processes, as VOCs take part in chemical photolysis reactions with hydroxyl (OH), nitrate (NO_3) radicals and O_3, they also transformed into various decomposition products (Atkinson, 2000).

A general scheme of VOC transformation/formation reactions of the troposphere is shown in Figure 2-1.

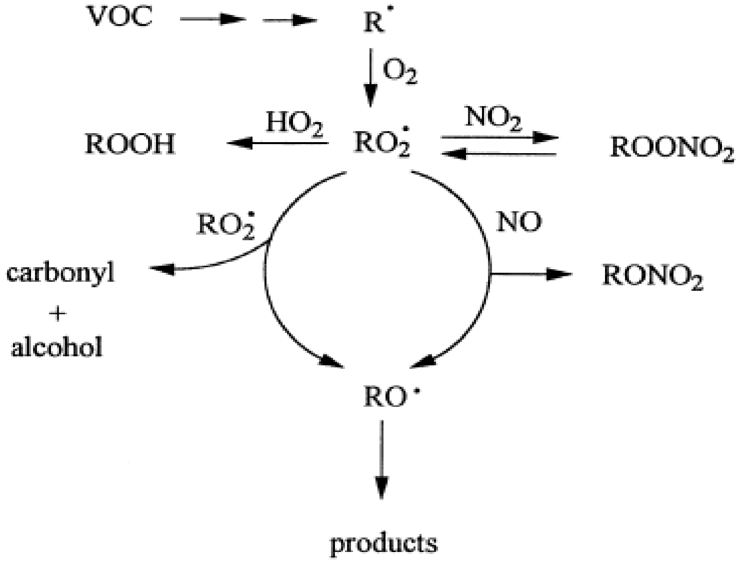


Figure 2-1 The transformation/formation reactions of VOCs in troposphere (Atkinson, 2000)

In these transformation/formation reactions, substituted alkyl radicals (R^*), alkyl peroxy/substituted alkyl peroxy (RO_2^*) or alxoy/substituted alxoy radicals are formed from alkanes, alkenes and other VOCs.

Tropospheric ozone considered a health hazard to both humans and animals due to adverse effects on lung and eyes. Ozone is one of the greenhouse gasses and it also damages trees, crops and other plants. Furthermore, ozone is the source of the OH radicals in troposphere (Reynolds, 1993).

In clean air, ozone is produced as a result of the photolysis of NO_2 (Figure 2-2a);

$$NO_2 + hv \rightarrow O + NO \qquad [1]$$

$$O + O_2 \rightarrow MO_3 + M \qquad [2]$$

However, addition of pollutants such as methane, VOCs and CO into the atmosphere will increase ozone concentrations in a complex and usually non-linear way (Reynolds, 1993). The most common route for the formation of ozone is the production of the hydroperoxies (HO_2) and methyl peroxies (RO_2), which occurs as follow;

$$OH + CO \rightarrow CO_2 + H \qquad [3]$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad [4]$$

$$HO_2 + O \rightarrow 2OH + 2O_2$$

$$\text{Net: } CO_2 + O_3 \rightarrow CO_2 + O_2$$

Alkyl peroxy (RO_2) and peroxy radicals, which are produced from other VOCs, act like methyl peroxy radicals. All of these radicals can react with NO to form NO_2 which produces ozone (Reynolds, 1993) (Figure 2-2b).

$$HO_2 + NO \rightarrow NO_2 + OH \qquad [5]$$

$$RO_2^* + NO \rightarrow RO + NO_2 \qquad [6]$$

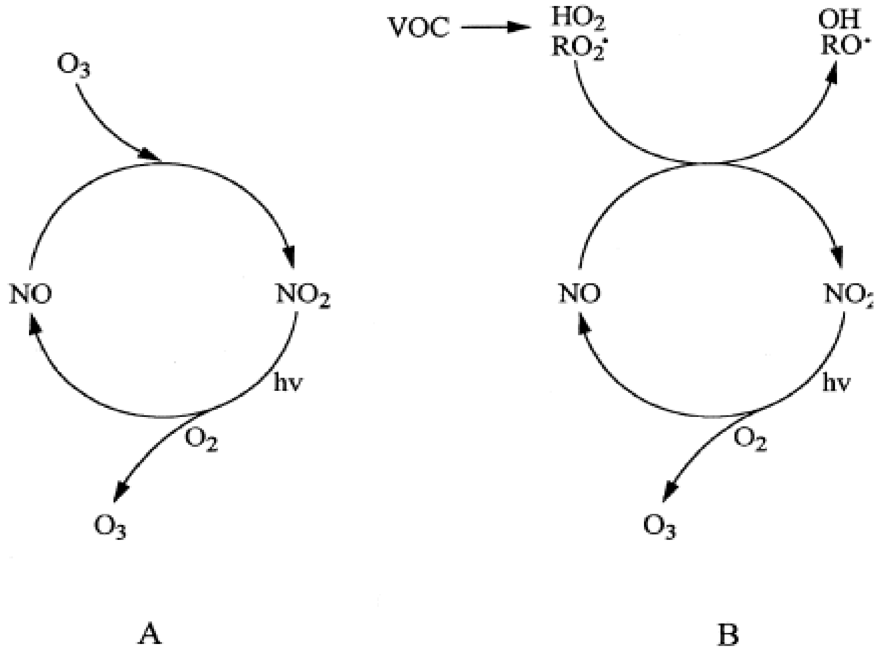


Figure 2-2 NO to NO_2 formation and ozone formation (Atkinson, 2000)

Therefore, there is a balance between photochemical ozone production and ozone depletion based on the HO_x and NO_x concentrations. In Figure 2-3, this relation can be clearly seen.

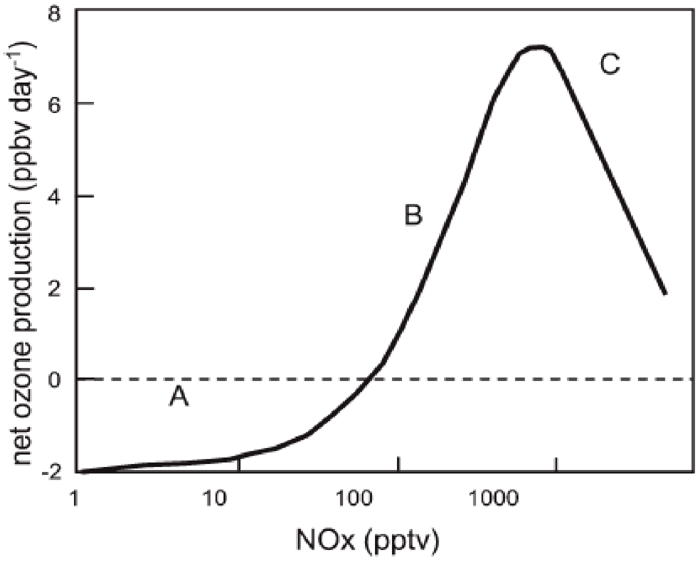


Figure 2-3 Relation of net ozone production/destruction based on the NO_x (Monks, 2005)

With participation of the VOCs in these chemical reactions, Figure 2-3 will transform into an isopleth where the axis represents VOC concentrations. The ozone isopleth diagram demonstrates that ozone formation is a non-linear function of NO_x and VOC concentrations (Figure 2-4). On the contrary, the relationship between NO_x, ozone and VOCs presents a challenge in that to reduce ozone concentrations, reduction in VOC concentrations is only operational under VOC-sensitive chemistry (High NO_x) and reduction NO_x concentrations is operational only under NO_x-sensitive chemistry (Monks, 2005).

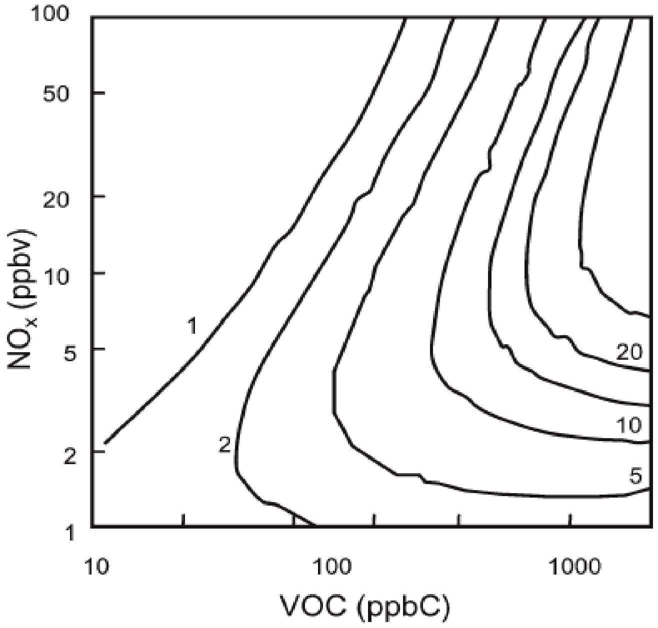


Figure 2-4 Ozone isopleth diagram for mean summer daytime meteorology, clear sky under urban conditions (Monks, 2005)

2.2 Sources of the VOCs in the Atmosphere

Fuel wood combustion and savanna burning are the biggest sources of the VOCs in atmosphere, followed by production and use of gasoline (traffic), refuse disposal and rubber manufacturing (Reynolds, 1993).

Many studies have been performed with the aim of identifying the ambient VOCs in different cities (Chang et al., 2005; Kerbachi et al., 2006; Parra et al., 2006; Brown et al., 2007; Guo et al., 2007; Hoque et alo., 2008; Parra et al., 2009). According to these studies, vehicle exhaust, gasoline evaporation, residential heating, biomass combustion, industrial emissions, solvent usage, dry cleaning and asphalting operations were found to be major sources of the ambient VOCs in cities.

Gue et al. (2007) examined the VOCs in Hong Kong ambient air and found that traffic emissions have a great contribution on the NMHVOC load of the urban (about 65%) and suburban (about 50%) atmospheres. Guo et al. also identified that other anthropogenic sources (petrol evaporation, industrial evaporations and solvent usage) had great contributions on the NMHVOC load of the urban and suburban atmospheres. On the other hand, combustion sources (vehicle and/or biomass combustion) were found to be responsible for half of the NMHVOCs in rural atmosphere (Guo et al., 2007). Chang et al. (2005) studied the ambient levels of VOCs in Kaohsiung in Taiwan. Chang et al. showed that vehicle exhaust and industrial emissions were major sources of ambient VOCs in Kaohsiung. 33% of the NMHVOCs were emitted from vehicles in Taiwan. In this study, the main sources of atmospheric butane and propane were also identified to be vehicle exhaust and LPG emissions (Chang et al., 2005). In Seoul, vehicle emissions (34.5%) and paint solvent emissions (46.2%) were found to be major sources of the ambient VOCs. In addition to these sources, gasoline evaporation (6%), printing solvents (3.3%), dry cleaning (2.1%) and asphalt paving (3.3%) were also identified (Na et al., 2004). Vehicles are also major source of the aromatic hydrocarbons in the urban area of Rome, Italy (Brocco et al., 1997). The contribution of traffic-related sources (evaporative, exhaust, unburned gasoline) was found to be 80% and 71% at Azusa and Hawthorne in Los Angles, USA, respectively. In addition to the mobile sources, industrial emissions, biogenic emissions and coating operations were also identified as ambient sources of VOCs (Brown et al., 2007). On the contrary, in South Korea, solvent sources constituted the major portion of NMHCs both in suburban and urban atmospheres. The contribution of the solvent sources to the total anthropogenic NMVOC emissions was given as 58.35%, followed by industrial processes (17.3%), transport (15.3%), waste (4.4%), fugitive emissions from fuel (3.3%), and stationary combustion (1.4%) (Choi et al., 2011). Consequently, VOC sources vary depending on sampling location, culture, traffic, economic level of the country, and meteorological parameters.

Accordingly, most studies in the literature have indicated that traffic-related emissions are major sources for VOCs in urban atmosphere (Martinez et al., 2000; Guo et al., 2007, Fernandes et al., 2002, Kelessis et al., 2006; Liu et al., 2008). 2-methylpentane and 1,3-butadiene are two of the tracers of vehicle exhaust (Liu et al., 2008). In urban areas, benzene, toluene, ethylbenzene, and xylene (BTEX) account for nearly 60% of NMHVOCs; therefore BTEX are also suitable tracers for traffic

(Lee et al., 2002; Mohamed et al., 2002). Moreover, Fernandes et al. (2002) also showed that traffic was major source for BTEX in urban atmosphere in Rio de Janeiro, Brazil. It has been also reported that near dense traffic, 75-85% of the benzene comes from traffic (Kerbachi et al., 2006). In addition to the traffic, BTEX, especially m,p-xylene and toluene, are also characteristic indicators of coating operations. Refineries are other important sources of benzene and n-aliphatics in the atmosphere (Martinez et al., 2000). Chlorinated compounds are mainly from industries, cleaning processes and chemical solvents (Lee et al., 2002). Heavy hydrocarbons, namely decane, dodocane and undacene, are mainly emitted from asphalting operations and diesel vehicles (Liu et al., 2008). Gasoline evaporation was identified as a source of C4-C7 alkanes and alkenes and aromatics, namely isobutene, n-butane, trans-2-butene, n-pentane, benzene and toluene. C2-C8 VOCs, namely ethylene, ethane, propylene, propane, acetylene, benzene and toluene are indicators of biomass and coal burning (Barrefors et al., 1995, Schauer et al., 2001). Propane and ethane are mainly originated from LPG, natural gas leakages, stationary combustion and vehicle exhaust (Na et al., 2004). C4-C5 alkanes and alkenes and aromatic hydrocarbons are possible tracers of solvent usage and industrial emissions in atmosphere. Heavy background aromatics indicate that the contribution of industrial emissions (Borbon et al., 2002). 1,3-butadiene and styrene were also found to be related with industrial emissions in different cities of the USA (Mohamed et al., 2002)

In addition to anthropogenic sources, biogenic sources are also important sources of VOCs in the atmosphere. Isoprene, terpenes and other molecules are emitted in large amounts by plants, mainly coniferous trees (Reynolds, 1993).

2.3 The Overview of the Temporal Variation of VOCs

Various factors affect the ambient concentrations of organic compounds in winter and in summer. For example, more rainy days in summer decreases the concentrations of organics relative to dry winter days. OH radicals are much more effective at removal of VOCs by chemical reaction during the summer season.

Indeed, higher temperatures and more sunlight will speed most chemical reactions. Accordingly, measured VOC concentrations in atmosphere are higher in winter than in the summer (Lee et al., 2002). Seasonal variations of organic compounds, with a maximum in winter and minimum in summer, have been reported in many studies (Brocco et al., 1997; Sharma et al., 2000; Fernandes et al., 2002; Lee et al., 2002; Mohamed et al., 2002; Ho et al., 2004; Chang et al., 2005; Na et al., 2005; Hoque et al., 2006; Kerbachi et al., 2006; Guo et al., 2007).

Sharma et al. (2000) investigated the seasonal variation of the C2-C6 saturated and unsaturated NHMCs in Happo/Japan. They observed a clear seasonal variation with minimum in summer for measured C2-C5 alkanes, n-hexane and acetylene. Clear seasonal variation of compounds with longer atmospheric lifetimes such as ethane, propane and acetylene was also observed in other studies (Goldstein et al., 1995; Klemp et al., 1997; Morikawa et al., 1997). Seasonal abundance of OH radicals and anthropogenic sources influence the observed seasonal variation. Furthermore, higher NMHC concentrations are observed at higher altitudes than at lower altitudes owing to low OH accessibility in higher altitudes (Sharma et al., 2000).

A seasonal variation of measured ambient hydrocarbons was also observed in different cities in the USA (Mohamed et al., 2002; Qin et al., 2007). Higher mean and median concentrations were observed at 12 to 13 sampling stations in winter and fall seasons than in the summer. However, ambient concentrations of halogenated hydrocarbons were not affected by season (Mohamed et al., 2002).

In Delhi, BTEX compounds also show a clear seasonal variation. Seasonal variation of the main meteorological conditions and source strength, accessibility of the OH radicals and strength of the insulation were used to explain the observed seasonal variation (Hoque et al., 2008).

In Hong Kong, higher VOC concentrations in winter than in summer were also explained by variation of the prevailing meteorological conditions and source strength (Lee et al., 2002; Ho et al., 2004; Guo et al., 2007). The results of VOC measurements in Shanghai, China also showed that the seasonal variations of atmospheric VOCs were mainly affected by meteorological conditions, including wind direction and precipitation (Cai et al., 2010).

Reduced emissions and meteorological conditions (increase in deposition/dispersion and chemical removal) have been shown to be a cause of low BTEX concentrations in Rio de Janeiro, Brazil during summer (Fernandes et al., 2002).

In Algiers, BTEX concentrations were 10% higher in winter than in summer; higher reactivities of VOCs with OH radicals during summer were assumed as a possible reason for this difference (Kerbachi et al., 2006).

Due to stagnant air conditions, higher aromatic hydrocarbon concentrations were also measured both in Rome, Italy and Thessaloniki, Greece in winter (Brocco et al., 1997; Kelessis et al., 2006).

On the contrary, different seasonal patterns have been detected in some cities depending on the location, meteorological and topographical properties of the sampling point and proximity of the sampling point to industrial sources. For example, at PolyU campus near a road in Hong Kong, concentrations of most organics such as xylenes, 1,3,5,-trimethylbenzene and methylene chloride were found higher in summer than in winter (Ho et al., 2004). A similar situation was also observed in Izmir (Elbir et al., 2007). Evaporative sources such as solvent usage, gasoline evaporation and gasoline spills are assumed to be the reasons of the weak seasonal variation (Ho et al., 2004; Na et al., 2005).

Several studies also showed that VOC concentrations are higher on weekdays than those on weekends, indicating that human activities have an important effect on VOC concentrations (Martinez et al., 2001; Cai et al., 2010). VOC concentrations also show variation through the day. The diurnal cycles of alkanes, alkenes and aromatics have a double peak pattern on weekdays, directly related with traffic rush hours (Cai et al., 2010). The two peaks are usually observed at 9:00am and between 15:00-20:00

pm during the morning and afternoon rush hours (Morikawa et al., 1997; Christensen et al., 1999; Barletta et al., 2002; Borbon et al., 2002; Ho et al., 2004; Lai et al., 2004; Kelessis et al., 2006; Cai et al., 2010; Li and Wang, 2012; Olumayede and Okuo, 2012). This situation can be explained by higher VOC emissions due to higher traffic density during the morning and afternoon, and dilution by increase of the assimilation capacity of the atmosphere; in other words, an increase of the mixing depth and photochemical activity during the noon time (Brocco et al., 1997; Na et al., 2003; Lai et al., 2004; Kelessis et al., 2006). Therefore, the two peak patterns in the diurnal variation of BTX indicate that the major sources of these organics are traffic emissions (Li and Wang, 2012). Furthermore, similar diurnal variations in BTEX concentrations related with traffic activity have also been observed in previous studies (Ho et al., 2004; Velasco et al., 2007; Li and Wang, 2012; Olumayede and Okuo, 2012).

However, on weekends, no clear double peak pattern is present, reflective of the change in the traffic pattern during the weekends. The two peak patterns in the diurnal variation of BTEX indicate that the major sources of these organics are traffic emissions (Li and Wang, 2012). Furthermore, similar diurnal variations in BTEX concentrations related with traffic activity were also observed in literature (Ho et al., 2004; Velasco et al., 2007; Li and Wang, 2012; Olumayede and Okuo, 2012). High concentrations of BTEX during the night time can be explained by calm atmospheric conditions and absence of photochemical activities (Tiwari et al., 2010).

2.4 Effects of VOCs

2.4.1 Health Effects

Based on the literature, some VOCs have some carcinogenic and non-carcinogenic effects at varying levels of exposure in humans and animals (Kolachana et al., 1993; Smith, 1996; Yin et al., 1996; Smith et al., 2011; Yang et al., 2012). For example, benzene has been accepted as a leukemogen for acute myeloid leukemia in adults. It has also found to be related with other disease subtypes such as chronic lymhocytic leukemia and childhood leukemia. Even at very low environmental benzene concentrations, increased leukemia risk has been identified (Vincenti et al., 2012). Moreover, VOCs have also some impacts on respiratory, digestive and central nervous system (Ayers et al., 2002). According to EPA reports, VOCs cause 35-55% of outdoor air cancer risk in USA. If VOC-containing mixtures are taken into account, the 79-81% of the cancer cases will be related with ambient VOCs in USA (EPA, 1990).

As stated in EPA reports, the major compounds responsible for cancer cases are the products of incomplete combustion, 1,3-butadiene and hexavalent chromium, in decreasing order of importance. Other major compounds are benzene, formaldehyde and chloroform (EPA, 1990).

2.4.2 Environmental Effects

The one of the important side effects of the presence of VOCs is the formation of the ground-level ozone which has negative side effects on both human health and plants such as the decreased ability of the plants to produce and store their food, making them more sensitive to illness, insects and other pollutants (Ayers et al., 2002).

The relative importance of each VOC on the formation of ozone is governed by its tendency to form radical species and by production of maximum amount of ozone by its reaction. These two consequences are due to reactions with other substances (Ayers et al., 2002). Therefore, ozone formation potential of each VOC is governed by its concentration and its reactivity (Qin et al., 2007).

Several methods are used to calculate the contribution of the each chemical compound to production of ozone (Na et al., 2003). The propylene equivalent method and the MIR method are commonly used in order to estimate the contributions of numerous VOCs in photochemical ozone formation (Na et al., 2003; Chang et al., 2005; Wu et al., 2006; Cai et al., 2010; Tiwari et al., 2010). The following equation is used to calculate propylene equivalent concentration;

$$\text{Propy-equiv}(i)=\text{conc}(i)\text{x}k_{OH}(i)/k_{OH}(C_3H_6) \qquad [7]$$

where Propy-equiv(i) is defined as a VOC compound i on an OH reactivity-based scale; conc(i) is the concentration of a VOC compound i; kOH(i) is the rate constant for the reactivity of VOC compound i with OH radical; and kOH(C_3H_6) is the rate constant for the reaction of propylene with OH radical (Cai et al., 2010). Therefore, the equivalent to propylene gives an upper limit of possible ozone formation (Na et al., 2003).

The ranking of VOCs according to their ozone formation potentials can be done by using Carter´s maximum incremental reactivity (MIR). MIR is the amount of ozone formed (in grams) per gram of VOC added to an initial VOC-NO_x mixture. It also shows the amount contributed to photochemical ozone formation in an air mass by each VOC (Carter 1994; Chang et al., 2005; Tiwari et al., 2010). These unitless MIR values are useful in an area which has high nitrogen oxide concentrations (Chang et al., 2005; Tiwari et al., 2010). The reactivity of each VOCs to its ozone formation potential is calculated by multiplication of its concentration by its MIR values (Wu et al., 2006).

The following equation is used to calculate ozone formation potential of each compound by using MIR method:

$$\text{OFP}(i)=\text{conc}(i)\text{x}\text{MIR}_{\text{value}}(i) \qquad [8]$$

Where OFP(i) is defined as the ozone formation potential of individual VOC i, MIRvalue (i) the maximum incremental reactivity coefficient of compound i, which is defined by Carter (Cai et al., 2010).

VOCs may also affect human health and environment through formation of particulates; VOC can account nearly 50% of the total fine particle (PM 2.5) mass in the atmosphere. Fine particles can penetrate into the lungs. Moreover, fine particles are more likely to be produced from toxic pollutants. Therefore, they have important health risk. Premature deaths and asthma are accepted as possible side effects of the exposure to particulate pollution. Furthermore, decrease in the visibility and growth and productivity of the plants have also been observed due increased particulate pollution.

2.5 Source Apportionment

To identify sources of VOCs in ambient air, different multi-receptor models are applied to data sets; Chemical Mass Balance (CMB), Factor Analysis (FA), Unmix and Positive Matrix Factorization (PMF) are some of the models used for the determination of sources. In the present study, PMF model was applied to a data set to identify sources of ambient VOCs in the atmosphere of Bursa. This technique is commonly used for the identification of ambient sources of VOCs (Brown et al., 2007; Song et al., 2007; Song et al., 2008; Ethirajan and Mohan, 2012; Dumanoglu et al., 2014).

2.5.1 Positive Matrix Factorization (PMF)

PMF is a least squares approach for solving factor analysis problems that determines the number of sources, contributions of the compounds and chemical composition of the sources without any source profile information (Paatero et al., 2002; Song et al., 2008). This tool has been implemented various data set in the literature, namely PM 2.5 data, aerosol data, deposition data, air toxic data and VOC data (Brown et al., 2007).

The solutions of PMF are dissimilar from solutions which are created by the customary factor analysis. Commonly, PMF creates a better fit to the data than FA. Besides, PMF eliminates all negative entries. For environmental data, error estimates of the data may change, though non-negativity is usually assumed as a main property of the models. Therefore, it is assumed that PMF is better model than the FA for most environmental studies (Paatero and Tapper, 1994).

PMF accepts a data set as an ixj data matrix X with i number of observations and j constituents of species. According to the model, the measured concentrations of specific samples were calculated as below,

$$X_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \qquad [1]$$

Where g is the amount of mass measured at each source, f is the profiles of the species from the each source, p is the number of sources and e is the residuals belonging the species (Xie and Berkowitz, 2006). The objective of PMF is to minimize the sum of the squares of the residuals weighted inversely with error estimates of the data points. Moreover, the model limits the g and f matrices. According to the model, sources cannot have negative species concentrations (fkj>0) and the sample cannot have negative source contribution (gik>0) (Paatero and Tapper, 1994). Consequently, it can be said that the objective of the model is to minimize the object function Q, given as

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{X_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right]^2 \qquad [2]$$

Where u_{ij} is the error estimate for xij. The solution of Eq. (2) continues until convergence. Determination of the factor numbers is one of the most important steps of PMF analysis because selecting too few factors can cause badly distinguished sources, while numerous factors can split up a real source into several unreal sources (Dikaia et al., 2009).

In PMF analysis, the main objective is to supply good correlation between modeled and real data. It is supposed to supply good correlation; correct estimation values of the errors should be used. If correct estimated values are used, the theoretical Q value is supposed to be about equal to the number of samples in the data set. Nevertheless, generally there are no consistent error estimates. Therefore, to handle both outliers and unreasonable error estimates, scales residues (eij/uij) are usually examined. For a well modeled data set, scaled residuals should be varying between +2 and –2 (Chueinta et al., 2000; Liu et al., 2003; Saraga et al., 2009).

PMF has been applied widely in the literature for identification of sources of ambient VOCs (Polissar et al., 2001; Kim et al., 2003; Yang et al., 2006; Brown et al., 2007). For example, Brown et al. (2007) applied PMF and CMB model to estimate sources of ambient VOCs at two sites in the Los Angeles air basin, Azusa and Hawthorne. In this study, five and six sources were obtained at Azusa and Hawthorne, respectively. At Azusa, evaporative emissions (31%), vehicle exhaust (22%), unburned/liquid gasoline (27%), coating (17%) and biogenic emissions (3%) were identified as ambient sources of VOCs. At Hawthorne, evaporative (34%), vehicle exhaust (24%), industrial emissions (15), natural gas (13%), liquid/unburned gasoline (13%) and biogenic emissions (1%) were identified as major sources. Elbir et al. (2007) assessed the urban and suburban sources of ambient VOCs in Izmir. To determine ambient sources of VOCs, PMF was applied and six (gasoline vehicle emissions, diesel vehicle emissions+residential heating, degreasing, dry cleaning and unidentified source) and three source (gasoline emissions, diesel emissions and paint emissions) factors were identified for the urban and suburban sites respectively. Song et al. (2008) applied PMF, UNMIX and CMB models for source apportionment of volatile organic compounds in Beijing. They estimated eight sources (gasoline exhaust (39.7%), liquid/evaporated gasoline (11.8%), LPG (11%), natural gas (4.6), petrochemical (19.9%), biogenic (1.6), painting (4.7%), diesel exhaust (3.2%)) when they applied PMF model to ambient sources of measured VOCs in Beijing. Xie and Berkowitz (2006) applied PMF to hourly average concentrations of VOCs in Texas. As a result, six to eight source categories were obtained in five sites in Texas.

CHAPTER 3

MATERIAL AND METHODS

Ambient concentrations of C2-C12 VOCs including aromatics, olefins, paraffins and halogenated compounds were measured hourly in the atmosphere of Bursa. For this purpose, an urban air sampling system was placed into Bursa Hygiene Center and hourly measurements were performed in two campaigns, generating about 3400 chromatograms. The first campaign was performed between September 14 and November 6, 2005 and the second campaign was performed between March 17 and May 10, 2006.

3.1 Sampling Site

An online GC-FID system was placed at the Bursa Hygiene Center (40.19^{o}N, 29.05^{o}E), which is located at the city center of the Bursa, and on-site measurements were performed. The nearest main avenue, which carries heavy traffic load of the city center, is approximately 1 km away from the station and the avenue lies in the north of the sampling station. The distance of the station to Ankara and Yalova highways, which are very busy roads joining downtown Bursa to its neighbor cities, is approximately 2 km. Other roads with heavy traffic are further away from the sampling location. The location of the sampling station is given in Figure 3-1.

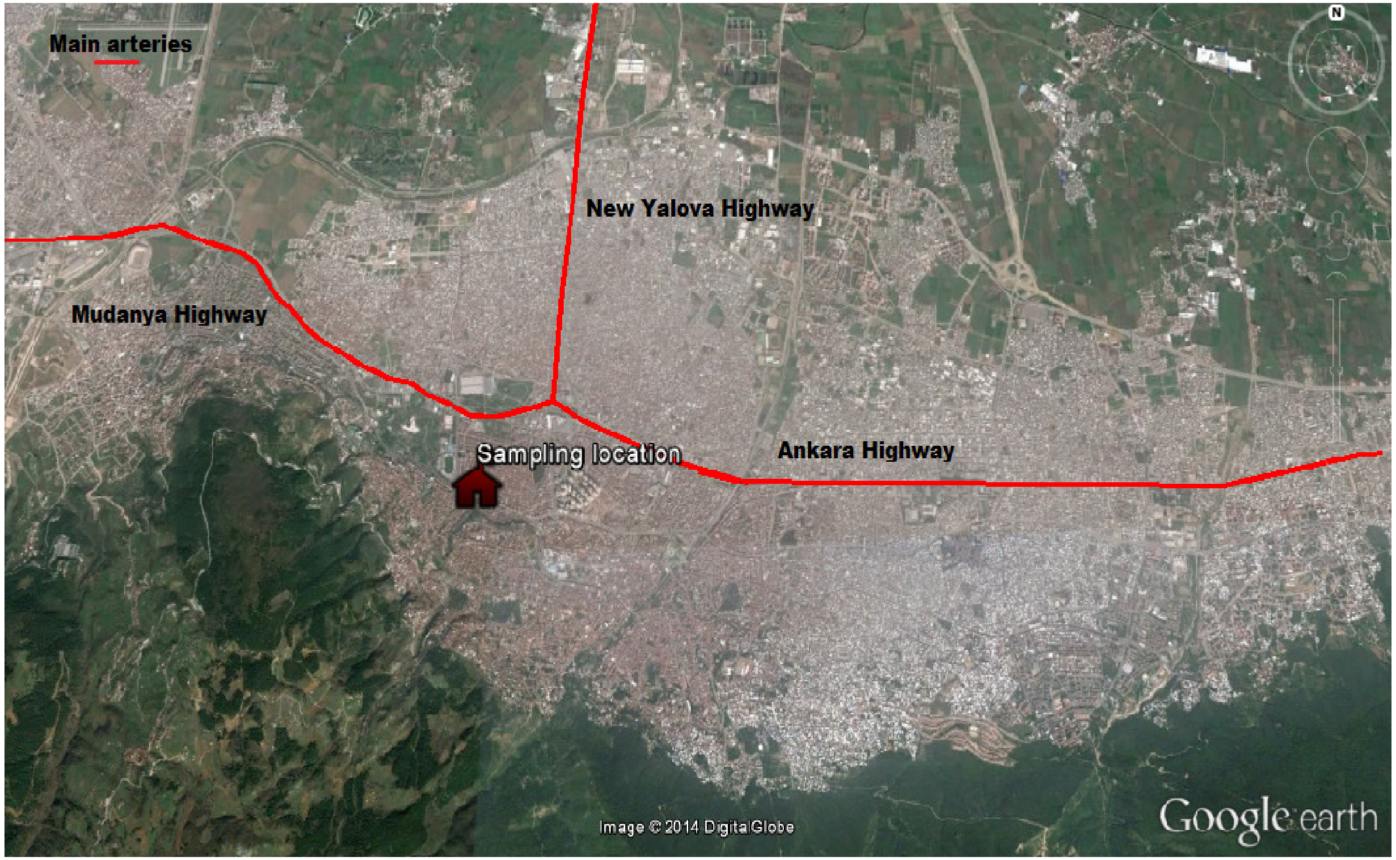


Figure -3-1 Location of the sampling point

3.2 Sampling Campaigns

Two sampling campaigns were performed during the study. Ambient air samples were collected on hourly basis. The first campaign, which is named as Fall campaign, was carried out between September 14 and November 6, 2005, and the second campaign, which is named as Spring campaign, was performed between March 17 and May 10 2006. 841 and 854 samples were collected during the first and second sampling campaigns, respectively during the study. Therefore, a total of 1695 samples (3390 chromatograms) were generated during these two campaigns.

3.3 Sampling Methodology

The VOCs were measured *in situ* using an online GC system. Measurements were hourly and each measurement cycle consisted of 45 minutes of sampling. The on-line measurement system consisted of an Agilent Model 6890 gas chromatograph equipped with 2 flame ionization detectors (FID) coupled to a Unity model thermal desorption and a Markes Air Server sampling system. The GC was obtained from Hewlett-Packard (Agilent Technologies Inc, Palo Alto, CA, USA). Thermal desorption system and air server sampling system were obtained from Markes International Limited, CF72 8XL, United Kingdom. Sample was collected directly on the cold trap through Air Server sampling system for 45 minutes. At the end of the collection period, cold trap was rapidly heated and trapped VOCs were transferred to the GC column. Once the trap finished it's desorption, it was cooled down, re-equilibrated to its temperature and began to collect a new sample while analysis of the prior sample was continuing.

3.4 Sample Analysis

GC-FID analyses were performed by Agilent Model 6890 GC equipped with 2 flame ionization detectors (FID) including a Deans Switch device and coupled to a Unity model thermal desorption and a Markes Air Server sampling system. Thermal desorption provides a higher sensitivity than chemical desorptionmethod and minimizes artifacts, losses and carry-over effects. A modified version of US EPA TO-17 method was used for the analysis.

Hourly measurements were performed. For each measurement, 450 ml sample was pulled directly from the air over 45 min onto a multilayer sorbent packed (12 cm x 2 mm i.d.) “Ozone Precursor/ Freons” trap at a 10 ml/min flow rate. Sample volume was electronically controlled by a mass flow controller (MFC). A Peltier electrical cold element was used to cool the trap to -15 ^{o}C. After samples were collected on the trap, the trap was rapidly heated at rates approaching 100 ^{o}C/sec from -15 ^{o}C to 300 ^{o}C and samples were sent to the inlet of GC equipped with Deans switch device for analysis. Once the trap finished it’s desorption, it was allowed to cool and re-equilibrate and then began to collect a new sample while analysis of the prior sample was continuing. Dean Switch system is used to obtain better resolution of the peaks with two different types of column. The GC/FID system had two columns. The analytical columns were obtained from J&W Scientific (Palo Alto, CA, USA). DB-1 (% 100 dimethylpolysiloxane, 122-1063 model) capillary column appropriate for hydrocarbons and HP-Al/S (HP-PLOT/Al_2O_3, sodium sulfate-deactivated, 19091P-S15 model) alumina PLOT column excellent use with light hydrocarbons (C1 to C8) and two FID detectors. Alumina PLOT columns do not require the cooling of the oven and they can enable to low GC start up temperatures; by this way dual column analysis can be performed in particular one GC oven (Latella et al, 2005). In the present study, light compounds (molecular weight smaller that of hexane) were held on an Alumina Plot capillary column and heavier compounds (molecular weights are higher than hexane) were held on a DB1 capillary column with the help of Dean Switch system.

Nitrogen was used as a carrier gas for the GC system. Dry air and hydrogen were used for the igation of flame. The purity of all gases was above 99.999% and high purity these gases were obtained from MITAN (MITAN A.Ş., Ankara, Turkey). Hydrocarbon and oxygen traps were also used for the supply of the gases to the system.

3.4.1. Optimization of GC/ FID System Parameters

For the optimization of the thermal desorption system, different parameters were examined based on the recommended operational values by the producer. The maximum operating temperature for the cold trap was 400 °C and typical desorption temperature range was 300-320 °C. The effect of the cold trap temperature on the recovery of the compounds on the trap was also investigated and optimum temperature was identified for the target compounds. -15 to -10 °C was mostly used for the quantification of ultra-volatile compounds such as ethene and acetylene. Therefore, the lowest temperature supplied the highest compound recovery. In Figure 3-2, the0 effect of desorption temperature on the recovery of the selected target compounds is given.

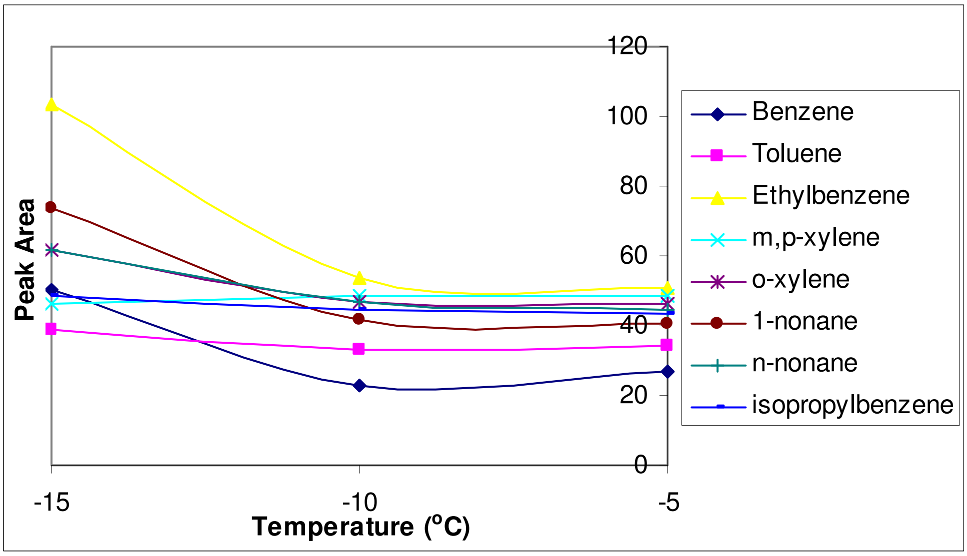


Figure 3-2 Effect of the cold trap temperature on the recovery of the selected target compounds

In addition to the effect of temperature, desorption time of the cold trap was also investigated for the selected target compounds (Figure 3-3).

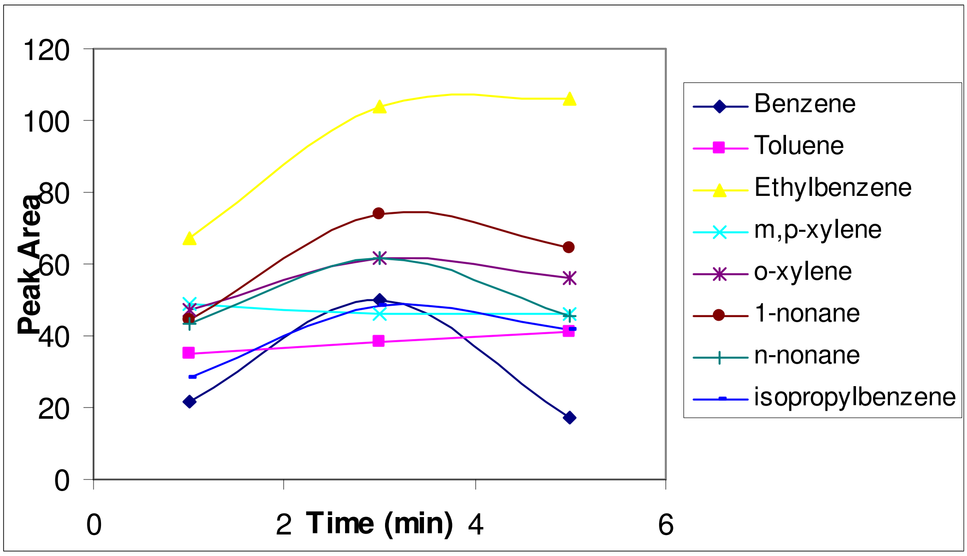


Figure 3-3 Effect of the desorption time on the recovery of the selected target compounds

1 min was found to be insufficient for the recovery of the compounds on the cold trap; after 2 min, similar values were obtained. For this study, 3 min was selected as an optimum time for the recovery of the target compounds on the cold trap. The sample chromatograms showing the effect of desorption time on the recovery of the compounds are given in Figure 3-4 for the selected compounds. Desorption temperature was selected as a 300 °C which was recommended by the manufacturer.

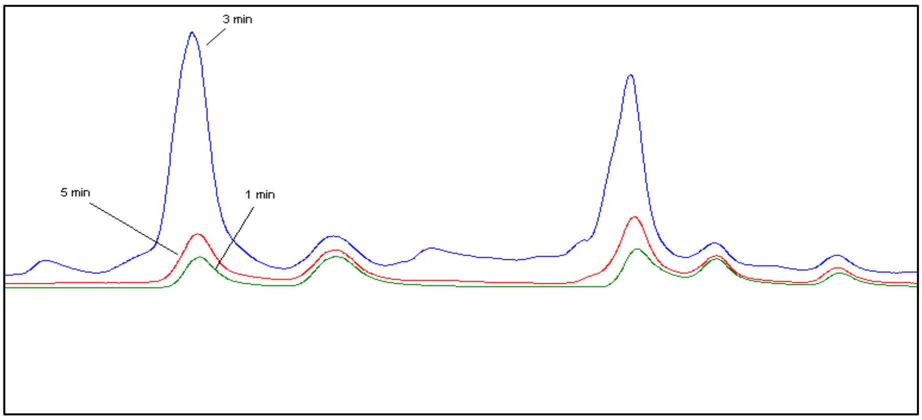


Figure 3-4 Sample chromatograms showing the effect of the desorption time of the cold trap

Due to the effect of the GC program (e.g. starting temperature, ramp values, holding temperature), column flow rate and injection temperatures, these parameters were identified based on the peak responses of the selected calibration standards. Flow rate of the sample tube and split tube were fixed to 30 ml/min and 50 ml/min, respectively. Therefore 8/3 split ratio which gave a good recovery was applied to all samples during the GC/FID analysis.

The GC program which was used in the present study and other optimized operational properties of the unity and GC-FID systems are given in Table 3-1.

Table 3-1 Optimized operational properties belong to unity and GC-FID system

Properties of Thermal Desorption System

	Dry Purge flow rate	120 ml/min
	Dry Purge Time/Pre-purge Time	1 min/1 min
	Cold Trap min temp	-15 °C
	Cold trap max temp	300 °C
	Cold trap desorption time	3 min
	Cold Trap Heating rate	100 °C/min
	Cold trap hold	3 min
	Sampling duration	45 min
	Sampling flow rate	10 ml/min
	Collected sample volume	450 ml
	Recollection split tube	Not used

Properties of GC

	Transfer Line Temp	120 °C
	Valve on/off times	Off at 13.2 min On at 45.5 min
	Detector Temperatures	300 °C
Column 1 (60mxi.d.,0.25mmxfilm, 1 μm)	Operating Temperature	30-325 °C
	Air flow rate	300 ml/min
	Hydrogen flow rate	30 ml/min
	Make-up (N_2) flow rate	2 ml/min
	Flow rate	2.8 ml/min
Column 2 (50mxi.d,0.32mmxfilm ,8 μm)	Operating Temperature	-60- 200°C
	Air flow rate	300 ml/min
	Hydrogen flow rate	30 ml/min
	Make-up (N_2) flow rate	2 ml/min
	Flow rate	5.2 ml/min
Temperature Program	40°C hold for 10 min, 10°C min^{-1} ramp to 195°C and hold 10 min.	

3.4.2. Quantification of Target Compounds

In the study External Standard Method was used for the quantification of each target compounds. In this method, the area or height response of the analyte versus concentration of the analyte in the standard are plotted. Then calibration factor which is the ratio of concentration to the area or the height response is calculated. Therefore, the concentration of the unknown analyte is calculated by comparing the response for unknown with that of standard within the linear range of the curve (Kuntasal, 2005; Civan 2009).

The GC was calibrated using a calibration gas mixture which included 148 VOCs, obtained from Environment Canada Analysis and Air Quality Division (AAQD). This gas mixture containing different VOCs with carbon numbers between 2 and 12 was prepared in a pressured 15 L summa canister. Gas mixture consisted of aromatic and halogenated hydrocarbons with concentrations between 2 and 20 ppb. For the identification of each target compounds different certified standards which include olefins, paraffin, halogenated VOCs mix, Benzene-toluene-Ethlybenzene-o-xylene mix, hydrocarbon mix were used. Retention time of n-hexane was used for setting of valve position time i.e., on/off time. Therefore, compounds whose molecular weight lighter than hexane were eluted from HP-AL/S column (when the valve position is on) and compounds whose molecular weight heavier than hexane were eluted from DB-1 column (when the valve position is off). Target compounds in this study are given in Table 3-2 and Table 3-3.

Table 3-2 Retention time and boiling points of the target compounds detected by FID-1

FID	Compound name	RT (min)	Boiling Point (^oC)
1	Ethylene	9.470	-103.70
1	Propane	11.626	-42.00
1	Propylene	13.017	-47.60
1	Isobutane	13.757	-159.60
1	n-Butane	13.757	-0.50
1	Acetylene	14.690	-84.00
1	trans-2-Butene	16.707	1.00
1	1-Butene	17.038	-6.47
1	Isobutylene	17.683	-6.90
1	cis-2-Butene	17.627	4.00
1	2,2-Dimethylpropane	18.222	9.50
1	Cyclopentane	19.159	49.00
1	n-Pentane	19.970	36.00
1	1,3-Butadiene	21.331	-4.40
1	2-Methylbutane	21.757	28.00
1	3-Methyl-1-butene	22.085	20.15
1	2-Methyl-1-butene	22.085	31.30
1	2-Methyl-2-butene	22.558	39.00
1	trans-2-Pentene	22680	36.00
1	Cyclopentene	23.160	45.00
1	1-Pentene	23.358	30.00
1	cis-2-Pentene	24.018	37.00
1	2,2-Dimethylbutane	24.749	49.73
1	2,3-Dimethylbutane	25.497	58.00
1	2-Methylpentane	25.661	60.00
1	3-Methylpentane	25.839	63.30
1	Isoprene	26.956	34.00
1	4-Methyl-1-pentene	27.076	54.00
1	3-Methyl-1-pentene	27.308	54.00
1	trans-4-Methyl-2-pentene	27.927	58.55
1	cis-4-Methyl-2-pentene	28.013	56.45
1	1-Hexene	28.661	63.00

Table 3-3 Retention time and boiling points of the target compounds detected by FID-2

FID	Compound name	RT (min)	Boiling Point (^oC)
2	n-Hexane	13.840	68.95
2	trans-2-Hexene	14.038	67.90
2	cis-2-Hexene	14.120	68.80
2	2-Ethyl-1-butene	14.120	62.00
2	trans-3-Methyl-2-pentene	14.346	70.45
2	cis-3-Methyl-2-pentene	14.522	67.70
2	2,3-Dimethylpentane	14.806	79.20
2	1,2-Dichloroethane	14.806	83.50
2	Methylcyclopentane	15.341	71.80

Table 3-3 (continued)

2	2,4-Dimethylpentane	17.008	80.50
2	1,1,1-Trichloroethane	15.748	74.00
2	1-Methylcyclopentene	16.414	75.50
2	Carbontetrachloroide	16.414	76.70
2	Benzene	16.587	80.10
2	Cyclohexane	17.079	81.00
2	Cyclehexene	17.257	83.00
2	2-Methylhexane	17.287	90.00
2	2,2,3-Trimethylbutane	17.441	80.90
2	2,3-Dimethylpentane	17.490	89.90
2	3-Methylhexane	17.758	92.00
2	Bromodichloromethane	17.891	90.00
2	Trichloroethylene	17.910	87.00
2	Dibromomethane	18.002	97.00
2	1,2-Dichloropropane	18.061	96.80
2	1-Heptene	18.381	93.64
2	2,2,4-Trimethylpentane	18.562	99.24
2	trans-3-Heptene	18.837	100.42
2	n-Heptane	18.991	98.42
2	cis-3-Heptene	19.016	95.70
2	trans-2-Heptene	19.231	95.70
2	cis-2-Heptene	19.713	98.00
2	cis-1,3-Dichloropropene	20.143	104.30
2	trans-1,3-Dichloropropene	20.180	112.00
2	Methylcyclohexane	20.414	100.90
2	2,2-Dimethylhexane	20.633	107.00
2	2,5-Dimethylhexane	20.659	109.12
2	2,4-Dimethylhexane	20.774	109.50
2	1,1,2-Trichloroethane	20.774	112.50
2	1-Methylcyclohexene	21.058	110.24
2	Bromotrichloromethane	21.459	105.00
2	2,3,4-Trimethylpentane	21.744	113.40
2	Toluene	22.092	110.60
2	2-Methylheptane	22.538	116.00
2	m-Chlorotoluene	22.459	161.00
2	p-Chlorotoluene	22.459	162.00
2	o-Chlorotoluene	22.625	158.5
2	Dibromochloromethane	22.625	119.00
2	4-Methylheptane	22.779	117.00
2	3-Methylheptane	22.779	115.00
2	trans-1,3-Dimethylcyclohexane	23.252	124.00
2	cis-1,3-Dimethylcyclohexane	23.252	120.00
2	trans-1,4-Dimethylcyclohexane	23.357	119.40
2	cis-1,4-Dimethylcyclohexane	23.357	124.00
2	1-Octene	23.483	121.30
2	Octane	24.039	125.70
2	trans-2-Octene	24.178	125.00
2	trans-1,2-Dimethylcyclohexane	24.325	123.00
2	cis-1,2-Dimethylcyclohexane	24.501	130.00
2	2,2,5-Trimethylhexane	24.638	124.00
2	1,2,4-Trimethylcyclohexane	24.688	140.00

Table 3-3 (continued)

2	Tetrachloroethylene	25.880	121.00
2	Chlorobenzene	26.021	132.00
2	Ethylbenzene	26.839	136.20
2	Bromoform	27.037	149.50
2	m-Xylene	26.749	139.00
2	p-Xylene	27.249	138.00
2	Styrene	28.114	145.00
2	1-Nonene	28.282	151.00
2	o-Xylene	28.379	144.00
2	1,4-Dichlorobutane	28.515	155.00
2	1,1,2,2-Tetrachloroethane	28.515	146.00
2	n-Nonane	28.681	150.80
2	Isopropylbenzene	29.624	154.20
2	3,6-Dimethyloctane	30.720	160,00
2	n-Propylbenzene	31.138	159.20
2	tert-Butylbenzene	31.300	169.00
2	3-Ethyltoluene	31.433	158.00
2	4-Ethyltoluene	31.555	162.00
2	1,3,5-Trimethylbenzene	31.753	164.70
2	2-Ethyltoluene	32.316	164.00
2	1-Decene	32.471	174.00
2	1,2,4-Trimethylbenzene	32.937	169.40
2	Decane	33.131	174.00
2	Benzylchloride	33.369	179.30
2	1,3-Dichlorobenzene	33.369	172.50
2	1,4-Dichlorobenzene	33.434	174.00
2	iso-Butylbenzene	33.622	170.00
2	sec-Butylbenzene	33.737	173.00
2	1,2,3-Trimethylbenzene	34.208	176.10
2	p-Cymene	34.208	176.50
2	1,2-Dichlorobenzene	34.687	180.50
2	Indan	34.878	180.00
2	1,3-Diethylbenzene	35.135	181.10
2	1,4-Diethylbenzene	35.450	184.00
2	n-Butylbenzene	35.505	183.00
2	1,2-Diethylbenzene	35.758	192.78
2	1-Undecene	36.736	162.00
2	Undecane	37.176	196.00
2	1,2,3,5-Tetramethylbenzene	38.154	198.15
2	1,2,4,5-Tetramethylbenzene	37.319	196.50
2	1,2,4-Trichlorobenzene	41.002	214.40
2	Naphthalene	41.461	218.00
2	Dodecane	43.166	216.00
2	Hexylbenzene	44.594	226.00

Absolute Response Factor (ARF) is used for the External Standard Method and analyte amounts were obtained by applying these response factors to the measured analyte amount. Due to the Unity Thermal Desorption system being directly connected with GC-FID system, gas standards could be directly analyzed and very high correlation constants (99.999) between mass of each compound and their area response were obtained for each compound during the calibration process. ChemStation software was used during the operation of the GC. By using this software, 6 point calibration curves were prepared for each compound. For the preparation of these calibration curves 100, 200, 300, 400, 500 and 700 ml gases were injected from the canister (Figure 3-5). Before each sampling campaign, six point calibrations were done on 08.09.2005 and 07.03.2006. However, it was not practical to perform six point calibrations frequently since each measurement was repeated at least two times which took 12 hours. Accordingly, calibration checks were done by mid-point injections by injecting 300 ml gas from the canister to GC. The mid-point calibrations were done on 18 October, 28 October and 4 November, 2005 for the first campaign. For the second campaign, they were injected on 7 March, 30 March and 11 April, 2006. When the deviations of the compounds were detected lower than 20%, the previous full calibrations were used for the calculation of VOCs.

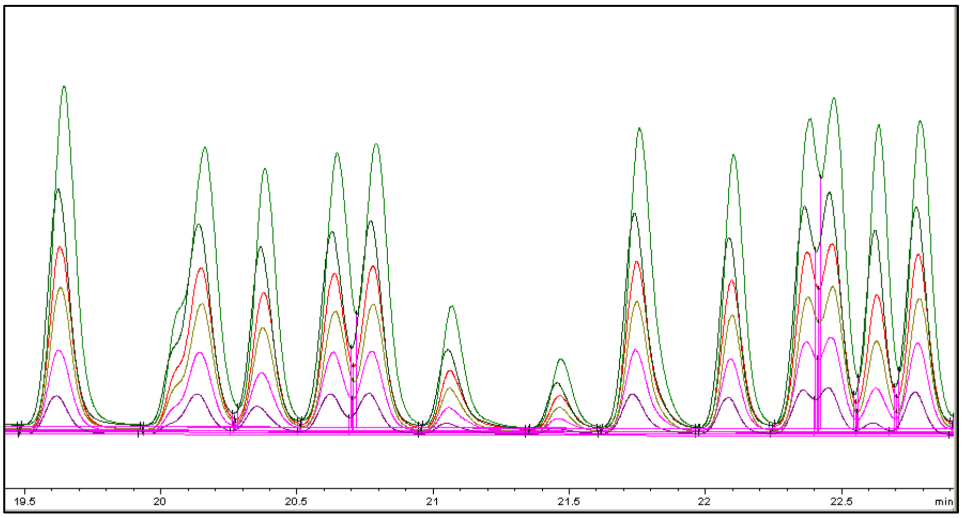


Figure 3-5 Peaks obtained from the injection of the calibration standard for the different VOCs

The produced chromotograms were drawn by the software. Area of the compound in each chromatogram versus mass of the compound as ng in the gas mixture was used for the preparation of the calibration curves. In Figure 3-6, calibration curves belonging to toluene for the both campaigns are given. Accordingly, the obtained slopes represent the ARF were used to calculate mass of the compounds in each sample. Then, these calculated values were divided by the volume of the air sample (450 ml). By this manner, concentration of each compound in the air sample was found. A sample chromatogram belongs to 2nd campaign period is given in Figure 3-7.

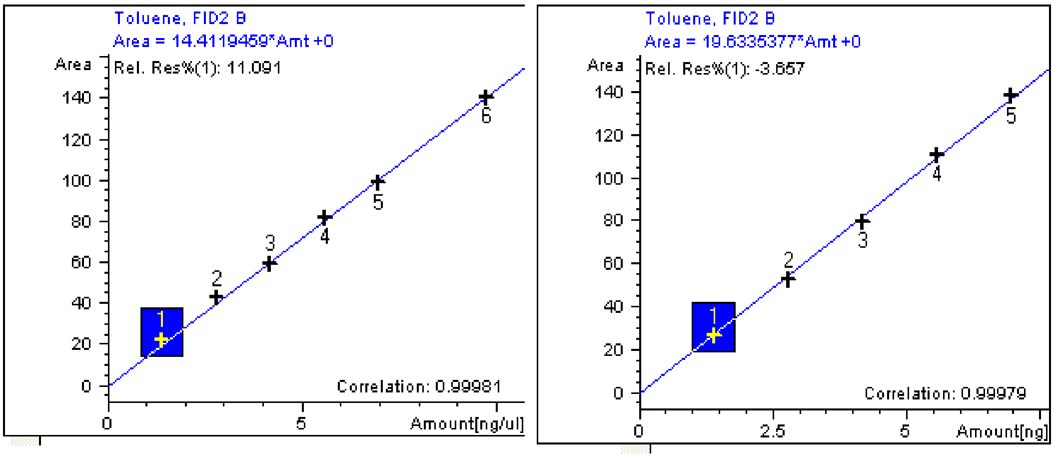


Figure 3-6 Toluene calibration curves for both campaigns, respectively

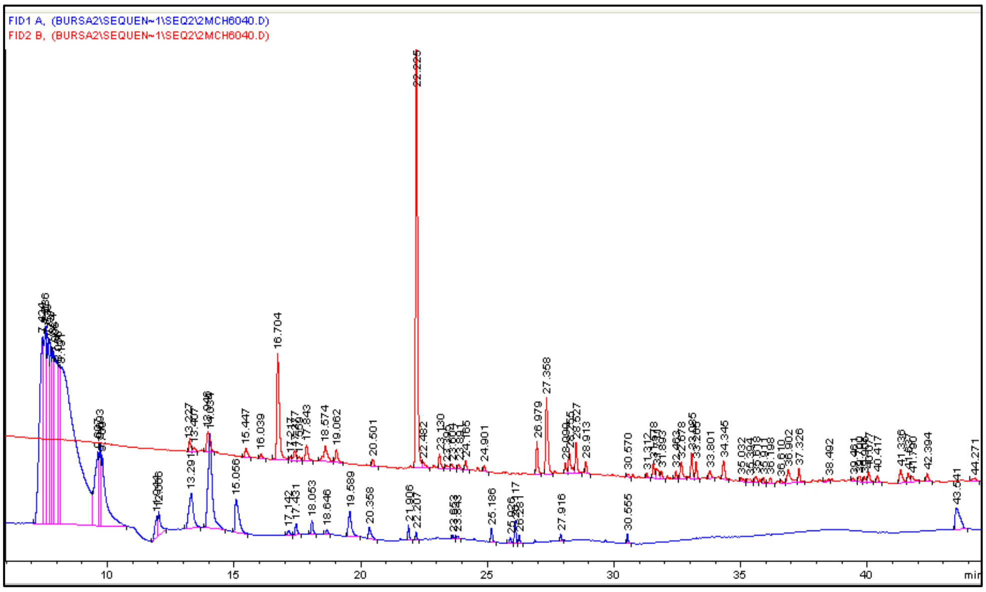


Figure 3-7 A sample chromatogram belongs to the second campaign

3.5 Quality Control and Quality Assurance (QA/QC)

Development and the use of QA/QC protocols refers to development of methodology to detect erroneous data points in the data set, which can arise from a multitude of sources including typological errors during transfer of data to a computer, errors in peak-fitting during processing of chromatograms, instrumental errors sampling errors, etc. QA/QC is an essential procedure, not only in determination of VOC concentrations in the atmosphere, but in all studies that include an experimental section. The form QA/QC can change from one work to another depending on the sampling and/or analytical techniques used, but it should exist in all studies.

In all experimental studies, a QA/QC procedure defines the procedures that will be applied to the data set and criteria that will be used in assessing accuracy and precision levels should be defined even before the experimental work starts. Then this protocol should be applied both during data generation and after the completion of data generation. The use of QA/QC procedures during data generation, such as using Standard Reference Materials (SRM), duplicate analysis, repeated analysis, field and laboratory blanks, is to ensure generation of reliable data. The QA/QC procedures that are applied after data generation is to assess the quality of the data (whether data meets predefined accuracy and precision criteria) and to eliminate any errors that can occur during data processing (such as typological errors during transfer of data to a computer, errors in peak-fitting during processing of chromatograms etc.). Accordingly, in the present study QA/QC procedure was examined under the two main headings namely, analytical system and produced data-set.

3.5.1 Analytical System QA/QC Procedure

3.5.1.1 Detection Limits of VOCs

In the present study, manual integration was done for the quantification of each peak in each chromatogram. However, the peaks whose areas are lower than the certain value were not integrated. These values were determined based on their signal/noise ratio. Different peaks were integrated and the variations in the percent differences in integrated peak areas having chromatographic signal/noise ratio of 3 compared to each other and low percent variation in peak areas were found. Accordingly, these values were used for the limit of quantification (LOQ) values (Dogan, 2013). Detection limits of individual VOCs varied between 0.021 μg m^{-3} for n-propylbenzene and 0.29 μg m^{-3} for dodecane (Table 3-4).

Table 3-4 Limit of quantification value for both campaigns (µg m^{-3})

Compound	The 1st campaign	The 2nd campaign
Ethylene	0.049	0.092
Propane	0.092	0.077
Propylene	0.053	0.058
Isobutane+n-Butane	0.125	0.137
Acetylene	0.076	0.079
t-2-Butene	0.073	0.085
1-Butene	0.082	0.090
Isobutylene	0.053	0.046
2,2-DiM-Propane	0.107	0.098
Cyclopentane	0.041	0.045
n-Pentane	0.058	0.059
1,3-Butadiene	0.088	0.076
2-Methyl-Butane	0.084	0.093
Cyclopentene	0.080	0.073
1-Pentene	0.098	0.103
2,2-Di-M-Butane	0.094	0.092
2,3-Di-M-Butane	0.087	0.095
2-M-Pentane	0.096	0.098
3-M-Pentane	0.094	0.175
3-M-1-Pentene	0.085	0.083
n-Hexane	0.067	0.053
Methylcyclopentane+2,4-Dimethylpentane	0.054	0.053
Benzene	0.074	0.052
Cyclohexane+Cyclohexene	0.096	0.181
2-Methylhexane	0.077	0.057
2,2,3-Trimethylbutane+2,3-Dimethylpentane	0.080	0.061
3-M-Hexane	0.084	0.062
n-Heptane+cis-3-Heptene	0.078	0.060
Methylcyclohexane	0.049	0.059
Toluene	0.077	0.057
2-M-Heptane	0.087	0.062
m+p-Chlorotoluene	0.173	0.090
4+3-M-Heptane	0.099	0.115
1-Octene	0.053	0.052
Octane	0.082	0.059
cis-1,2-Dimethylcyclohexane	0.048	0.054
2,2,5-Trimethylhexane	0.055	0.056

Table 3-4 (Continued)

Chlorobenzene	0.057	0.052
Tetrachloroethylene	0.035	0.044
Ethylbenzene	0.083	0.060
m+p-Xylene	0.073	0.053
Styrene	0.051	0.038
1-Nonene	0.075	0.059
o-xylene	0.041	0.029
n-Nonane	0.075	0.058
n-Probylbenzene	0.029	0.021
3-Ethyltoluene	0.073	0.053
4-Ethyltoluene	0.076	0.057
1,3,5-Tri-M-Benzene	0.073	0.056
2-Ethyltoluene	0.074	0.055
1,2,4-Tri-M-benzene	0.039	0.028
n-Decane	0.085	0.057
1,2,3-Tri-M-benzene+p-Cymene	0.087	0.062
Indan	0.049	0.059
1,3-Di-E-Benzene	0.080	0.057
1,4-Di-E-Benzene	0.054	0.069
n-Butylbenzene	0.083	0.063
1,2-Di-E-Benzene	0.059	0.067
1-Undecene	0.149	0.132
Undecene	0.030	0.070
1,2,3,5-Tetramethylbenzene	0.087	0.065
1,2,4,5-Tetramethylbenzene	0.077	0.056
1,2,4-Tri-Cl-Benzene	0.266	0.145
Naphthalene	0.121	0.072
Dodecane	0.289	0.214
Hexylbenzene	0.151	0.199

3.5.1.2 Precision of Linearity

The precision of the system was determined by 5 replicate measurements. For the determination of the precision, 100 ml gas was injected from the canister containing the AAQD standard to the system 5 times and Relative Standard Deviations (RSDs) were calculated for each compounds. RSD values were found lower than the 15%.

For selected compounds, RSD values for the peak area and retention time are given in Table 3-5.

Table 3-5 Performance of the system for the selected compounds

Compound	**Relative Standard Deviation (%)**	
	Peak area	**Retention time**
Ethylene	4.3	0.11
Propane	1.1	0.35
Acetylene	5.0	0.63
1,3-Butadiene	7.9	0.30
Benzene	2.6	0.05
Toluene	2.1	0.03
Ethylbenzene	1.0	0.02
m,p-xylene	4.6	0.02

Before each sampling campaign, 6 points calibration curves were prepared. During each sampling period, to check whether there was a problem in the GC, mid-point calibrations were also performed. Obtained areas from the mid-point calibrations were compared with the results of the 6 point calibrations and RSD values were found to be lower than the 15%

According to the EPA 8000b standard method, if there is difference bigger than the 20% between the areas, a new calibration must be prepared. The RSD values for the areas belong to the calibrations and mid-point calibrations for the selected compounds are given in Table 3-6.

Table 3-6 The RSD values belonging the calibration and midpoint calibrations

Compound	Relative Standard Deviation (%)	
	Peak area	Retention time
Ethylene	3.2	0.64
Propane	5.8	1.4
Acetylene	4.0	2.3
1,3-Butadiene	8.8	1.9
Benzene	15.8	0.22
Toluene	7.9	0.20
Ethylbenzene	5.9	3.8
m,p-xylene	8.2	0.19

3.5.2 Data Set QA/QC Procedure

QA/QC is particularly important in large data sets which are processed statistically. In such data sets, data usually cannot be investigated point by point. So, one must have tracers that will allow detection of suspicious data points in an aggregate of data. Since environmental data is log-normally distributed, deviations from expected concentrations, deviations from expected enrichment factors in a trace element data set, deviations from expected correlations, and deviations from expected ratios can all be used to detect the data that are not reliable. Please note that none these alone are conclusive evidence for a datum to be incorrect, but a flag should be put on the data (particularly if more than one of these test points to the same datum) and at the end of the QA/QC analysis flagged data should be investigated for the possible source of the observed deviation. If everything is normal and no possible source was found, then that datum becomes real.

Another important issue during data processing is the examination of the all measured data because due to erroneous data, very significant errors in the results can be observed.

The QA/QC procedures used after data generation included inspection of three different plots, including time series plots, scatter plot matrices, finger plots and diurnal profiles, to detect suspicious data points (PAMS Workbook, 2000; EPA, 2007).

In this study, for the QA/QC of the data, firstly univariate outliers were determined for each compound by using SPSS 15.0 software. By this method, outliers which are very different from the rest of the data set were identified by conversion of all the scores for a variable to standard scores. In the current study, all data set were examined for two campaigns and the sample whose standard score is ±2.5 or beyond was flagged as an outlier and then these flagged samples reprocessed. After outlier analysis, time series plots, scatter plot matrices, finger plots and diurnal profiles of the measured compounds were also investigated to detect problematic data.

3.5.2.1 Time Series Plots

Time series plots of the compound are good indicators of the possible outliers, spikes, abrupt changes in the concentrations, misidentified peaks and extended periods of unexpected high or low concentrations. In this approach, time series plots of several VOCs that are correlated with each other are inspected together for unusually high concentrations. Since atmospheric data is log-normally distributed, very high concentrations do not necessarily indicate an error in sampling or measurement. However, since the time-series plots investigated together belong to highly correlated VOCs, then a high datum which is real should be high in all of these VOCs; on the other hand if one datum corresponds to a very high concentration for one of these correlated VOCs that is highly suspicious datum should be flagged (Figure 3-8).

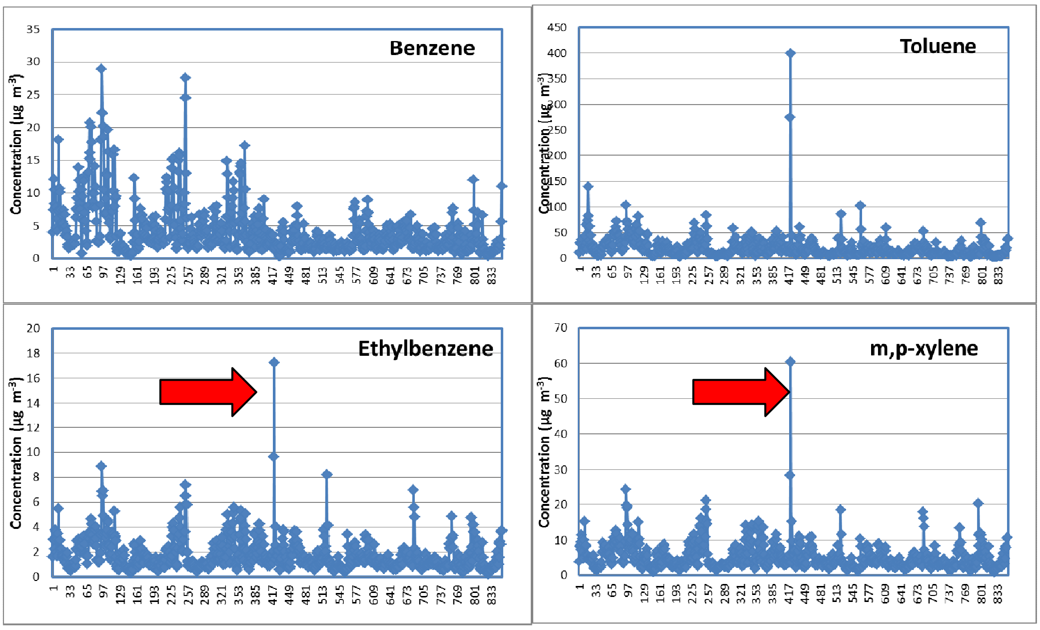


Figure 3-8 Times series of the BTEX compounds for the second campaign

Consequently, preparing time series plots for every species in the data set provided very useful information to detect problematic data points.

3.5.2.2 Scatter Plot Matrices

For the preparation of the scatter plots, several compound groups are plotted and relations among the variables and distribution of the variables are examined. This type of matrix is a compact summary of the variables. By this manner, outliers can be easily identified.

In this approach, scatter plot matrices were prepared for all data sets (Figure 3-9). For all plots, data points which are scattered to the general correlation trend were identified and the suspicious samples were flagged and then reprocessed.

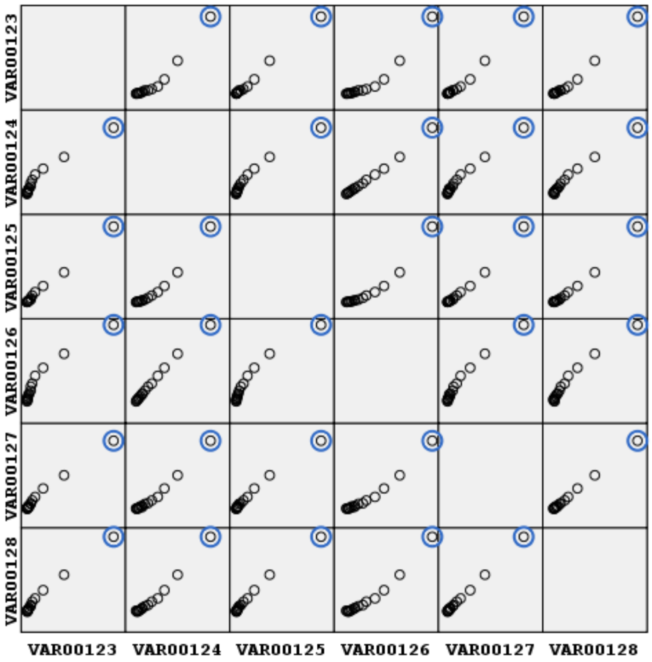


Figure 3-9 Scatter plot matrices for the selected compounds

3.5.2.3 Finger plots

Finger plots give an idea about the composition of the sample. Thus, unique characteristics of the samples can be identified and determined outliers were examined by means of time series and scatter plots.

In the current study, compositions of the samples were also determined by using finger plots. Thus, unique characteristics of the samples were identified. In Figure 3-10, a finger plot belonging to the second campaign is given.

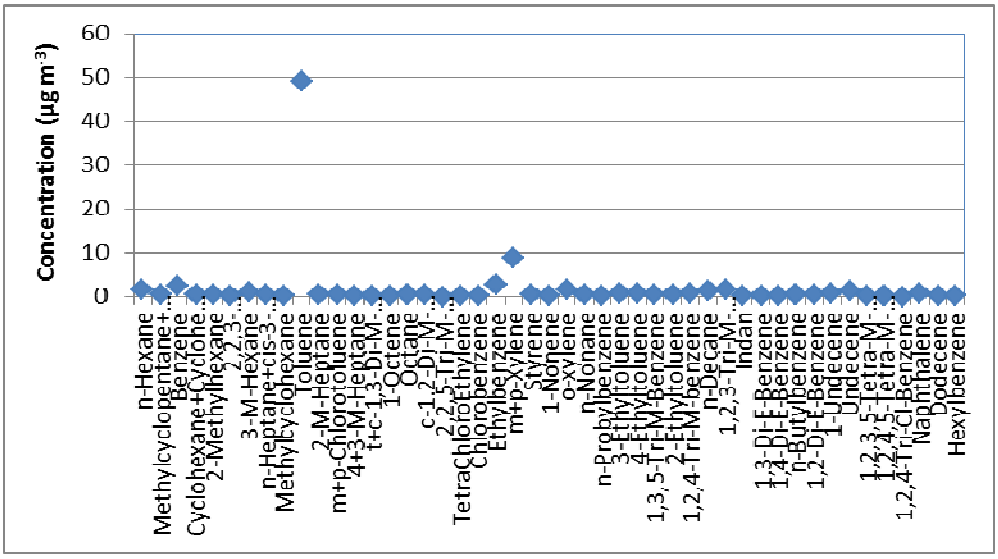


Figure 3-10 Finger plot of the selected compounds for the second campaign

3.5.2.4 Diurnal Profiles

Diurnal profiles provide an opportunity to compare mean values of the different variables between different monitoring sites, different years or weekday vs. weekend. In this approach, diurnal profiles of all the compounds are prepared and morning, noon and night periods of the pollutants are examined separately; in this manner, suspicious samples which caused unexpected deviation from common pattern were identified (Figure 3-11).

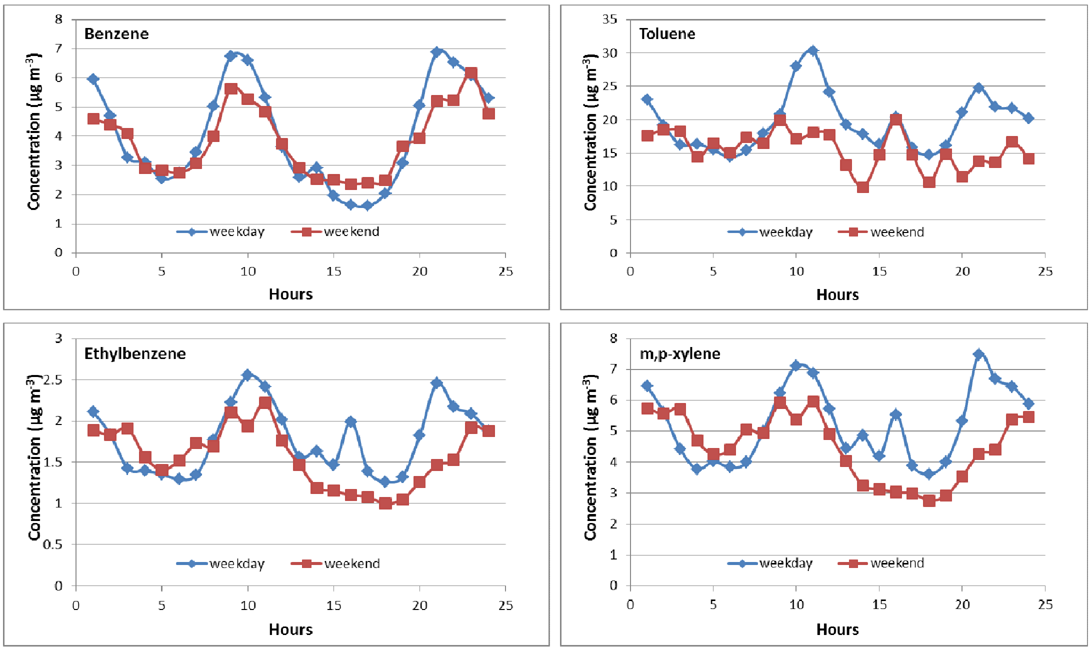


Figure 3-11 Diurnal profile of the BTEX compounds for the first campaign

In here an outlier was assumed as an unusually extreme value for a variable, given the statistical model in use. The outliers detected with SPSS software were also compared with the results of the time series, scatter plots, finger plots and diurnal profiles of the compounds. The same outliers (constituting 10% of the data set) were also identified as a result of these procedures. After identification of these anomalies, chromatograms which contained these anomalies were re-evaluated to control any misidentification or quantification of the peaks. If any problems could not be observed as a result of these re-examination and no problems could be found during the collection of these samples or during the analyses, these anomalies were attributed to changes in the source strength of the compounds or meteorological activities. Accordingly, these samples were not eliminated from the data set.

CHAPTER 4

RESULTS AND DISCUSSION

The fates of atmospheric VOCs are affected by various factors. Variations in ambient concentrations of VOCs in urban atmospheres are the consequence of temporal and spatial changes such as variations in source strength, meteorological parameters and topography. Therefore, it is crucial to perform measurement campaigns to characterize temporal and spatial variation of atmospheric concentrations of VOCs, both to assess their health effects and to validate models as a tool for understanding and prediction of future trends (Jones et al., 1998). Consequently, concentrations of VOCs measured in Bursa atmosphere and factors affecting these concentrations are extensively discussed in the remainder of this chapter. Levels of VOCs, episodic, diurnal and seasonal variability in their concentrations, effects of meteorology and source apportionment of measured VOC concentrations are the topics discussed in the following sections. Spatial distribution of VOCs can also provide valuable information on their sources in an urban airshed. Such a study on spatial distribution of VOC concentrations in the atmosphere of Bursa was previously performed in a separate study (Civan et al., 2011) which helped us to understand temporal variability of VOC concentrations in this work.

4.1 Meteorological Parameters

Air pollution is not a merely an emission problem, it is also meteorology-related situation and the VOC concentrations in air is strongly affected from changes in meteorological conditions (Lashkova et al., 2007; Manju, 2002). Meteorological parameters that controls dispersion and reactivity of VOCs in atmosphere include, wind speed, wind direction, temperature, mixing height, solar flux, and atmospheric stability (Jones et al., 1998). Temporal variations of measured VOC concentrations in Bursa atmosphere are also affected by these meteorological parameters and variations in source strength, namely the variation in traffic pattern of the city.

Consequently, it is important to understand variations in meteorological parameters in order to understand variations of VOC concentrations in the Bursa airshed. Bursa has a temperate climate which can be described as a transition between the Mediterranean and Black Sea climates. Köppen , a climate classification which is based on the hottest and coldest months classifies Bursa as an Mediterranean climate type (Caliskan et al., 2012). Average temperature in January, which is the coldest month in Bursa province, is 5.5^{o}C and the average temperature in July, which is the hottest month, is 24.6^{o}C.

Average lowest and highest recorded temperatures are 1.7^{o}C in February and 30.6^{o}C in June. The annual average temperature of the central province is 14.4 ^{o}C (DMİ, 2010). There is no month where the average temperature drops below zero. According to the Erinç drought index (Öztürk, 2010), January, February, November and December are very moist, March and April are moist, May is semi-humid, June and September are arid and finally June and August are fully-arid. The prevailing wind direction is NE (%49.3). Local topography has a strong effect on the wind characteristics of the city. Northern winds are very effective for the ventilation of the city (Öztürk, 2010).

Winds were very slow during both measurement campaigns. Average wind speed for the first and second campaigns was 1.3 and 1.8 m/s, respectively. These were lower than annual average wind speed for the city, which is 3 m/s (Caliskan et al., 2013). The highest wind speeds were recorded in April and the lowest in March.

During the sampling campaigns, precipitation was low; very few rain events were observed. Total precipitation was 68 mm and 25 mm for fall and spring campaigns, respectively. Moreover, no statistical meaningful ($p<0.5$) correlation between measured VOC concentrations and precipitation data was obtained. Therefore, the effect of the precipitation on measured organic compound concentrations was not examined in the rest of the thesis.

Although the highest temperature (30°C) was recorded in April, most of the midday temperatures in September were higher than those recorded in April. In September and May, average temperatures were similar. The lowest temperatures were observed in March (-0.9°C). The summary of the meteorological parameters recorded at the Yunuseli meteorological station in Bursa during the sampling periods is given in n Table 4-1.

Wind roses for Bursa are given in Figure 4-1 for both sampling campaigns. The prevailing wind direction was East-Northeast (ENE), while West-Southwest (WSW) and East-Southeast (ESE) were the next most frequent wind directions during the first campaign. On the other hand, winds from WSW were dominant during the second campaign. During both sampling campaigns, northerly winds were also frequently seen. A higher frequency of calm conditions (WS < 1.0 m s^{-1}) was observed during the first campaign than during the second campaign (2.43% vs. 0.23%).

Table 4-1 Meteorological parameters belong the sampling period

	Temperature (°C)			**Wind speed (m s^{-1})**			**Mixing Height (m)**		
Sampling period	Avg	Max	Min	Avg	Max	Min	Avg	Max	Min
Sept-Oct,2005	15.8 ± 5.0	29.2	1.2	1.3 ± 1.2	5.1	0.0	816 ± 393	1640	71
March-May,2006	13.5 ± 5.2	30	-0.9	1.8 ± 1.4	6.9	0.0	769 ± 480	2666	94

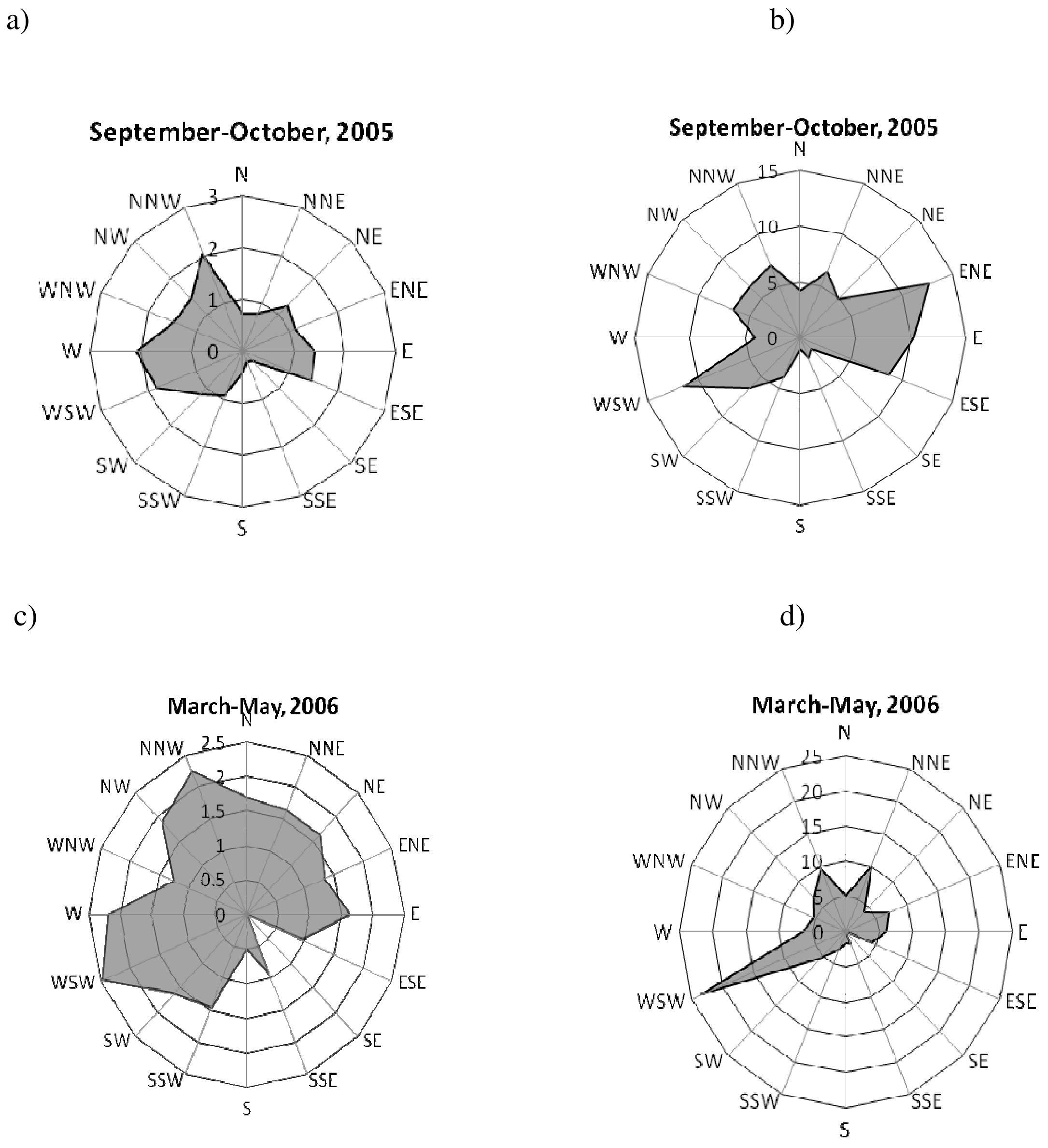
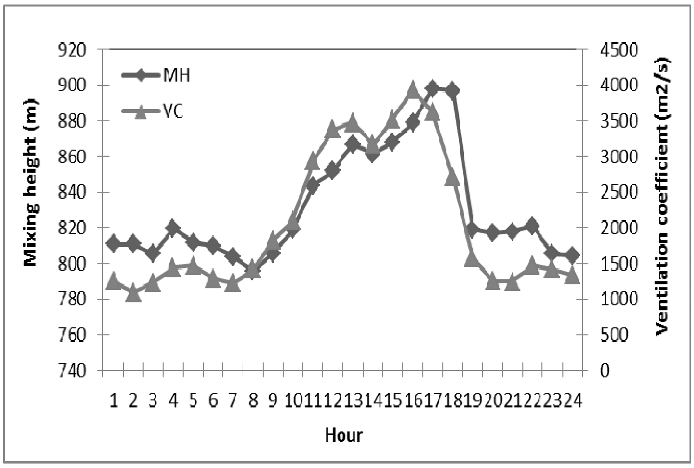


Figure 4-1 a;c) Rose diagrams of wind speed (m/s) for the first and second campaigns, respectively, b;d) wind direction (%) for the first and second campaigns, respectively

Meteorological processes in the boundary layer have a very important role in identifying diffusion, transport and chemical transformation of pollutants in the atmosphere (Rao et al., 2003). Mixing height, ventilation coefficient and cloud cover are the essential boundary layer parameters that can affect air quality. Therefore, hourly mixing height and ventilation coefficients were calculated to identify dispersion and hence ventilation characteristics of the Bursa atmosphere during the study.

Mixing height is defined as the depth where pollutants released into the atmosphere are well mixed. It determines the vertical range of the dispersion which occurs due to the release of pollutants below that height (Nath, 2006; USEPA, 2004). Mixing height generally shows systematic diurnal and seasonal variations with shallow mixing height during night hours and in winter and deeper mixing height during noon hours and in summer (Genc et al., 2010). Correlation of this pattern with lower summer and day-time concentrations of pollutants is frequently reported in literature (Harrison, 2001; Chou et al., 2007; Davies et al., 2007).

Mixing height values in this study were calculated using rawinsonde data measured at Göztepe Meteorology Station in İstanbul. Rawinsonde data consisted of transmissions from twice daily balloon rises (at 00 UTC, and 12 UTC). Using these values, hourly mixing heights were then calculated using the meteorological pre-processor PCRAMMET developed by the US EPA. Diurnal variations of the mixing height for both sampling campaigns are given in Figure 4-2.



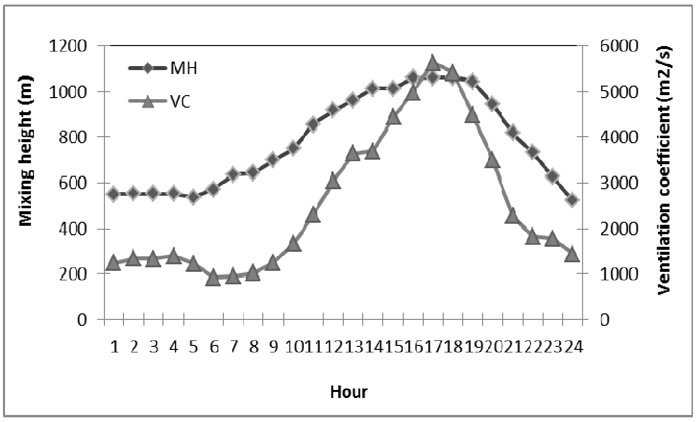


Figure 4-2 Diurnal variation of the MH and Ventilation Coefficient for Fall and Spring campaigns, respectively

The mixing height and ventilation coefficient depicted a very typical diurnal pattern with lower values at night and higher values during day-time. Inversions that occur at ground level limit the dispersion of pollutants vertically in the atmosphere. In addition to ground level inversions, calm winds, which mostly happen during night, increase the cooling of the ground (Krishna et al., 2004; Pandey, 2008). For these reasons, the night time mixing heights were found to be lower as compared to afternoon mixing heights for both sampling campaigns. Deep mixing heights were observed between 08:00 am and 08:00 pm, with a maximum between 15:00-18:00 in both sampling campaigns. After the sunrise, mixing height increased rapidly and reached its maximum depth of 900 m and 1000 m by the mid-afternoon of both sampling campaigns. After sunset, depth of the mixing height was lower than 820 m and 600 m for the first and second campaigns, respectively. Daily variations of mixing height during the two campaigns were not significantly different. This was probably due to the timing of the two campaigns. Normally mixing height is expected to be higher in summer and lower in winter. However, neither of our campaigns took place in true summer and true winter periods. In the present study, assimilative capacity of the Bursa atmosphere during the two sampling campaigns was also investigated. Assimilative capacity of the atmosphere is explained as a maximum pollutant load that can be emitted the atmosphere without disturbing the use of air resources in the territory (Krishna, 2004). Therefore, assimilative capacity of the atmosphere controls dispersion and the dilution of pollutants discharged from their local sources (Pandey, 2008). Ventilation coefficient is the parameter that is commonly used to express assimilative capacity of the atmosphere under different meteorological conditions (Manju et al., 2002; Goyal and Rao 2007a; Genc et al., 2010).

Ventilation coefficient is the product of the mixing height and wind speed. In the current study, Ventilation coefficient was calculated on an hourly basis by multiplying mixing height with the wind speed at half the mixing height. Interpolation method was applied to calculate wind speed at half mixing height (Ashrafi et al., 2009; Manju 2002). High ventilation coefficients indicate good dilution, resulting in lower pollutant concentrations (Rao et al., 2003) and low ventilation coefficient indicate poor dispersion conditions. In Figure 4-2, diurnal variation of the ventilation coefficients is also presented. Diurnal variation in ventilation coefficient was similar to the diurnal pattern of mixing height. The VC values increased during the daytime and decreased during nighttime and early morning due to low mixing height and light prevailing wind (Pandey, 2008), indicating that the atmosphere of Bursa has a poor dispersion capacity at these times. The maximum ventilation coefficient values occurred between 15:00 and 18:00 for both campaigns. Some differences such as height and shape of curve between diurnal VC patterns of the two sampling campaigns were observed. These differences were probably due to smaller contribution of the wind speed to ventilation coefficient than mixing height (Manju, 2002).

State of Colorado Department of Health in Denver (EPA, 1999) devised an air quality index which relates ventilation coefficient values to dispersion conditions in the city. In this scheme, VC values between 0 and 2000 m^2 sec^{-1} represent poor air quality (poor dispersion conditions), values between 2,001 and 4,000 represent fair air quality, VCs between 4,001 and 6,000 indicate good air quality and VC values >6,000 indicate excellent air quality in an airshed. Based on this scheme, VC values in Figure 4-2 indicate that dispersion conditions, in Bursa Atmosphere, were poor at night time and became “fair” and “good” during day-time. This variation in ventilation conditions in the city did not seem to change between the two campaigns.

Seasonal variations in mixing height and ventilation coefficient are depicted in Figure 4-3. Both MH and VC demonstrated systematic seasonal variations with higher values in summer. Among the monthly averages shown in the figure, the lowest values were observed in March and the highest mixing height and ventilation coefficients were observed in September and May. However, it should be noted that our campaigns did not include the whole year; even smaller MH and VC values can be seen in December, January and February in winter and higher than our maximum MH and VC can be expected in summer months (June, July and August). When the values given in Figure 4-3 are compared with the Colorado Department of Health index, VC < 2000 observed in March indicates that dispersion conditions are poor in Bursa during winter season. Since higher ventilation coefficients are not expected in other winter months, “poor” dispersion conditions are expected to prevail throughout winter season in Bursa atmosphere. Monthly average ventilation coefficients reached to approximately 3000 cm^2 sec^{-1} in March, which corresponds to “fair” dispersion conditions. VC values are expected to be “good” in June, July and August, which are not covered in this study. Frequency of occurrence of different dispersion conditions in Bursa are given, for both campaigns, in Figure 4-4. Frequencies of occurrence values were found by comparing VCs with the Colorado Department of Health index on an hourly basis. “Poor” dispersion conditions were by far the most common ventilation category, which were followed by “fair”, “good” and “excellent” conditions. Contributions of “fair”, “good” and “excellent” dispersion conditions are approximately 20%, 10% and 8%, respectively. Poor ventilation conditions, on the other hand, prevailed the remaining 60% of the time. Poor ventilation conditions were more frequent and other ventilation conditions were less frequent in the first campaign, which was due to lower mixing height and VC values in winter.

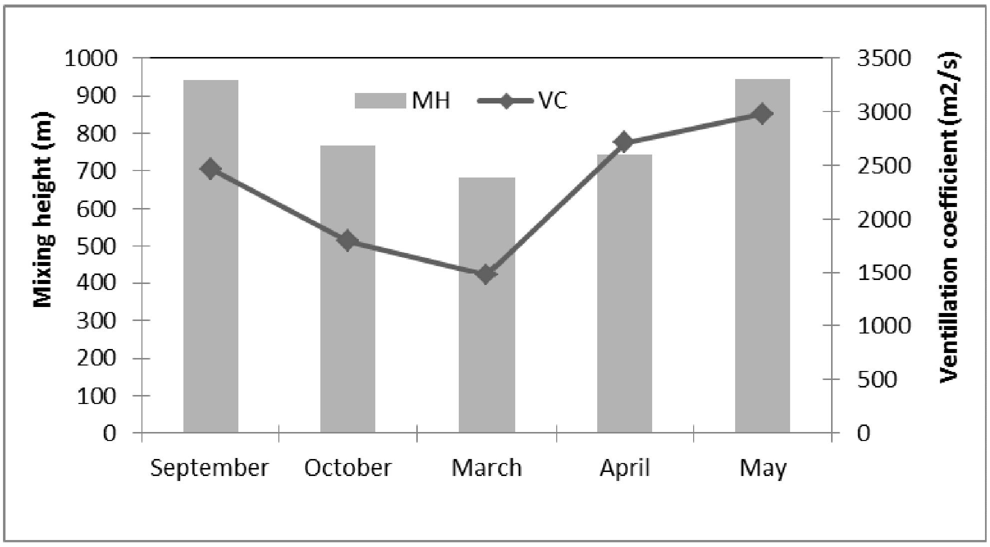


Figure 4-3 Monthly variation of the MH and Ventilation Coefficient

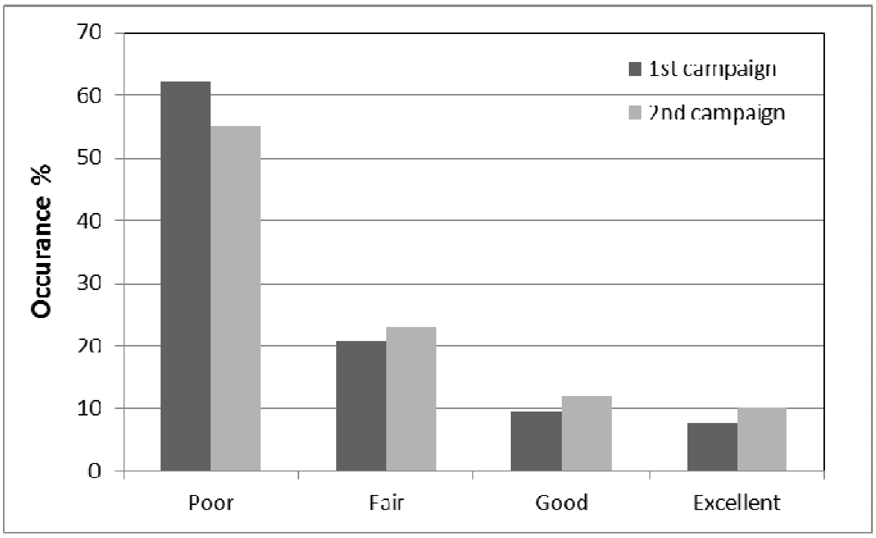


Figure 4-4 Comparison of the dispersion levels of Bursa for both sampling campaigns

Pasquil (1974) stability classes, which are also a measure of atmospheric dispersion characteristics, were also calculated on an hourly basis for our study period using the meteorological pre-processor PCRAMMET. The processor recognizes seven stability classes. They ranged from very unstable (A) to very stable (F). The last class (G) indicates strong, ground-based nocturnal inversion with non-definable wind flow. Diurnal variations of the stability classes for the sampling periods are given in Figure 4-5 and Figure 4-6 for the first and second campaign, respectively.

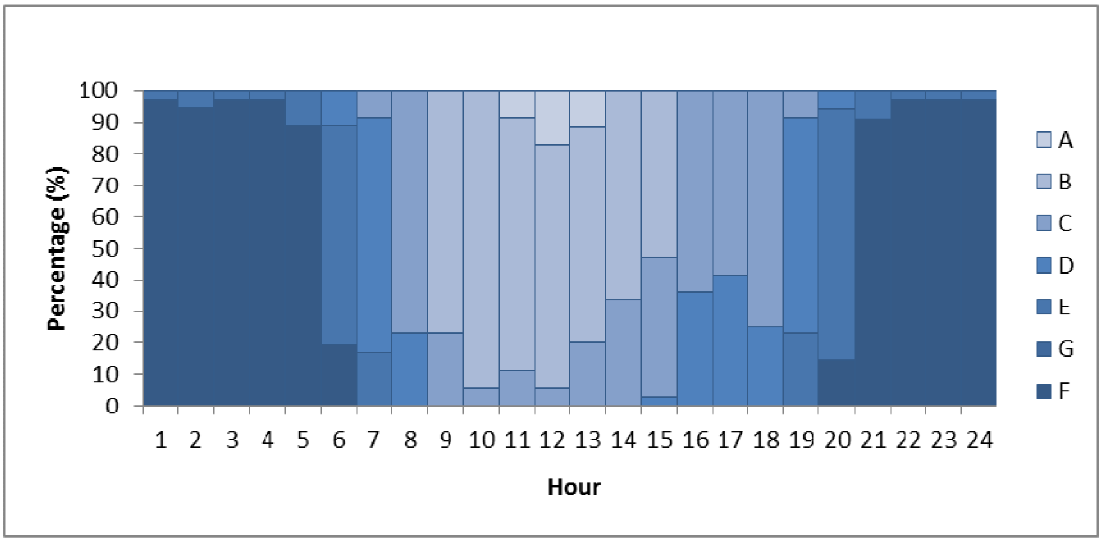


Figure 4-5 Diurnal variation of the stability classes during the first campaign

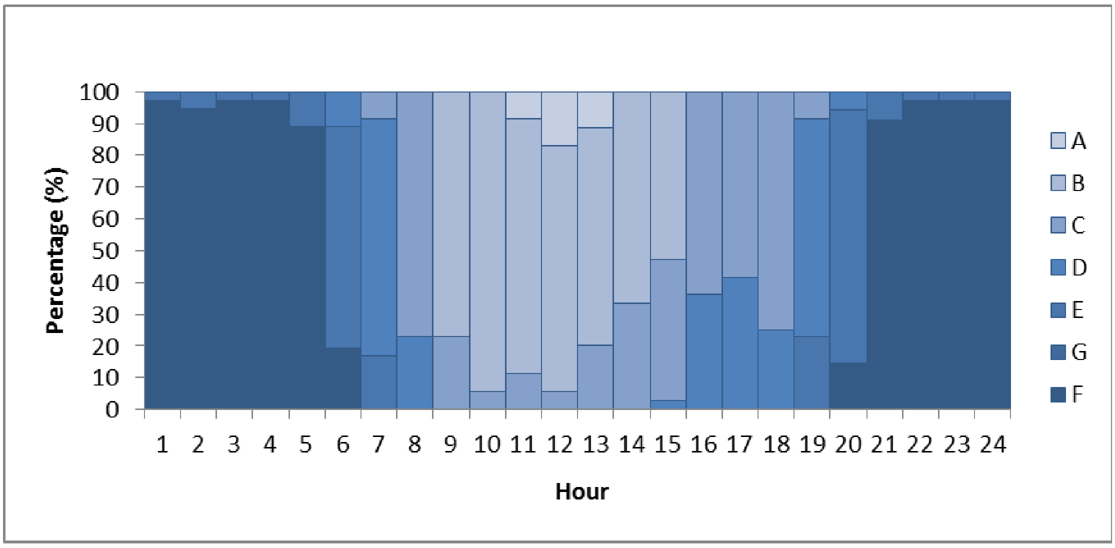


Figure 4-6 Diurnal variation of the stability classes during the second campaign

It is clear from both figures that unstable conditions prevailed during day-time, particularly at noon. However, no unstable conditions were observed during night time. For the second campaign, unstable condition was found more frequently as compared to the first campaign, which is consistent with the seasonal variations of ventilation coefficient. Therefore, it might be concluded based on both of these discussions that the assimilative capacity of the Bursa airshed is the higher during spring season than fall. However, the length of the good atmospheric conditions was very limited even during spring season. It should also be noted that worse dispersion conditions should generally be expected during winter months and better dispersion conditions should be expected during summer months, periods which were not covered by our campaigns.

4.2 Descriptive Statistics of the Measured VOCs Concentrations

The mean, median, minimum and maximum concentrations of the measured compounds for both campaigns are given in Table 4-2.

Table 4-2 Descriptive Statistics of the Collected Data (µg m^{-3})

	1st Campaign			2nd Campaign		
Compound name	**Mean**	**Med.**	**range**	**mean**	**Med.**	**range**
Ethylene	8.96±9.19	6.17	0.21-58.9	16.5±14.0	11.9	1.4-92.9
Propane	3.71±4.42	2.11	0.14-33	2.56±2.94	1.48	0.14-20.97
Propylene	5.31±5.61	3.56	0.22-35	4.78±4.24	3.52	0.5-57.4
Isobutane+n-Butane	27.84±30	18.44	0.45-185	25.6±21.8	18.5	1.34-177
Acetylene	3.96±5.11	2.087	0.14-35.8	4.54±4.6	3.02	0.13-33.6
trans-2-Butene	0.85±0.72	0.65	0.08-4.81	0.42±0.34	0.30	0.07-2.53
1-Butene	0.76±0.82	0.48	0.06-0.63	0.79±0.65	0.58	0.08-4.94
Isobutylene	0.70±0.51	0.57	0.14-3.67	0.55±0.33	0.44	0.15-2.40
2,2-Dimethylpropane	0.62±0.57	0.44	0.06-3.68	0.45±0.37	0.323	0.17-2.56
Cyclopentane	2.23±2.36	1.48	0.07-20.7	1.96±1.56	1.46	0.17-11.8
n-Pentane	0.87±0.91	0.58	0.04-7.34	0.89±0.67	0.69	0.09-5.09
1,3-Butadiene	0.51±0.84	0.47	0.05-5.90	0.74±0.67	0.69	0.09-5.09
2-Methyl-Butane	-	-	-	0.86±0.87	0.55	0.08-6.63
Cyclopentene	0.51±0.53	0.32	0.054-4.43	0.26±0.23	0.19	0.04-1.95
1-Pentene	0.36±0.30	0.25	0.05-2.45	0.25±0.23	0.19	0.04-1.63
2,2-Dimethylbutane	1.28±1.36	0.87	0.06-11.1	1.03±0.85	0.78	0.05-6.44
2,3-Dimethylbutane	0.48±0.54	0.29	0.05-5.12	0.39±0.31	0.29	0.07-2.72
2-Methylpentane	1.59±2.0	0.92	0.03-21.9	1.45±1.28	1.06	0.11-3.08
3-Methylpentane	0.83±1.19	0.38	0.03-13.6	0.79±0.82	0.56	0.087-10.3
3-Methyl-1-pentene	0.57±0.58	0.39	0.04-3.37	0.37±0.26	0.31	0.04-2.11
n-Hexane	3.20±2.43	2.73	0.31-14.0	1.13±0.99	0.82	0.12-12.9
Methylcyclopentane	0.62±0.82	0.35	0.05-5.35	0.50±0.46	0.37	0.07-5.38
Benzene	3.68±5.27	1.52	0.12-40.1	4.03±3.78	2.79	0.32-28.86
Cyclohexane+Cyclohexene	1.14±1.08	0.80	0.12-5.09	0.59±0.58	0.41	0.08-9.59
2-Methylhexane	0.93±0.78	0.74	0.1-6.23	1.06±1.68	0.50	0.08-20.5
2,2,3-T-M-butane+2,3-Dimethylpentane	0.51±0.52	0.37	0.043-2.93	0.38±0.57	0.19	0.04-7.3

Table 4-2 (continued)

3-Methylhexane	2.24±1.35	1.86	0.25-8.2	0.99±0.50	0.84	0.36-3.38
n-Heptane	0.69±0.79	0.42	0.03-5.98	0.56±0.36	0.46	0.096-2.80
Methylcyclohexane	0.45±0.48	0.26	0.04-4.30	0.26±0.19	0.19	0.045-1.21
Toluene	27.86±48.7	16.3	2.1-949	19.15±21.87	13.34	2.35-399
2-Methylheptane	0.88±0.60	0.73	0.07-3.4	0.36±0.26	0.28	0.035-1.90
m-Chlorotoluene	1.12±1.06	0.78	0.13-7.2	0.38±0.25	0.31	0.084-2.01
4+3-Methylheptane	0.78±0.59	0.63	0.05-4.9	0.31±0.23	0.23	0.06-1.57
t,c-1,3-Dimethylcyclohexane	0.39±0.25	0.31	0.06-1.4	0.14±0.08	0.12	0.039-0.797
1-Octene	0.44±0.52	0.28	0.07-3.0	0.21±0.25	0.12	0.02-2.17
Octane	0.56±0.40	0.44	0.1-2.50	0.40±0.21	0.34	0.11-1.68
cis-1,2-Dimethylcyclohexane	1.32±1.32	0.92	0.07-8.2	0.74±0.63	0.52	0.099-5.21
2,2,5-Trimethylhexane	0.18±0.13	0.15	0.055-0.98	0.11±0.054	0.10	0.063-0.352
Tetrachloroethylene	0.21±0.16	0.16	0.03-1.0	0.11±0.066	0.087	0.023-0.54
Chlorobenzene	0.25±0.27	0.17	0.053-2.34	0.13±0.10	0.10	0.063-1.25
Ethylbenzene	2.39±3.97	1.57	0.15-79	1.73±1.30	1.35	0.24-17.25
m,p-Xylene	6.38±11.8	3.89	0.13-226	5.07±3.88	3.94	0.80-60.33
Styrene	2.94±2.08	2.90	0.18-13.2	1.43±2.29	0.54	0.10-23.62
1-Nonene	0.97±1.17	0.50	0.08-7.2	0.36±0.29	0.24	0.04-1.77
o-Xylene	1.09±1.4	0.68	0.05-24.3	0.87±0.62	0.68	0.17-8.67
n-Nonane	0.65±0.49	0.53	0.09-3.48	0.61±0.37	0.52	0.16-3.73
n-Propylbenzene	0.18±0.18	0.13	0.07-2.58	0.11±0.099	0.086	0.063-1.47
3-Ethyltoluene	1.37±1.18	0.95	0.25-8.15	0.88±0.58	0.69	0.019-4.21
4-Ethyltoluene	0.81±0.79	0.54	0.09-4.73	0.64±0.38	0.52	0.15-2.92
1,3,5-Trimethylbenzene	0.54±0.53	0.36	0.07-3.5	0.43±0.28	0.34	0.09-2.17
2-Ethyltoluene	0.62±0.58	0.44	0.08-4.0	0.39±0.28	0.31	0.06-2.24
1,2,4-Trimethylbenzene	1.03±1.1	0.70	0.07-6.8	0.82±0.52	0.65	0.16-3.57
n-Decane	1.27±1	1.01	0.17-7.8	1.21±0.72	1.01	0.34-6.41
1,2,3-Trimethylbenzene+p-Cymene	1.95±1.89	1.34	0.07-15.6	1.27±0.88	1.0	0.17-8.57

Table 4-2 (continued)

Indan	0.38±0.31	0.29	0.09-3.48	0.20±0.17	0.15	0,053-2.47
1,3-Diethylbenzene	0.48±0.43	0.35	0.08-6.8	0.21±0.36	0.14	0.03-6.53
1,4-Diethylbenzene	0.69±0.57	0.55	0.05-7.5	0.38±0.41	0.29	0.06-7.16
n-Butylbenzene	0.43±0.38	0.35	0.06-6.64	0.36±0.40	0.29	0.08-7.6
1,2-Diethylbenzene	0.37±0.39	0.29	0.06-6.9	0.41±0.40	0.34	0.08-6.94
1-Undecene	16.79±20.1	8.72	1.69-113	2.03±2.53	1.24	0.18-27.68
Undecane	0.32±0.29	0.24	0.07-2.49	1.15-0.88	0.96	0.32-16.51
1,2,3,5-Tetramethylbenzene	0.45±0.50	0.31	0.034-9.01	0.22±0.56	0.14	0.028-11.04
1,2,4,5-Tetramethylbenzene	0.42±0.38	0.34	0.01-4.74	0.18±0.37	0.13	0.02-6.90
1,2,4-Trichlorobenzene	29.93±39.29	14	0.38-289			
Naphthalene	0.88±0.43	0.82	0.15-4.6	0.80±0.95	0.63	0.18-17.0
Dodecane	4.23±4.99	2.71	0.17-27.1	1.28±2.27	0.34	0.096-18.32
Hexylbenzene	1.81±1.6	1.39	0.17-10.2	0.85±2.85	0.35	0.06-29.68

The median total VOC concentrations were 115 and 86 µg m^{-3} for the first and second campaigns, respectively. In the first campaign, total VOC concentrations were higher than the second campaign even though more stable weather conditions were present in the second campaign. This discrepancy was likely due to asphalting operations, which would be expected to lead to significantly higher concentrations of organics, particularly heavy hydrocarbons, such as dodecane and 1-undecene. Higher concentrations of solvent-originated compounds (i.e., for example toluene, m,p-xylene, 1,2,4,-trichlorobenzene and styrene) were recorded during the first campaign than the second. However, traffic-originated VOCs such as benzene, acetylene and 1,3-butadiene were higher in the second campaign than in the first campaign. Therefore, data highlights the importance of source strength and meteorology on VOC concentrations.

Taken as a sum, isobutane and n-butane were the most abundant compounds for both campaigns. However, this measured value is the sum of both compounds. Toluene was the most abundant single compound with a median concentration varying from 16.3 to 13.3 µg m^{-3} for the first and second campaigns, respectively. High toluene concentrations have been commonly observed in most studies related with urban air (Kellessis et al., 2006; Fernandes et al., 2002). Levels of toluene in atmosphere range from 1 to 30 µg m^{-3} (EPA, 1994). There are no regulations on atmospheric levels of toluene in Turkish Air Quality Regulation, European Commission Air Quality Standards and World Health Organization Regulations because toluene is not accepted as a carcinogen. The International Agency for Research on Cancer (IARC) is not accepting toluene as a human carcinogen. However, there are studies related with the potential of toluene to create teratogenicity/embryotoxicity in humans exposed in occupational environments (CCOHS, 2011). It also contributes to formation of tropospheric ozone and other photooxidants (Baltaretu et al., 2009).

Mean benzene concentrations range between 5 and 20 µg m^{-3} in urban atmospheres. There is no safe exposure level of benzene in atmosphere because it is accepted as a human carcinogen (Air Quality Guidelines for Europe, 2000). In this study, benzene concentrations of 1.52 and 2.79 µg m^{-3} were measured for the first and second campaigns, respectively. According to the EU Air Quality Standard and Turkish Air Quality Assessment and Management Regulation (Directive, 2008), annual benzene concentration is restricted to below 5 µg m^{-3}. Therefore, in this study, measured benzene concentrations were found lower than the limit values. 62 and 64 compounds out of the 148 target compounds were detected in more than 50% of the samples for the first and second campaigns, respectively. As samples collected on an hourly basis, the concentration of each compound showed great variation. Concentration of each compound ranged from 0.4 to 399 µg m^{-3}. This situation points out the diurnal, weekday/weekend, and seasonal variations in Bursa atmosphere.

The percentage of the most 15 observed compounds are given in Figure 4-7. The top 15 compounds were found to be mostly the same in either campaign. Only n-hexane, 3-m-hexane, cyclopentane and 2-m-pentane were not observed in both campaigns. The first notable issue was the high abundance of the heavy hydrocarbons such as dodecane and 1-undecene, indicating a specific potential source in the first campaign. Probably because of asphalting operations in the city center, the percentages of heavy hydrocarbons were found to be higher in the first campaign than the second campaign. Similar results were also obtained for n-hexane, 3-m-hexane, cyclopentane and 2-m-pentane, because these organics are solvent originated pollutants. The larger loads of benzene, ethylene, acetylene, ethylbenzene, and m,p-xylene in the second campaign show stronger influence of traffic emissions in the second campaign, because these VOCs are well documented tracers of traffic-related emissions.

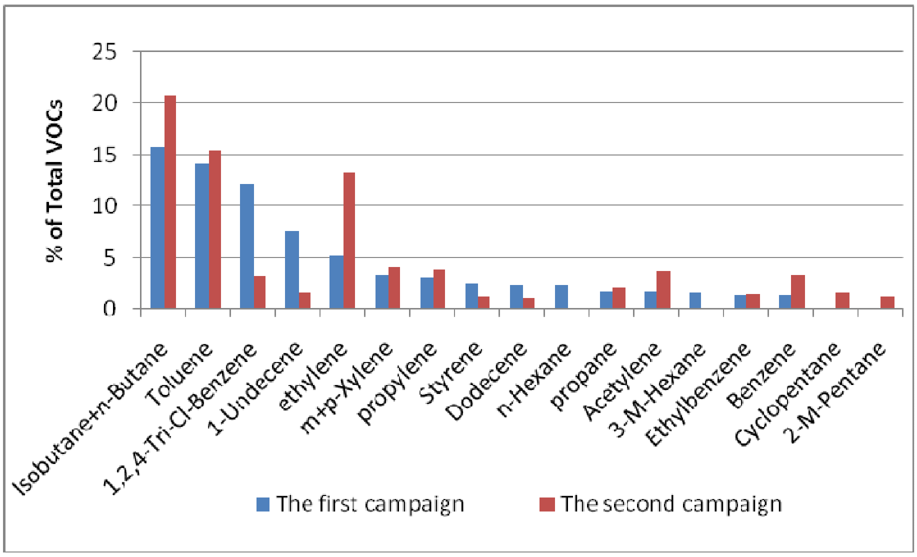


Figure 4-7 The percentage of the most observed 15 compounds

Investigation of VOCs is very informative because each class has different oxidation pathways, rates, products and different contributions to ozone and aerosol production (Lurmann and Main, 1992). Fractions of the four main VOC groups are presented in Table 4-3. Approximately 31 percent of the VOCs were accounted for by alkanes and 22, 2, 31 and 13 of total VOC concentration are accounted for by alkenes, alkynes, aromatics and halogenated compounds in the first campaign. Similar fractions were also observed for the second campaign except for halogenated compounds. In the second campaign, 37 percent of the VOCs were accounted for by alkanes and 23, 3, 34 and 2 percent were accounted for by alkenes, alkynes, aromatics and halogenated compounds. Therefore, percent contribution of the halogenated compounds was about 7 times higher than the second campaign. This situation indicates a local source for the halogenated compounds during first measurement period. Alkanes are the most abundant group of organic compounds in the Bursa atmosphere, which is followed by aromatics, alkenes and halogenated compounds. Once in the atmosphere, aromatics compounds and alkenes are more reactive than alkanes and chlorinated compounds (Lurmann and Main, 1992). Therefore, high alkane contributions, which was observed in both campaigns is probably due to slower oxidation rates of the alkanes compared to aromatics and alkenes. Lonneman et al. (1986) found that the average HC for non-converter-equipped cars were 39.1%, 21.8%, and 35.3% for alkanes, alkenes and aromatics, respectively. Therefore, in this study, composition of the NMVOCs was found consistent with non-converter equipped cars for both campaigns.

Table 4-3 Percent contributions of the organic compounds

Group	**1st campaign (%)**	**2nd campaign (%)**
Alkanes	31.45	37.36
Alkenes	22.05	23.22
Alkynes	1.82	3.4
Aromatics	31.48	34.25
Halogenated compounds	13.16	1.77

4.3 Comparison of the Data with Literature

The comparison of the average concentration values of the selected organic compounds for the both campaigns with the measured outdoor concentrations of

VOCs in different cities is given in Table 4-4. As can be seen from Table 4-4, average concentrations of the VOCs included in the table cover wide ranges. This is expected because VOC concentrations measured in any city depends on a variety of factors, including differences in weather conditions, the major source types (i.e. vehicle, fuel type and industrial sources), atypical traffic conditions, quality of the gasoline, percentage of catalyst-equipped cars, location of the sampling point (i.e. urban/suburban or rural area), proximity of the sampling location to industrial areas, highways and residential areas, duration of the sampling, and the level of the development of the city (Gee and Sollars, 1998; Son et al., 2003; Jo et al.,2012). Therefore, comparison of the measured VOC concentrations in Bursa urban atmosphere with another results measured in different cities is not completely relevant. For example, In Hong Kong, measurements were performed in PolyU campus at an urban station affected from heavy traffic (Ho et al., 2004). However, in the present study, measurements were performed in the city center and sampling location was tagged as urban and affected from moderate traffic.

Civan (2010) measured atmospheric levels of organic compounds at Bursa urban atmosphere at summer and winter. Weekly passive sampling campaigns at 52 sites were performed during the study. According to the Table 4-4, the measured VOC concentrations in this study were found to be higher than the reported VOC levels of Bursa by Civan (2010) except that the traffic originated compounds i.e., benzene and 1,3-butadiene. Please note that, as asphalting operations were performed during the first campaign, higher NMTVOC concentrations were recorded in the present study. However, since traffic route was changed due to asphalting activities, emissions from gasoline exhaust decreased at our station. Therefore, the reasons for such a difference in measured concentrations of organics in Bursa atmosphere may be explained by differences in sampling methodology, source strength and meteorology.

It can be said that the average VOC concentrations measured in European and North American cities are quite similar to those measured in the present study. However, the levels of VOCs in developing countries in South America and Asia are much higher than those in developed countries. As the measured VOC concentrations in the present study were compared with the VOC levels of other cities, in general, measured values were found relatively lower than in developing countries such as Manila and Sau Paulo. Moreover, measured concentrations are relatively similar or a bit higher than those measured in developed cities such as Paris and Berlin. There is one point to note in such a comparison. Since VOC levels in any city is a strong function of traffic activity, one would expect to see lower VOC concentrations in Bursa than those measured in cities like Berlin, Paris or Toronto, because in an earlier study in our group it was demonstrated that number of vehicles in those cities are a factor of four higher than the number of cars in in Bursa traffic (Kuntasal et al., 2013). Similar VOC concentrations in Bursa with those cities probably indicate uncontrolled emissions in Bursa.

Table 4-4 Comparison of the measured concentrations of the VOCs with literature (mean concentrations, µg m^{-3})

	This Study		**Literature**														
Compound name	**Bursa, Turkey**		**4 sites in Ankara, Turkey**[1]	**İzmir, Turkey**[2]		**Bursa**[5] **W/S**	**3 sites in Canada**[4]	**Hong Kong, China**[3]		**Manila, Philippin.**[6]	**Kolkata, India**[7]	**Sao Paulu, Brazil**[6]	**Caracas, Venez.**[6]	**London, UK**[8]	**Paris, France**[8]	**Berlin, German.**[8]	**Pamplona, Spain**[8]
	1st	**2nd**		**W**	**S**			**W**	**S**								
Ethylene	8.96	16.51					4.61-5.52										
Propane	3.71	2.57					8.34-37.64										
Acetylene	3.96	4.54					3.28-6.16										
Propylene	5.31	4.78					1.09-1.82										
Isobutane+n-butane	27.84	25.65					4.59-19.37										
Cyclopentane	2.23	1.96					0.50-2.15										
n-Pentane	0.87	0.90				0.97/0.34	3.05-21.18										
1,3-Butadiene	0.74	0.51				0.39/0.16	0.19-0.36										
Cyclopentene	0.51	0.26					0.08-0.09										
1-pentene	0.36	0.25					0.22-0.25										
2,2-Di-M-Butane	1.28	1.03					0.31-0.81										
2,3-Di-M-Butane	0.48	0.39					0.72-1.70										
2-Methylpentane	1.59	1.46	1.76-3.72				2.42-6.75										
3-Methylpentane	0.83	0.79					1.48-3.78										
n-Hexane	3.20	1.13	3.62-11.96			0.66/0.46	1.55-6.32			9.5			18.8				
Benzene	3.68	4.03	7.32-21	10.4	3.31	8.21/2.26	2.03	5.07	2.97	12.6	33.56	16.7	14.2	2.7	4.0	6.9	2.84
2,2,3-Tri-m-butane+ 2,3-Di-m-pentane	0.51	0.38				0.28/0.36	1.26-1.49										
2-Methylhexane	0.93	1.06				0.73/0.74	0.90-1.57										
3-Methylhexane	2.24	0.99				0.92/0.89	0.37-0.69										
Heptane	0.69	0.56				0.85/0.61	0.86-2.30			8.4		11.1	10.5				
M-cyclohexane	0.45	0.26				0.33/0.16	0.53-2.54										
Toluene	27.86	19.15	7.05-23.96	13.5	15.39	23.41/25.21	4.54-5.38	26.44	26.22	168	41.41	28.1	28.9	7.2	15.0	13.8	13.26

Table 4-4 (Continued)

2-M-Heptane	0.88	0.36				0.81/0.45	0.37-0.69										
1-octene	0.44	0.21					0.05-0.08										
Octane	0.56	0.40	0.53-1.14	0.04	0.07	0.65/0.32	0.37-0.91										
Chlorobenzene		0.13				0.51/0.59											
Ethylbenzene	2.39	1.73	1.36-4.21	1.60	3.65	3.37/3.77	0.91-1.38	2.61	3.18	21.9	10.96	6	5	1.4	3.0	2.8	2.15
M,p-Xylene	6.38	5.07	4.16-5.63				3.32-4.80	2.78	3.99	55.8	15.69	18.5	16.4	3.7	7.0	7.5	3.38
Styrene	2.94	1.43	2.62-4.33	1.57	ND	1.32/0.36	0.92										
1-nonene	0.97	0.36				8.87/10.87	0.06-0.07										
o-Xylene	1.09	0.87	1.49-5.75			1.52/1.33	1.15-1.70	2.03	3.06	16.8	12.49	6.2	55.8	1.5	4.0	2.9	2.63
n-Nonane	0.65	0.62	0.68-1.13			0.41/0.18	0.33-0.91										
1,2,4-Trimethylbenzene	1.03	0.82	1.67-4.25	0.43	0.80	3.21/0.57	1-1.62	2.15	2.59								
n-decane	1.27	1.22				1.98/0.7	0.51-3.88										
1,2,3-trimethylbenzene	1.95	1.27					0.3-0.38										
1,3-Di-E-Benzene	0.48	0.22					0.07-0.09										
1,4-Di-E-Benzene	0.69	0.38				0.37/0.13	0.19-0.23										
1,2-Di-E-Benzene	0.37	0.42					0.04										
Undecane	0.32	1.15															
Dodecane	4.23						0.18-0.32										
Napthalene	0.88	0.81	1.94-7.38	0.61	0.90	0.21/0.13											
Hexylbenzene	1.81	0.85					0.12-0.14										

[1] Kuntasal, 2005; [2] Elbir et al., 2007; [3] Ho et al., 2004; [4] Ayers, 2002; [5] Civan, 2010; [6] Gee and Sollars, 1998; [7] Dutta et al., 2009; [8] Kerbachi et al., 2006; [8] Parra et al., 2009;
1st: 1st campaign; 2nd: 2nd campaign; W:winter; S:summer; ND: Not Detected.

4.4 Relation of the Pollutant Concentrations with Meteorological Parameters

4.4.1 Light Hydrocarbons

4.4.1.1 Effect of Temperature on the Measured Light Hydrocarbon Concentrations

Variation of selected light hydrocarbon concentrations (with carbon numbers between 2 and 5) with temperature is given in Figure 4-8. Almost all VOCs measured in this study depicted a statistically significant ($p<0.05$) decrease with increasing temperatures in both campaigns. The only exception to this common trend was observed in temperature dependence of 3-m-1-pentene for the first campaign. This compound, in the first campaign, behaved differently from other VOCs not only in its temperature dependence, but also in its diurnal pattern, which will be discussed in coming sections. It did not display a diurnal traffic pattern with two rush-hour maxima as observed in most of the other VOCs, indicating that traffic emissions were not the main source of this compound. An important source of 3-methyl-1-pentene, especially for the first campaign, is probably solvent evaporation with minor contribution from traffic. 3-methyl-1 pentene can be utilized for the production of aerosol coating materials and aerosol propellants (EPA, 2007). These types of evaporative sources proved to be effective in this study as there was a hospital in the close proximity of our station. High concentrations of 3-m-1-pentane can also be attributed to an increase in evaporation of 3-m-1-pentene from fugitive sources at higher temperatures (Cetin et al., 2003). In the source apportionment exercise which will be discussed in Chapter 5, 3-m-1-pentane was found to be associated with industrial sources and gasoline evaporation but not with vehicle exhaust. Both of these sources of 3-m-1-pentane are consistent with its increasing concentration with temperature. As mentioned above, remaining VOCs showed decreasing concentrations with increasing temperature in both campaigns. There may be several reasons for such behavior, three of which are relevant to this study:

1. Enhanced photochemistry during summer
2. Seasonal variations in source strengths
3. Dilution due to meteorology

High temperatures and high solar flux promote the photochemical removal of VOCs and thus facilitate faster removal of VOCs from the atmosphere (Ho et al., 2004; Parra et al., 2006). Although higher solar flux and not temperature is the main reason for enhanced photochemistry, it can appear as if it is dependent on temperature because solar flux itself is closely related with temperature.

Seasonal variations in source strength can also appear to be temperature dependent if they decrease in the summer. Such dependence is frequently observed for conventional pollutants that are emitted from combustion. Since combustion decreases in urban areas in summer, less pollutant will be emitted from combustion in summer when temperature is high. However, seasonal variation of VOC sources is probably not an important factor in observed dependence of VOC concentrations on temperature, because the two most important VOC sources in urban airshed, namely traffic and solvent evaporation are not expected to decrease in summer when temperature is high. On the contrary, evaporative sources are expected to increase in summer with increasing temperature.

Dilution due to meteorological factors is one of the most important reasons for the observed temperature dependence of VOC concentrations. As discussed in the previous section, mixing height and ventilation coefficient are both higher in summer. This means that pollutants emitted to the atmosphere will be diluted in a larger volume in summer. This will result in lower concentrations of VOCs in summer, thus an inverse dependence of VOC concentrations on temperature. The effect of variations in mixing height on VOC concentrations are frequently cited in literature (Sistla et al., 1995; El-Fadel et al., 2002; Yuan et al., 2009). Relative contributions of meteorology and photochemistry on the apparent dependence of concentration on temperature are difficult to assess.

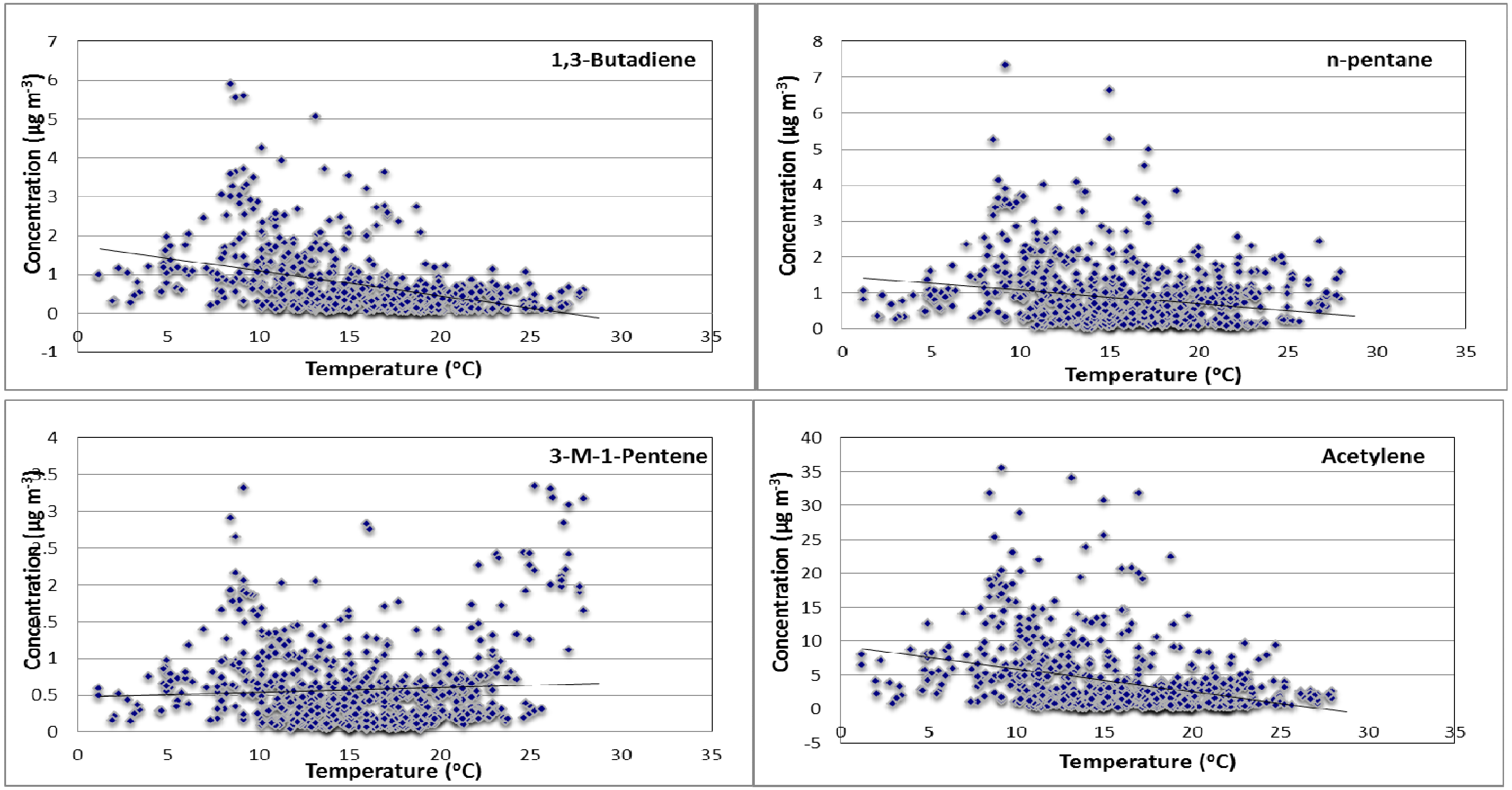


Figure 4-8 Relation of the selected light hydrocarbons concentrations with temperature

4.4.1.2 Effect of Wind Speed on the Measured Light Hydrocarbon Concentrations

A variation of concentrations of selected VOCs with wind speed is depicted in Figure 4-9. Although concentrations of light VOCs shown in the figure decreased with increasing wind speed, high VOC concentrations were also detected at very low concentrations (bimodal distribution). Bimodal distribution indicates that there would be two sources of organic compounds in the atmosphere. Similar patterns were observed in concentrations of all measured species in a statistically significant manner ($p<0.05$). Decreasing concentrations of pollutants with increasing wind speed is very frequently reported in literature and is not specific for Bursa (Filella and Penuelas, 2006; Wang et al., 2009; Ojiodu and Uwadia, 2013). Observed pattern is due to more effective ventilation of the city with faster winds. Consequently, higher wind speed produced stronger ventilation in Bursa as reported for other cities (Filella and Penuelas, 2006).

4.4.1.3 Effect of Mixing Height on the Measured Light Hydrocarbon Concentrations

Mixing height (MH) determines the volume in which pollutants, including VOCs, are present. Deeper MH indicates that emitted pollutants are diluted in larger volume and results in low concentrations of pollutants. Shallow mixing height on the other hand leads to emitted pollutants being dispersed in a small volume, resulting in higher concentrations. Based on this argument, one would expect to see an inverse relation between MH and VOC concentrations (VOC concentrations are expected to decrease with increasing mixing height). Variation of concentrations with MH is depicted in Figure 4-10 for selected VOCs in Bursa atmosphere. The patterns for VOCs included in the figure are typical and most of the remaining VOCs showed similar patterns. The decrease in VOC concentrations with increasing MH was statistically significant ($p<0.05$). .

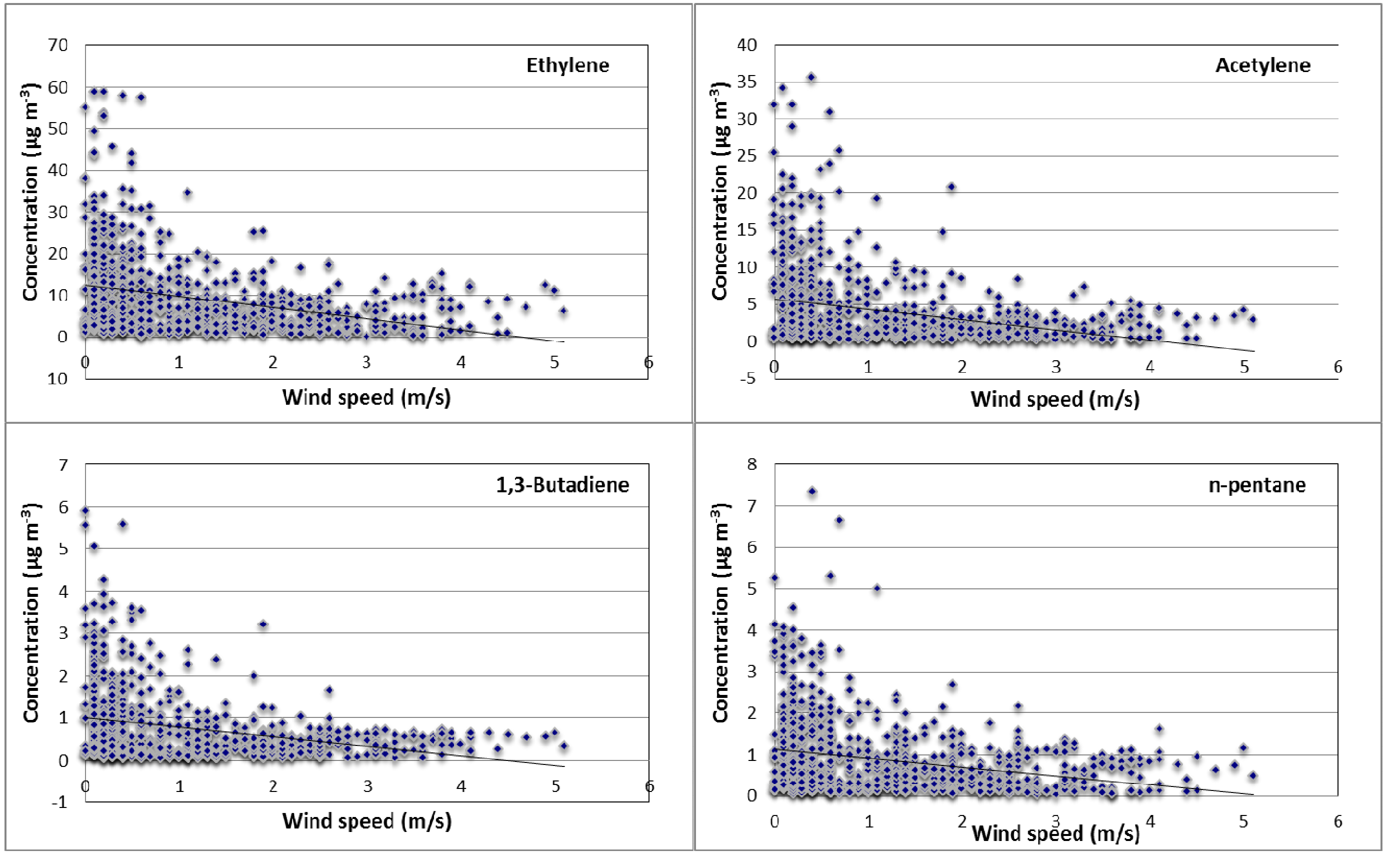


Figure 4-9 Relation of the selected light hydrocarbons concentrations with wind speed

The observed pattern clearly demonstrates that mixing height is an important meteorological parameter controlling concentrations of VOCs. The only exception to this pattern was the behavior of 3-m-1-pentene concentrations in the first campaign. Although 3-m-1-pentane also showed a slight decrease with increasing MH, the variation was not statistically significant. There are two important point to note regarding the MH dependence of VOC concentrations; (1) this dependence was the same for all VOCs and thus weakens the source-related correlations and source apportionment using multivariate statistical tools such as FA and PMF. (2) Since the MH varied both seasonally and diurnally, seasonal and diurnal variations in VOC concentrations should be affected from temporal variation in MH.

Dependence of pollutant concentrations on MH is not unique to this study. Since variation in meteorology is more or less same in everywhere (at least in temperate latitudes), such dependence has been observed in many studies (for example, Yang et al., 2005; Filella and Penuelas, 2006).

4.4.1.4 Effect of Wind Direction on the Measured Light Hydrocarbon Concentrations

The “pollution rose” is a useful and simple method for relating pollutant concentrations to wind direction. That relation, in turn, provides information on locations of potential sources of pollutants. In this approach, average concentrations of VOCs were calculated for each wind sector. For the preparation of the pollution roses, only winds >3 m s^{-1} were considered because low wind speed periods can cause lack of directionality in the source contributions. However, in the present study, winds > 3m s^{-1} constituted only about 10% of the total samples. Therefore, winds > 2 m s^{-1} was taken for preparation of the pollution roses for both campaigns. This increased the percentage of usable wind data to 35. Wind roses prepared for the first and second campaigns are given in Figure 4-11. Wind direction was discussed in detail in section 4.1. Discussion of wind roses in this section involves winds faster than 2 m s^{-1}. Discussion in section 4.1 was necessary to understand meteorology in the study area. Discussion of direction of fast winds in this section is also necessary, because these are the winds that can be related to pollution sources. Wind roses given in Figure 4.11, is not exactly the same with roses given in Figure 4.12, owing to different percentages of clams (or winds with speeds < 2 m s^{-1}) in different wind sectors. As can be seen, there was no wind (>2 m s^{-1}) passing through SSE, SE and S sectors. Wind frequency from these sectors was zero for both campaigns. Furthermore, as the frequencies of N and SSW sectors were very low (<1%), these sectors were also excluded from pollution roses as their uncertainty would be very high.

Dominant wind direction in both campaigns was from WSW. However, there were significant differences between the wind roses prepared for the two campaigns. In the first campaign (fall) there was a fair percent of flow from W, WNW, NW, N, ENE, E and ESE sectors. However, in the wind rose prepared for the second campaign (spring), the main flow was from WSW (as in the first campaign) with a minor flow from NNW sector; flow percentages from all other sectors were negligibly small. This type of flow pattern indicates that we can expect to have intercepted emissions from more diverse sources in the first campaign and from a more limited number of sources in the second campaign. Low frequency of winds from certain sectors suggests that contributions of these sectors to measured concentrations of VOCs at our receptor will be low, no matter how high emissions in these sectors are.

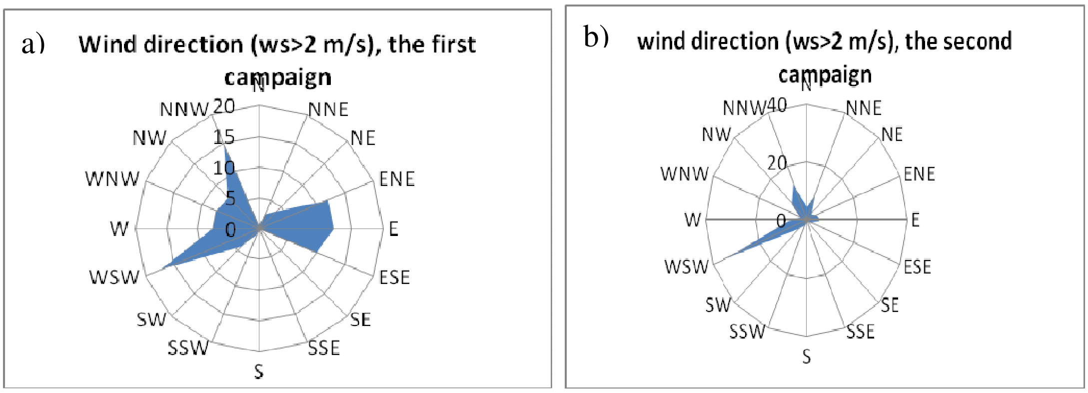


Figure 4-10 Wind direction (%) for a) the first and b) second campaigns

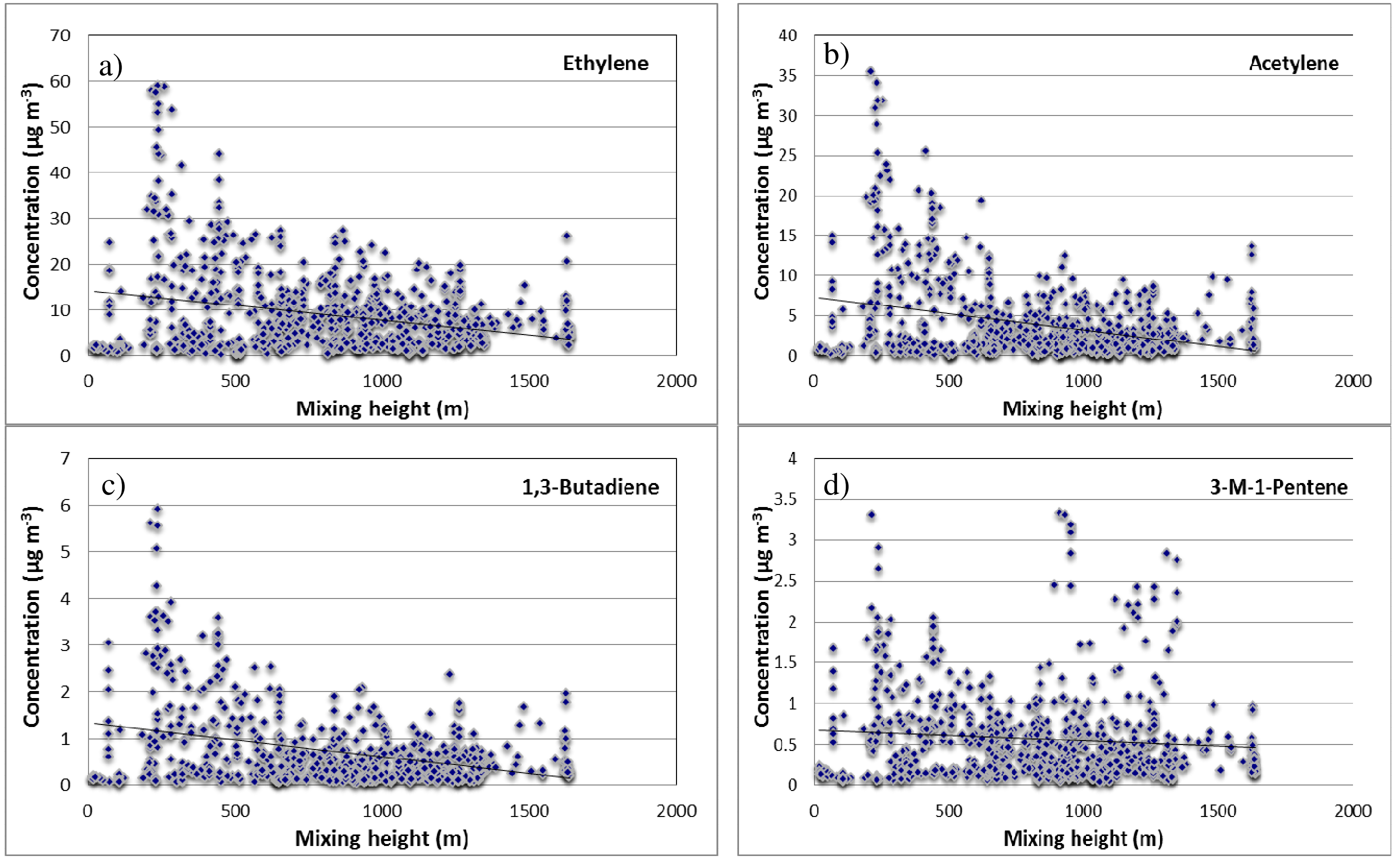


Figure 4-11 Relation of the selected light hydrocarbons concentrations with mixing height

Pollution roses for the light hydrocarbons for the first and second campaigns are given in Figures 4-12 and 4-13, respectively. Pollution roses were prepared for all measured compounds, although only selected compounds are displayed in the Figures. Distributions of potential sources that can affect our station are depicted in Figure 4-14. Bursa is an industrial city, but industry is not randomly distributed around the city. Three large "organized industrial districts" host most of the industrial emissions in Bursa. The largest of these strong industrial source areas is located 10 km to the NW of our station. The second one is located 9 km to the NE of the station and the third one is 12 km to the E of the station. Another important source area is the city center. The highest density of population and traffic activity occurs in the city center, which is approximately 3 km to the NE of the station. Winds from city center are expected to bring high concentrations of VOCs, which are associated with traffic and residential emissions. Another important source that can contribute to measured concentrations of VOCs at our station is the hospital. Bursa state hospital might have been an important source of some of the VOCs measured at our site, because it is only few hundred meters from the station and solvents are used in its laboratories. However, contribution of the hospital on concentrations of some of the VOCs is unclear. Bursa State hospital is located to the SW of the station.

Compounds with similar sources are expected to have similar pollution roses. There are similarities between pollution roses of many of the VOCs in the first campaign due to their common sources. The most obvious common source for the light VOCs is light duty traffic emissions. Compounds that are good markers for light duty vehicle emissions, such as, 1,3-butadiene, n-pentane, acetylene, ethylene, propane and isobutane+n-butane (Borbon et al., 2002), demonstrated similar pollution roses shown in Figures 4-12b, 12c and 12d. These roses indicate that contributions of NNE, NE, ENE, E and ESE to light duty vehicle emissions recorded at our station were high. A smaller contribution was also observed from sectors WNW, W, WSW and SW. It should be noted that lack of contributions in the remaining sectors is not due to lack of sources in those sectors, but rather due to lack of winds faster than 2 m/s. The first group of sectors, which extends from NNE to ESE includes most populated part of the city, including the “Heykel” area, which is considered as the city center. The traffic density in these sectors is the highest among all sectors

3-m-1-pentene had a unique pattern, with a specific source at NNE sector. The diurnal pattern displayed by this compound was also significantly different from diurnal patterns depicted by other compounds, which were associated with traffic emissions. Moreover, correlations between 3-m-1-pentene and other traffic markers are fairly low as will be discussed in the coming sections. Although the main source of 3-m-1-pentene was traffic (Watson et al., 2001), in this campaign, evaporative sources were also identified.

In the second campaign, compounds related to motor vehicle emissions such as ethylene, 1,3-butadiene, and acetylene had higher average concentrations at ESE sector due to the presence of the city center, where traffic density and hence emissions occurred (Figure 4-13). In addition to the ESE sector, NNE sector had the second greatest contribution for most of the traffic related target compounds.

Pollution roses between the two campaigns have both similarities and differences. Some of these differences may be partly due to significantly different wind patterns during the two campaigns and partly due to asphalting operations, which will be discussed in the coming sections. NNE, NE, ENE, E and ESE are the sectors with high concentrations of majority of VOCs in both campaigns. Although concentrations of VOCs were high in these sectors in both campaigns, fall concentrations of VOCs in each of these sectors were significantly lower than corresponding concentrations in spring season On the other hand, sectors WNW, W, WSW and SW, had fairly low concentrations in the first campaign (fall) but, had higher average VOC concentrations in the second (spring) campaign.

Since fast winds did not blow from the remaining six sectors in the first campaign average concentrations of VOCs in these sectors were not calculated. Concentrations of VOCs in these six sectors were low. Pollution roses of traffic markers, such as BTX compounds, from the two campaigns are fairly similar to each other. However, there are some small differences in pollution roses prepared for VOCs that have potential sources other than traffic. For example, compounds that are well documented markers for gasoline evaporation, n-pentane, 2-m-pentane, 3-m-pentane and 3-m-1-pentene (Watson et al., 2001) also had slightly different sector averages due to differences between locations of exhaust emissions and evaporative emissions (mostly gas stations).

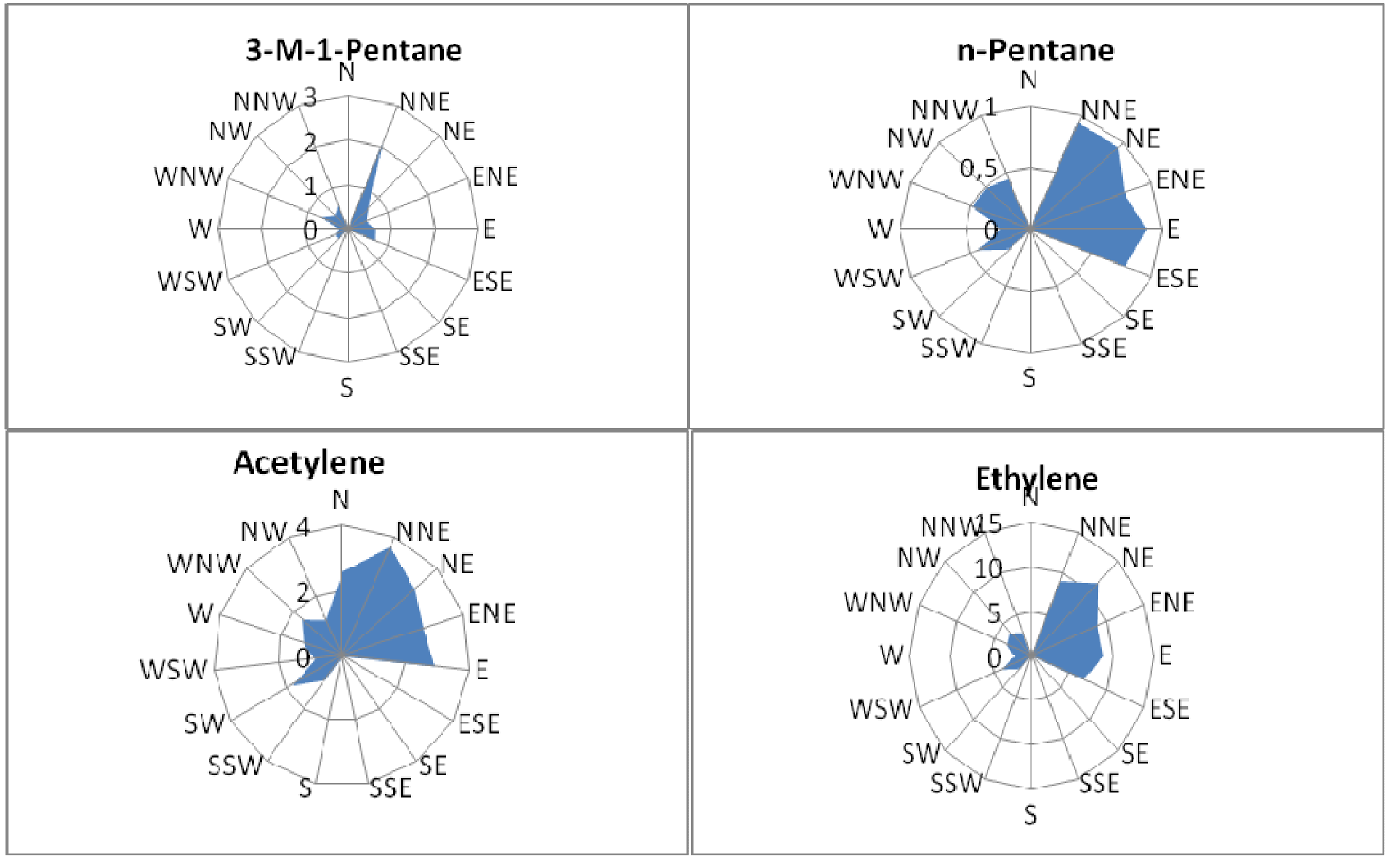


Figure 4-12 Pollution roses prepared for the selected light compounds during the first campaign (µg/m^3)

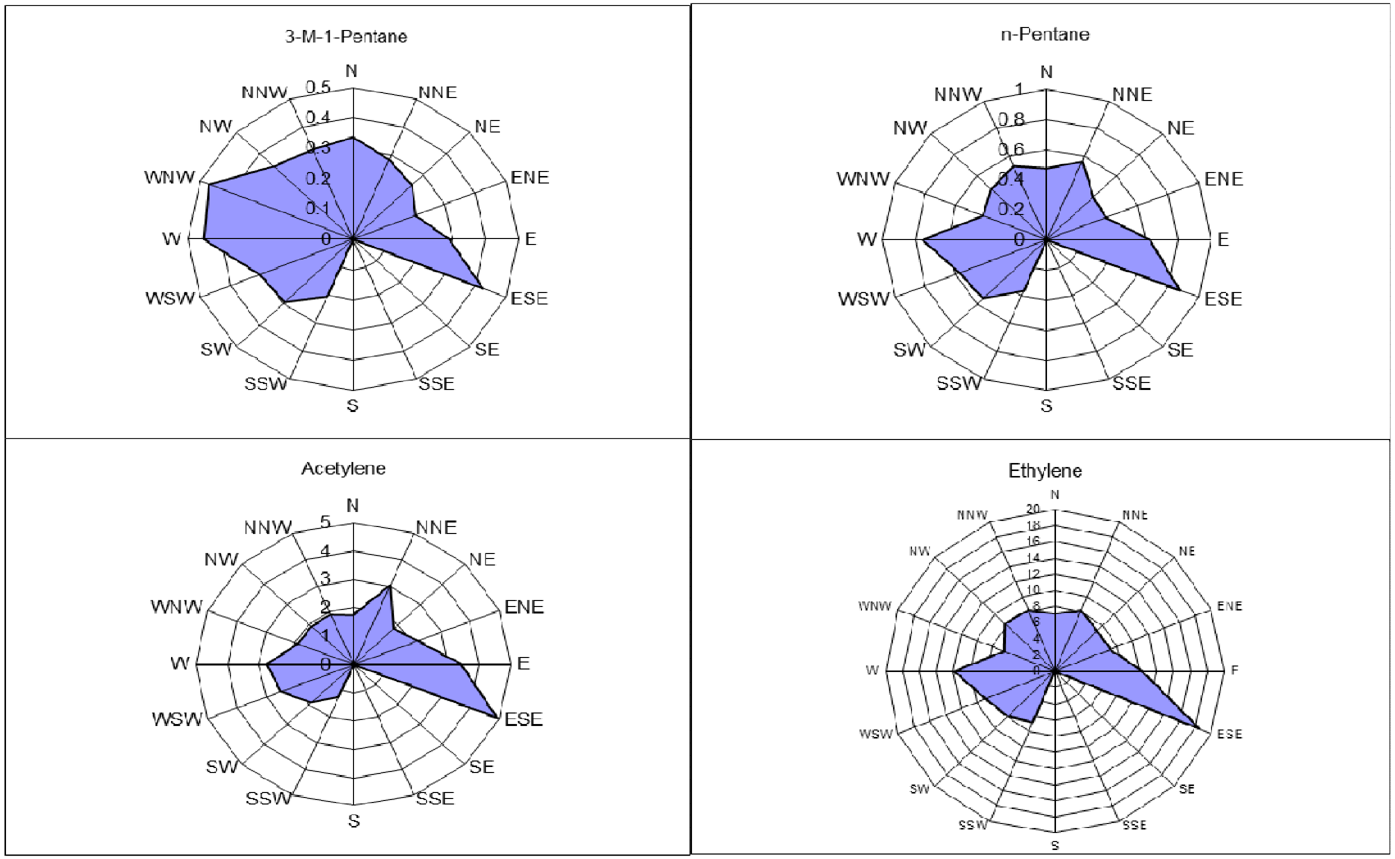


Figure 4-13 Pollution roses prepared for the selected light compounds during the second campaign (μg/m^3)

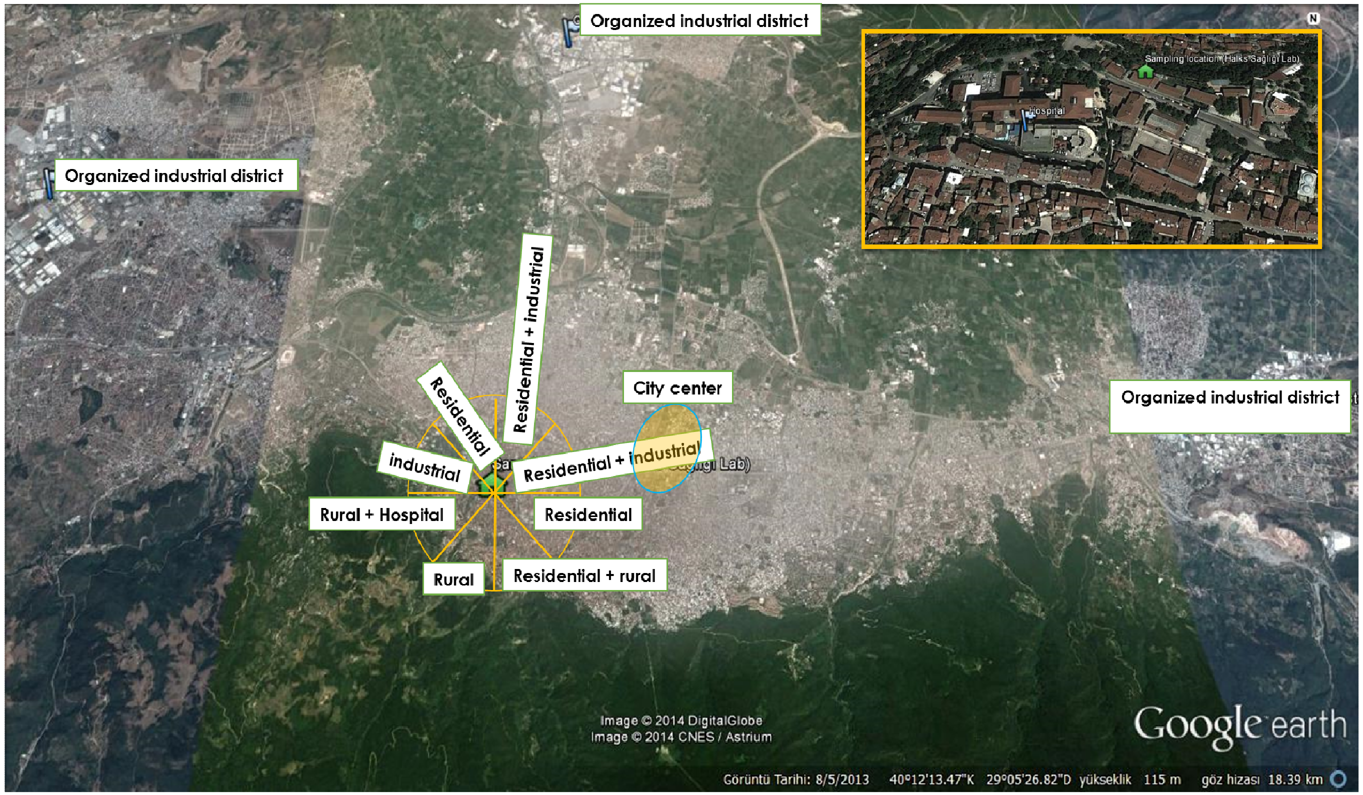


Figure 4-14 Distribution of sources among wind sectors

Contribution of wind frequencies to the Pollutant Rose

During the study, sometimes low frequencies of winds which carried high organic load from certain sectors were observed. If these winds were directly used for the preparation of pollution roses, they would not represent the real situation at our receptor point because receptor point was mostly affected by the prevailed wind direction with the highest percent of frequency. Therefore, in order to see the effect of the wind frequencies on pollutant roses, frequency of each wind sector was normalized and obtained values were multiplied with average concentration of the pollutants on each wind sector. In this way, contribution of low frequency of winds from certain sectors to measured concentrations of VOCs at our receptor would be low, no matter how high emissions in these sectors are. Normalized pollution roses for the selected light compounds are shown in Figure 4.15.

The main sectors were found to be ENE, E, ESE and WSW for the first campaign. In addition to these sectors, NNW sector had a smaller contribution. Due to low frequencies of the winds from N, NNE and NE sectors, contributions from these sectors to measured concentration of VOCs at sampling point was very low although very high emissions were recorded in these sectors. In the study, normalized pollutant roses of the many light VOCs were found to be similar to each other. Since compounds with similar sources are expected to have similar pollution roses, VOCs at our receptor were found to be related with traffic: Because city center where the traffic density is very high was located between NNE and ESE sectors. Major differences were not observed between with (Figure 4.15) and without normalized (Figure 4.12) pollutant roses for the selected compounds. Therefore, contributions of ENE, ESE and E sectors to light duty vehicle emissions measured at sampling location were found to be high. .

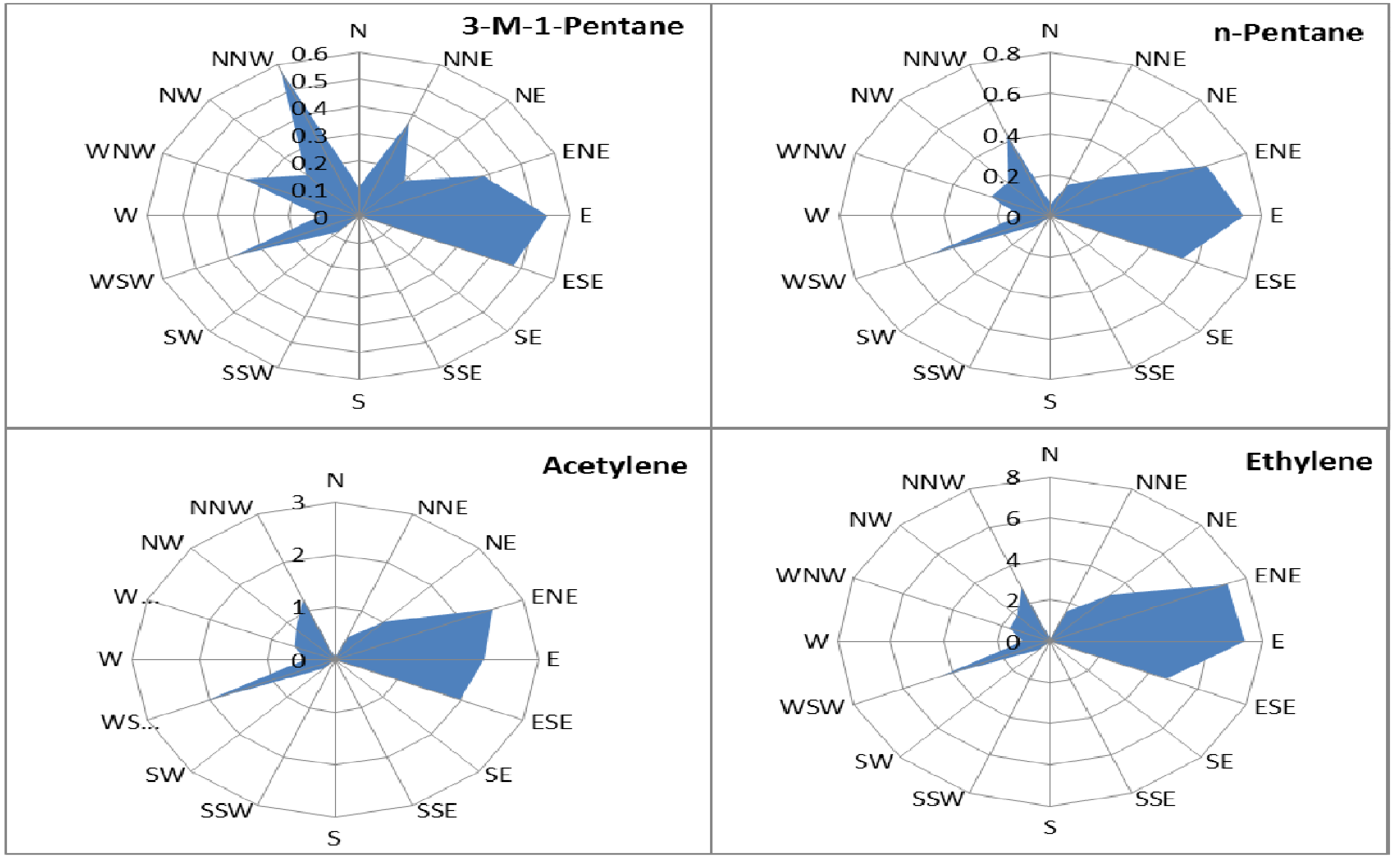


Figure 4-15 Normalized pollution roses prepared for the selected light compounds during the first campaign

The pattern of the 3-m-1-pentene had also found to be different than the other VOCs. The dominant sectors were NNW, NNE, ENE, E and ESE. Although very low wind frequency from NNE sector, contribution from this sector was also found to be high like the pollution rose of the 3-m-1-pentene (Figure 4.12a) due to very high concentration on this wind sector. As the diurnal pattern of the 3-m-1-pentene is different than the traffic, the evaporative source of this compound was identified as NNE sector in addition to WSW, NNW, ENE, E and ESE which are the dominant wind sectors. Dominant sectors had the highest contributions. Therefore, frequencies of the wind were found to be very effective on the measured concentration of VOCs at receptor point.

In the second campaign, the dominant sector is WSW for all of the measured light hydrocarbons. In addition to WSW, minor contributions from NNW and NNE were also identified on these plots (Figure 4-16). In the second campaign due to low frequency of winds from certain sectors, very low VOC concentrations were obtained at our sampling point although no matter how high emissions were measured in these sectors and normalized pollutant roses of the light hydrocarbons (Figure 4-16) were found to be very similar to wind rose of the second campaign (Figure 4-11b).

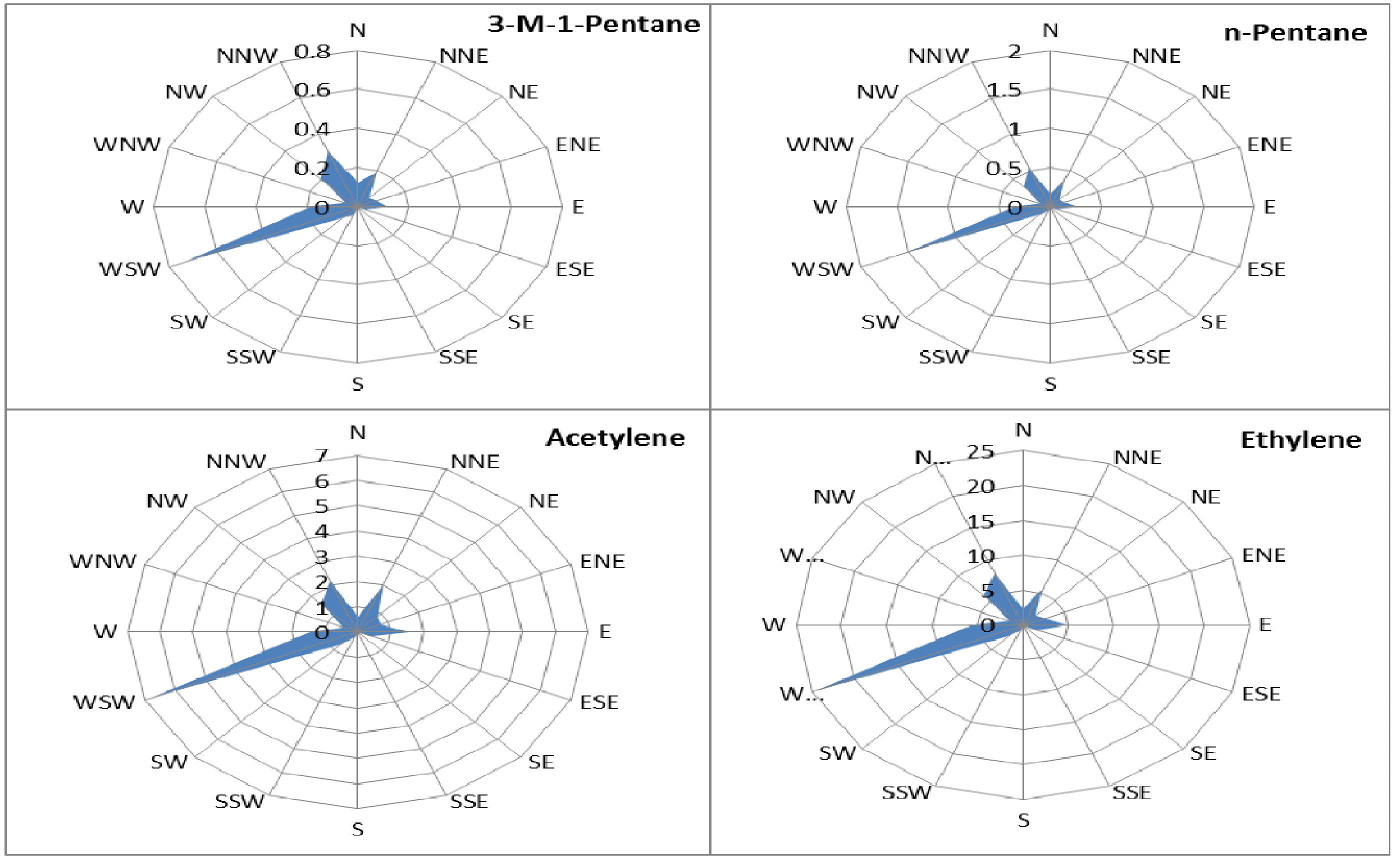


Figure 4-16 Normalized pollution roses prepared for the selected light compounds during the second campaign

4.4.1.5 Effect of Ventilation Coefficient on the Measured Light Hydrocarbon Concentrations

Ventilation coefficient is the product of mixing height and wind speed. Since it is a combined measure of both vertical and horizontal ventilation process in an urban atmosphere, it is expected to be an important parameter that strongly affects concentrations of VOCs (and other airborne pollutants). Ventilation coefficient is considered as an indicator for assimilation capacity of atmosphere (Goyal and Rao, 2007)

Ventilation coefficient in this study was calculated on an hourly basis by multiplying the wind speed, which was obtained from the Bursa meteorological station, with the mixing height, which was calculated using the software RAMMATE, which is meteorological preprocessor used in most dispersion models (Turner, 1994). Calculation of ventilation coefficient and its diurnal and seasonal variation in Bursa atmosphere were discussed earlier in the manuscript and will not be repeated here.

Variation of light hydrocarbon concentrations with ventilation coefficient is given in Figure 4-17. All light hydrocarbons, except for 3-m-1-pentene, showed statistically significant negative correlation ($p<0.05$) with ventilation coefficient, indicating that ventilation process is an important component in temporal and spatial variation of VOC concentrations in Bursa atmosphere. However, it should also be noted that it is not the only source of variability in VOC concentrations, because concentrations are also correlated with sources, as will be discussed later in the manuscript.

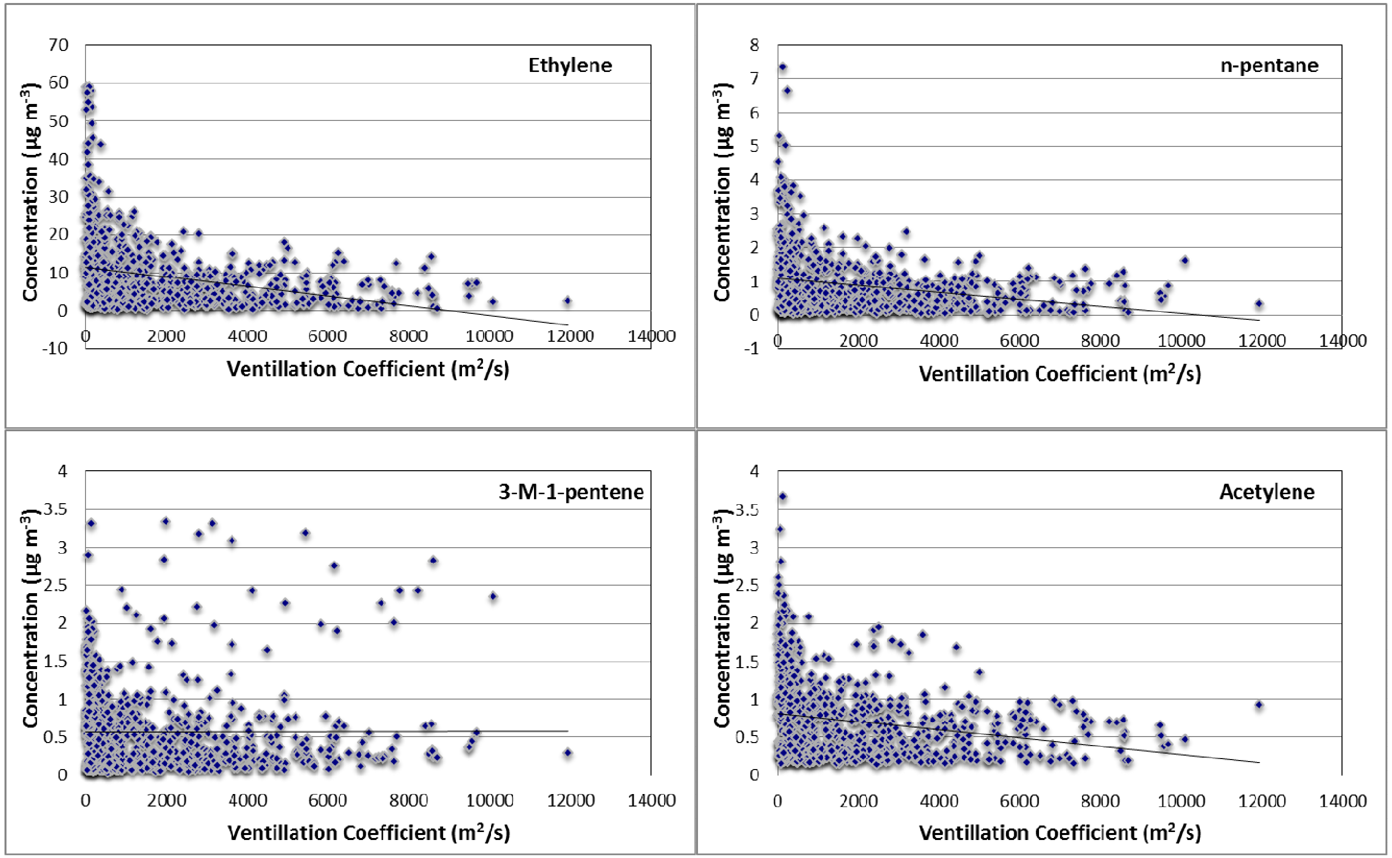


Figure 4-17 Relationship of selected light hydrocarbon concentrations with ventilation coefficient

4.4.2 Heavy Hydrocarbons

4.4.2.1 Effect of Temperature on the Measured Heavy Hydrocarbon Concentrations

Variation of C_6 – C_{12} hydrocarbon concentrations with temperature is depicted in Figure 4-18. Most of the heavy hydrocarbons (62%) carbon numbers between 6 and 12 were found to be inversely proportional ($p<0.05$) with temperature in the first campaign. On the contrary, n-hexane and m,p-chlorotoluene were found to be positively correlated with temperature. Hexane and chlorinated toluene are not only released from the vehicle exhausts, but also used as solvents in both industrial processes and certain domestic activities (Borbon et al, 2022; Guo et al., 2004). Therefore, these compounds may have been released from evaporative sources which were closely located to the sampling location. For the rest of the compounds, namely; 2,2,3-trimethylbutane+2,3-dimethlypentane, 3-m-hexane, toluene, 2-m-heptane, 1-octene, chlorobenzene, ethylbenzene, m,p-xylene, styrene, 1-nonene, 1,3-di ethylbenzene, 1,2-di-ethylbenzene, 1-undecene and undecane, did not show statistically significant relationship ($p>.05$) with temperature during the first campaign. During the second campaign, an inverse relationship ($p<0.05$) was found between the temperature and most of the measured VOC concentrations (48%). However, for 3-methylhexane, 2,2,3-trimethylbutane+2,3,-dimethlypentane, n-butylbenzene, 1,2-diethylbenzene, undecane and n-decane, a statistically significant positive correlation ($p<0.05$) with temperature was observed. As in the first campaign, n-hexane, methylcyclopentane+2,4-dimethylpentane, cyclohexane+cyclohexene, toluene, 1-octene, octane, 2,2,5-tri-m-hexane, chlorobenzene, ethylbenzene, m,p-xylene, 1-nonene, o-xylene, n-nonane, 4-ethyltoluene, 1,4-diethylbenzene, 1,2,3,5-tetra-methyl-benzene, 1,2,4,5-tetra-methyl-benzene, did not show a statistically significant relationship with temperature. These observations suggest that VOCs with carbon number >5 can be divided into three groups based on their dependence on temperature. Concentration of benzene compound and other VOCs which originate primarily from traffic showed a statistically significant negative correlation with temperature. This is typically the case for all VOCs, which has similar emissions in summer and winter and can be explained by more effective ventilation of the city in summer. Since traffic load do not significantly change between summer and winter, higher concentrations of traffic-related VOCs in winter is not surprising. Organic compounds that also have non-traffic sources, particularly from evaporative sources, are expected to increase with temperature as evaporation is enhanced in warm summer months (Cetin et al., 2003). VOCs that did not show a statistically significant relation with temperature and VOCs, for which concentration increase with increasing temperature, are believed to be in this second group.

4.4.2.2 Effect of Wind Speed on the Measured Heavy Hydrocarbon Concentrations

Variation of benzene, toluene, n-nonane and n-decane with wind speed is given in Figure 4-19. An inverse relationship ($p<0.05$) was detected between wind speed and nearly all of the VOC concentrations (94%) due to the dilution effect of wind speed. There were few exceptions to this general feature. Chlorinated compounds such as chlorobenzene and m,p-dichlorotoluene and few non-chlorinated compounds, such as 1-octene, n-decane and 2,2,5-tri-m-hexane did not show any statistically significant correlation with the wind speed in both first and second campaigns. 1,2-di-ethylbenzene and undecane, on the other hand, depicted a statistically significant ($p < 0.05$) increasing trend. No significant relation with wind speed or increase in concentrations of VOCs with increasing wind speed, demonstrate that temporal variation in emissions of these compounds are more influential on variability of their measured concentrations than meteorological parameters. One likely source that can alter meteorology dependence of concentrations of these VOCs is the hospital, which is fairly close to our sampling point.

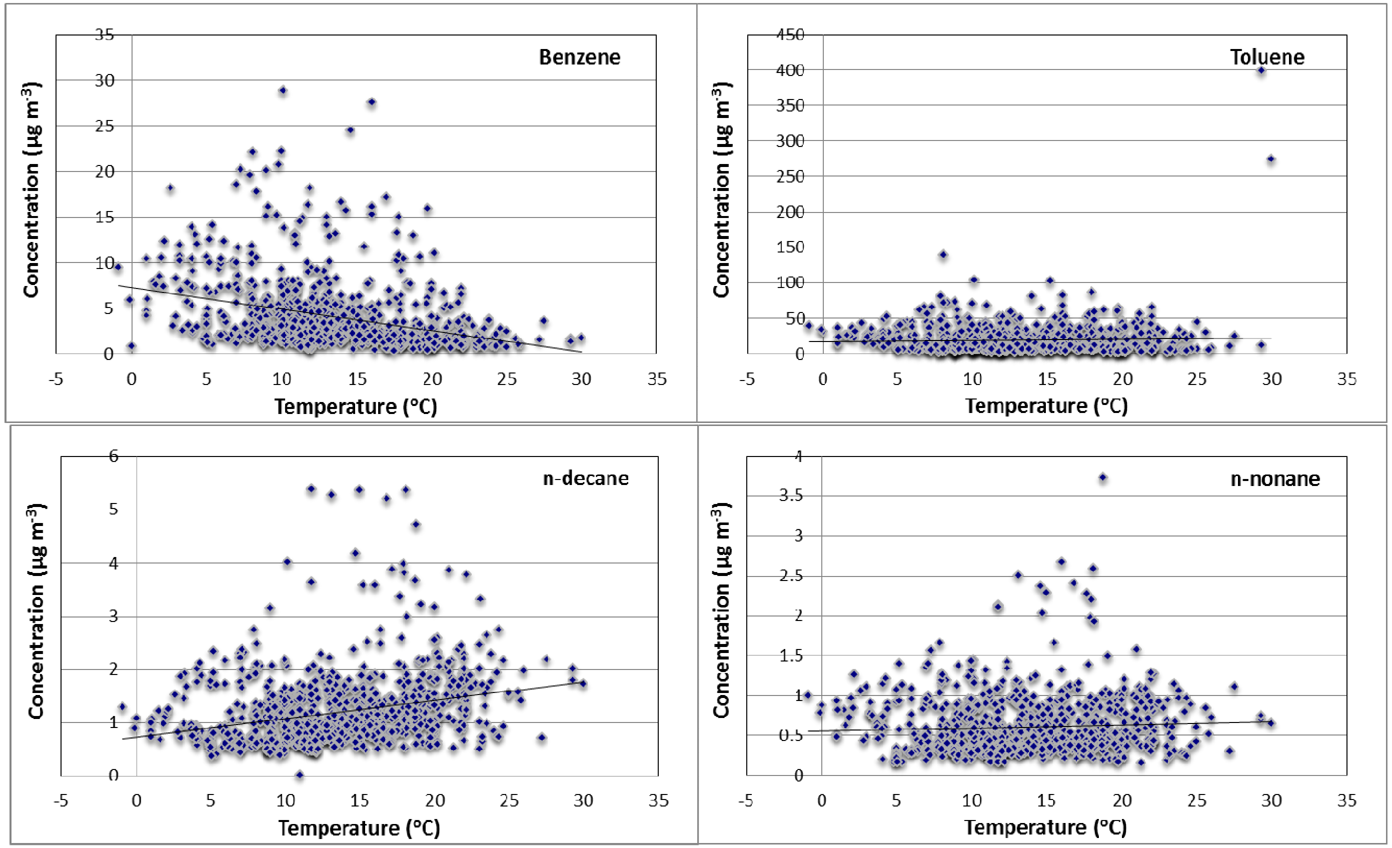


Figure 4-18 Relationship of selected heavy hydrocarbon concentrations with temperature

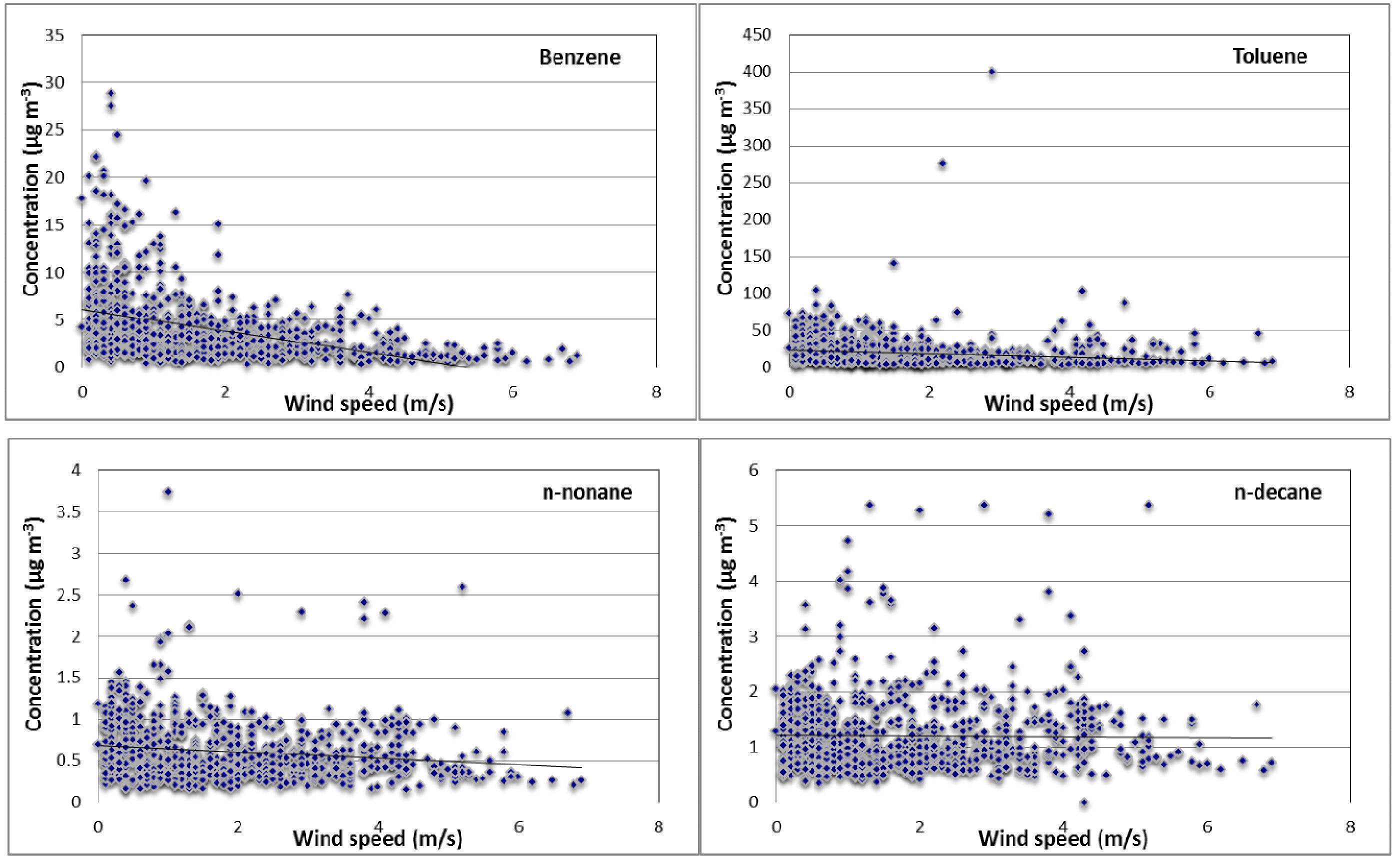


Figure 4-19 Relationship of selected heavy hydrocarbon concentrations with wind speed

4.4.2.3 Effect of Mixing Height and Ventilation Coefficient on Heavy Hydrocarbon Concentrations

Variation of measured heavy hydrocarbon concentrations with mixing height is given in Figure 4-20. With few exceptions concentrations of VOCs decreased with increasing mixing height with a 95% or better statistical significance. The only exceptions to this general trend is m,p-chlorotoluene and 1,2,4-trichlorobenzene in the first campaign and 1,2-diethylbenzene, undecane and n-decane in the second campaign. Please note that these compounds, which are not correlated with mixing height, are the compounds that showed good correlation with temperature.

Variation in concentrations of selected VOCs with ventilation coefficient is given in Figure 4-21. Hydrocarbon concentrations showed stronger negative correlations with mixing height, than those found between light VOC concentrations and mixing height. This is probably because concentrations of heavy VOCs were also strongly correlated with wind speed as discussed in the previous sections.

Since high ventilation coefficient values indicate effective ventilation and good dispersion (Rao et al., 2003), ventilation coefficient, together with variations in emissions, is the most important meteorological parameter in determining temporal variations in concentrations of measured parameters. Statistically a very significant negative correlation ($p<0.05$) was observed for most of the VOCs (95%) in both sampling campaigns. However, for some of the VOCs, including; n-hexane, toluene, m,p-chlorotoluene, chlorobenzene, m,p-xylene, 1-undecene and 1,2,4-tri-chlorobenzene, relationship with ventilation coefficient was not statistically significant, particularly in the first campaign. Furthermore, other meteorological parameters such as temperature, mixing height and wind speed were also found ineffective or positively correlated with some of these identified seven VOCs. In the second campaign, again for most of the VOCs, a significant negative relation ($p<0.05$) was observed between the ventilation coefficient and measured VOC concentrations. For only 2,2,3-trimethylbutane+2,2-dimethylpentane, 2-m-heptane and 1,2,3,5-tetra-m-benzene, no relationships were identified. Therefore, we probably could not detect the effect of meteorology on the measured concentrations of these VOCs because of the fact that these VOCs are used as solvents and are released to the atmosphere from close to sampling station.

4.4.2.4 Effect of Wind Direction on Concentrations of Heavy Hydrocarbons

Pollution roses of the first campaign are given in Figure 4-22. Pollution roses are plotted for all target compounds for both campaigns, however only selected compounds are displayed in the Figure. Compounds originated from motor vehicles had similar sector contributions. For example benzene, TEX, 1,2,4-trimethylbenzene and 1,2,3-trimethylbenzene showed high contributions for both NNE and NE sectors, implying high traffic density at the city center. Concentrations of heavy VOCs in N sector was not calculated owing to lack of winds faster than <2 m s^{-1} in that sector. Some of the heavy hydrocarbons such as 1-undecene, 1,2,4-trichlorobenzene and dodecane had a different pollution roses. Please note that these compounds also had different temporal patterns and diurnal variations from other traffic markers. Sources of these compounds and others were investigated using a multivariate statistical tool, namely positive matrix factorization (PMF), results of which will be extensively discussed later in the manuscript. These three compounds were strongly correlated with the factor that represents asphalting activity around our sampling location. Obviously asphalting operations which took place to the SE of our station are probably the main sources of 1-undecene, 1,2,4-trichlorobenzene and dodecane.

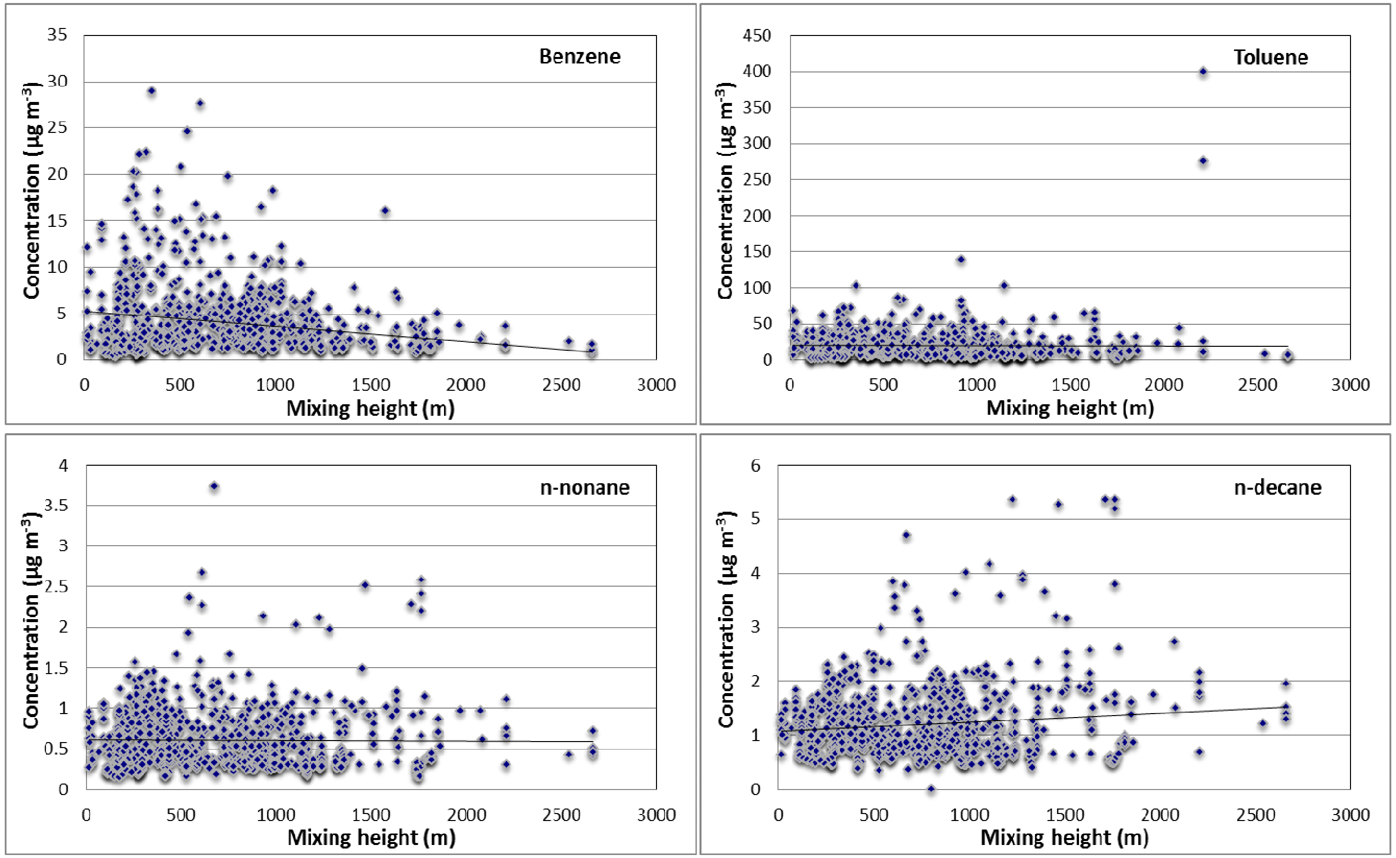


Figure 4-20 Relationship of selected heavy hydrocarbon concentrations with mixing height

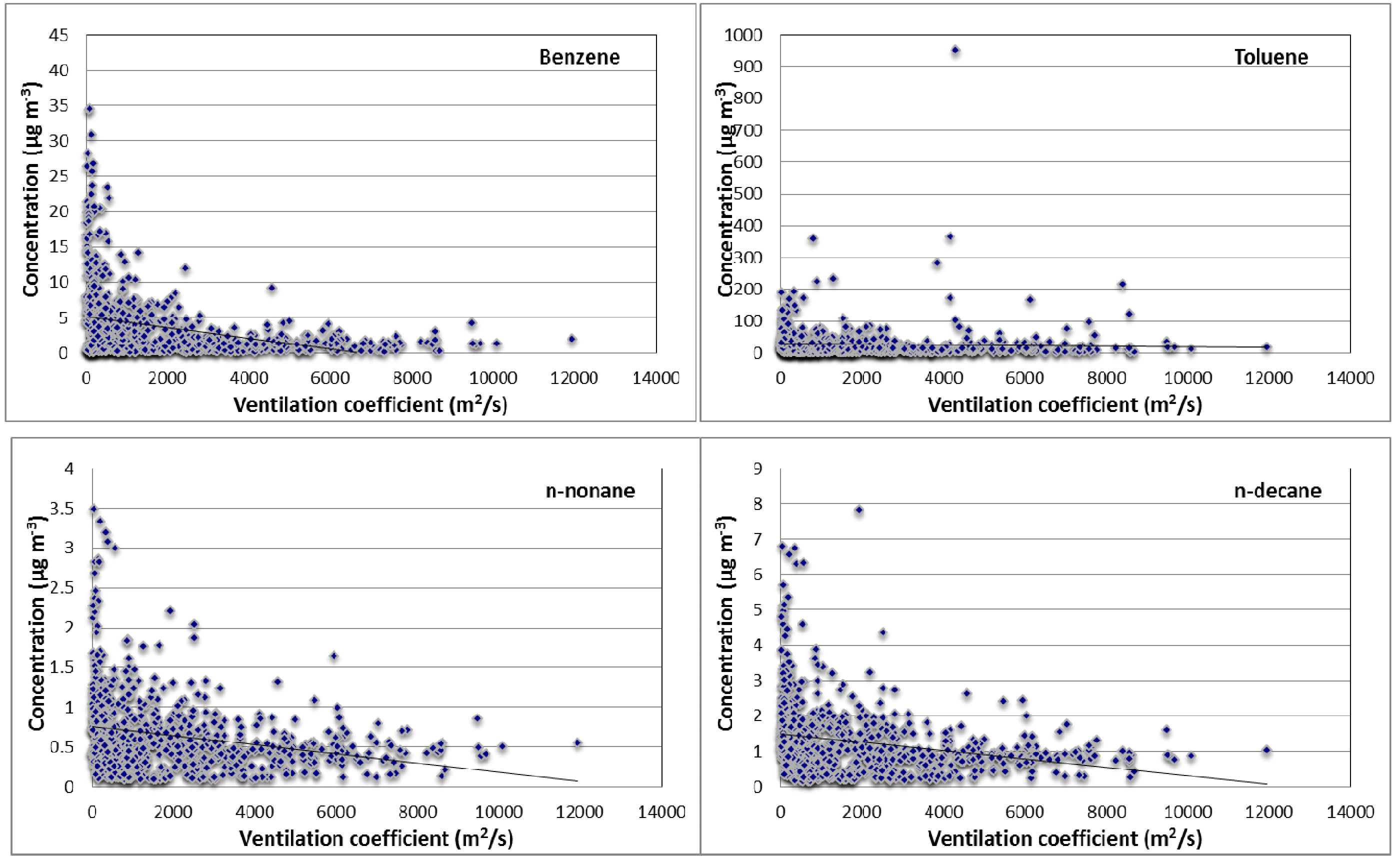


Figure 4-21 Relationship of selected heavy hydrocarbon concentrations with ventilation coefficient

A slightly different pollution rose of n-hexane, with higher concentrations at the NNE sector indicates a source other than traffic. Although traffic is the main source of n-hexane, it is also emitted from variety of solvents used in printing, manufacturing of furniture, toys, shoes, and electronics (Chan et al., 2006). Some of the compounds such as 1-nonene, styrene, 3-m-hexane, m,p-chlorotoluene and 2-m-heptane also had slightly different profiles, with higher concentrations at SSW and NW sectors. These deviations from usual traffic distribution were not observed in Ankara study, which is a city without significant industrial activity. In Ankara VOC study, most of the VOCs, which are also measured in this study, were strongly associated with traffic emissions and their pollution roses were very similar to each other (Kuntasal, 2006). In this study, on the other hand, directional concentrations of many VOCs suggested non-traffic contributions to their measured concentrations. This can be partly due to high intensity of industrial activity and partly due to presence of nearby non-traffic VOC sources, such as hospital and plywood factory. In the study average toluene-to-benzene (T/B) and m,p-xylene-to-ethylbenzene (X/E) ratios were also calculated for each sector, because these ratios are demonstrated to be good tools to assess contribution of non-traffic sources on measured VOC concentrations. Typical T/B value for urban traffic exhaust varies between 1.5 and 3 (Kelessis et al., 2006). Higher T/B ratio indicates that there is a significant non-traffic source of toluene in the study area.

Although traffic is the most important source of both ethylbenzene and xylenes, X/E ratio demonstrate the age of the sampled air, because their decay rates are significantly different (Monod et al., 2000; Nelson and Quigley, 1983; Laowagul et al., 2008), X/E ratios between 2 and 4 are reported for fresh emissions from variety of sources (Nelson and Quigley, 1983; Monod et al., 2000). Directional dependence of T/B and X/E ratios are given in Figures 4-22i and 22j, respectively, for the first campaign.

High T/B ratios were observed at NE, ENE and E directions in this study. This observation indicates the presence of additional sources of the toluene emissions which are emitted from different type of industries or evaporation from painted surfaces (Laowagul et al., 2008). Lower T/B ratios, representative for traffic emissions were observed in other sectors. NE, ENE and E sectors include both residential, traffic and industrial sources. Obviously, there are significant non-traffic sources of toluene in Bursa Atmosphere. These non-traffic sources can both be industrial and/or evaporative in residential areas. The zero contribution at the N sector was because of the lack of winds >2 m s^{-1} blowing from this sector.

The calculated X/E ratio was between 3 and 4 in all sectors during the first campaign. This is expected because transport time of emissions to our sampling point is not different enough to cause a change in X/E ratio. These observations imply that these sectors were under influence of fresh emissions, which is typical in urban environment.

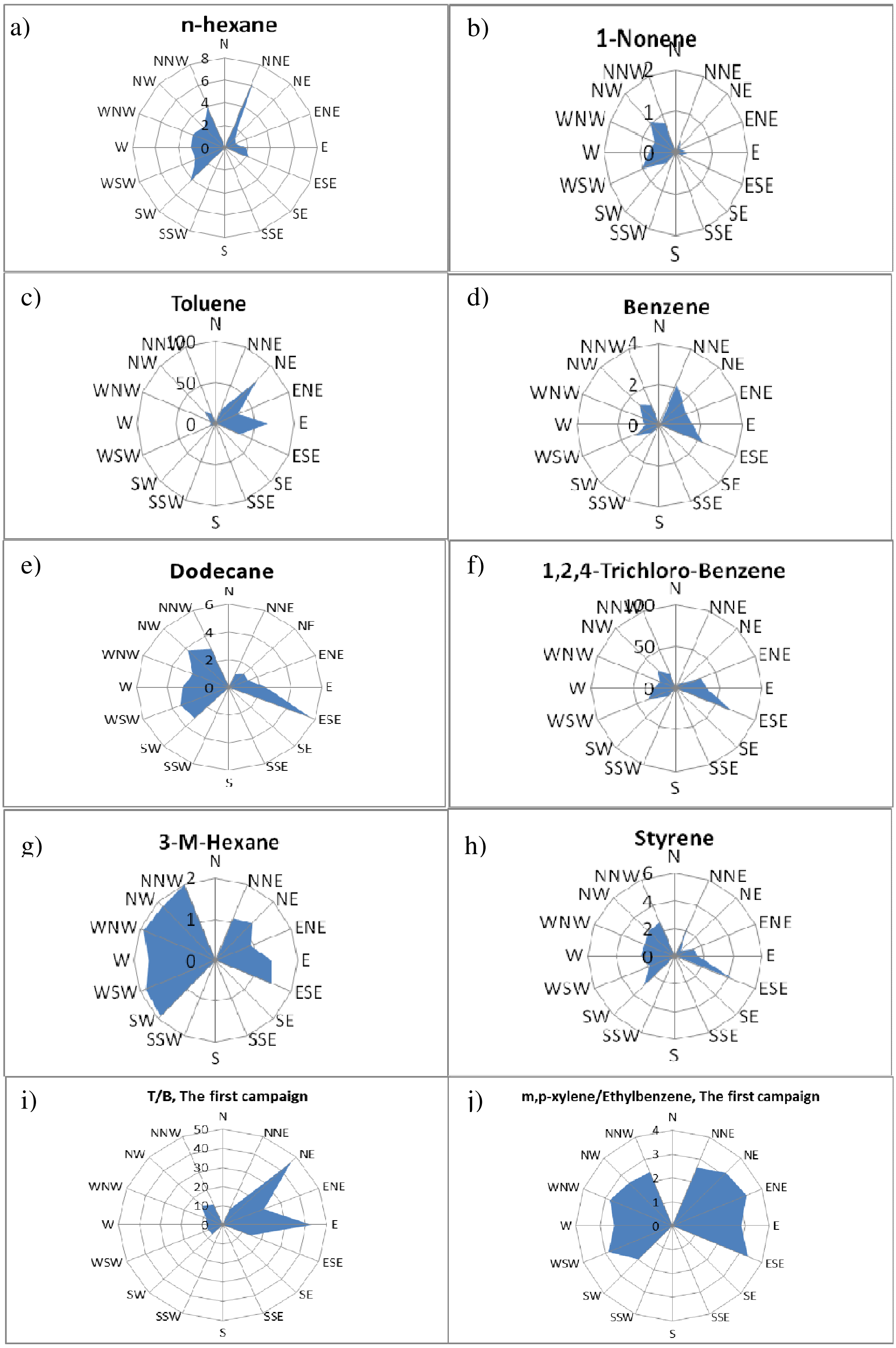


Figure 4-22 Pollution roses for selected heavy hydrocarbons for the first campaign ($\mu g/m^3$)

Pollution roses for selected VOCs during the second campaign are given in Figure 4-23. BTEX compounds, except for toluene have similar distributions of their concentrations in wind sectors. Their concentrations are high in sectors between NNE and E and also in sectors between SSW and NNW. The first range points to the city center and urban traffic and the second range of sectors suggest emissions from Bursa Organized Industrial District, which is located to approximately 10 km to NW of our sampling point. This second high concentration sector, which extends from SSW to NNW is contributed by the Bursa State Hospital which is situated to the SSW of our station. Contributions of these sources to both heavy and light VOCs will be discussed in more detail later in the manuscript, when PMF is discussed.

Directional dependence of T/B and X/E ratios are also depicted in Figure 4-23. The ratio of T/B was about 5 at all sectors except sector SSW, highlighting non traffic sources of toluene in Bursa atmosphere. The most notable point in sectorial distribution of T/B ratio is the very high value of this ratio at SSW sector, demonstrating very high evaporative sources of Toluene in the hospital. The ratio of m,p-X/E was about 3 for all sectors, suggesting that heavy hydrocarbons intercepted at our station are fresh emissions, which is not surprising in an urban environment. These ratios were not calculated for the sectors between E and SSW sectors, because no winds blew from these sectors during the second campaign.

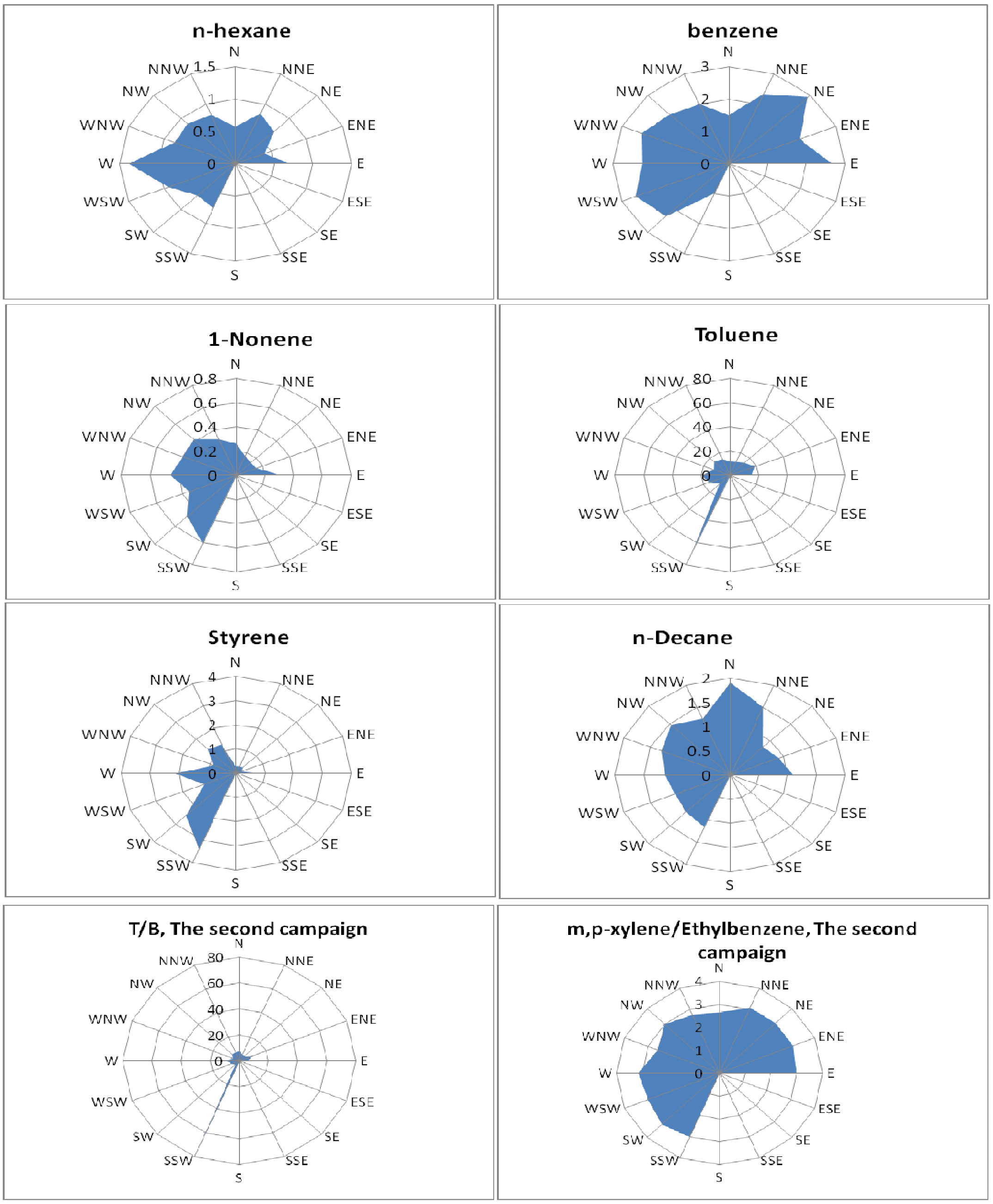


Figure 4-23 Pollution roses for selected heavy hydrocarbons for the second campaign (μg/m^3)

Contribution of wind frequencies to the Pollutant Roses

The effect of the wind frequency is also clearly seen from the pollutant roses of selected heavy hydrocarbons during the first campaign (Figure 4-24). Similar contributions were observed nearly for most of the measured heavy hydrocarbons. WSW, NNW, ENE, E and ESE sectors are the dominant wind directions during the first campaign (Figure 4-11). According to the normalized pollutant roses of heavy hydrocarbons these sectors are also dominant wind sectors. However, some deviations were also observed on pollution roses during the first campaign. For example, compounds originated from traffic such as benzene, 1,2,3-trimethylbenzene and ethylbenzene had higher contributions at ENE, E and ESE as compared to NNW and WSW sectors. Also, E is the dominant sector for toluene. Therefore, although wind frequency is the dominant factor to indicate location of potential sources of pollutant at the receptor, concentration of the compounds was also found to be important for some of the compounds such as toluene, benzene, ethylbenzene and 1-nonene.

The similar pollutant roses for the other heavy hydrocarbons i.e. high contributions from WSW, NNW and ESE clearly imply lack of winds faster than 2 m s^{-1} in other sectors.

Same pattern was also observed during the second campaign (Figure 4-25) and WSW sector which is dominant wind direction had the greatest contribution in that sector at the receptor for all of the measured VOCs.

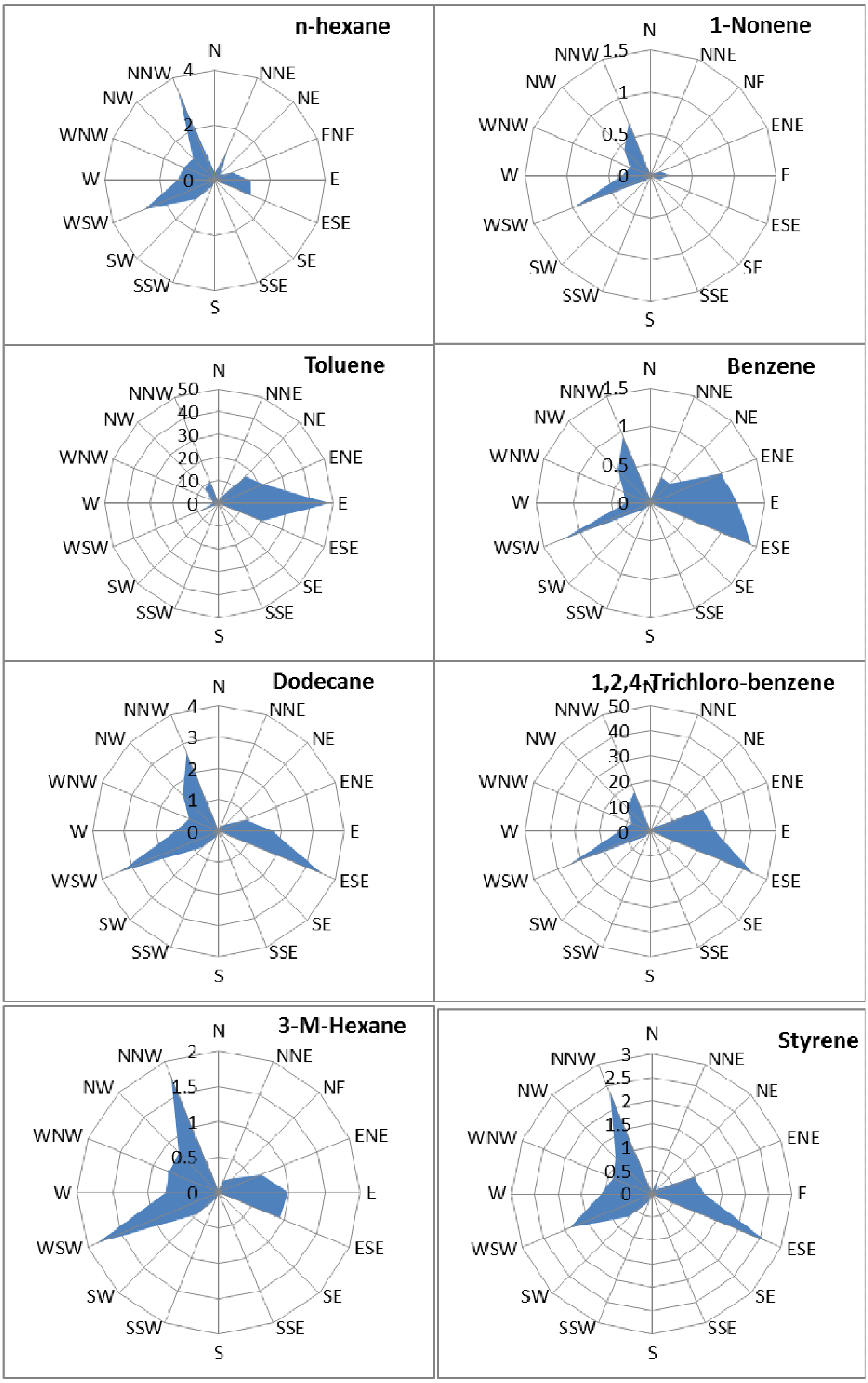


Figure 4-24 Normalized pollution roses prepared for the selected heavy hydrocarbons during the first campaign

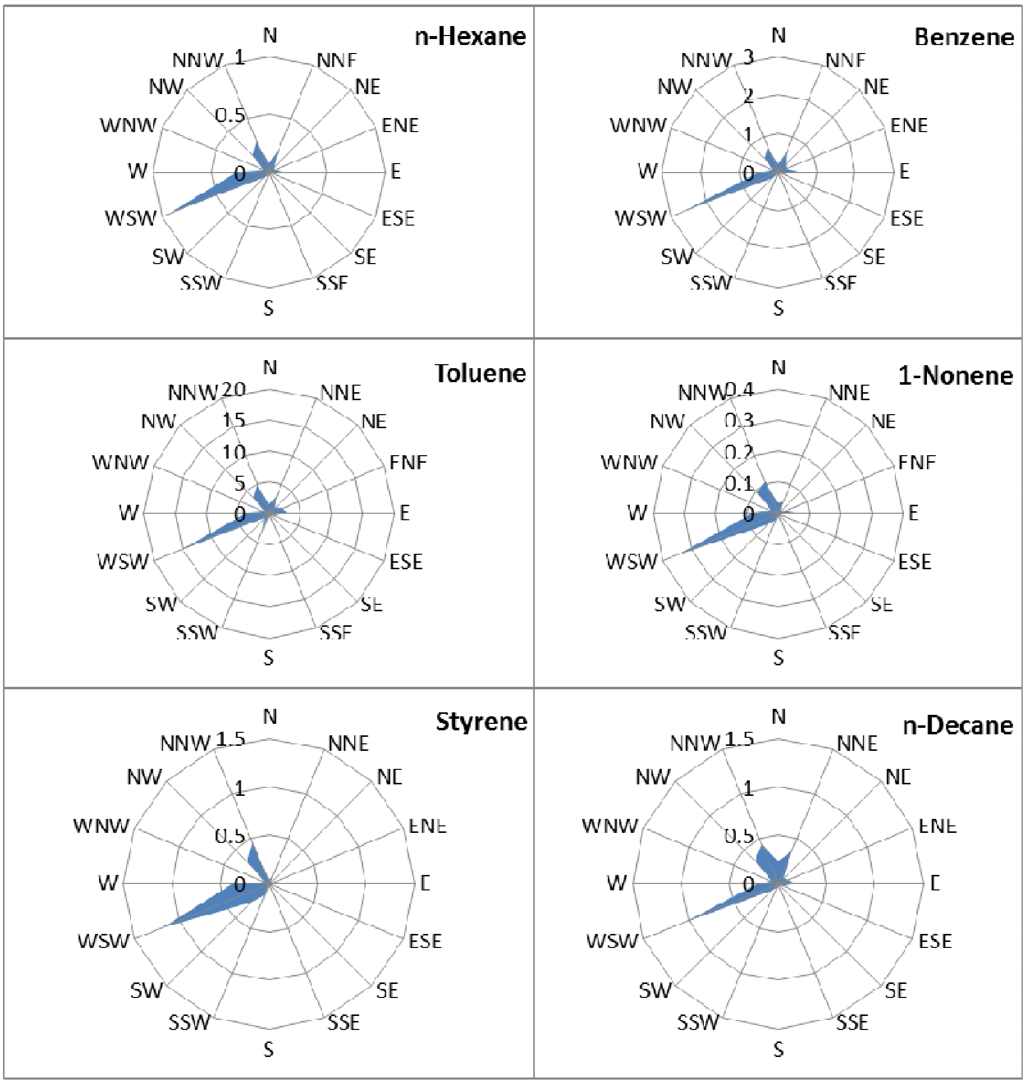


Figure 4-25 Normalized pollution roses prepared for the selected heavy hydrocarbons during the second campaign

4.5 Temporal Variations of the Measured VOCs Concentrations

4.5.1 Difference between the First and Second Campaigns

Total concentrations of measured VOCs were obtained by summation of the average concentration of the compounds. Monthly average concentration of the measured NMTVOCs is given in Figure 4-26.

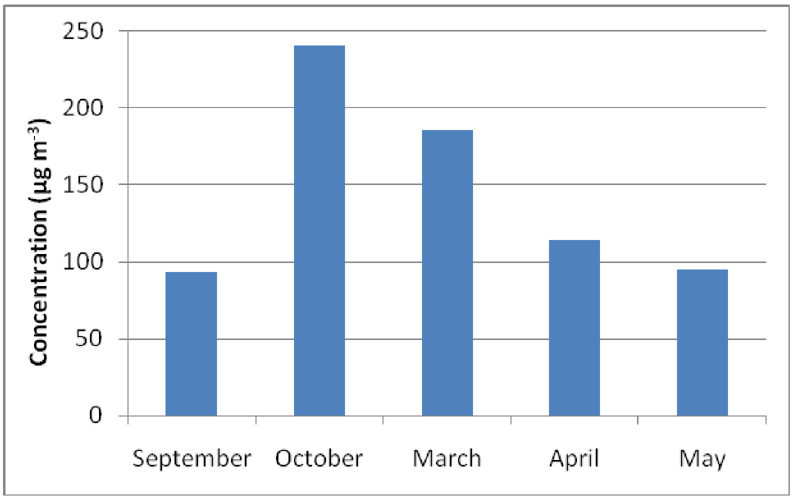


Figure 4-26 Monthly average concentration of NMTVOCs

Higher mixing height and better assimilative capacity of the atmosphere favor lower pollutant concentrations in summer months (Hoque et al., 2008). During the sampling campaigns, calm conditions and stable atmospheric properties were frequent. However, depending on the atmospheric properties of the city, a variation in VOC concentrations were also observed during the sampling campaigns. Conditions that favor accumulation of pollutants (i.e., the lowest mixing heights, lowest ventilation coefficients, the most stable weather conditions) were more frequent in winter months, particularly in March. Moreover, conditions that favor effective dispersion of pollutants gradually improved from winter towards summer. Average temperatures recorded during sampling campaigns, were 19 °C, 14 °C, 10 °C, 14 °C and 15 °C for September, October, March, April and May, respectively. Therefore, observed variations in concentrations of VOCs are expected be at least partially affected from such variation in ventilation characteristics of the Bursa atmosphere. Such dependence of measured VOC concentrations on local meteorology is frequently reported in literature (Cetin et al., 2003; Hoque et al., 2008; Tiwari et al., 2010). Measured VOC concentrations in urban atmosphere are also strongly affected from variations in source strength. As will be discussed in coming paragraphs, VOC concentrations we measured in Bursa atmosphere are under the influence of both of these factors.

Although assimilative capacity of the atmosphere was the worst in March in Bursa, the highest NMTVOC concentrations were observed in October. This is because asphalting operations in the proximity of the station may have led to an increase in VOC concentrations in atmosphere. This effect is not observed for all VOCs, but for the ones that are affected by asphalting operations. This is a good example of how temporal variations in source strengths of VOCs strongly affect variations in their measured concentrations.

To view difference between the first and second campaign clearly, the measurement period was divided into hot and cold, or summer and winter months. September was assumed as a summer season and March was assumed as a winter season. In many studies the year is divided into four seasons as in our everyday life. However, atmospheric concentrations of pollutants depend usually on heating emissions, ventilation potential and rain, which effectively scavenge pollutants from atmosphere. Almost all of these parameters show dramatic differences between summer and winter. Spring and fall are transition periods and because of this their information value is limited. With this logic, the year is divided to two seasons as summer and winter in most of the studies in our group, including this study. Analysis of Variance (ANOVA) analysis was performed (using SPSS version 17.0) to test statistical significance of the differences between winter and summer concentrations of VOCs measured in this study. Winter-to-summer ratios of selected VOC concentrations are given in Figure 4-27.

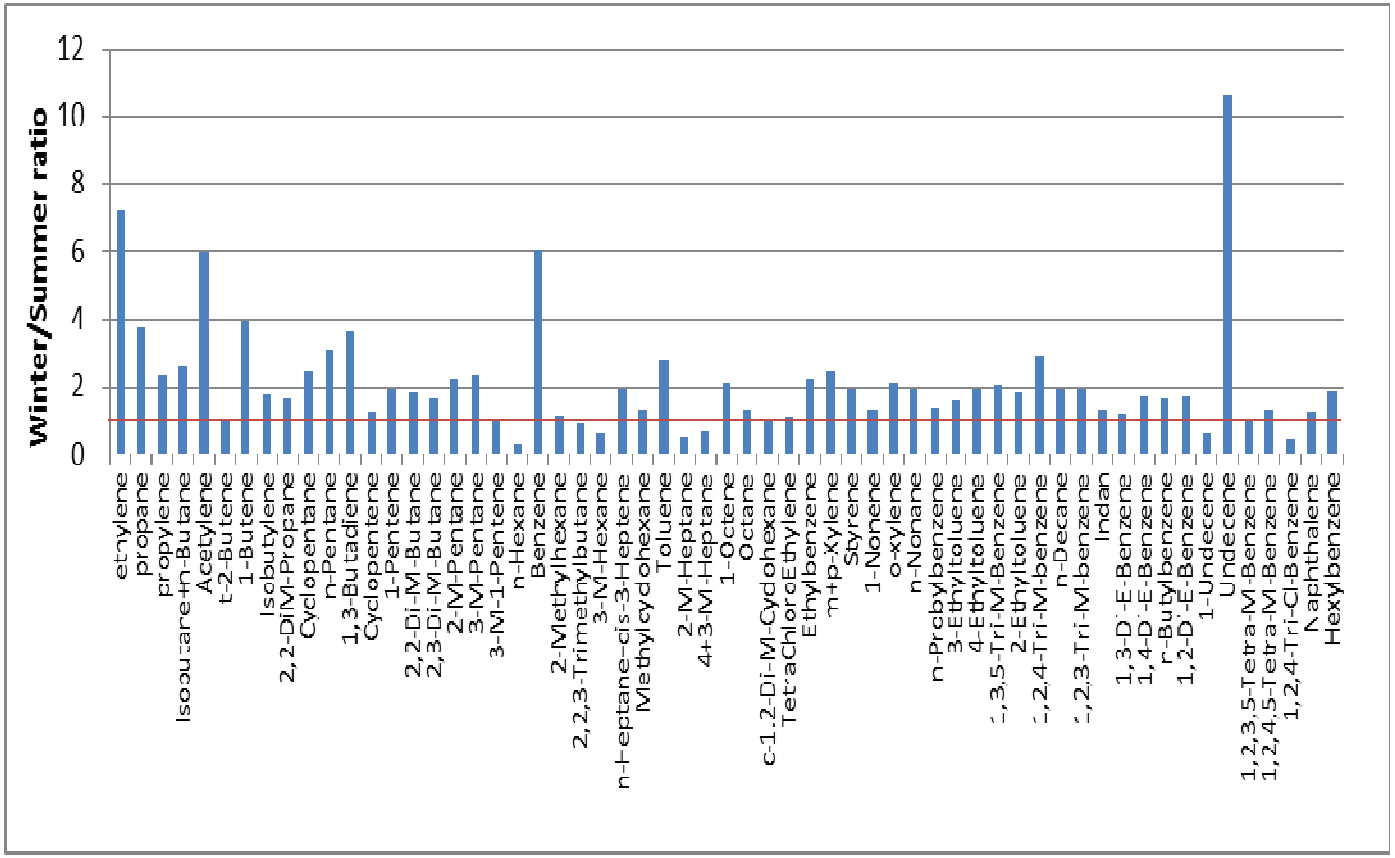


Figure 4-27 Winter to summer ratio of selected VOCs

For 97 out of 101 VOCs, which were measured in more than 10% of samples in both summer and winter seasons, difference between winter and summer mean concentrations of measured VOCs were statistically significant with better than 95% probability ($p<0.05$). Only four of the measured VOCs, namely t-2-butene, 3-m-1-pentene, c-1.2-di-m-cyclohexane and 1,2,3,5-tetra-m-benzene did not show a statistically significant difference between seasons. Please note that if emissions of a VOC are the same in winter and summer seasons, its concentration is expected to be higher in winter, owing to meteorology, as discussed previously in the manuscript. No variation actually means higher emission of that VOC in summer season. Consequently, lack of variation in concentrations of t-2-butene, 3-m-1-pentene, c-1.2-di-m-cyclohexane and 1,2,3,5-tetra-m-benzene, indicate that they are emitted at a higher rate in summer, suggesting an evaporative source for them.

Most of the measured VOCs have higher concentrations in winter. Nine of the measured compounds have W/S ratio > 4. Sixty-three of the compounds have W/S ratio between 1.5 and 4.0 and 18 compounds have ratios between 0.9 and 1.5 and there are only 7 VOCs with ratios < 0.9. There are several factors that can lead to higher winter concentrations of these compounds.

1. Meteorology; lower mixing height, lower winds and lower ventilation coefficient in winter (Yu et al., 2014).)
2. Faster destruction of VOCs with increased solar flux in summer season (Lee et al., 2002)
3. Season dependent increase in source strengths of VOCs in winter season (Filella and Penuelas, 2006)

The role of meteorology on concentrations of VOCs (and other atmospheric pollutants for that matter) were discussed previously in the manuscript and will not be repeated here. Briefly, higher mixing height in summer leads to dilution of VOCs and other pollutants and other pollutants resulting in lower concentrations in summer season. Precipitation is another meteorological factor that can affect measured concentrations of pollutants in general and VOCs in particular. More frequent rain events in winter results in more effective scavenging of VOCs from atmosphere.

Rain scavenging and dilution due to increased mixing height are two opposing factors in terms of measured VOC concentrations. Rain scavenging favors higher VOC concentrations in summer, whereas seasonal variation in mixing height favors for higher VOC concentrations in winter. Although we did not investigate relative contributions of these two met parameters, from literature we concluded that the effect of mixing height on VOC levels is more important than the effect of rain (Sangiorgi et al., 2011; Apel et al., 2010; Sangiorgi et al., 2011; Yang et al., 2013).

Photochemical destruction of VOCs in summer is expected to be higher due to boosted solar flux and increased temperatures (Lee et al., 2002). This also leads to higher concentrations in winter season.

The third factor that can affect variations in concentrations of VOCs is the variation in source strengths of some of the VOCs. Winter-to-summer ratio of the some compounds, such as, n-hexane, 3-m-hexane, 2-m-heptane, 3-m-heptane, 4-m-heptane, 1-undecene and 1,2,4-tri-chlorobenzene were lower than 1, indicating their higher concentrations in summer and the ratio was statistically sound ($p<0.05$) This result is not surprising because these compounds are one of the main elements of solvents; evaporation also increases with increasing temperature, and high temperatures led to an increase in the concentrations of the solvent originated compounds in the atmosphere. Monthly variations in different VOC groups are given in Figure 4-28. Monthly variations of the groups were small; however, contributions of aromatics and alkenes were lower in summer when compared with colder months (i.e., march). This pattern is consistent with observations reported in literature and is probably due to high reactivity of aromatics in the atmosphere (Lurmann and Main, 1992). Unlike aromatics, halogenated hydrocarbons did not show strong temporal variation; probably due to their industrial sources.

4.5.2 Diurnal variation

Diurnal variations of NMTVOCs are given in Figure 4-29 and Figure 4-30. High concentrations were observed at morning (8:00-11:00), and evening (19:00-21:00) hours in both campaigns. Moreover, in addition to the rush hours, high concentrations were also observed just after midnight. Diurnal pattern observed in VOC concentrations is typical and observed in most of the studies in the literature (Demir et al., 2011; Fares et al., 2013; Li et al., 2014; Patokoski et al., 2014; Na et al., 2003). This diurnal pattern is dictated by diurnal variations in VOC source strengths, particularly emissions from traffic. With the increase in the traffic intensity, VOC concentrations start to increase in the morning. After 10:00, NMTVOC concentrations started to decrease. Relatively low concentrations were observed between 12:00 and 18:00, most likely owing to decrease in the traffic density, lower concentrations were observed in noon time as compared to morning and evening rush hours. Concentrations then increase after 18:00 hours due to afternoon rush hour. This second peak which occurred between 18:00 and 21:00 is slightly later than we expected. It should be real, because a similar afternoon rush hour peak was also observed in earlier studies in Ankara (Kuntasal et al., 2013). Meteorology do not play an important role on observed variation in Non-methane Total Volatile Organic Compounds (NMTVOCs) concentrations, because observed diurnal pattern is not consistent with diurnal variation in mixing height and

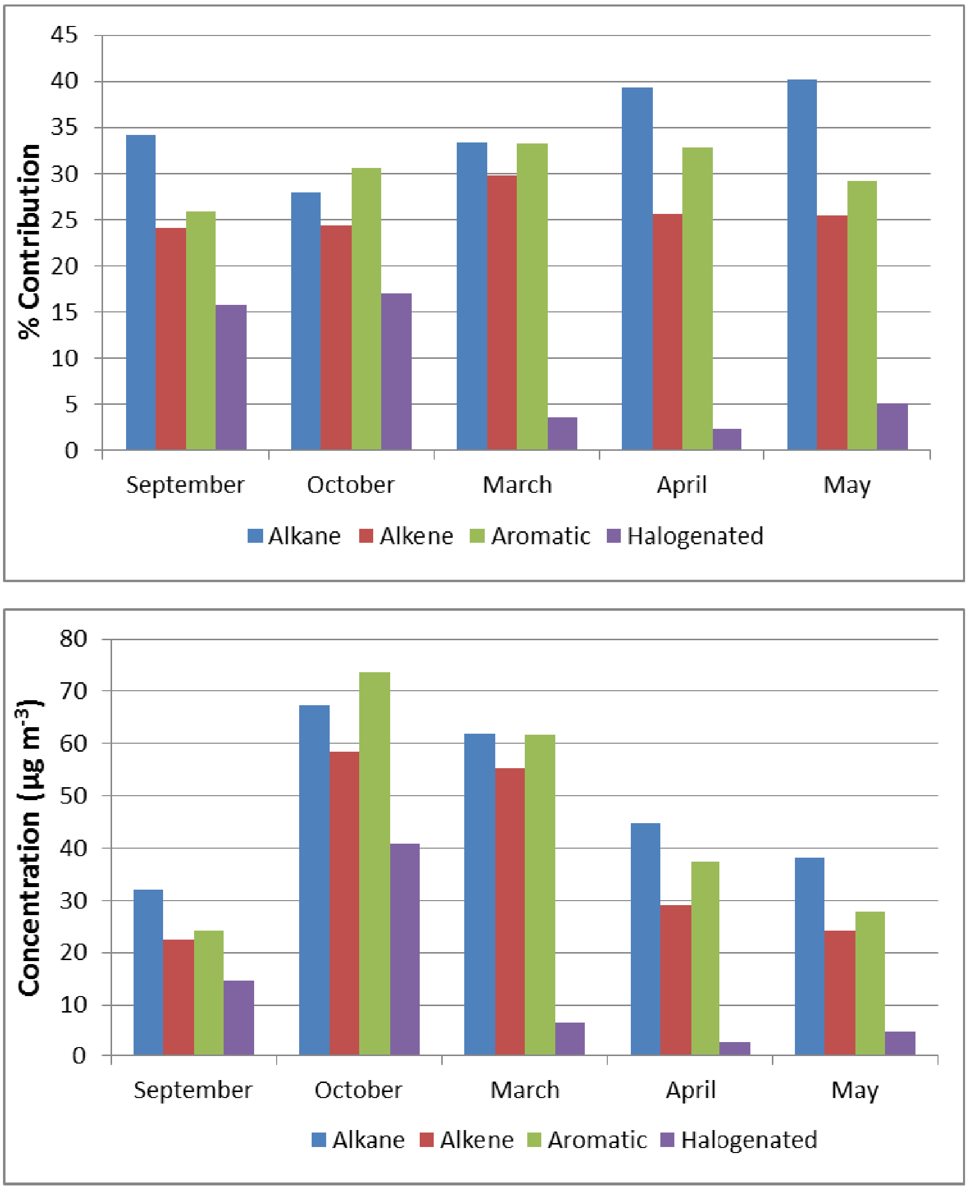


Figure 4-28 Monthly variation of the hydrocarbon groups

ventilation coefficient, which were discussed earlier in the manuscript. However, contribution of meteorology, particularly variation in mixing height and ventilation coefficient cannot be ruled out entirely. Although contribution of meteorology is small and insignificant during day time, when measured VOC concentrations are dominated by variations in traffic emissions, it may contribute to measured VOC concentrations at night when traffic emissions are low. In fact, relatively high concentrations of NMTVOCs and in individual VOCs at midnight, when traffic emissions are in its minimum, can be due to low mixing height and low ventilation coefficient at that time of the day. Furthermore, meteorology may also contribute to low VOC concentrations observed at noon hours, because ventilation of the atmosphere is the highest at noon, due to high wind speed, deeper mixing height and high ventilation coefficient values at noon.

Enhanced photochemistry at noon hours also contributes to low concentrations of VOCs, by speeding up their oxidation. These all indicate that although diurnal pattern in VOC concentrations is determined by diurnal variations in their emissions, the pattern is modified by both local meteorology and photochemical activity.

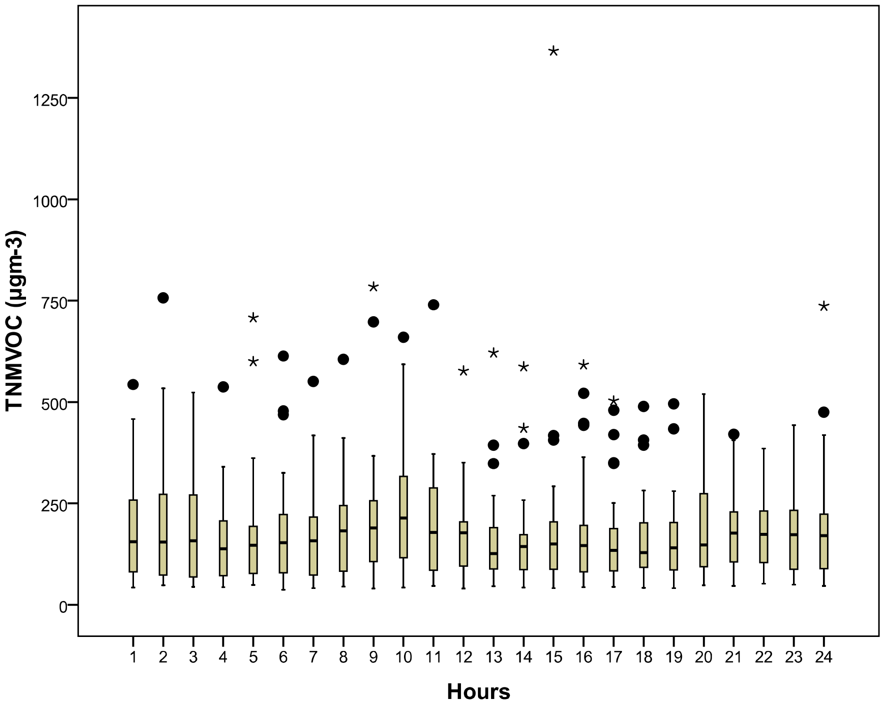


Figure 4-29 Diurnal variation of the NMTVOC concentrations in the first campaign (Extreme values and outliers marked with star and round dot, respectively)

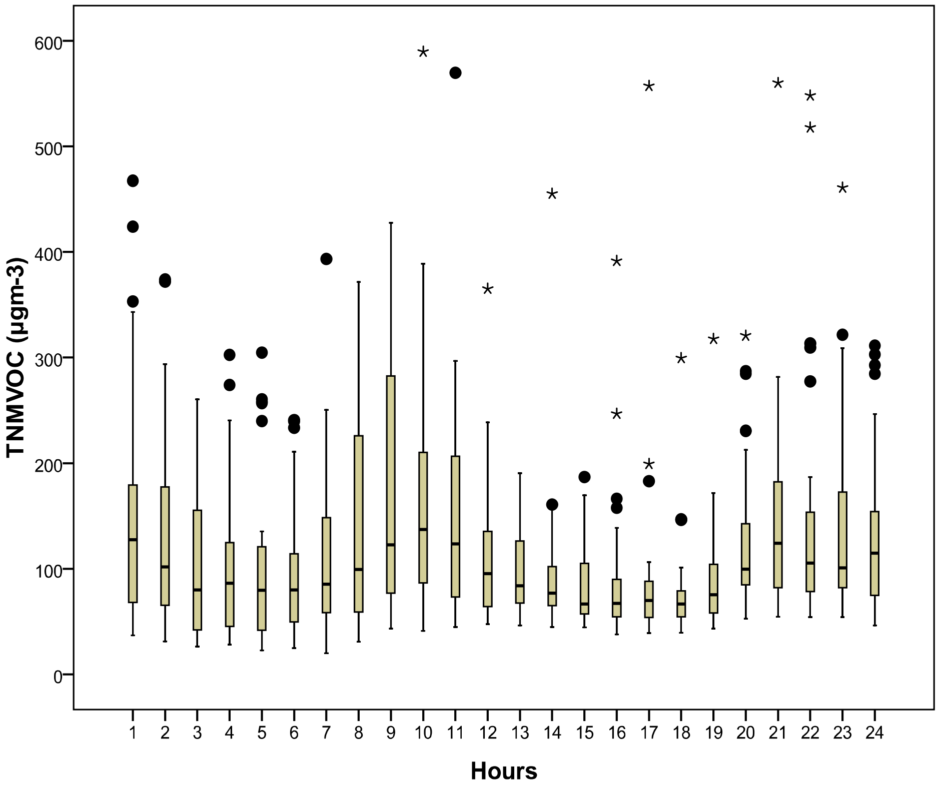


Figure 4-30 Diurnal variation of the NMTVOC concentrations in the second campaign (Extreme values and outliers marked with star and round dot, respectively)

Diurnal variation of BTX compounds in the first campaign is given in Figure 4-31. Diurnal variations of the aromatics are effected many factors such as traffic density, meteorological conditions and rush hours (Nguyen et al., 2009). Usually, double peaks are reflective of the typical traffic pattern (Chang et al., 2006) in diurnal profiles. In addition to traffic originated emissions, evaporative sources are also important in diurnal patterns depicted by some of the VOCs. Since evaporative emissions are expected to increase in the afternoon with increasing temperature, (Nguyen et al., 2009), any increase in concentrations of VOCs can be attributed to their evaporative sources.

When diurnal patterns of the BTEX compounds are compared with each other, it can be seen that the diurnal pattern of the benzene is different from other BTEX (referred to as TEX compounds) compounds. As the major source of benzene in the atmosphere is traffic (Skov et al., 2001); diurnal profile of the benzene closely mimics daily changes in traffic density. The difference in diurnal patterns in concentrations of benzene and TEX compounds are due to non-traffic sources of TEX compounds.

Diurnal variations of selected light hydrocarbons are given in Figure 4-32. Diurnal patterns in concentrations of ethylene, propane, acetylene and n-pentane are not very different from diurnal behaviors of total VOC and BTEX compounds, indicating that traffic activities are also the main source of these compounds in Bursa atmosphere. Although there are evaporative sources for ethylene, emissions from LPG and natural gas strongly contributes to ambient propane levels, traffic emissions dominate over the other sources in this study, because diurnal variation in ethylene, propane and pentane concentrations are very similar to diurnal variations in acetylene concentration, which is a combustion product and best available marker for traffic emissions.

When diurnal profiles of all VOCs were examined, some unusual profiles that did not follow the usual traffic pattern were also identified. One example for this non-traffic behavior was observed for heavy hydrocarbons, such as 1-octene, 1-nonene, 1-undecene, n-nonane, n-decane, 1,2,3-trimethylbenzene, undecane and dodecane. Diurnal variations in concentrations of these compounds are given in Figure 4-33. Diurnal variations in concentrations of these compounds are significantly different from diurnal patterns depicted by BTEX compounds, with higher concentrations during day time, rather than at rush-hours. These compounds were found to be strongly associated with asphalting operations in PMF exercise, which will be discussed in more detail in Chapter 5 of the manuscript. This may be the main reason for non-traffic diurnal variations in concentrations of these compounds. Actually this is an expected situation because these compounds were mainly emitted from the asphalt paving operations as well as diesel exhaust (Liu et al., 2005; Liu et al., 2008; Vega et al., 2000).

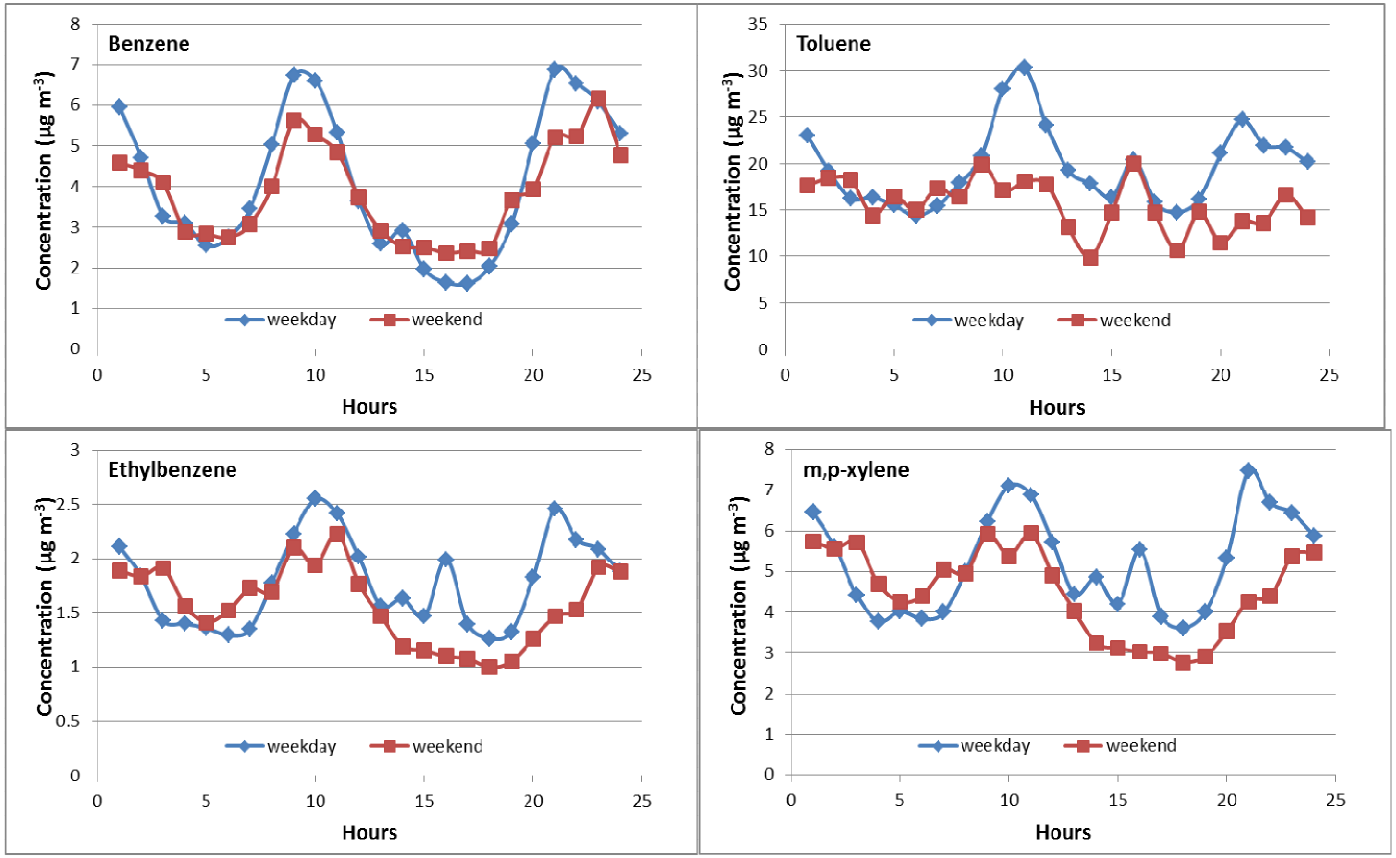


Figure 4-31 Diurnal profile of the BTEX compounds for the first campaign

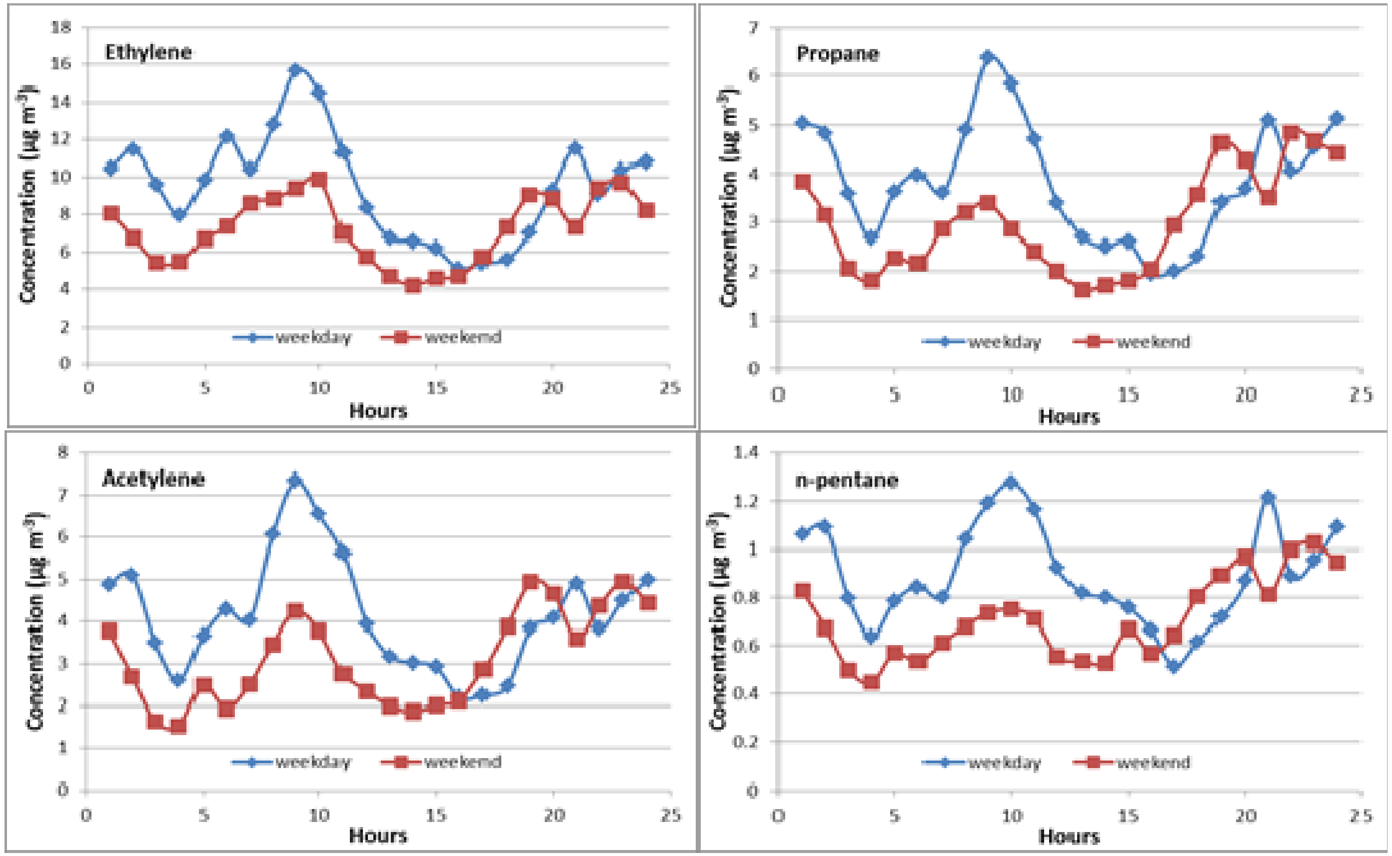


Figure 4-32 Diurnal profile of selected light HCs in the first campaign

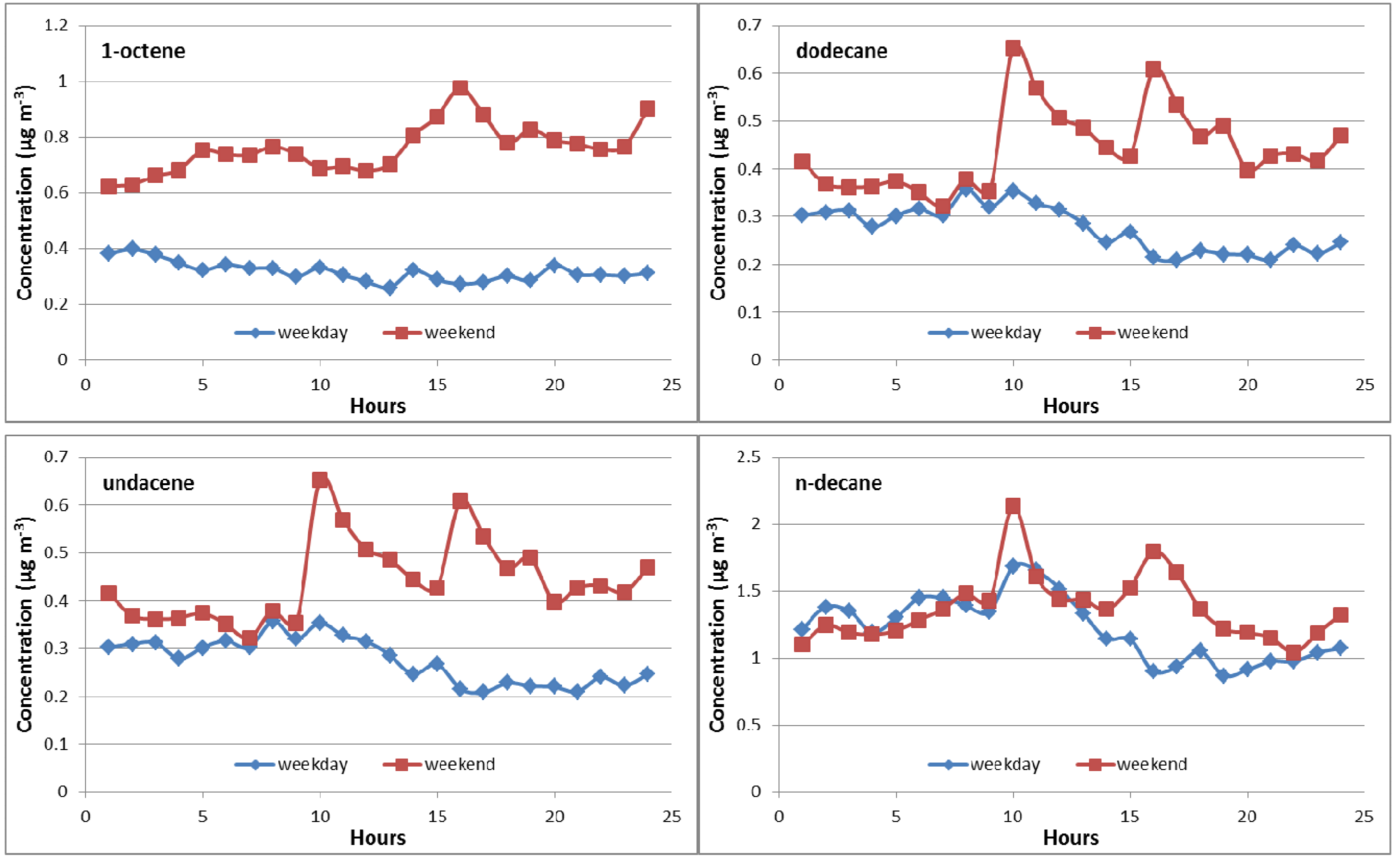


Figure 4-33 Diurnal profiles of the selected compounds for the first campaign

As will be discussed later in the manuscript, concentrations of 1-octene, 1-nonene, 1-undecene, n-nonane, n-decane, 1,2,3-trimethylbenzene, undecane and dodecane were higher during weekends than their concentrations in weekdays, probably because paving works were performed during the weekend.

In addition to the heavy hydrocarbons, different diurnal patterns were also observed for some other VOCs, such as n-hexane and styrene. Diurnal behavior of these two compounds is given in Figure 4-34. Styrene and n-hexane do not show typical traffic diurnal pattern with two maxima during morning and afternoon rush hours. They have a fairly uniform distribution of concentrations throughout the day.

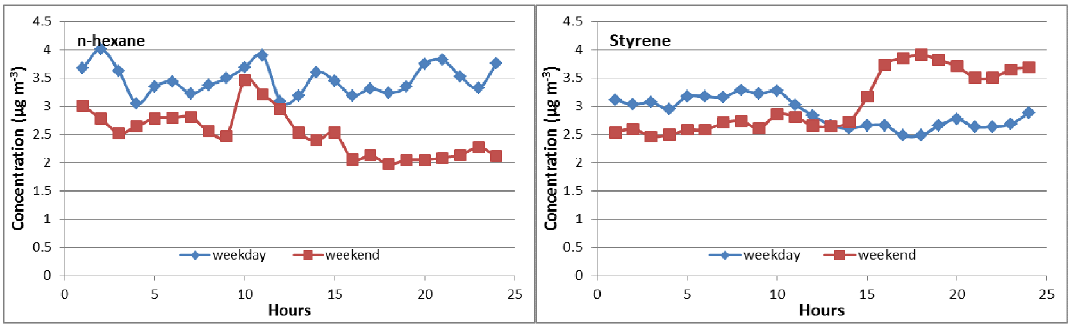


Figure 4-34 Diurnal profiles of n-hexane and styrene for the first campaign

Traffic is the major source of the hexane in urban atmospheres. However, it is also commonly used as a solvent in industrial processes and domestic activities (Borbon et al, 2022; Guo et al., 2004). Consequently, uniform distribution of hexane concentrations in 24-hour period can be explained by the contribution of evaporative sources between morning and afternoon rush-hours.

Contribution of evaporative sources can also explain diurnal pattern, or lack of significant diurnal pattern, observed in styrene concentrations, because ambient styrene concentrations have also strong contributions from industrial evaporative emissions in urban atmosphere (Guo et al., 2004). Industrial evaporation is also confirmed as a significant source of styrene in this study, because it is strongly associated with evaporative emission factor in the PMF exercise, which will be discussed in Chapter 5 of this manuscript.

3-m-1-pentene was another VOC that did not follow the usual traffic pattern with two rush-hour maxima. Diurnal variation in 3-methyl-1-pentene concentrations are given in Figure 4-35. Daily pattern of 3-methyl-1-pentene was clearly different from the diurnal variation of other light VOCs. The lack of traffic cycle with two rush hour maxima suggests that traffic emissions were not the main source of this VOC. An important source of 3-methyl-1-pentene, especially for the first campaign, was probably solvent evaporation rather than traffic. 3-methyl-1 pentene can be utilized for the production of the aerosol coating materials and is used as propellants (EPA, 2007). Therefore, high daytime concentrations of 3-m-1-pentene may indicate an evaporative source.

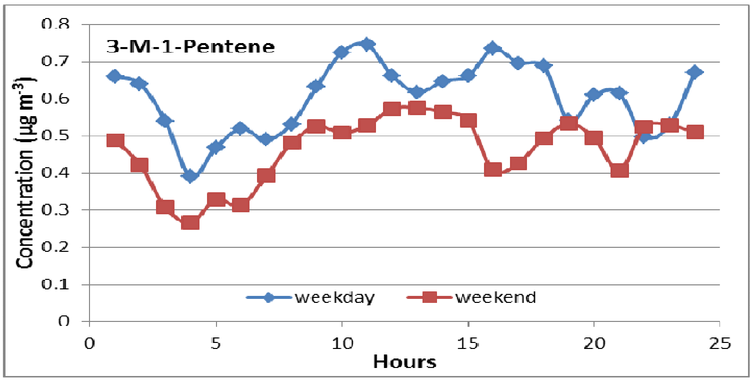


Figure 4-35 Diurnal profile of the 3-M-1-Pentene

As in the first campaign, most of the VOCs were found to be related with traffic in the second campaign also. Diurnal variation in BTX concentrations in the second campaign are given in Figure 4-36. Like in the first campaign, concentrations of BTEX compounds started to increase at 05:00 am. The highest concentration peaks occurred between 09:00 and 11:00. After these maximum concentrations remained low until everybody returned to their homes and started to increase at 18:00, reached to a maximum between 20:00 and 21:00, then decrease to the lowest concentrations after midnight. This pattern is very similar with the pattern observed in the first campaign.

Diurnal patterns of selected light hydrocarbons are given in Figure 4-37. Ethylene, acetylene, propane and n-pentane which are the VOCs included in this group depict a very clear traffic pattern like BTX compounds, demonstrating that traffic is their major source. This pattern shown for BTX compounds and other light hydrocarbons is observed in diurnal variations of most of the light and heavy VOCs and is the common diurnal profile for organic compounds measured in this study. This means that traffic pattern is the common pattern for a large majority of the VOCs in Bursa atmosphere. As discussed earlier in the manuscript, this common pattern, which is generated by traffic emissions in the city, is probably modified by diurnal variations in meteorology and photochemistry. However, these modifications are generally not large enough to change the traffic pattern significantly. However, there are non-traffic emissions which can dominate the diurnal variations in concentrations of some of the VOCs. In these cases traffic pattern, can be entirely masked by these sources. The most obvious of these non-traffic emissions is the evaporative sources. Evaporative emissions include both gasoline evaporation at gas stations and solvent evaporation in daily domestic activities, such as painting, photocopying etc. and in industry. Since Bursa is a heavily industrialized city, these sorts of non-traffic emissions are more important than that observed in most of the cities where industrial activity is not very extensive. Some examples of such non-traffic daily patterns are presented in the coming paragraphs. VOCs that did not follow typical traffic pattern with two maxima include c-1,2-di-m-cyclohexane, 1-nonane, n-nonane, styrene, undecane, 1-undecene, 1,2-di-e-benzene, n-butylbenzene, n-decane, 1,3-di-e-benzene, 1,4-di-e-benzene, 1,2,3,5,-tetra-m-benzene, 1,2,4,5,-tetra-m-benzene, 1,2,4-tri-Cl-benzene, 1-octene, hexylbenzene and napthalene. Diurnal patterns for some of these compounds are given in Figure 4-38. High concentrations were observed after sunrise until sunset, suggesting an evaporative source for them. Availability of these groups of compounds in both campaigns suggests that a variety of VOCs are released to atmosphere in Bursa from evaporative sources as well as from vehicle exhausts.

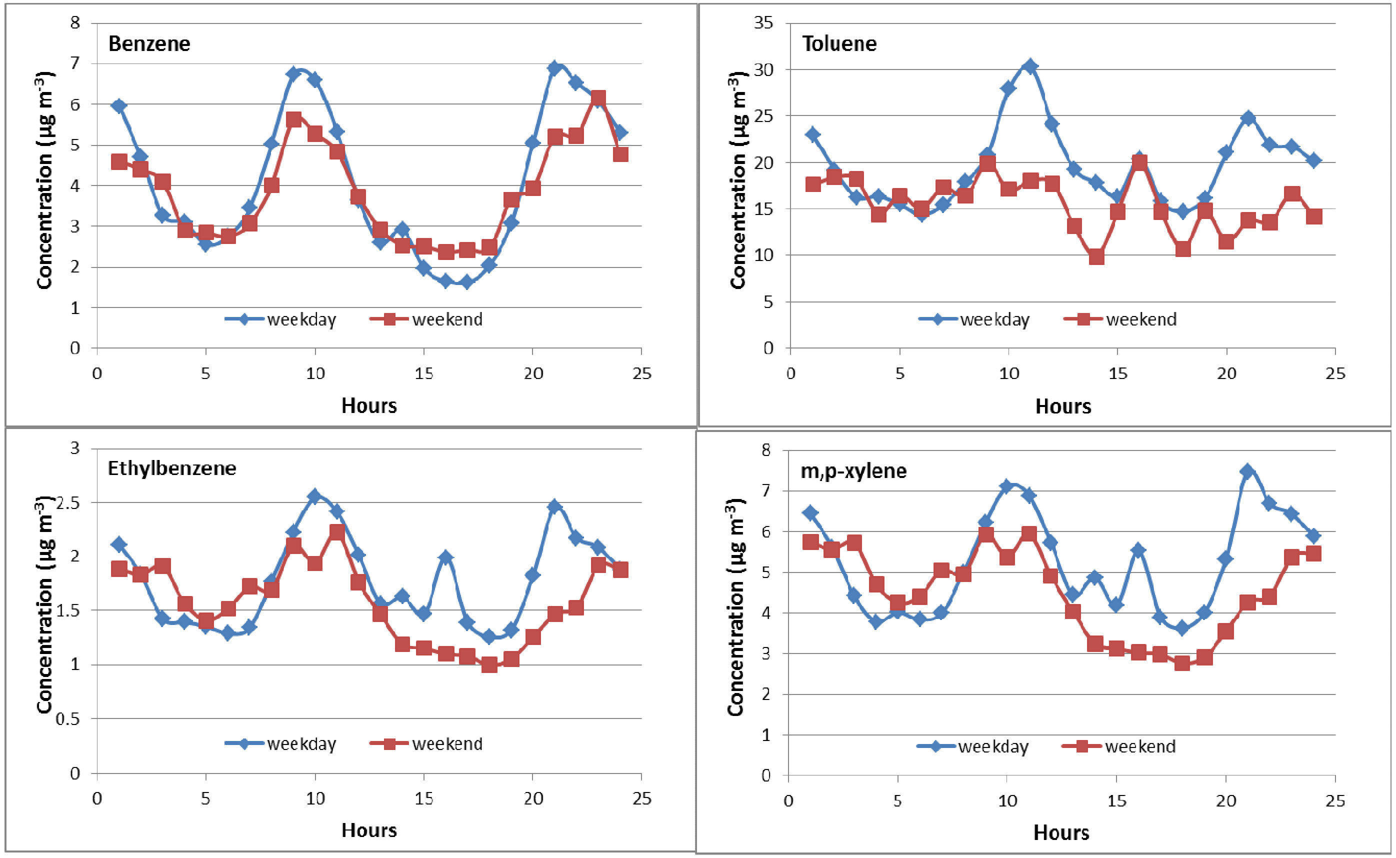


Figure 4-36 Diurnal profile of the BTEX compounds for the second campaign

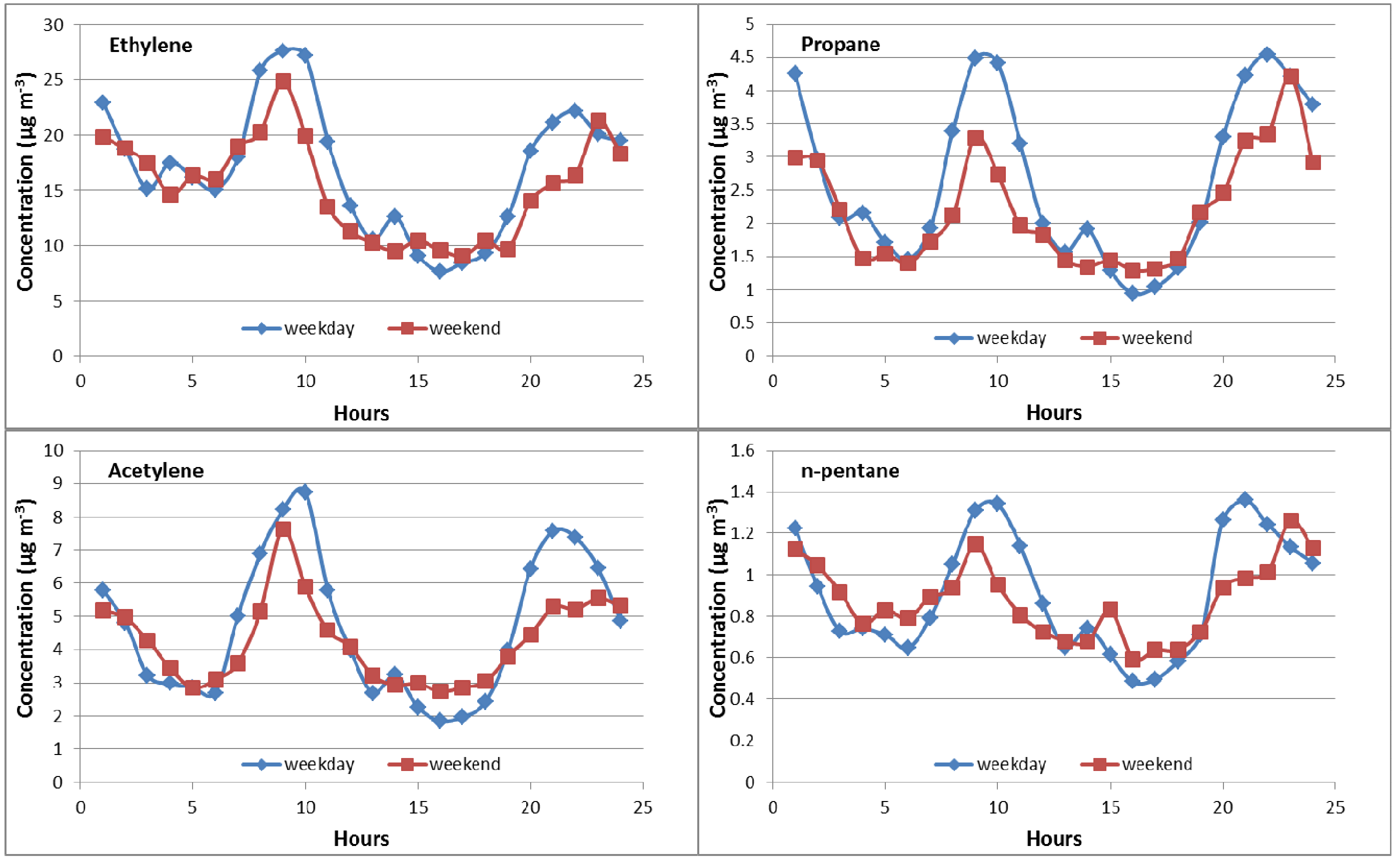


Figure 4-37 Diurnal profiles of selected light VOCs in the second campaign

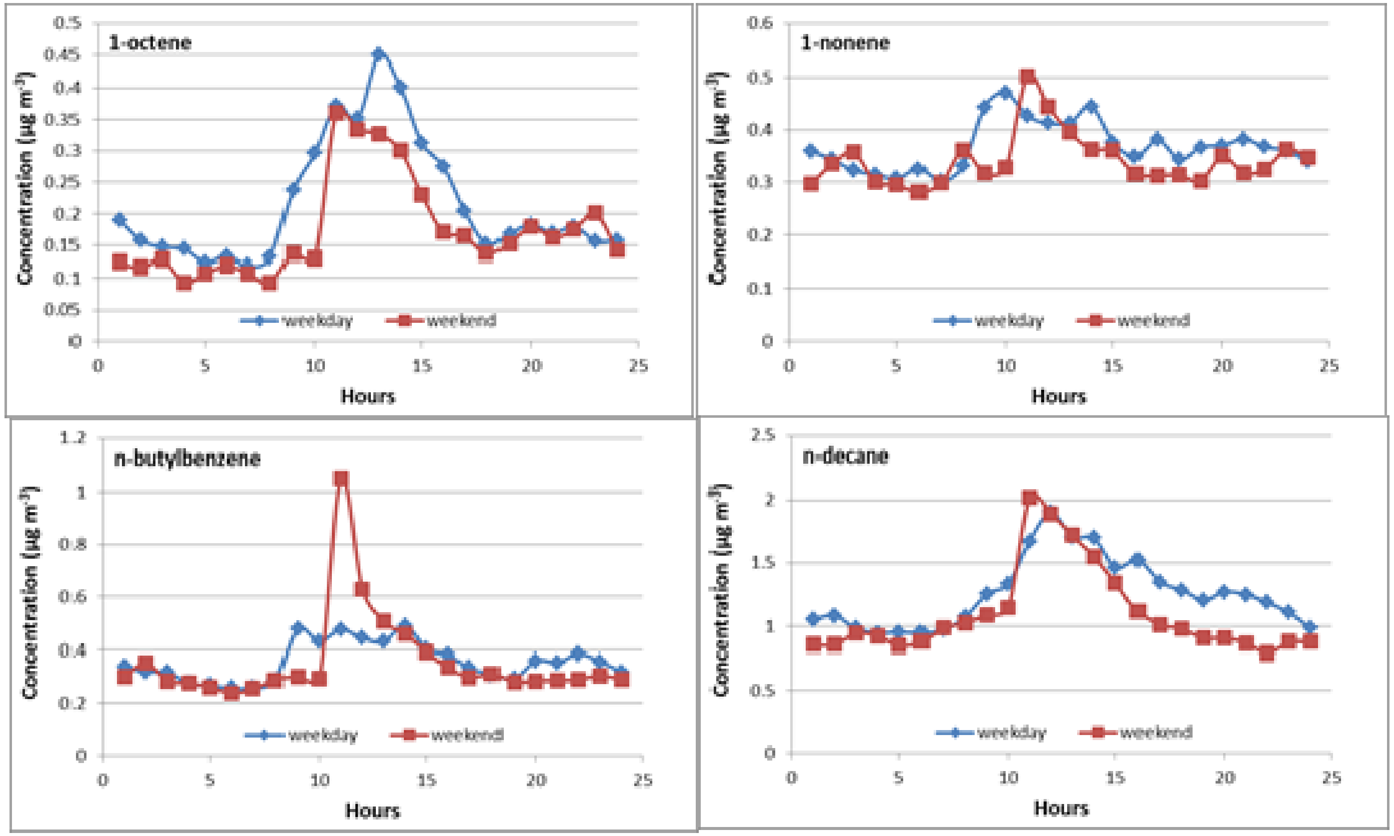


Figure 4-38 Diurnal profiles of the selected compounds with non-traffic diurnal patterns in the second campaign

Diurnal variation of the alkane, alkene, aromatic and halogenated fractions and concentrations of VOCs for the first and second campaigns are given in Figure 4-39 and Figure4-40, respectively. Significant diurnal variation was observed for all of the organic groups in both campaigns. The Figures 4-39 and 40 demonstrate that observed concentrations of VOCs are affected from factors such as meteorology photochemical activity as well as diurnal variation in emission strengths. ΣVOC concentration showed a well-defined traffic pattern with clear morning and afternoon maxima related to increased traffic activity during morning and afternoon rush hours. Although observed diurnal pattern in ΣVOC concentrations and in concentrations of individual VOCs is strongly associated with variations in traffic density, diurnal variations in meteorology and photochemical activity may also contribute to this pattern. Deeper mixing height, enhanced ventilation conditions and unstable conditions during noon hours results in dilution of VOC concentration (and concentrations of other pollutants as well) contributing to low VOC concentrations observed at mid-day. Similarly, increased solar flux and resulting enhanced photochemical activity at noon hours may result in more extensive degradation of VOCs and thus contribute to observed low concentrations at noon.

It should also be noted that halogenated hydrocarbons do not show clear diurnal patterns in their concentrations as aromatics, alkanes and unsaturated hydrocarbons, because contribution of traffic activity to concentrations of halogenated hydrocarbons is not as high as its contributions to other VOC groups.

Another interesting point that should be pointed in this section is the diurnal variations in VOC profiles. As pointed in previous sections, saturated hydrocarbons have the highest percent contribution to total VOC concentrations, which is followed by contributions of aromatic compounds, alkenes and halogenated compounds. These relative contributions of VOC groups are valid throughout the day, except for noon hours. At noon hours, contributions of alkanes and alkenes decrease and that of aromatics increase. This is probably faster oxidation of saturated and unsaturated linear chain hydrocarbons

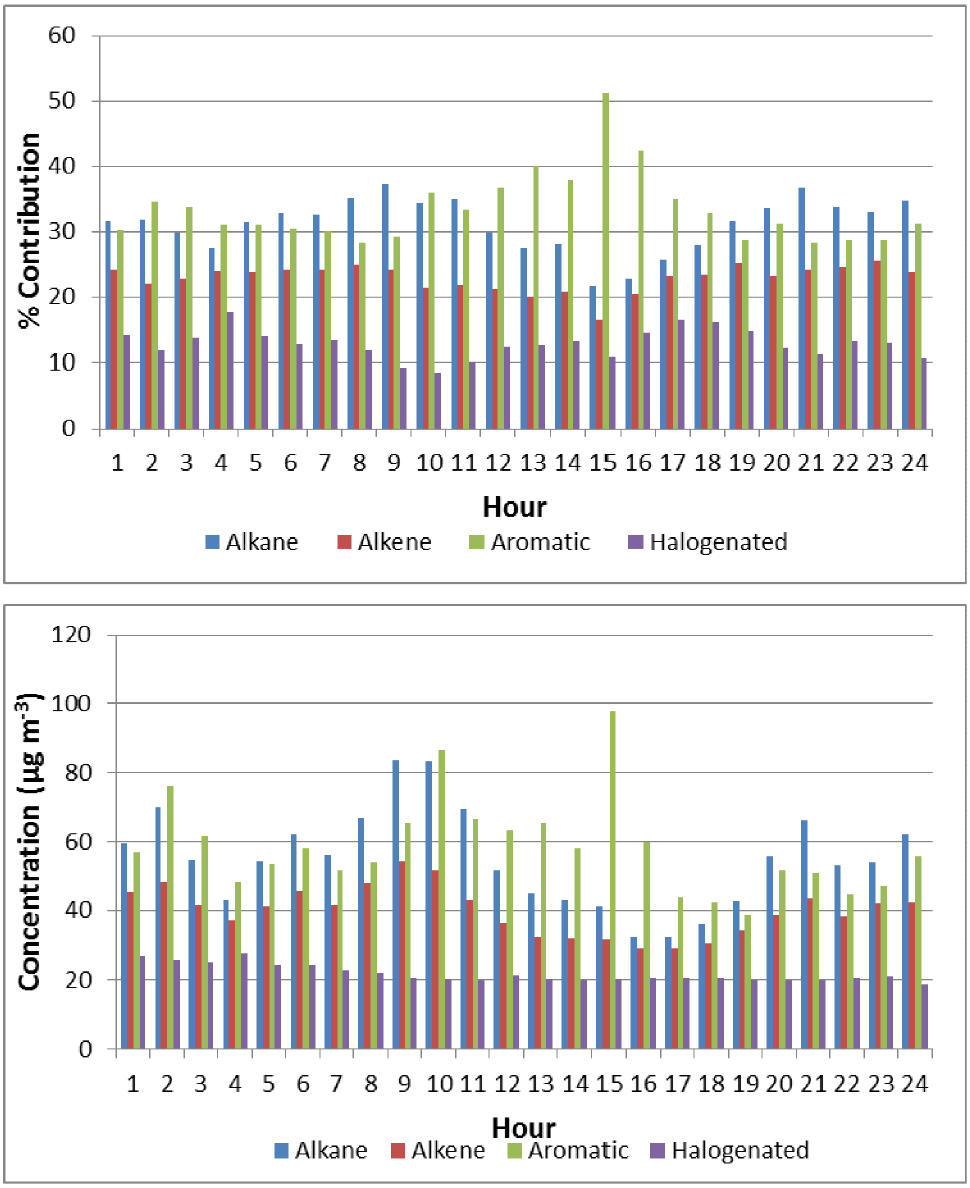


Figure 4-39 The diurnal variance in alkane, alkene, aromatic and halogenated fractions and concentrations of VOCs for the first campaign

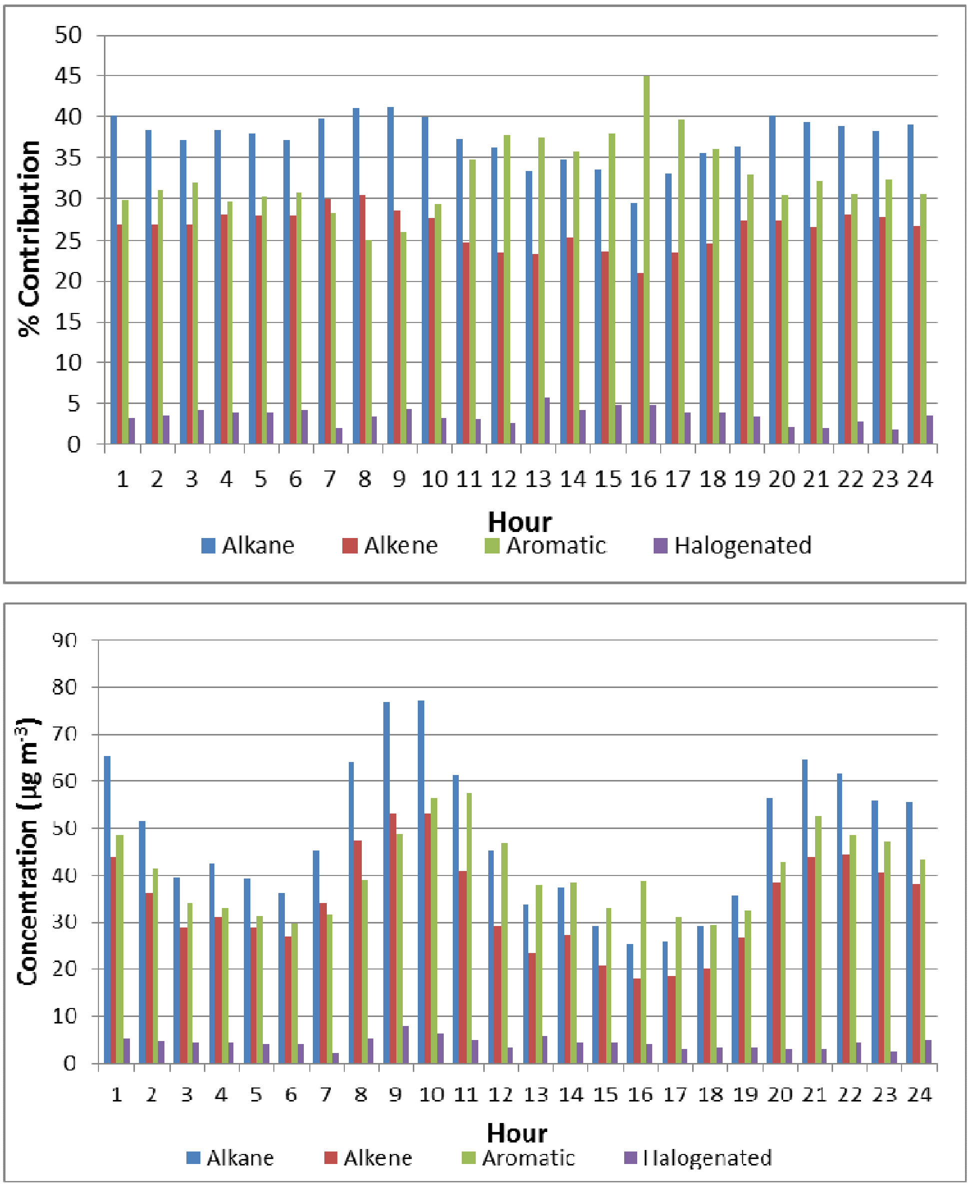


Figure 4-40 The diurnal variance in alkane, alkene, aromatic and halogenated fractions and concentrations of VOCs for the second campaign

4.5.3 Weekday vs. Weekend Variation

Most of the compounds measured during the first campaign showed statistically significant weekday to weekend variation at 90% statistical confidence level ($p<0.1$). Weekdays to weekend ratios (WD/WE) of measured target compounds are given in Figure 4-41. As can be seen from the Figure, higher average concentrations were obtained on weekdays than the weekend for most, if not all VOCs, indicating that the traffic is the major source of many organic compounds. Concentrations of traffic-related pollutants are often higher on weekdays than on weekends. Heavy-duty diesel truck activity and light duty passenger vehicle activity on highways have been found to be 70–80% and 10% lower on weekends, respectively (Marr and Harley, 2002). Therefore, in this study, a possible reason of the lower concentrations related with the traffic based organics on weekends is the reduction of traffic density in city center.

On the other hand, there are also non-traffic activities that can lead to an increase in concentrations of certain VOCs during weekends. Best example for such a weekend source in this study is asphalting operations. Although the influence of asphalting operations on observed concentrations of VOCs will be discussed in more detail later in the manuscript, at this point it may be sufficient to state that such a source did exist and affected VOC concentrations and their temporal variability during our measurements in the Bursa atmosphere.

Some of the solvent-based hydrocarbons, namely; t-2-butene, isobutylene, toluene, c-1.2-di-m-cyclohexane, indane, 1,4-diethyl-benzene, 2,2,5-tri-m-hexane+1,2,4-tri-m-cyclohexane, tetrachloroethylene, 3-ethyltoluene, 4-ethyltoluene, 2-ethyltoluene, 1,3,5-tri-m-benzene, 1,4-di-e-benzene and 1,2,4,5-tetra-m-benzene did not show statistically significant weekday to weekend variation ($p>0.1$). Since concentrations of these VOCs are strongly contributed by evaporative sources both in domestic activities and in industry, reduction in traffic density during weekends does not alter their Week day/Weekend ratios significantly.

Furthermore, weekday/weekend ratios of some of the compounds, such as 2-m-hexane, 2,2,3-trimethylbutane+2,3-dimethylpentane, 3-m-hexane, 2-m-heptane, m+p-chlorotoluene, 1-octene, 1-nonene, n-nonane, n-propylbenzene and most of the heavy hydrocarbons, namely; n-decane, n-butylbenzene, 1-undecene, undecane, 1,2,3,5-tetra-m-benzene, 1,2,4-tri-Cl-benzene, naphthalene, dodecane and hexylbenzene are smaller than unity. Majority of these VOCs are associated with the asphalting operations in the city. We observed strong influence of asphalt pavement activities close to our station on a number of VOCs during the first campaign. These activities were performed during weekend days. These results indicate that there were additional VOC sources other than traffic. Actually, results of the PMF exercise, which will be discussed in subsequent sections, demonstrated that motor vehicle related sources contributed only about 41% of the NMTVOC concentrations in the first campaign. Rest of the NMTVOC concentrations (59%) is accounted for by other, non-traffic sources, such as solvent use, asphalt operations, paint and other industrial activities in the first campaign.

Weekday-to-weekend concentration ratios of VOCs in the second campaign are depicted in Figure 4-42. As in the first campaign, average weekday concentrations of VOCs are higher than their weekend concentrations, in the second campaign as well. The difference is statistically significant in 95% confidence level ($p<0.05$) for most of the VOCs measured in this study. However, WD/WE ratios for some of the VOCs, including ethylene, propane, acetylene, n-pentane, 1,3-butadiene, 2-methyl-butane, benzene, n-heptane, chlorobenzene, n-propylbenzene, 1,3,5-tri-m-benzene, 1,2,4-tri-m-benzene, 1,2,3-tri-m-benzene, indane, 2-ethyl-toluene, 1,3-di-e-benzene, 1,4-di-e-benzene, 1,2-di-e-benzene, n-butylbenzene, 1,2,3,5-tetra-m-benzene, 1,2,4,5-tetra-m-benzene, naphthalene and hexylbenzene are also >1, but the difference is not statistically significant at 90% or greater confidence level. Among these compounds acetylene, 1,3-butadiene and benzene are typical tracers of motor vehicle emissions (Schauer et al., 2001). Therefore, lack of statistically significant difference between weekday and weekend concentrations of these species imply either lack of difference between traffic counts in weekdays and weekends during the second campaign or imply contribution of non-traffic sources, even to there well defined traffic markers. The reason is not very clear.

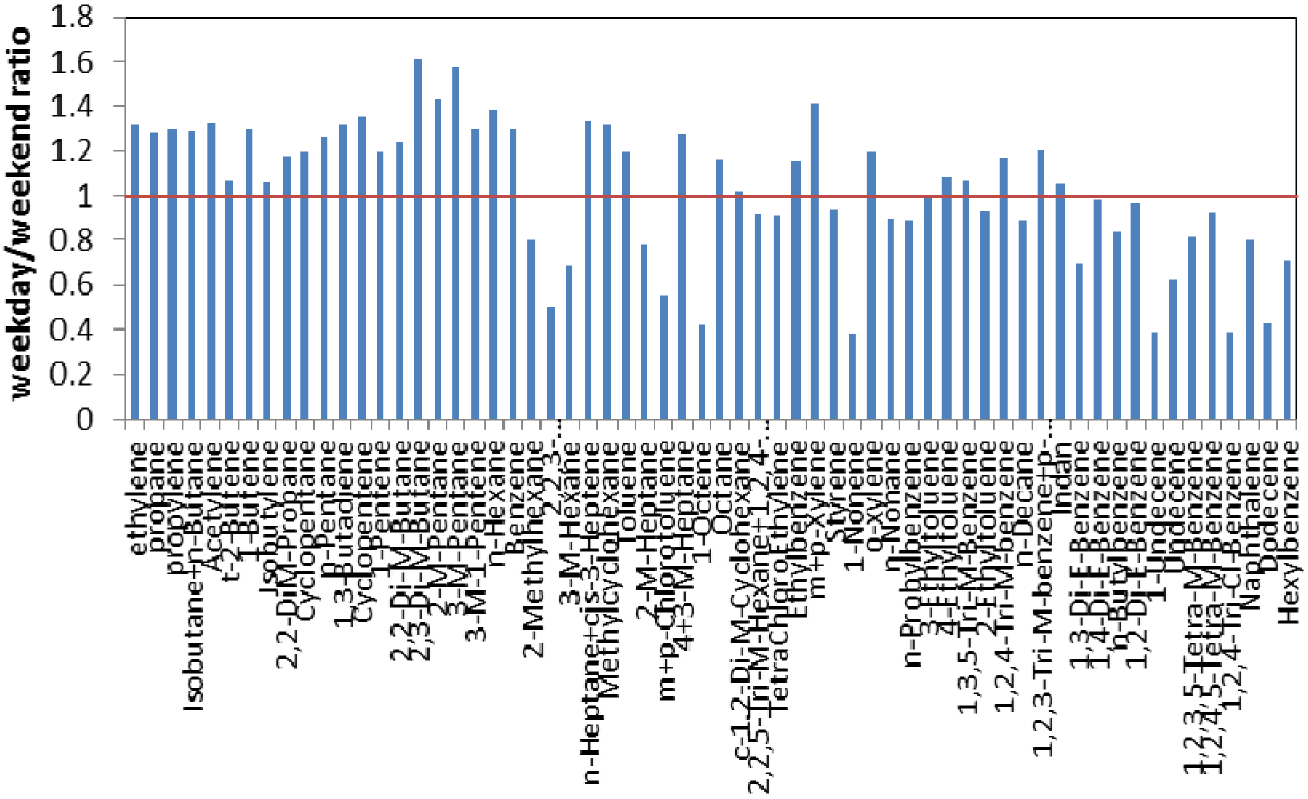


Figure 4-41 Weekday to weekend ratio of the target hydrocarbons for the first campaign

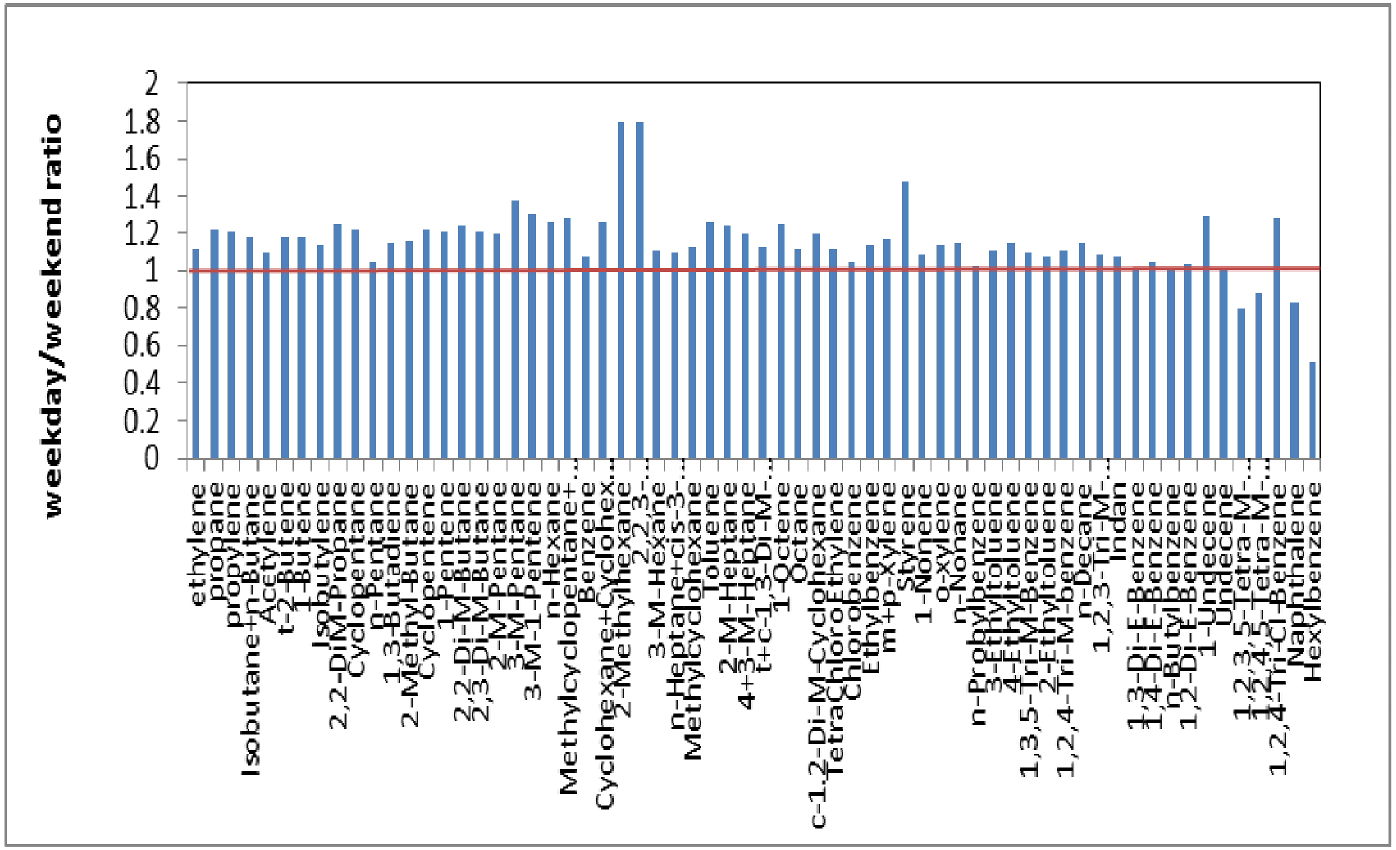


Figure 4-42 Weekday to weekend ratio of the target hydrocarbons for the second campaign

4.5.4 Short-term (Daily) Variation in VOC Concentrations

Short term variations or time series plots of parameters can provide useful information on episodic changes in concentrations of species. Such information can be very useful to understand factors affecting measured concentrations of VOCs (or other pollutants) in an urban airshed.

Daily variation in ΣVOC concentration during the first campaign is given in the Figure 4-43. NMTVOC concentrations gradually increase from September 14 to October 28. The reason for the observed increasing pattern in ΣVOC concentration is probably due to meteorology. As pointed out before, concentrations of most of the VOCs are high in winter and low in summer. Since the period that covered by our first campaign corresponds to a transition from summer to winter (between early September to the end of October) a gradual increase in VOC concentrations is not surprising. A similar gradual increase from beginning to the end of the first campaign is also observed in individual light and heavy VOCs.

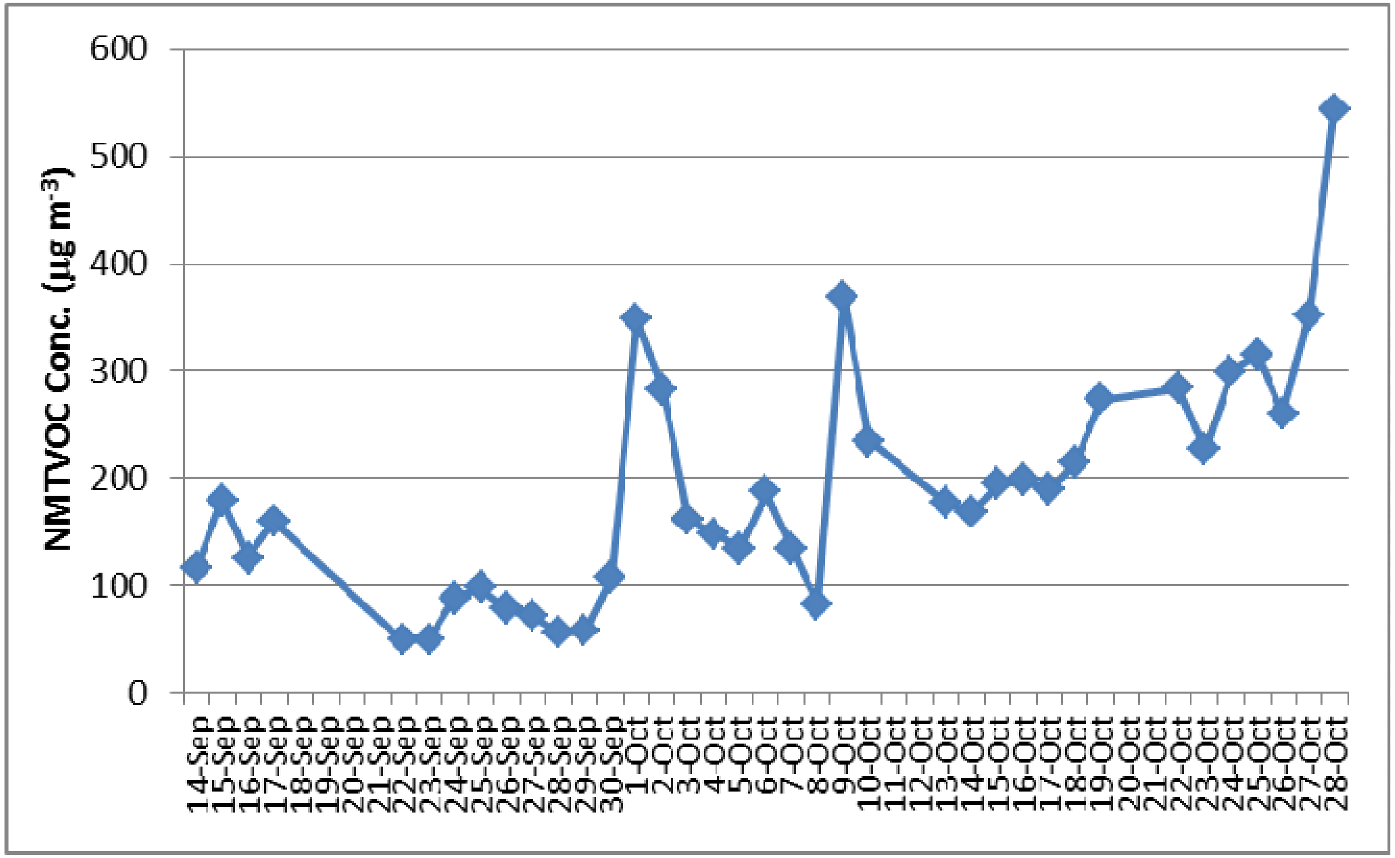


Figure 4-43 Daily variation of the NMTVOCs during the first campaign

Episodic variations in BTEX concentrations are given in Figure 4-44. As observed in time series plot of the NMTVOC concentration, concentrations BTEX compounds also gradually increase from beginning to the end of the first campaign. As can be seen from the Figure, episodic high TEX concentrations were observed in 6th, 11th and 21th of October. Please note that these peaks were observed in all BTEX compounds, except for benzene. Although traffic is the best documented source for all BTEX compounds, benzene is the only BTEX compounds that are emitted solely from gasoline burning. Toluene, ethylbenzene and xylenes have also non-traffic sources, such as solvent evaporation. Since these episodes were not observed in time series plot of benzene concentration, but observed in concentrations of all other BTEX compounds, we can state that they are generated by some industrial activity rather than traffic emissions. It should also be noted that these episodes observed in TEX concentrations do not appear in time-series plot of the ΣVOC concentrations in Figure 4-43.

Concentrations of other light hydrocarbons, which are also known as good markers of light duty traffic emissions, including acetylene, 1,3-butadiene, 1,2,4-trimethylbenzene and heptane are given in Figure 4-45. Time-series plots of these compounds closely resemble that of benzene in the previous figure and thus confirm their traffic source in the Bursa atmosphere. Although concentrations of some of the traffic markers are affected from industrial activities in Bursa, these four compounds are not among them. Exhaust emissions from light-duty vehicles appears to be the dominating source of acetylene, 1,3-butadiene, 1,2,4-trimethylbenzene and heptane in Bursa atmosphere, at least during the first campaign.

Time-series plots of selected heavy hydrocarbons, including 1-undecene, 1-octene, dodecane and 1-nonane are given in Figure 4-46. Time-series plots of these compounds (and also of some of the other heavy VOCs, which are not shown in the figure due to space limitation) are characterized by two very strong episodes in 2nd of October and in 10th of October. These two peaks in time series plots of these heavy VOCs coincide with the episodes observed in ΣVOC concentration, which is shown in Figure 4-39. In those days ΣVOC concentrations reached to 350 and 380 $\mu g\ m^{-3}$

levels, respectively. Two minor episodes in heavy VOC concentrations are also observed in September 24 and October 16, 17 and 18. Although these episodes are also observed in concentrations of all of these compounds concentrations during these days are not as high as the ones observed in the first two episodes. These episodes in heavy VOC concentrations do not match with the episodes observed in TEX compounds in Figure 4-44. Also they did not show an increase with time. Probably these heavy hydrocarbons were influenced by very strong source and did not show a temporal variation.

These episodes in heavy VOCs are believed to be due to asphalting operations that took place. There was an intense asphalt pavement activity at Altıparmak Boulevard and at smaller roads that connect to Altıparmak Boulevard, between September 20 and October 10. Altıparmak Boulevard is one of the busiest roads in Bursa. Its distance to our station is approximately 1000 meters. Episodes were observed when wind blew from the direction of the Altıparmak Boulevard. During these periods station is strongly influenced by emissions from hot asphalt.

Heavy hydrocarbons are good markers of emissions from heavy duty vehicles (Pekey et al., 2013). However, trucks and buses or diesel engine in general is not their only source. These VOCs are also emitted in operations that involve asphalt, both during its production and its application to the roads (Liu et al., 2005; Liu et al., 2008; Vega et al., 2000). In addition to the findings of Liu and et al (2005, 2007, 2008), Profile number 1007 in EPA VOC Profile Speciation Report also demonstrate that heavy hydrocabons, such as isomers of dodecane, isomers of tetradecane, n-decane, n-undecane, n-dodecane, naphthalene, methyl napthelenes and trimethyldecene accounts for approximately 64% of the asphalt mass (EPA, 1990). Consequently data generated in this study clearly demonstrated that some of the heavy hydrocarbons can be used as good tracers of asphalt application in urban airshed. However, contribution of these operations on ΣVOC mass was striking in this study because of the close proximity of asphalt application to our station. It can be a significant VOC source for the urban atmosphere in general, as most asphalt applications are done during summer season, when traffic activity is at minimum.

VOC emissions during activities are enhanced by warm temperatures and circulation over the city is easier due to deeper mixing height.

Asphalt applications have an opposite effect on concentrations of light hydrocarbons. After September 21 for about 10 days, very low concentrations were observed, especially for the light hydrocarbons. This is obvious in Figures 4-44 and 4-45, where short-term variations in concentrations of BTEX compounds and other light VOCs are shown. These low concentrations are also due to asphalting operations. Light VOCs are not emitted from asphalt, so paving asphalt do not affect their ambient concentrations. However, traffic route was changed and Altıparmak Boulevard and connecting roads were closed off to traffic during asphalting operations. Therefore, concentrations of light hydrocarbons originating from emissions from gasoline exhaust decreased at our station.

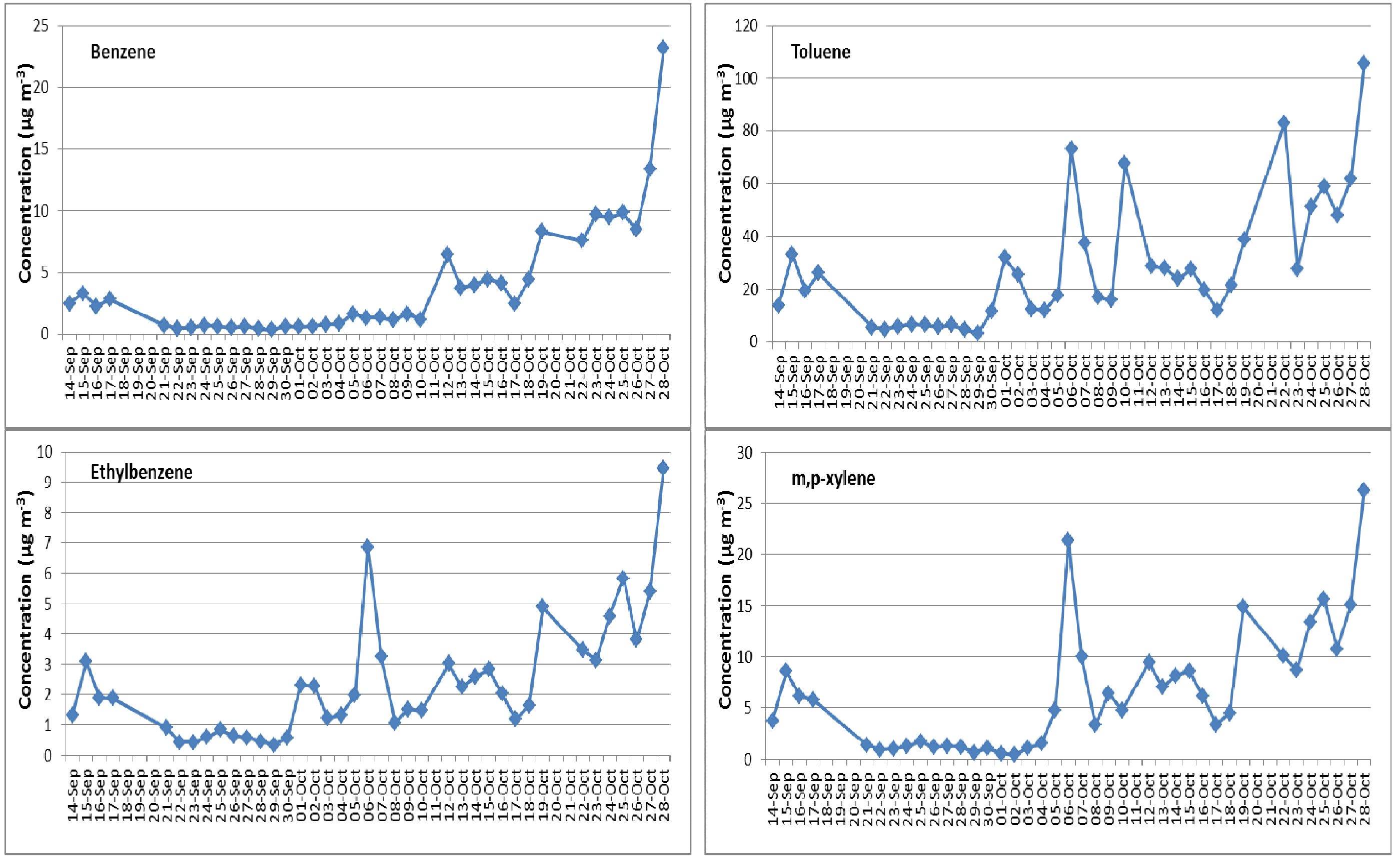


Figure 4-44 Daily variation of the BTEX group for the first campaign

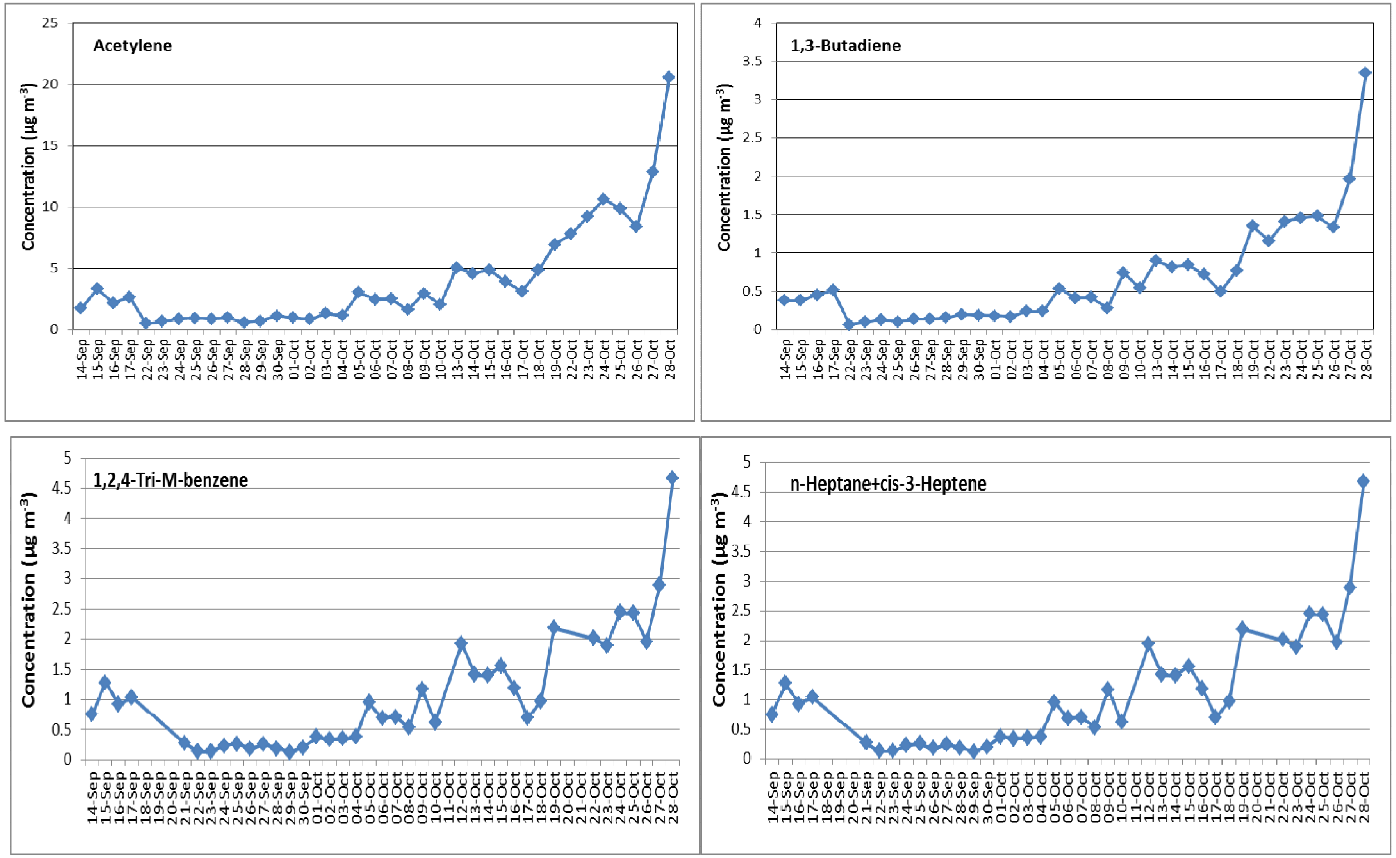


Figure 4-45 Time series of the selected VOC group for the first campaign

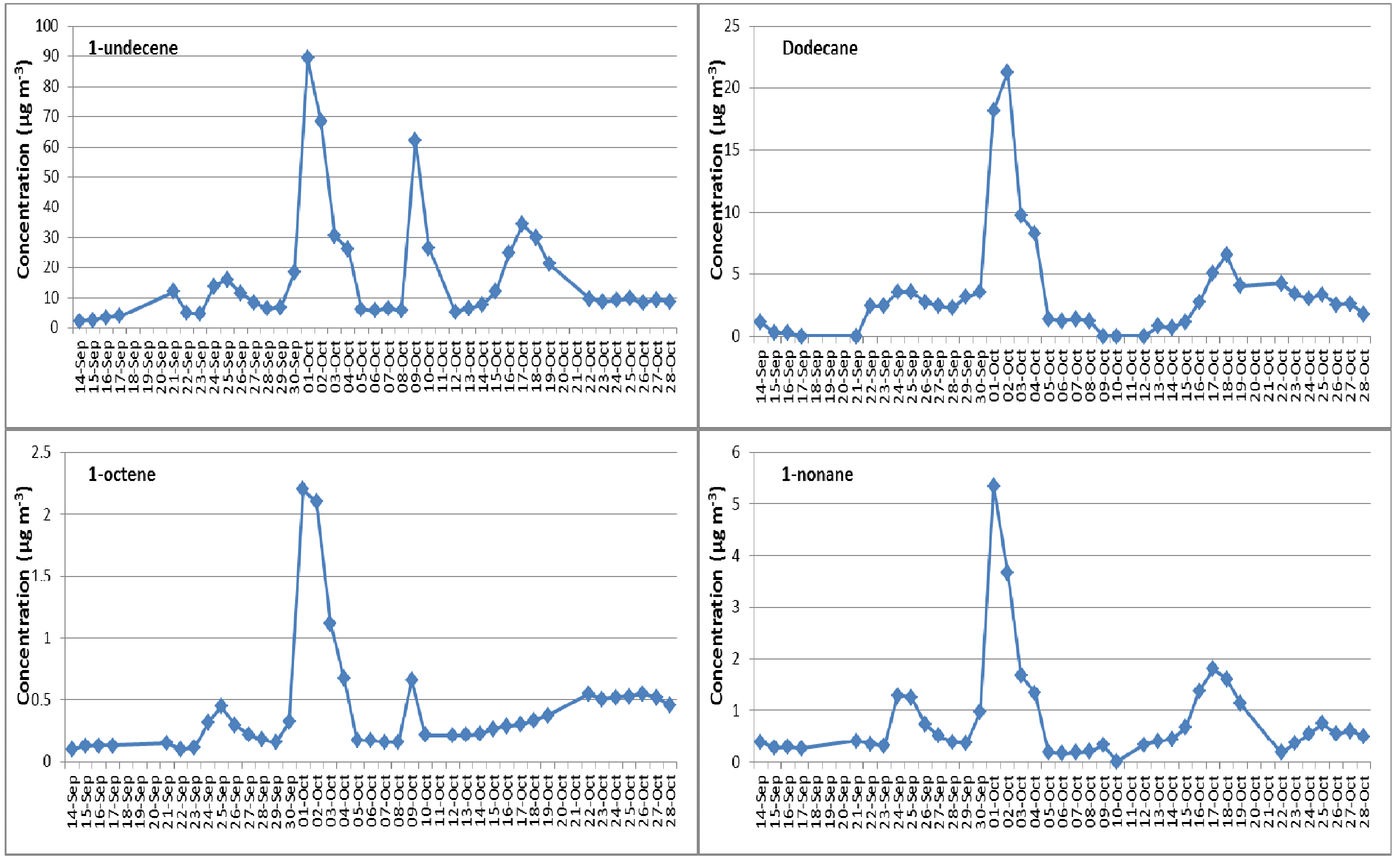


Figure 4-46 Times series of the selected compounds for the first campaign

Short-term (daily) variation of the ΣVOCs during the second campaign is presented in Figure 4-47. As can be seen from Figure ΣVOC concentration decrease with time during the sampling campaign. As discussed earlier in the manuscript, if emissions are equal, VOC concentrations in the winter are higher than those measured in summer because higher temperatures increase the evaporation of VOCs and strong solar radiation increases the photochemical oxidation rates of VOCs and deeper mixing height and higher ventilation coefficients in summer enhances ventilation.

Short-term variations in concentrations of BTEX compounds during the second campaign are given in Figure 4-48. As in the first campaign, very high toluene, ethylbenzene and o-and m,p-xylene concentrations were observed on 21st of March, 6th of April and 18th of April . Such episodes were attributed to evaporative sources (i.e., solvent usage, gasoline spill, and industrial activities) in the first campaign. The difference between BTEX episodes in the first and second campaigns is in benzene concentrations. In the first campaign, episodes observed in TEX compounds were not associated with episodes in benzene concentrations. This ruled out exhaust source for observed episodes. However, in the second campaign, episodic increases in TEX concentrations were correlated with similar increases in benzene concentration. Although evaporative sources cannot be ruled out entirely, association of TEX concentrations with that of benzene, in the second campaign may indicate that episodes observed in concentrations of BTEX compounds may also be due to exhaust emissions.

Short-term variations in concentrations of selected light hydrocarbons that are also documented tracers for vehicle exhaust are given in Figure 4-49.

As daily variations of all the compounds during the second campaign are examined, a decreasing trend can be seen for most compounds (Figure 4-49). However, 2,2,3-trimethyl-butane+2,3-di-m-pentane and 1-nonane showed a different trend (Figure 4-50).

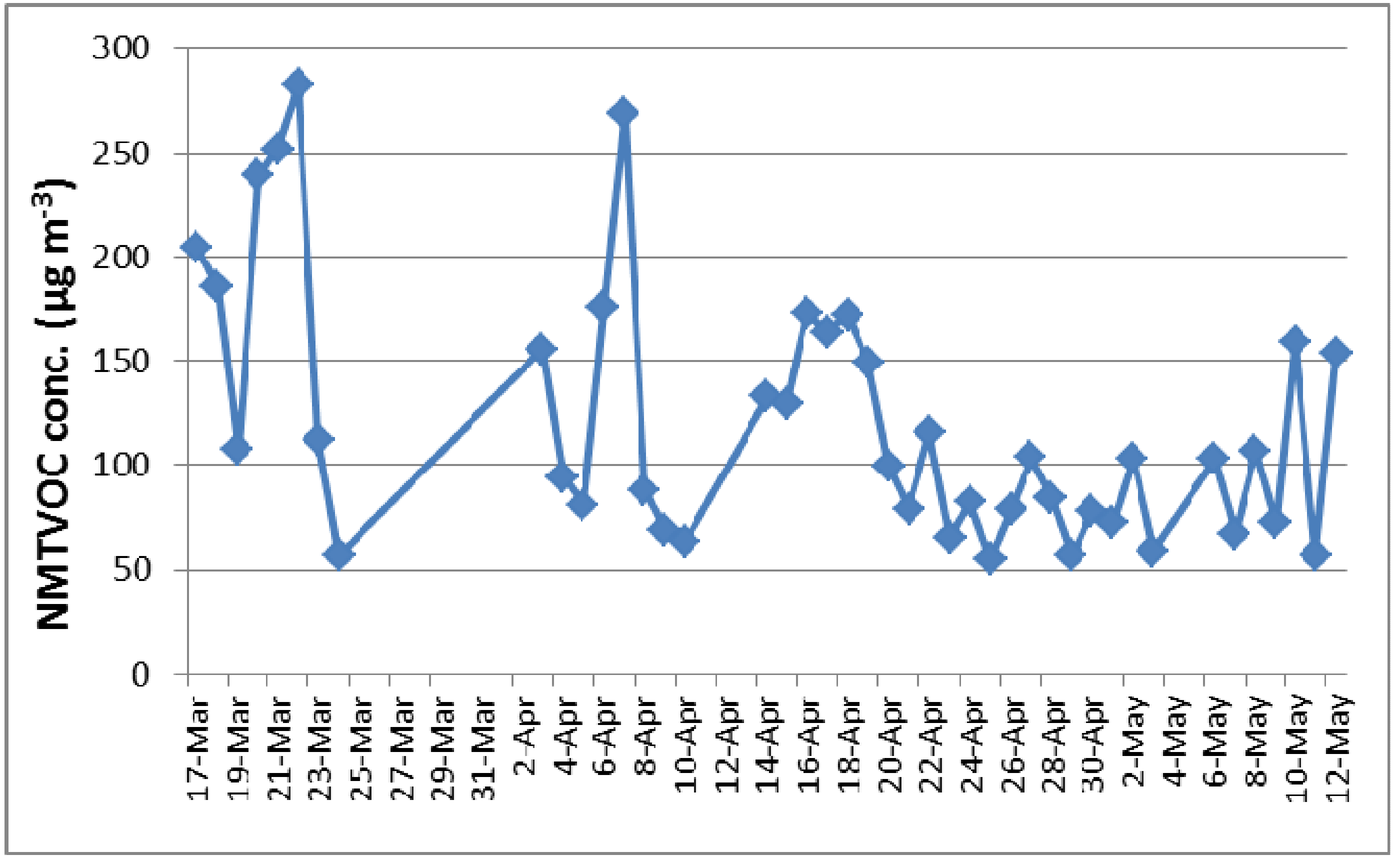


Figure 4-47 Daily variation of the NMTVOC during the second campaign

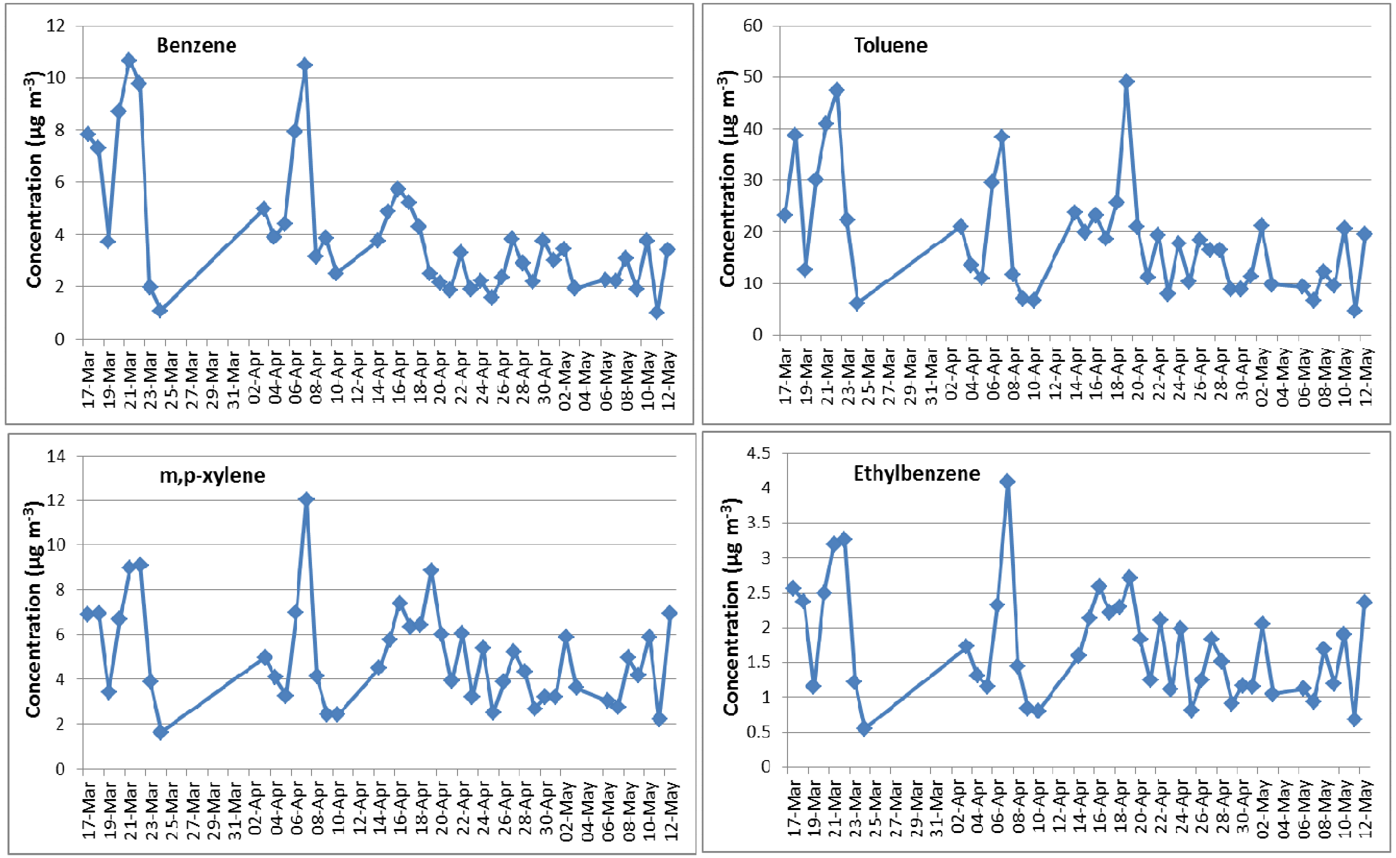


Figure 4-48 Daily variation of BTEX compounds during the second campaign

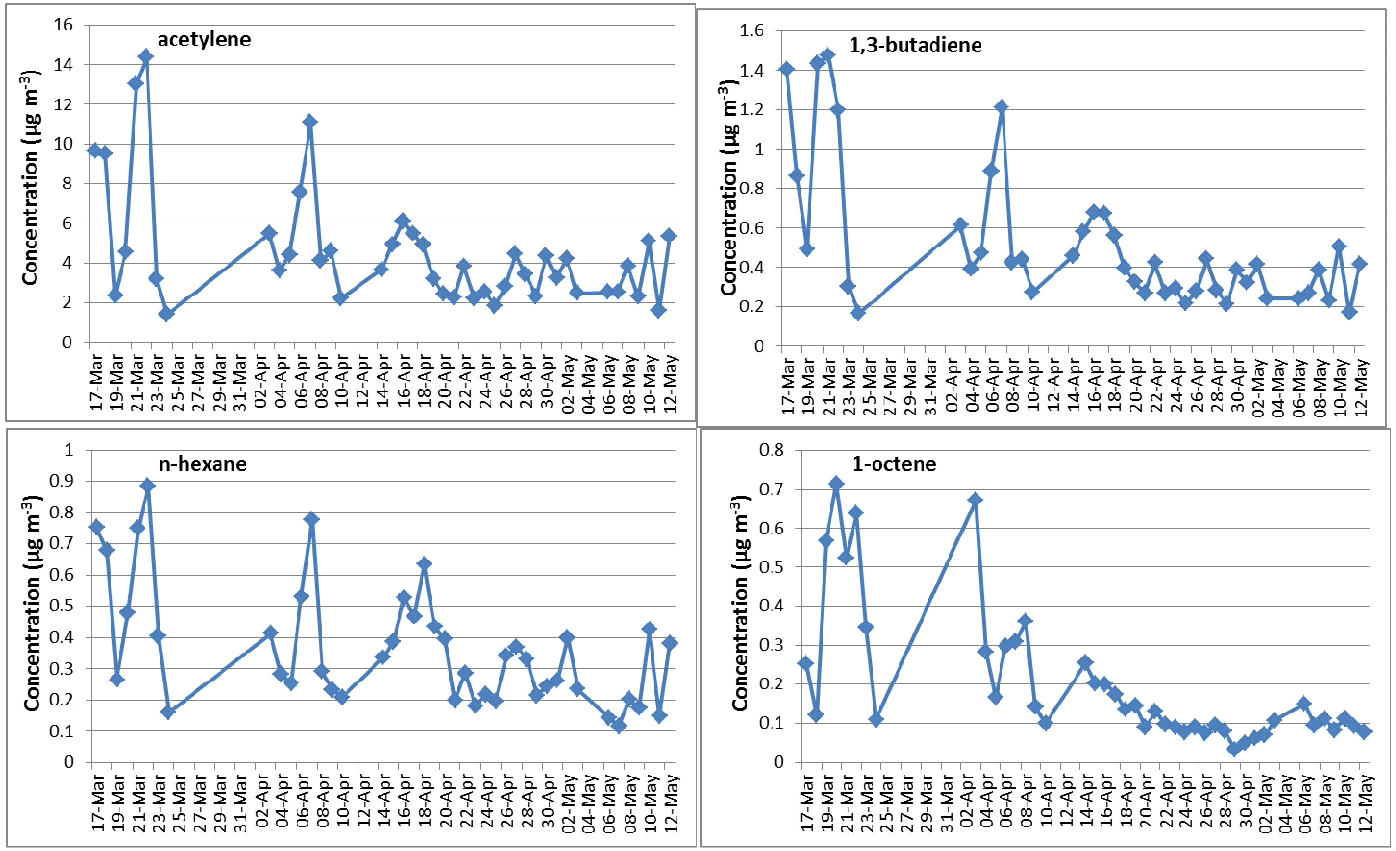


Figure 4-49 Daily variation of selected light VOCs during the second campaign

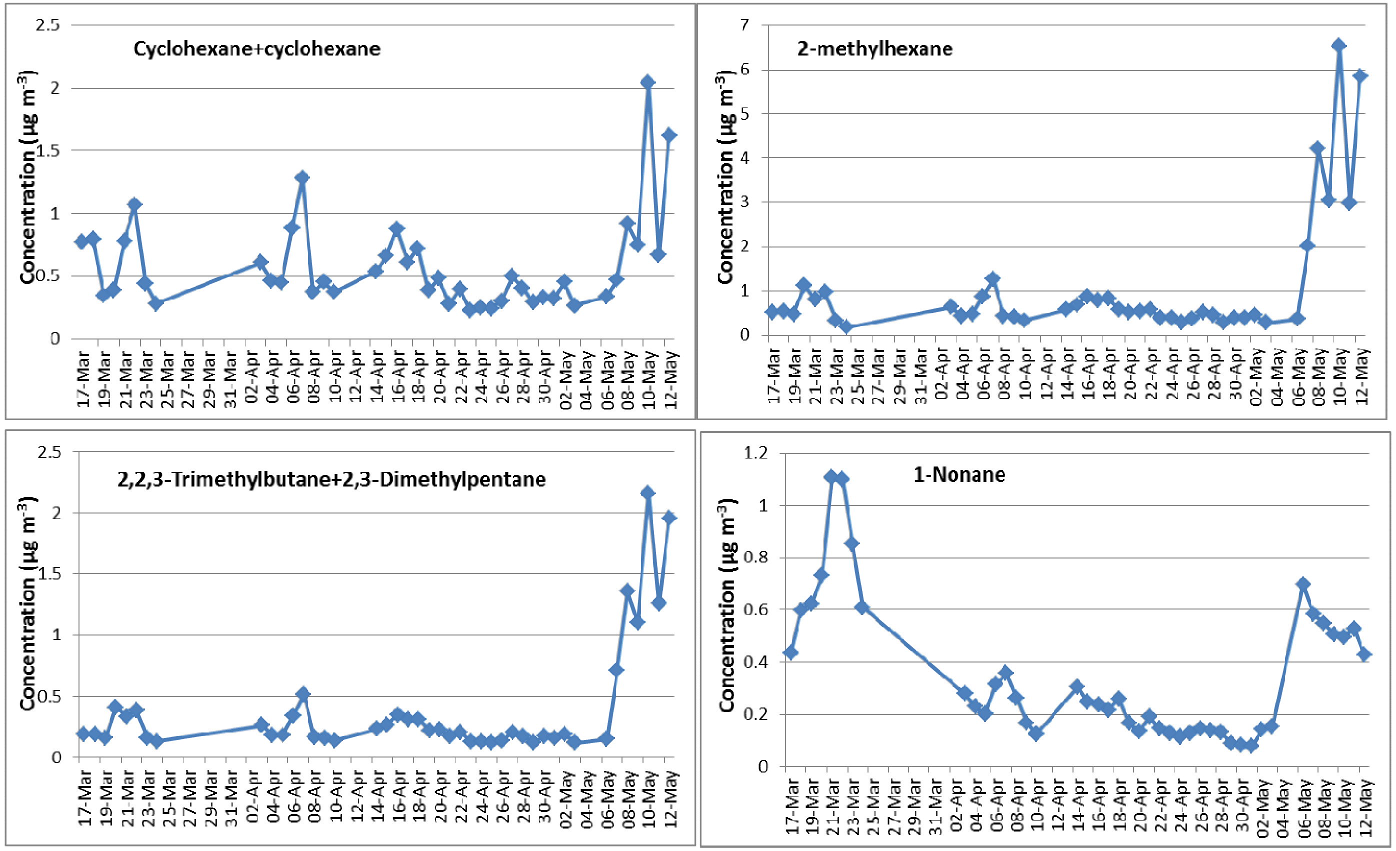


Figure 4-50 Daily variation of selected heavy compounds during the second campaign

Episodes observed in BTEX concentrations in 21st of March, 6th of April and 18th of April also occur in concentrations of acetylene, 1,3-butadiene, hexane and 1-octene. This also confirms that episodes observed in both of these groups are likely to be due to traffic emissions. The reason they appear as episodes is the transfer of these traffic emissions to our station, which strongly depends on wind direction.

C_3-C_6 alkanes are emitted to atmosphere from both traffic activities and evaporative sources (Brown et al, 2007; Borbon et al., 2002; Srivastava et al., 2005). Daily variation in concentrations of cyclohexane, 2 methylhexane, 2,2,3-trimethylbutane and 1-nonane, which are among this group, are given in Figure 4-50. Episodes observed in BTEX concentrations in March 21st and in April 6th are also observed in concentrations of these species, indicating that at least some of their concentrations are from traffic emissions. However, BTEX episode in April 18th, which is observed in BTEX compounds does not exist in concentrations of cyclohexane, 2 methylhexane, 2,2,3-trimethylbutane and 1-nonane. Similarly strong episodes observed in concentrations of these compounds at the end of May do not exist in BTEX concentrations. This observation suggests that traffic is not the only source of cyclohexane, 2 methylhexane, 2,2,3-trimethylbutane and 1-nonane.

4.6 VOC Ratios: Temporal Pattern

Chemical species in the atmosphere show different reactivity. As a result of photochemical reactions, concentrations of the reactive compounds will decrease faster than concentrations of less reactive ones (Elbir et al., 2007). Ratios of VOCs with different reactivity can provide information on aging of VOCs and thus relative distances between the source and receptor (Guo et al, 2007). In the atmosphere m,p-xylene and ethylbenzene have higher reaction rates with OH radicals compared to benzene; therefore, their removal in the atmosphere will be faster than that of benzene (Elbir et al., 2007). This means that xylene-to-benzene (X/B) and ethylbenzene-to-benzene (E/B) can be used for this purpose. However, the ratio that is most widely used to assess aging of air parcels is xylene-to-ethylbenzene ratio (X/E ratio) (Ho et al., 2004; Hsieh et al., 2011).

Similarly ratios of VOCs with different sources can provide information on relative contributions of these sources. Benzene-to-toluene ratio (B/T ratio) is the most widely used ratio for this purpose. Benzene is emitted exclusively from motor vehicles, particularly from light duty vehicles. Although emissions from motor vehicles are also source of toluene in the atmosphere, it also has non-traffic sources, such as evaporation from painted surfaces. Consequently, low B/T ratios indicate strong contribution of non-traffic sources on the VOC composition of the atmosphere (Guo et al., 2004; Guo et al, 2007; Hoque et al., 2008).

Hourly variation of VOC ratios during first campaign are depicted in Figure 4-51. The X/E ratio decrease after the compounds (xylene and ethylbenzene) is emitted to atmosphere, because xylenes react faster with HO radicals (Ho et al., 2004). Hence, low X/E ratios are measured at a receptor which is far from the source (Huo et al., 2004). In the first campaign, X/E ratios vary between 0.05 and 5.83 with an average value of 2.51 ± 0.9. Average X/E ratio suggests a mix of fresh emissions from traffic in the city and relatively aged emissions from distant sources. Time series of X/E values in the first campaign demonstrate that the ratio does not follow a homogeneous pattern, but increases and decreases in time, indicating that there are times when local traffic emission dominate measured concentrations of VOCs and there are times when their concentrations are influenced from distant emissions. The episodic increases observed in concentrations of TEX compounds, which were discussed in previous section corresponds to low X/E ratios suggesting that those episodes are generated by emissions away from the city center. This conclusion agrees with the industrial evaporative sources suggested in that section.

T/B ratio is usually preferred to determine traffic emissions because both are main constituents of gasoline. However, the ratio is modified in the atmosphere, because toluene can originate from solvent emissions via evaporation. Toluene-to-benzene ratios reported for fresh exhaust emissions are approximately 2, but the ratio increases with increasing non-traffic toluene contributions (Sweet and Vermette, 1992; Scheff and Wadden, 1993).

The T/B ratios, in the first campaign, change between 1.50 and 449.30 with an average value of 15.49±29.33. The average T/B ratio of approximately 15 is significantly higher than 2.0 which is the value used for fresh traffic emissions and suggest that there is persistent non-traffic toluene in the Bursa atmosphere. Please note that toluene is an indicator for non-traffic VOC emissions, but it is not the only VOC which has non-traffic sources. Consequently, presence of a continuous influence of non-traffic sources on toluene concentrations also indicates the contribution of these non-traffic sources on other VOCs as well.

One point to note in Figure 4-51 is the T/B and X/E ratios between September 30 and October 2. Between these days very high T/B ratios are measured. These high T/B ratios correspond to unusually low X/E ratios. Anomalous ratios in this period is due to asphalt pavement operations around our station and will be discussed in more detail in PMF section of the manuscript, because one of the factors in PMF clearly related to asphalt operations.

Time series plots of T/B and X/E ratios are depicted in Figure 4-52. Temporal variation of the ratios in the second campaign is not as variable as their temporal variation in the first campaign. Median values of T/B ad X/E ratios in the second campaign are 4.61 and 2.92 respectively. The median value of X/E ratios is not significantly different from the X/E values in the first campaign.

However, T/B ratios in the first campaign are a factor of two higher than T/B ratios in the second campaign. The median T/B ratio in the first campaign is approximately 8 whereas median T/B ratio in the second campaign is approximately 4. The value of 8 indicate that there is a significant contribution by non-traffic sources on measured VOC levels, whereas average value of 4 indicate more important contribution from traffic sources. Even the value of 4 indicates that traffic is not the only source of toluene in the atmosphere. Higher contribution of non-traffic sources in the first campaign is partly due to episodic industrial releases of solvents, as the one occurred between September 30 and October 2, 2005 and partly due to limitation of traffic activity at Altiparmak Boulevard for asphalting operations.

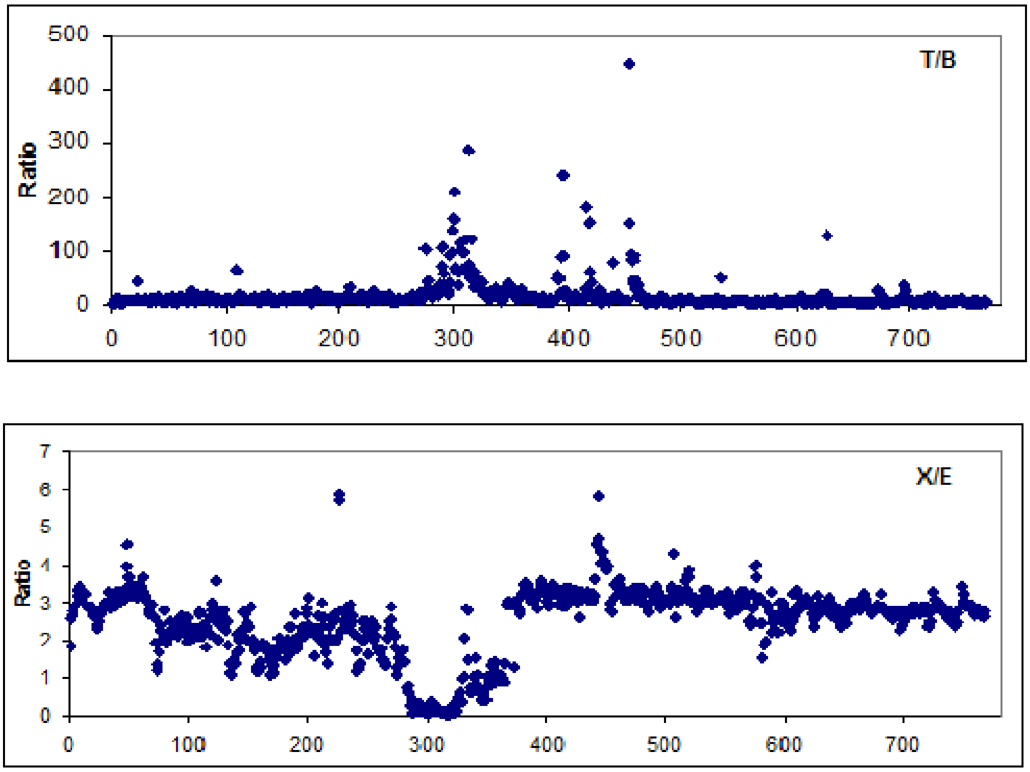


Figure 4-51 Ratios of the BTEX group for the first campaign

T/B ratio of between 4 and 8 and X/E ratio of approximately 3 are typical for the city of Bursa all year around. These values indicate that VOC concentrations measured at our station are result of a mixing of traffic emissions with non-traffic evaporative emissions. In most of the cities studied by our group traffic emissions have dominating influence on measured VOC levels. Only in Bursa non-traffic emissions, most likely from extensive industrial activities in the city, have observable contribution to measured VOC levels.

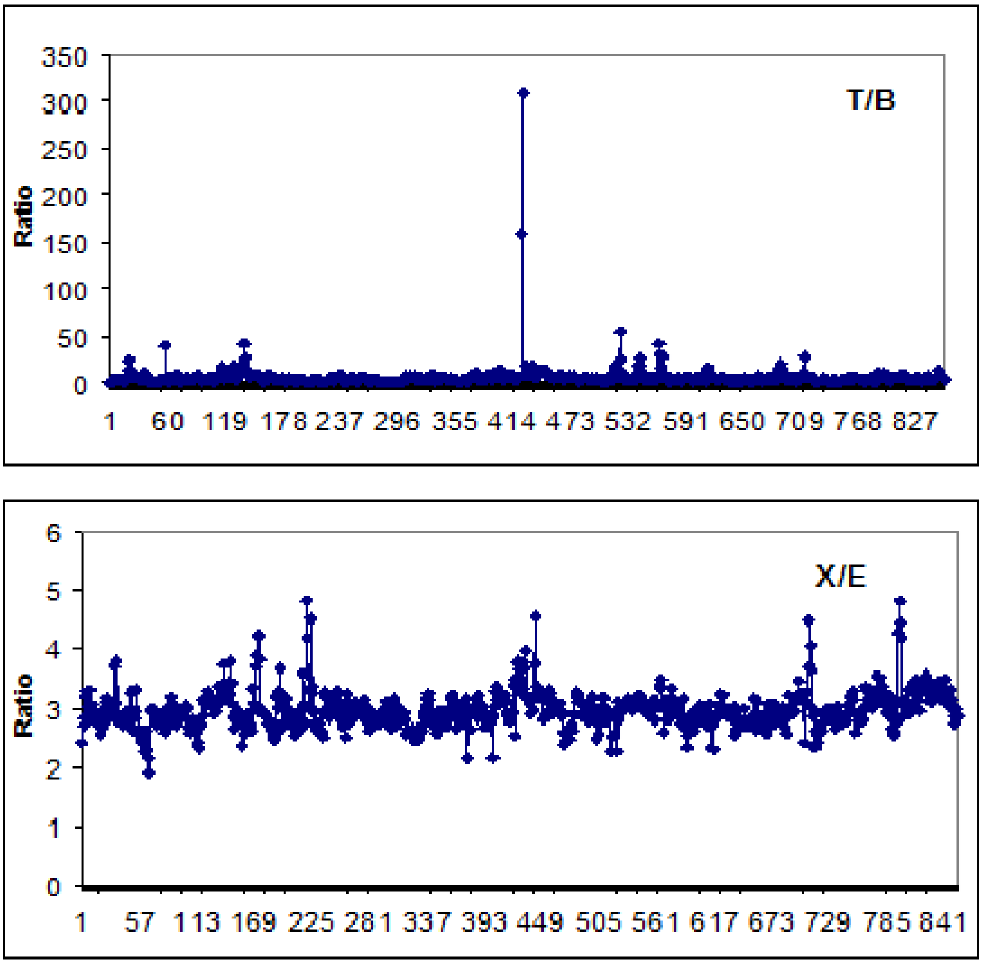


Figure 4-52 Ratios of the BTEX group for the second campaign

Diurnal variations in T/B and X/E ratios are given in Figure 4-53. X/E ratios do not show any variation during the day. Its value is constant at around 3 in both seasons. Constancy of X/E ratio demonstrate that there is no significant variations in the age of air parcels arriving to our station, which is expected in an urban atmosphere, where distribution of VOC sources do not change throughout the day. There may be episodic changes in transport distances, as discussed earlier in the manuscript (unusually low X/E ratios between September 30 and October 2), but these observations are too short-time to modify the general pattern. Such episodic variations are mostly confined to the first campaign and not observed in the second one.

T/B ratio, on the other hand, depicted a well-defined diurnal pattern with maximum values were reached between 15:00 and 16:00 in both campaigns. In the first campaign maximum T/B ratios reaches to 35, but in the second campaign they increased up to 18. The diurnal pattern observed in T/B ratio is probably due to diurnal variation in temperature. Since non-traffic sources of toluene include evaporation from painted surfaces and solvents, these are expected to increase with temperature. The striking point in this diurnal pattern is that it shows that evaporative sources of toluene and other VOCs is more important than we anticipated.

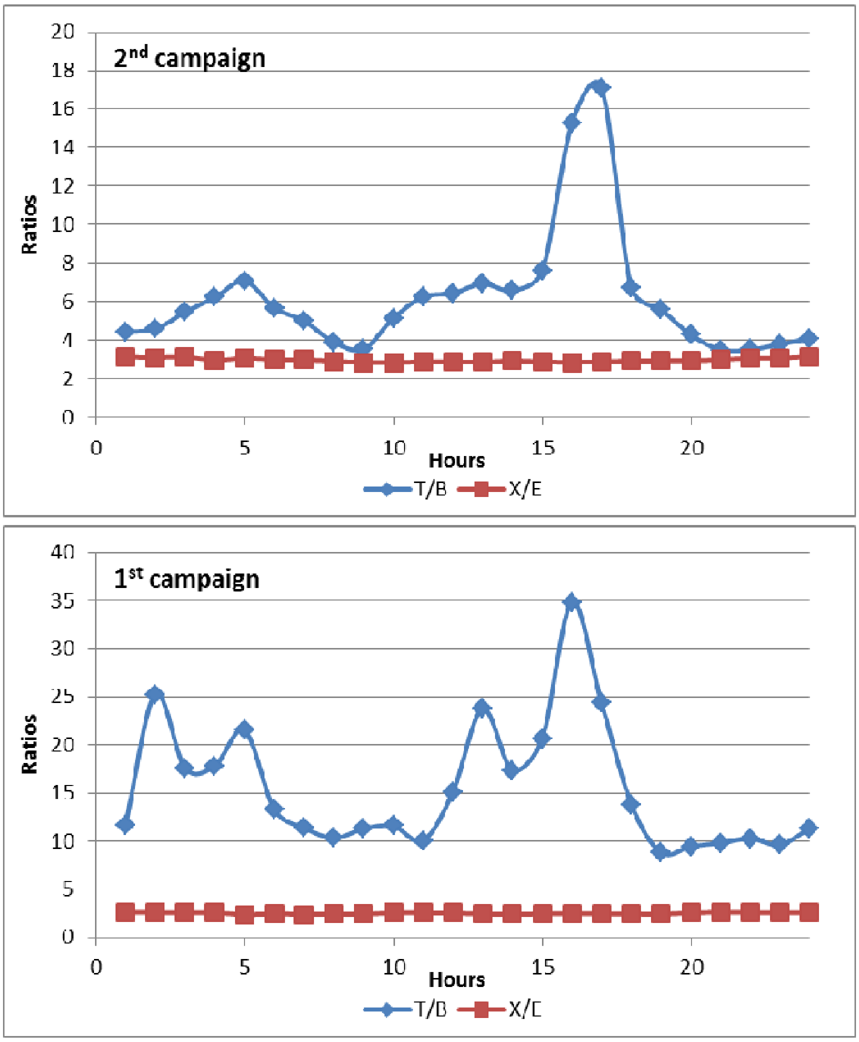


Figure 4-53 Diurnal variation of the VOC ratios for both campaigns

The T/B ratios found in this study are generally higher than those measured in Italy (1.5), France (2) (Mulder, 2000), Germany (<3), (Seilet et al., 2002), India (<1) (Chattopadhyay et al., 1997), Santiago (2.1) (Hoque et al., 2008), Hanoi (1.2-1.3) (Truc and Oanh, 2007), Copenhagen (2.2), Mortsel (3-4) (Buczynska, 2009), Toronto (2.4), and Los Angeles (2.5) (Pilar and Graydon, 19873). Although T/B ratios obtained in the present study are generally higher than T/B ratios for different parts of the world, there are some studies where calculated T/B ratios are even higher than those found ın this study. These few studies include; T/B ratio fond in Hong Kong (avg 5) (Lee et al., 2002), in Southern Taiwan (0.9-8.6) (Hsieh et al., 2006), and Hong Kong (37) (Ho et al., 2004).

4.7 Inter-species Correlation

Correlation coefficients between selected compounds during the first and second campaigns are given in Table 5. Binary correlation coefficients between compounds are close to unity, indicating a strong correlation ($P<0.001$) between most of the VOCs. This situation is probably due to the strong source in the city center, most likely the traffic. Benzene is mostly assumed as a marker for heavy traffic, which is generally the major source of the BTEX compounds (Khoder, 2007). Low r values between benzene and toluene for both campaigns is due to supplementary sources toluene other than the traffic (Hoque et al., 2008). Please note that discussion of VOC ratios demonstrated that these supplementary sources are particularly important in Bursa due extensive industrial activity in the city. In addition to industries, small commercial activities in city center or motor vehicle service stations are also supplementary sources of toluene.

Table 4-5 Summary of the BTEX correlation coefficients during the both sampling campaigns

The first campaign					
	Benzene	Toluene	Ethylbenzene	m,p-Xylene	o-Xylene
Benzene	1.00				
Toluene	0.532	1.00			
Ethylbenzene	0.640	0.877	1.00		
m,p-Xylene	0.618	0.857	0.985	1.00	
o-Xylene	0.710	0.827	0.963	0.978	1.00
Undecane	-0.001	0.088	0.06	0.046	0.082
1,2,3,5-Tetra-M-Benzene	0.085	0.040	0.060	0.046	0.089
1,2,4,5-Tetra-M-Benzene	0.129	0.074	0.099	0.081	0.132
1,2,4-Tri-Cl-Benzene	0.231	0.097	0.196	0.169	0.270
Naphthalene	-0.01	0.014	-0.009	-0.020	0.029
Hexylbenzene	0.032	0.002	-0.005	-0.022	0.029
The second campaign					
	Benzene	Toluene	Ethylbenzene	m,p-Xylene	o-Xylene
Benzene	1.00				
Toluene	0.465	1.00			
Ethylbenzene	0.672	0.817	1.00		
m,p-Xylene	0.624	0.830	0.982	1.00	
o-Xylene	0.719	0.807	0.955	0.964	1.00
m,p-chlorotoluene	-0.043	-0.054	-0.058	-0.099	-0.060
1-octene	-0.003	0.140	0.094	-0.082	-0.029
1-nonene	-0.137	0.06	0.027	-0.212	-0.134
1-undecene	-0.178	-0.018	-0.051	-0.155	-0.135
1,2,4-trichlorobenzene	-0.188	-0.013	-0.080	-0.185	-0.139
Dodecane	-0.166	0.042	-0.002	-0.262	-0.204

Correlations between some compounds and BTEX compounds were found low for both campaigns. In the first campaign, for example correlation between heavy hydrocarbons and other BTEX compounds were poor ($p<0.18$) and mostly negative during the first campaign. However, there was a good correlation ($p>0.91$) among the heavy hydrocarbons, indicating that they were emitted from the same source, likely asphalting operations.

Similar results are also observed in the second campaign. In the second campaign, correlations (i.e., $p<0.27$) between BTEX and undecane, 1,2,3,5-tetra-m-benzene, 1,2,4,5-tetra-m-benzene, 1,2,4-tri-Cl-benzene, naphthalene and hexylbenzene are low (not statistically significant). This is due to industrial sources of undecane, 1,2,3,5-tetra-m-benzene, 1,2,4,5-tetra-m-benzene, 1,2,4-tri-Cl-benzene. Industrial sources of these compounds are confirmed in the PMF exercise, which will be discussed in Chapter 5. These VOCs are associated with industrial factor in PMF. Furthermore, most of the chlorinated compounds are emitted from sources where solvents are used (Kuntasal, 2006).

4.8 VOC Reactivity and Ozone Formation Potential

Organic compounds are emitted into the atmosphere from different types of natural and anthropogenic sources. These emissions are affected by a variety of physical processes and chemical reactions during their lifetimes in the atmosphere. Gas phase organic chemicals are removed from the atmosphere by dry and wet deposition and various chemical reactions, especially with hydroxyl radicals, nitrate radicals and ozone.

The main loss process of gas phase organic compounds is reaction with OH radicals (Stockwell et al., 2012). The tropospheric life time of the organic compounds is very important because it verifies the transport of the compound to remote regions and accumulation of the compounds and absorption of IR in the atmosphere (Kwok and Atkinson, 1995; Atkinson, 1990).

Rate constants and half-life of the VOCs measured in the atmosphere of Bursa are given in Table 4-6. Constants were obtained from the literature (Kwok and Atkinson, 1995; Atkinson, 1990). The reactions were assumed to be of second order with reactant lifetime of (=1/k[OH]. The OH concentration was taken as a $2x10^6$ molecule cm^{-3} (which is the measured OH concentration value in spring and september in Europe) for the calculation of life times (Simpson, 1995).

Table 4-6 Rate constants and half-lives of organic compounds due to reaction with OH radicals (Kwok and Atkinson, 1995)

Compound	**k_{OH} (cm^3 molecule^{-1} s^{-1})**	**Half life (hr)**
Propane	1.15E-12	120.77
n-Butane	2.54E-12	54.68
Acetylene	0.9E-12	154.32
t-2-Butene	64 E-12	2.17
1-Butene	31.4 E-12	4.42
2,2-DiM-Propane	0.849 E-12	163.59
Cyclopentane	5.16 E-12	26.92
n-Pentane	3.94 E-12	35.25
1,3-Butadiene	66.6 E-12	2.09
Cyclopentene	67 E-12	2.07
1-Pentene	31.4 E-12	4.42
2,2-Di-M-Butane	2.32 E-12	59.87
2,3-Di-M-Butane	6.3 E-12	22.05
2-M-Pentane	5.6 E-12	24.80
3-M-Pentane	5.7 E-12	24.37
n-Hexane	5.61 E-12	24.76
Benzene	1.23 E-12	112.92
2-Methylhexane	6.79 E-12	20.45
2,3-Dimethylpentane	4.87 E-12	28.52

Table 4-6 (continued)

3-M-Hexane	7.16 E-12	19.40
n-Heptane+cis-3-Heptene	7.15 E-12	19.43
Methylcyclohexane	1.04E-11	13.35
Toluene	7.09 E-12	19.59
Octane	8.68 E-12	16.00
Ethylbenzene	7.1 E-12	19.56
m-Xylene	2.36E-11	5.89
p-xylene	1.43E-11	9.71
Styrene	5.80E-11	2.39
o-xylene	1.37E-11	10.14
n-Nonane	10.2 E-12	13.62
n-Probylbenzene	6.00E-11	2.31
1,3,5-Tri-M-Benzene	5.75E-11	2.42
1,2,4-Tri-M-benzene	3.25E-11	4.27
n-Decane	11.6 E-12	11.97
1,2,3-Tri-M-benzene+p-Cymene	3.27E-11	4.25
Naphthalene	2.16E-11	6.43

In Table 4-6, the long atmospheric times indicate stable compounds in the atmosphere. Therefore, benzene, propane, acetylene and 2,2-di-m-propane had the longest atmospheric life time in Bursa atmosphere.

Ground level ozone is a very important problem. Ozone is not directly emitted into the atmosphere; it is a secondary pollutant that is formed from the photochemical reactions between VOCs and nitrogen oxides. As there are different types of the VOCs with different types of reaction mechanisms and each VOC has different contribution to the formation of ozone. These differences on the formation of ozone are stated to as the “ozone reactivities” of the VOCs (Carter, 1994).

The ranking of organic compounds can be performed according to the ozone formation potential by using Carter’s maximum incremental reactivity (MIR) (Tiwari et al., 2010). Carter’s MIR is the amount (in grams) of ozone formed per gram of VOC added to an initial VOC–NO_x mixture and is a unitless constant. MIR indicates the amount contributed to the total ozone formation in an air mass by an individual compound (Carter, 1994). MIR coefficients used in the present study were obtained from the literature (Carter, 1994; Tiwari et al., 2010) (Table 4-7).

Table 4-7 MIR values of measured species during the sampling campaigns (Carter, 1994; Tiwari et al., 2010)

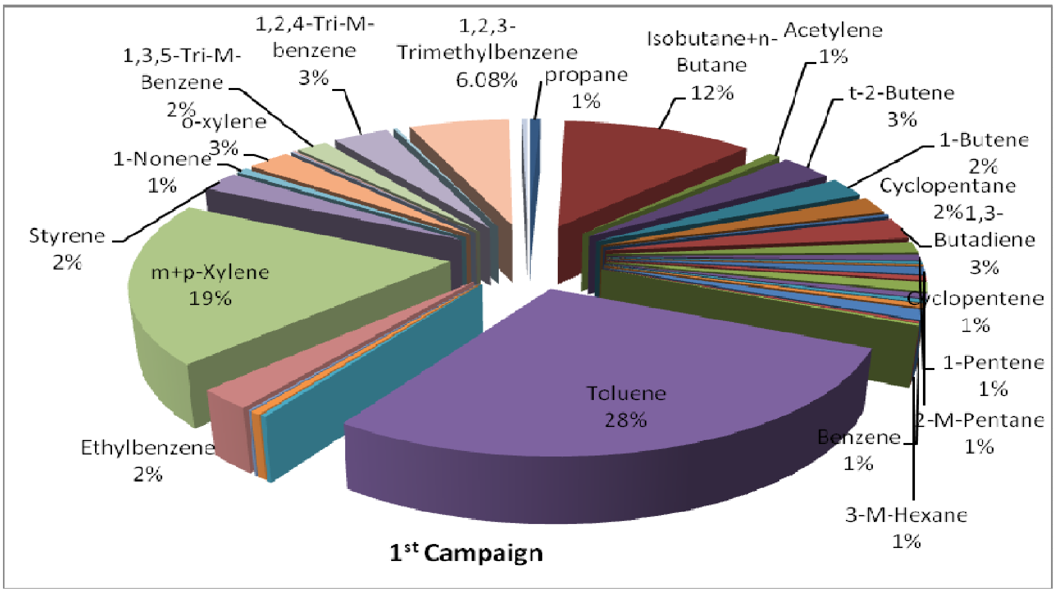
Compound	MIR (gr O3/ gr VOC)	Compound	MIR (gr O3/ gr VOC)
Propane	0.48	2-M-Heptane	0.96
Isobutane+n-Butane	1.12	2,2,3-Trimethylbutane+2,3-Dimethylpentane	2.63
Acetylene	0.5	3-M-Hexane	1.4
t-2-Butene	10	n-Heptane+cis-3-Heptene	0.81
1-Butene	8.9	1-Octene	2.7
Cyclopentane	2.4	Octane	0.6
n-Pentane	1.04	Ethylbenzene	2.7
1,3-Butadiene	10.9	m+p-Xylene	8.2
Cyclopentene	7.7	Styrene	2.2
1-Pentene	6.2	1-Nonene	2.2
2,2-Di-M-Butane	0.82	o-xylene	6.5
2,3-Di-M-Butane	1.07	n-Nonane	0.54
2-M-Pentane	1.5	n-Probylbenzene	2.1
3-M-Pentane	1.5	1,3,5-Tri-M-Benzene	10.1
n-Hexane	0.98	1,2,4-Tri-M-benzene	8.8
Benzene	0.42	n-Decane	0.46
2-Methylhexane	1.08	1,2,3-Tri-M-benzene+p-Cymene	8.9
Methylcyclohexane	1.8	Naphthalene	1.17
Toluene	2.7		

Ozone formation potential of the measured VOCs in the atmosphere of Bursa in both campaigns is given in Figure 4-54. Based on the MIR scale, toluene (28%) is the dominant VOC for ozone formation as compared to other organics. According to the PMF profiles which are given in Chapter 5, the main sources of the toluene are the industrial activities and vehicle exhaust. Therefore, more effective control strategies of solvent originated products will supply more efficient ozone reductions in Bursa atmosphere.

The m,p-xylene (19%) is the second largest contributor followed by isobutene+n-butane (12%). The BTEX group alone contributed about 50% of the total ozone formation potential.

Although the contribution of 1,3-butadiene, 1,3,5-Tri-M-Benzene and t-2-butene to ozone formation potential were the highest, the ozone formation potential of these compounds were found to be lower than 5% due to their low atmospheric concentrations. Furthermore, the contribution of the benzene to the ozone formation potential was also calculated lower than 1% for both campaigns although benzene is the most dangerous volatile organic compound in the atmosphere.

The difference in ozone formation potentials VOCs in the first and second campaigns and species that have the highest contribution for ozone formation are not very different between the first and second campaigns.



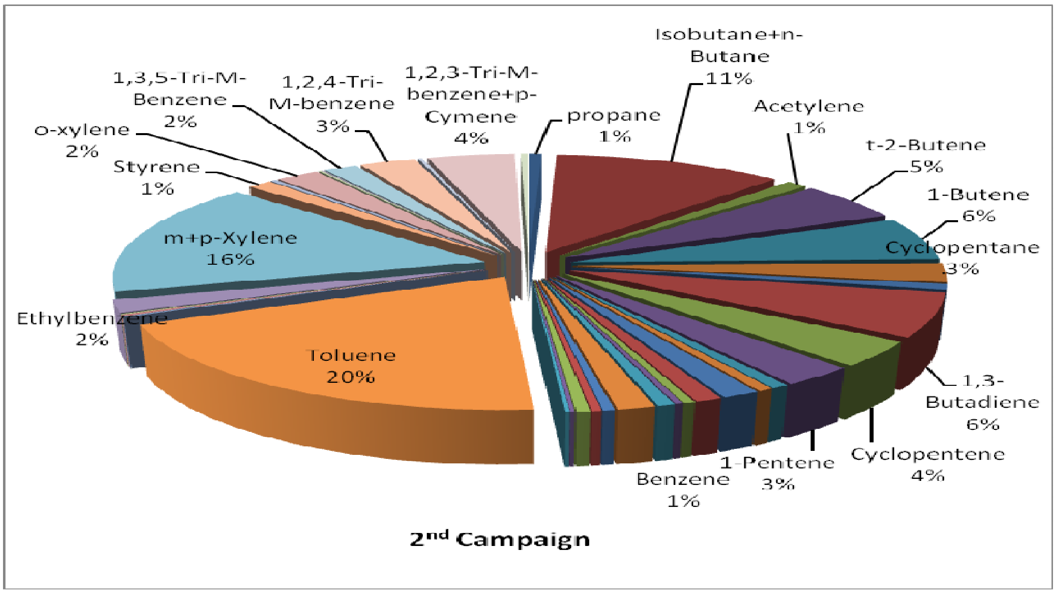


Figure 4-54 Ozone formation potentials of the measured VOCs in both campaigns (contributions below the 1% are not shown in the figure)

CHAPTER 5

RECEPTOR MODELLING

5.1 Source Apportionment

Sources contributing to measured concentrations of VOCs in Bursa atmosphere were investigated using receptor modeling approach. There is a variety of receptor modeling tools, such as chemical mass balance, factor analysis, principal component analysis, multi linear engine, cluster analysis, positive matrix factorization (PM), which are used in source apportionment studies. Each of these has their own advantages and disadvantages. Among them, most commonly used receptor modeling tools are factor analysis CMB, cluster analysis and more recently PMF.

In this study PMF was used to identify and quantify sources of VOCs. The PMF is a multivariate statistical instrument like factor analysis. Factor analytical modeling was in use since early 80's and because of this its advantages and disadvantages are fairly well established. PMF, on the other hand, appeared in last 10 years, but it replaced FA in most receptor modeling studies. The PMF has several advantages over conventional FA. It is quantitative, whereas FA is qualitative (unless some additional statistical calculations are done). The most important superiority of PMF over other multivariate tools like FA and PCA is that it can operate with incomplete data sets.

In environmental samples all parameters are not necessarily measured in all samples. Some were not measured because their levels in the atmosphere can be lower than detection limits of the instruments. Some are not measured due to analytical problems. Some may be considered in some of the samples. Because of these reasons, there is fairly large number of below detection limits (BDL) and undetects in environmental, including atmospheric data sets. Multivariate techniques like FA and PCA cannot use such data sets with large number of non-detect and undetect values. When there is a sample with even one missing datum that sample is not included in the FA. In a typical atmospheric data set 80-90% samples can be excluded with those criteria. Data can be filled in, but fabricated data is not as good as measured data and increase unique variance of the system. However, PMF can operate with even very high missing data points (up to 50% of 60%). Because in PMF individual data points can be weighted separately. Generally high uncertainty can be assigned to uncertain data and contribution of that data point on the model fit is minimized. This means that when there is a missing datum and arbitrary number can be entered, and very high uncertainty is assigned to it. Then, that arbitrary number does not contribute to generation of factors. The real data of the same parameter, which has a reasonable uncertainty, do contribute to model fit.

As can be understand from this discussion; assignment of uncertainty to data points is a crucial step in PMF and has to be done with extreme caution, because accuracy of the output is strongly related to uncertainties assigned to parameters. How this is done is explained in the next section

5.2 Positive Matrix Factorization

EPA PMF v3.0, which was developed by the United States Environmental Protection Agency's Office of Research and Development, was used in this study to investigate sources of VOCs measured in Bursa atmosphere. There are two types of input to the program, namely concentrations and error estimates. Methodology developed by Pollisar et al., (2001) was used to generate uncertainties of each datum. Briefly, when a data is above the detection limit concentration value is directly used and uncertainty of the datum is set equal to summation of the detection limit for each compound and a certain ratio of concentration of that compound. This ratio was selected as a 0.05 for this study. Data below the detection limit were replaced with half of the detection limit and 5/6 of the detection limit was used as its uncertainty. For missing data, the concentration was replaced with the geometric mean of the measured concentrations and 4 times of the geometric mean value was used as error.

5.2.1 Input Parameters

Two approaches were used to prepare data set for PMF analysis. Firstly, compounds and samples with 15% or higher missing or BDL values were excluded from the PMF analysis. In the second step, variables with high noise were down-weighted. (Paatero and Juntto, 2000; Paatero and Hopke, 2003). According to the suggested method, compounds with a weak signal-to-noise ratio (between 0.2 and 2) should be down weighted and compounds with a poor signal to noise ratio (lower than 0.2) should be entirely removed from the input data set. In this way, contribution of weak compounds to PMF fit is reduced to obtain better modeling results (Brown et al., 2007). For the first campaign, t-2-butene, 2-m-heptane, m,p-chlorotoluene and naphthalene and for the second campaign 2-methylhexan, 2,2,3-trimethylbutane and 1,3-di-ethylbenzene are classified as bad variables and removed from the input data set.

Determination of factor numbers is a crucial step in PMF analysis. Variation of the goodness-of-fit parameter (Q) is the key factor to assess optimum number of factors. Therefore, Q values are used for the evaluation of how well the model fits the real data. EPA PMF gives two Q values for each run, namely Q(robust) and Q(true). Q(robust) is the goodness of fit parameter and is calculated by the model. And changes from one run to another. Theoretical Q value (Q_{true}) is calculated using the following relation:

$$Q_{true\,=}\ nm - p(n+m),$$

where n is the number of parameters (in this case VOCs), m is the number of samples, and p is the number of factors. Ideally, Q_{true} should be less than $1.5xQ_{robust}$, otherwise if $Q_{true} > 1.5Q_{robust,}$ it shows that peak events might be disproportionately manipulating the model (EPA, 2008).

In PMF, the FPEAK parameter is used to control rotation. In this study, for the assessment of the Q value, different FPEAK values varying between -2 and +2 were examined. When the Q value did not change significantly, the corresponding FPEAK value was selected as an optimum solution.

5.2.2 Application of the Model

To determine the proper number of sources, three main criteria were applied, which is in line with the methodology used by Zhao et al. (2004). First, different numbers of factors were tried and number of factors where Q values did not change significantly was retained. In the second step various values of F-peak between -2 and +2 were tried. FPEAK affect autocorrelation between factors. Positive values of FPEAK did not affect the Factor Score plots significantly. However, negative values beyond -1.5 increased the Q-value by more than 100 units. Therefore, by using different FPEAK values, oblique edges were examined and given that Q value did not change significantly, optimum FPEAK value was selected as -1.4. Moreover, a value of -1.4 supplied the highest increase in the independence of factors without increasing the Q value more than 100 units (EPA, 2008).

In the third step scaled residuals were investigated. For a good fit, more than the 99% of the scaled residuals should be within ±2 around the mean value for all parameters. The fourth and the final criteria is interpretability of the retained factor compositions. (Paatero, 2000; Zhao et al., 2005; Xie and Berkowitz, 2006). Additionally, 5% extra modeling uncertainty was applied. Application of these criteria led to the selection of 8 factors for both campaigns.

The model was run 20 times with eight factors for both campaigns and all runs were converged. The Q(robust) was within 1% and 1.1% of the Q(true) for the first and second campaign, respectively. Therefore, outliers did not heavily impact the Q value. Both were within 50% of their Q theoretical value.

5.2.3 Results of the Model for the First Campaign

As a result of the PMF analysis, eight physically meaningful factors were generated at the urban site of Bursa during both the first and second sampling campaigns. The remainder of this chapter focuses on these eight factors of each campaign. The relation between factors and physical sources were based on investigation of source profiles, fractions of measured concentrations of each VOC accounted by factors (This corresponds to “explained variance” (EV) in conventional factor analysis), diurnal variation and time series plots of factor scores (also known as G-scores) were prepared. Source profiles were also compared with other profiles obtained from literature, U.S. Environmental Protection Agency’s (EPA) Version 4.0 of the Speciate Data Base, UK National Atmospheric Emission Inventory database (NAEI) and US California Environmental Protection Agency (Cal/EPA) gas and particulate matter organic speciation profile database in order to confirm the proposed source for a particular factor.

Factor 1 loadings, fraction of concentrations of VOCs accounted for by the factor, time-series plot of Factor 1 G-scores and diurnal variation of g-scores are presented in Figure 5-1. The source profile plot which was prepared for Factor 1 points out that n-hexane is the most abundant compound in this factor, which is followed by toluene and isobutane+n-butane.

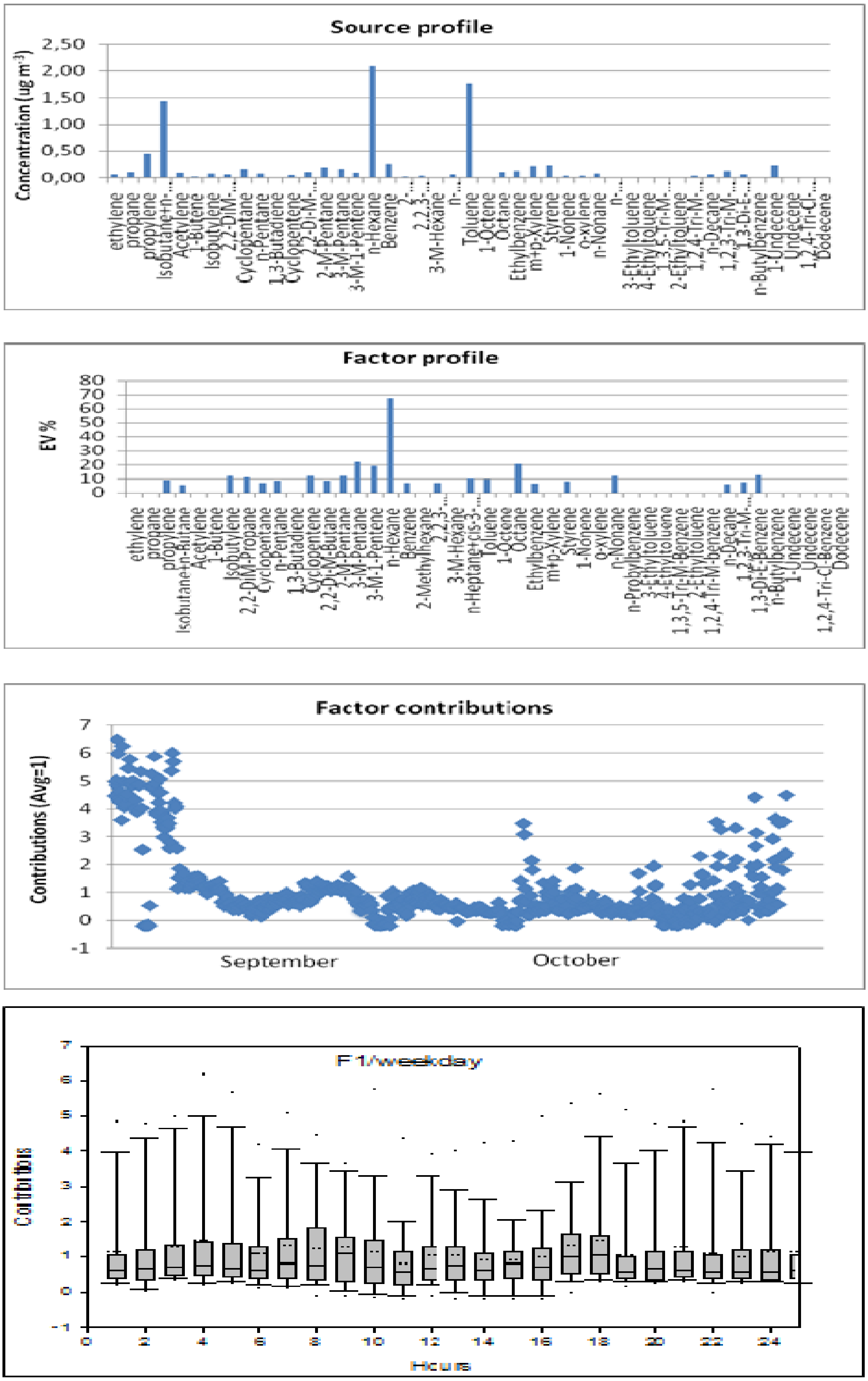


Figure 5-1 PMF, Campaign 1 FL, EV TS and Diurnal variation in Factor 1

It can be seen in Figure 5-1b that Factor 1 accounts for >65% of the measured n-hexane concentration in the data set. Factor also accounts for approximately 20% of the concentrations of 3-m-pentane and octane. It should be noted that although concentrations of toluene and isobutene is high in Factor 1, this factor is not the primary source of these species. This is the difference between factor loadings and EV in PMF. It also shows why EV is more important than factor loadings in assignment of factors to specific sources. Time series plot of G-scores (which shows source contributions in each sample) indicate that source strength of Factor 1 is high in early September and late October, but low throughout September and October, which covers the bulk of our campaign 1 period. Figure 5-1d shows that there is no significant diurnal variation in the source strength for factor 1. Hexane is commonly used for industrial processes as a solvent and in solvent-related domestic activities (Borbon et al, 2022; Guo et al., 2004). In this factor, n-hexane (67%) is the most abundant constituent. Moreover, abundance of toluene was 6.4%. Organic solvents such as n-hexane, toluene and xylene are found in many commercial products owing to their industrial uses in the production of adhesives, glues, paints, cleaners, thinners, and plastics (Liu et al., 2008; Gomes et al., 2010).

Lack of any diurnal pattern in source strength is a good indication of an industrial activity (Brown et al., 2007). Another point to note is that hexane is a good organic solvent, which has numerous applications in both industry and in laboratories. Toluene and isopentane, which have high concentrations in Factor 1 (although Factor 1 is not their primary source) are also well-known markers for solvent evaporation. Based on these arguments the source of the Factor 1 is identified as **industrial process**. Representing solvent emissions in one or more industrial activity. There are about 4080 source profiles in the Speciate 4.0 database which was developed by US EPA (EPA, 2006) and 2,000 source profiles in the Cal/EPA Organic Gas Speciation Profiles database (Cal/EPA, 2014). UK National Atmospheric Emission Inventory (NAEI) includes 111 species profiles (Passant, 2002). Factor profiles generated in this study are compared with profiles from these databases and literature to confirm the assigned sources.

Among the various profiles which were used for identification, Factor 1 shows the best fit with profiles related with solvent usage. The relation is statistically significant at 95% confidence level ($p<0.05$). The source profile for Factor 1 together with solvent source profile acquired from the NAEI is given in Figure 5-2.

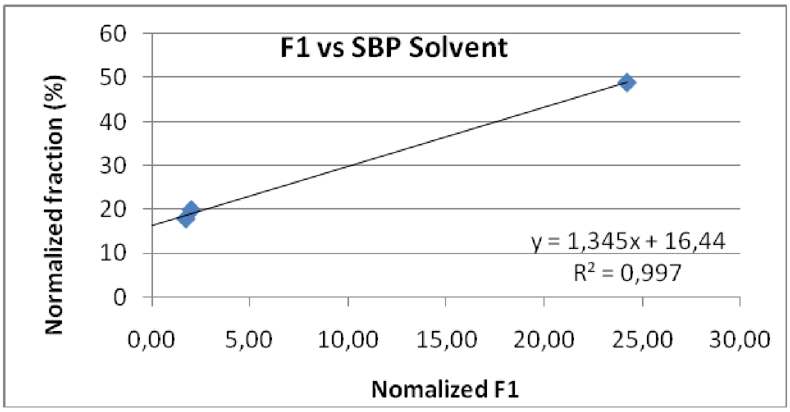


Figure 5-2 Correlation between F1 and solvent source profiles obtained from the literature

SBP 65/70 solvent profile was obtained from NAEI database profile number 116. This profile has been used for solvents which are mixtures of low boiling point aliphatic distillates. The main constituents of the SBP 65/70 solvents are n-hexane (49%), 2-methylpentane (20%), 3-methylpentane (18%) and methylcyclopentane (8%). According to the NAEI database, the profiles of adhesives, painting manufacture, printing and rubber process also contain SBP solvents.

The source profile, EV and g-score plots (both time series and diurnal variations) for **Factor 2** are given in Figure 5-3. Concentrations of some heavy hydrocarbons, namely 2,2,3, trimethylbutane, 1-octene, 1-nonene, 1-undecene, 1,2,4-trichlorobenzene, and dodecane are mostly accounted for by factor 2. Abundance of heavy compounds, scarcity of BTEX and traffic-related trace compounds such as ethylene, acetylene, and 1,3-butadiene indicate that this profile was not associated with light duty motor vehicle emissions.

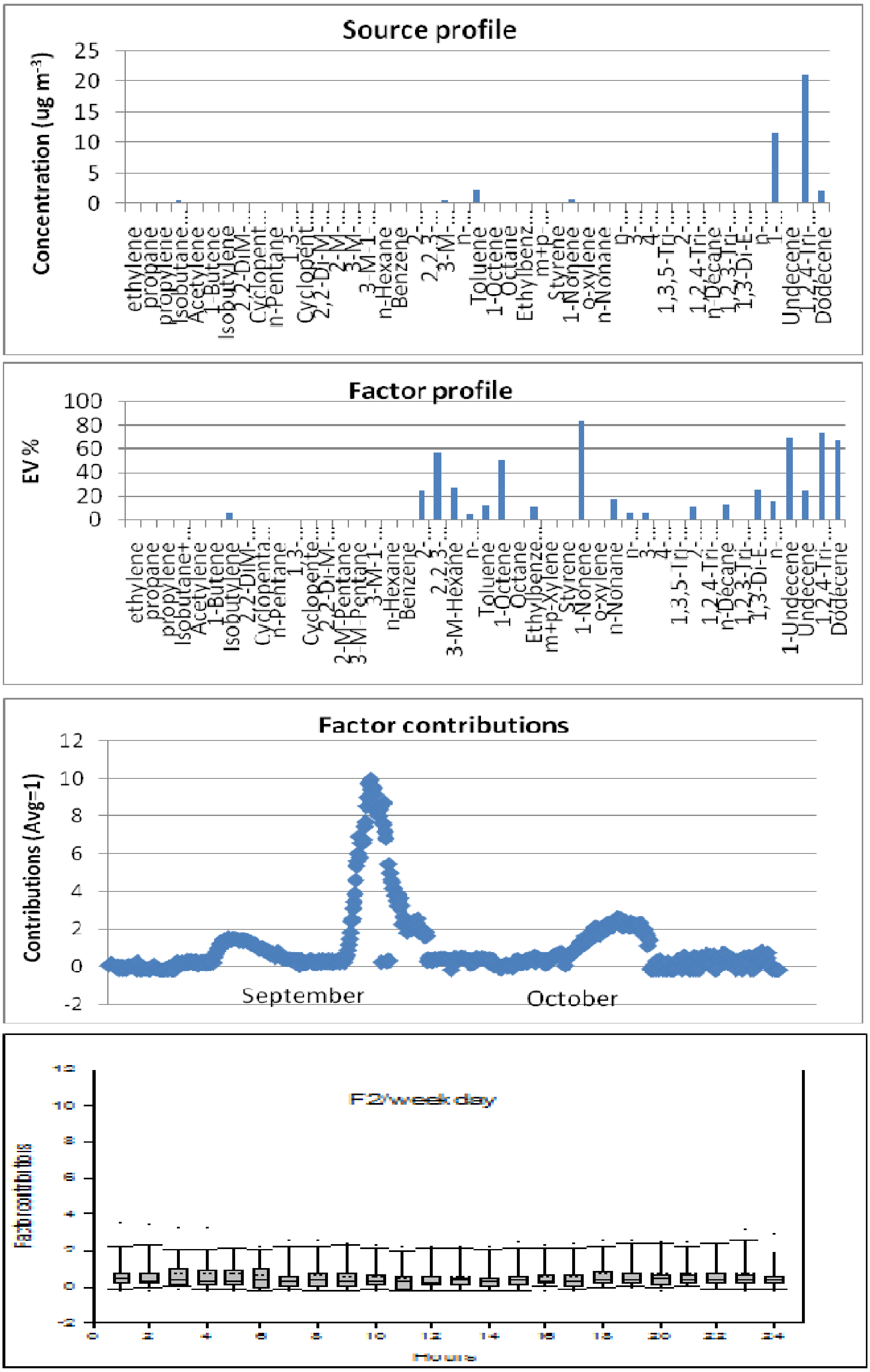


Figure 5-3 Factor loading, percentage of species accounted for by each factor, time-series and diurnal plots of factor 2 scores

Furthermore, diurnal variation of Factor 2 scores, depicted in Figure 5-3d do not show a significant variation within a day, which also confirms that Factor 2 is not related to traffic emissions.

Time-series plot of factor scores is given in Figure 5-3c. The scores are rather unusual. There is very strong episodic increase in source strength between September 30 and October 4, 2005. There are also two other peaks, one at early September and the other one late October. This factor emerged due to these episodes and is probably a transient feature of the Bursa atmosphere. Time series plot of the VOCs loaded in this factor is depicted in Figure 5-4. These peaks are obvious in all VOCs shown in the figure.

Temporal variations of acetylene and benzene, two well-known gasoline exhaust markers, are plotted in Figure 5-5, together with 1-undecene and 1,2,4-t-chlorobenzene, which are among the elements that have high loadings in Factor 2. The difference between the two groups of VOCs is very clear in the figure. Traffic markers do not show the peaks, which are obvious in Factor 2 VOCs.

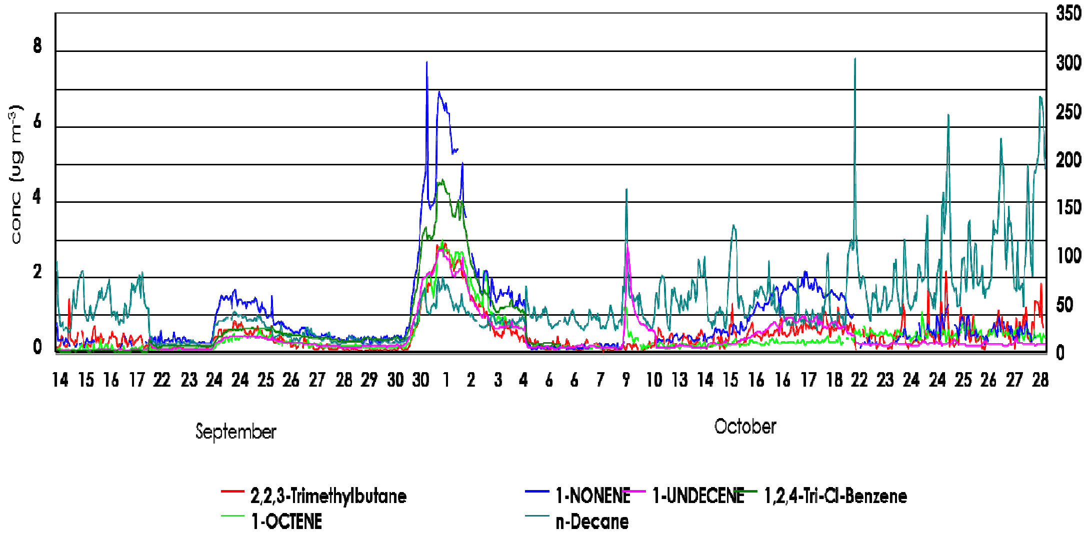


Figure 5-4Figure 5-5 Time-series plots of VOCs that are heavily loaded in PMF factor 2

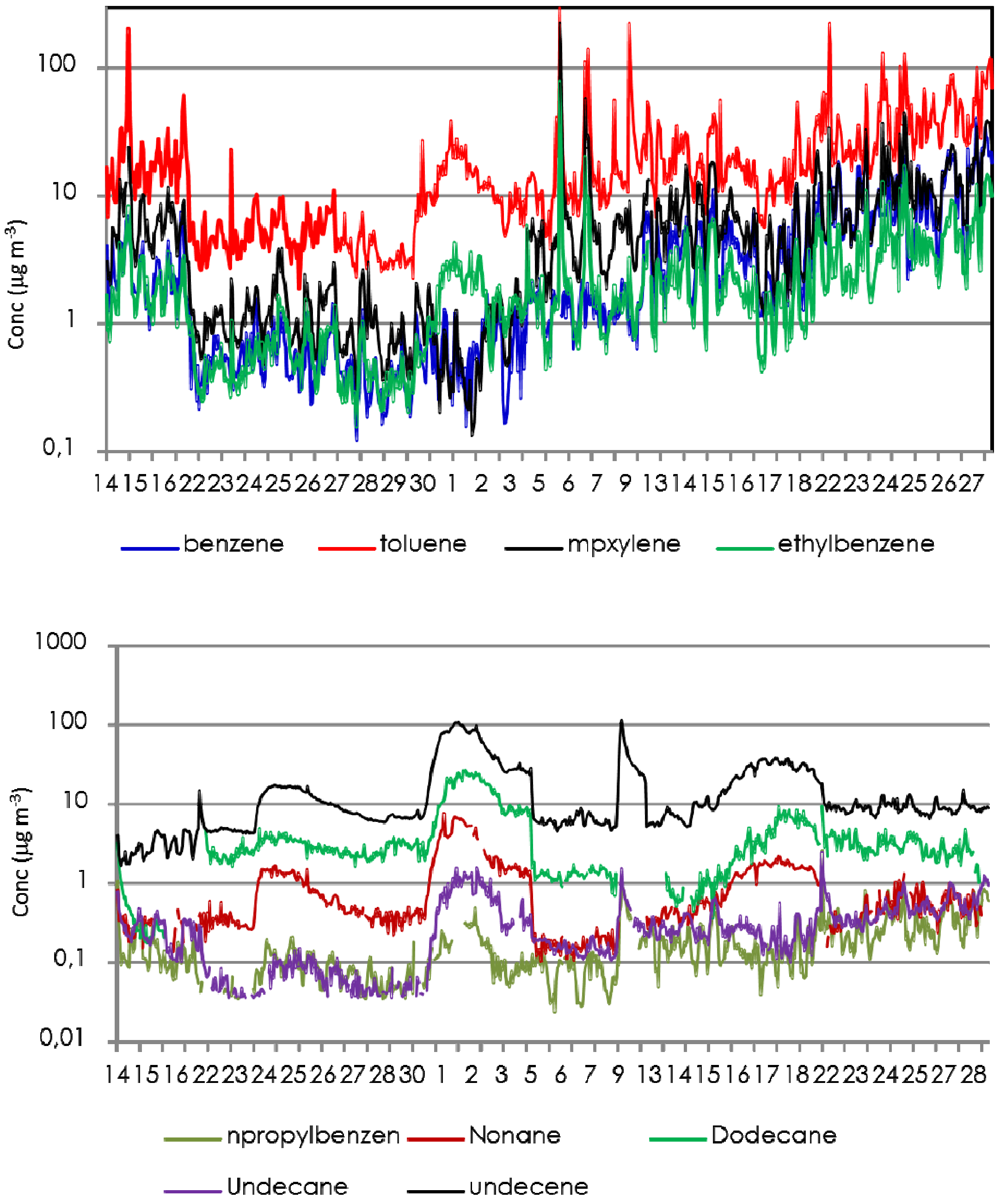


Figure 5-6 Temporal variations of acetylene, benzene, 1-undecene and 1,2,4-t-chlorobenzene during first campaign

Factor 2 is associated with asphalt pavement operations in the close proximity of our station. Records of the Bursa Municipality show that there were asphalt pavement activities on the Altıparmak Boulevard, which is within 1 km from the measurement point, between September 30 and October 4. During this period traffic was cut on the Altıparmak Boulevard. Asphalting activity continued on side streets around our station.

Heavy hydrocarbons are generally associated with emissions from heavy-duty vehicles (Pekey et al., 2013). However they are also emitted from other sources such as coal combustion (Liu et al., 2008), production and pavement of asphalt (EPA, 1996). Asphalt source of Factor 2 is confirmed by comparing factor 2 profile with asphalt profiles in the literature. Comparison with asphalt profile generated in Mexico City is depicted in Figure 5-6. The agreement between the two profiles is statistically significant at 99% confidence level (p<0.001). Although only Mexico City profile is depicted in Figure 5-6, Factor 2 profile also showed fairly good agreement with an asphalt profile generated in Beijing, China (Liu et al., 2005) another asphalt profile from Mexico City (Wega et al., 2000) and EPA SPECIATE profiles #1007 and #023 (EPA, 2006).

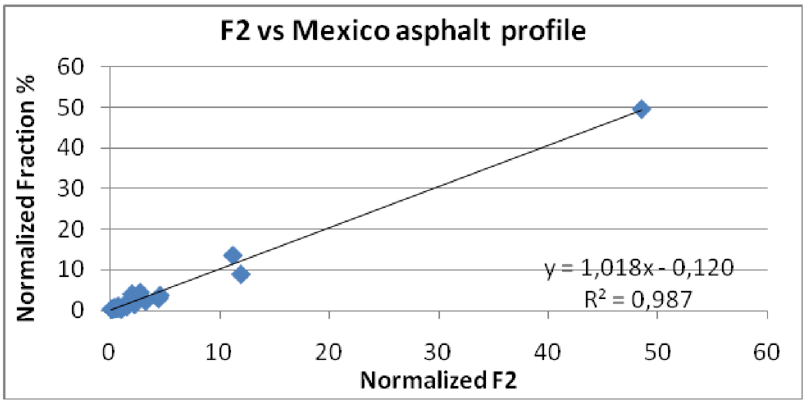


Figure 5-7 Correlation between F2 and asphalt source profile

During asphalt pavement operations, the traffic on the Altıparmak Boulevard was transferred to other roads. This is expected to result a decrease in concentrations of traffic related VOCs at our station during asphalt pavement operations. This can be seen in Figure 5-5. Concentrations of acetylene and benzene are low in the period when asphalt peaks occurred. Their concentrations started to increase after October 10, when the effect of the major peak is diminished. It is also worth pointing that concentration of acetylene and benzene are high during the small peak observed in October. This also suggests that small peak in October is not due asphalting operations in the Altıparmak Boulevard; it is probably due to asphalt pavement in side streets which does not affect traffic flow significantly.

T/B and X/E ratios, which were discussed in Section 4.5 of this manuscript also have unusual values in the period between September 30th and October 4th.

These two ratios indicate that unusual domination of non-traffic sources. They also indicated that those VOCs coming from non-traffic sources spent unusually long periods of time in the atmosphere before they are intercepted at our sampling point. We also attempted to determine the approximate regions where these distant source areas are located.

The median values of ratios and meteorological parameters that can affect transport of these species to our site are presented in Table 5-1. Median value of T/B ratio in campaign 1 is 8.7 which imply that there is strong contribution from non-traffic sources. However the median value of the ratio between September 30 and October 2 is approximately 40. Such a high value in T/B ratio in the middle of a city with a strong traffic activity is only possible by an accidental release of solvents during an industrial activity or by a high-temperature operation that can release solvents. The X/E ratio for whole campaign 1 is 2.8 which indicates that the station do not receive very fresh emissions in general. However, the ratio decrease to 0.2 in the period between September 30 and October 2, suggesting that air parcel carrying non-traffic emissions spent several hours in the air before it is intercepted at our station.

Table 5-1 Median values of VOC ratios and meteorological parameters for whole campaign 1 period and for the period between 30 September and 2 October

	Campaign 1	September 30
T/B ratio	8.7	39.5
X/E ratio	2.8	0.2
Temp (°C)	16.0	18.8
WS (m s^{-1})	1.0	0.75
MH (m)	816	579

Average temperature in those days is 19°C, which is not significantly different from the average temperature for campaign 1, which is 16°C. Winds were calm in that particular period (WS 0.8 m s^{-1}), but winds were calm during entire campaign 1 as well (average WS in campaign 1 was 1.0 m s^{-1}). Although slow or calm winds increase the residence times of these compounds in the air and results in smaller X/E ratios, if this is the only reason for the observed anomaly, then similarly low X/E ratios should prevail during entire campaign. Similarly the mixing height also cannot explain this unusual event, which occurred between September 30 and October 2.

Time series plots of benzene, toluene, m,p-xylene and ethylbenzene are depicted in Figure 5-7. There is one interesting point in the figure. Benzene and m,p-xylene concentrations do not change in the period between September 30 and October 4. However, concentrations of both toluene and ethylbenzene make a peak in this period. This explains why T/B ratio reaches to values as high as 40 between September 30 and October 4 and clarifies the non-traffic source of toluene in that period. Obviously toluene is emitted from asphalt pavement operations.

Ethylbenzene peak between September 30 and October 4 also indicates that ethylbenzene is also emitted from asphalt pavement operations at the Altıparmak Boulevard. However, emission of ethylbenzene from asphalt pavement operations ruins the usefulness of the X/E ratio, because X/E ratio is a measure of the age of the air parcel only if there is no additional source of both m,p-xylene and ethylbenzene between the source and receptor. In this case there is an additional source of ethylbenzene and very low X/E ratios recorded between September 30 and October 4 are due to this additional ethylbenzene source and do not indicate an old air parcel.

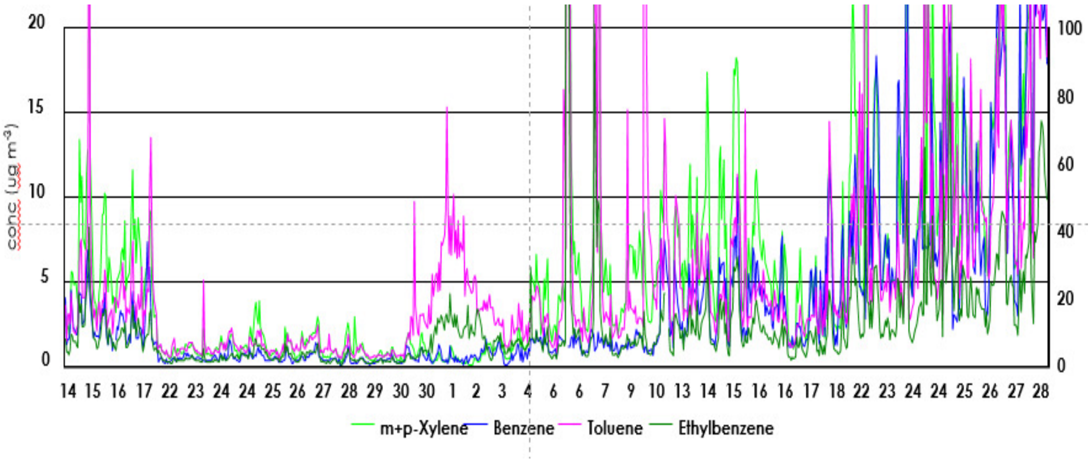


Figure 5-8 Time-series plots of VOCs that are used in T/B and X/E ratios

The results of PMF run for **Factor 3** are given in Figure 5-8. 1-undece, 1,2,4-trichlorobenzene, toluene and isobutene+n-butane are the most abundant compounds in the source profile of Factor 3. EV plot indicates that Factor 3 accounts for approximately 25% of the concentrations of 1-undecene and 1,2,4-ttichlorobenzene in Bursa atmosphere. The factor also accounts for approximately 15% of the styrene concentration and >10 of the concentrations of 2-ethyltoluene, n-propylbenzene. Diurnal variations in G-scores indicate that source strength if this factor does not follow a typical traffic pattern.

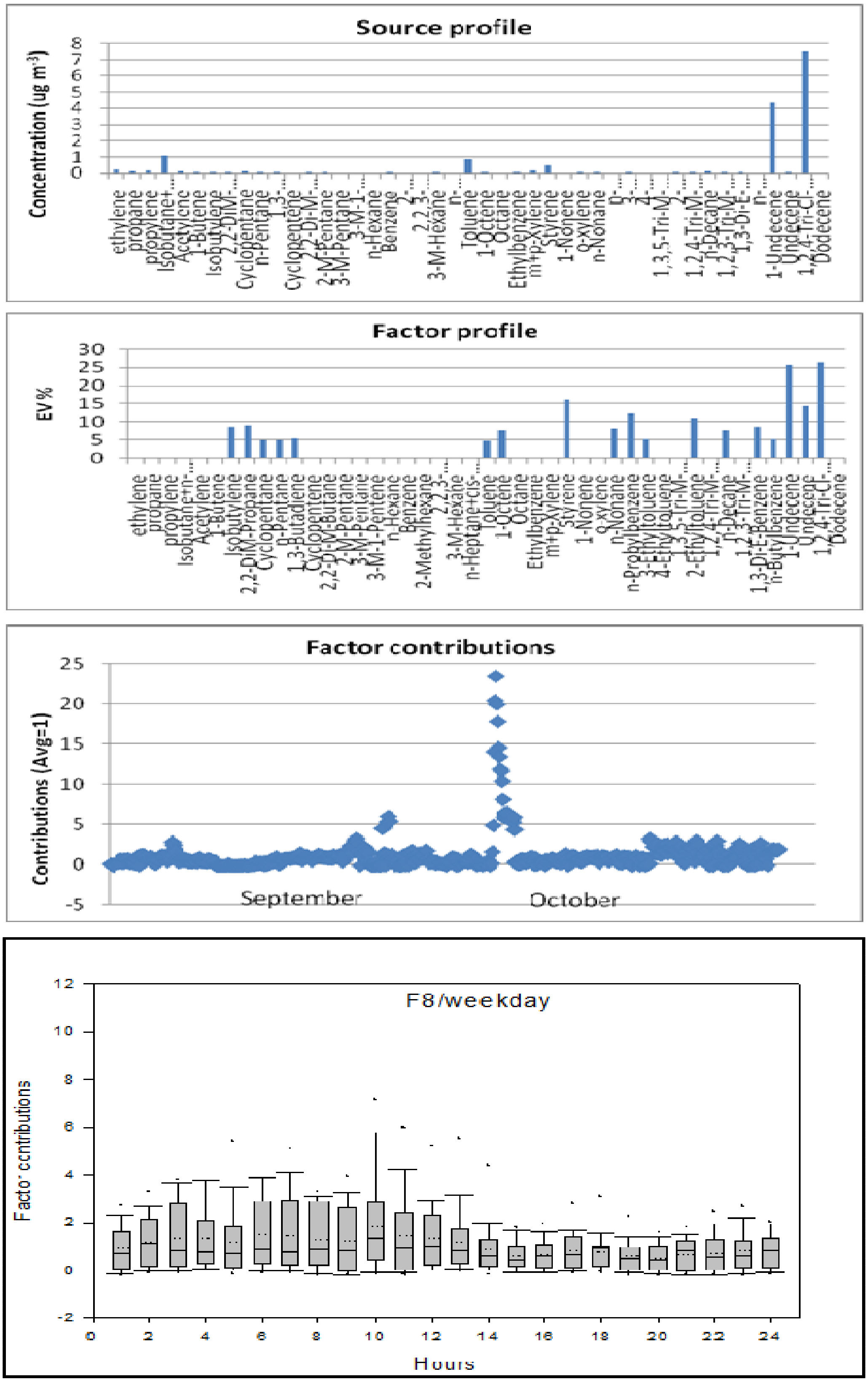


Figure 5-9 Factor loading, percentage of species accounted for by each factor, time-series and diurnal plots of factor 3 scores

Time-series plot of the g-scores shows an interesting temporal variation in source strength. Source strength is low throughout the campaign, except for the period between October 8 and October 10. In this period there is a huge peak in g-scores. Temporal variations in concentrations of 1-undecane and 1,2,4-trichlorobenzene are given in Figure 5-9. Both of these compounds show a very rapid increase in their concentrations starting in October 8 at 17:00. Concentrations reach to a maximum in October 9, 13:00 then gradually decrease, reaching to baseline levels at October 10. Please note that both 1-undecene and 1,2,4-trichlorobenzene are also associated with asphalt emissions and because of that they show episodic increases between September 30 and October 4, but factor 3 has nothing to do asphalt operations, because timing of the episode in Factor 3 do not match with asphalt pavement activities in the area.

The dependence of the factor to one large episode suggests that this factor, like factor 2, also represents a transient feature in Bursa atmosphere. Pollution rose prepared using g-scores in the episode period is depicted in Figure 5-10. Throughout 24 hours of measurements (there are only 26 hour worth of data between October 8, 17:00 and October 10, 13:00, because there are some gaps in the measurement in that period), winds blew only from NNE, E and ESE sectors. Although the rose in the figure restricts the emissions to the east of the city, it is not very helpful because bulk of the city lies to the east of our measurement point. These discussions suggested three potential sources for the episode that generated factor 3. (1) one of the organized industrial districts are located to the east of the city. Accidental release of solvents in that district can generate the episode observed in factor 3 scores. (2) Release of solvents from one of the numerous small manufacturing units, which are distributed within the city, can also generate such an episode, provided that the manufacturing unit is located to the east of our station. (3) Although the hospital do not exactly located in the sectors indicated in the pollution rose and contribution of organics originated from hospital is not clear, hospital is very strong source and it is very close to the measurement point, release of solvents from one of the labs in the hospital can be intercepted from E, ESE and ENE sectors, at calm winds, prevailed at that time. The distance of the sampling station to potential sources is given in Table 5-2.

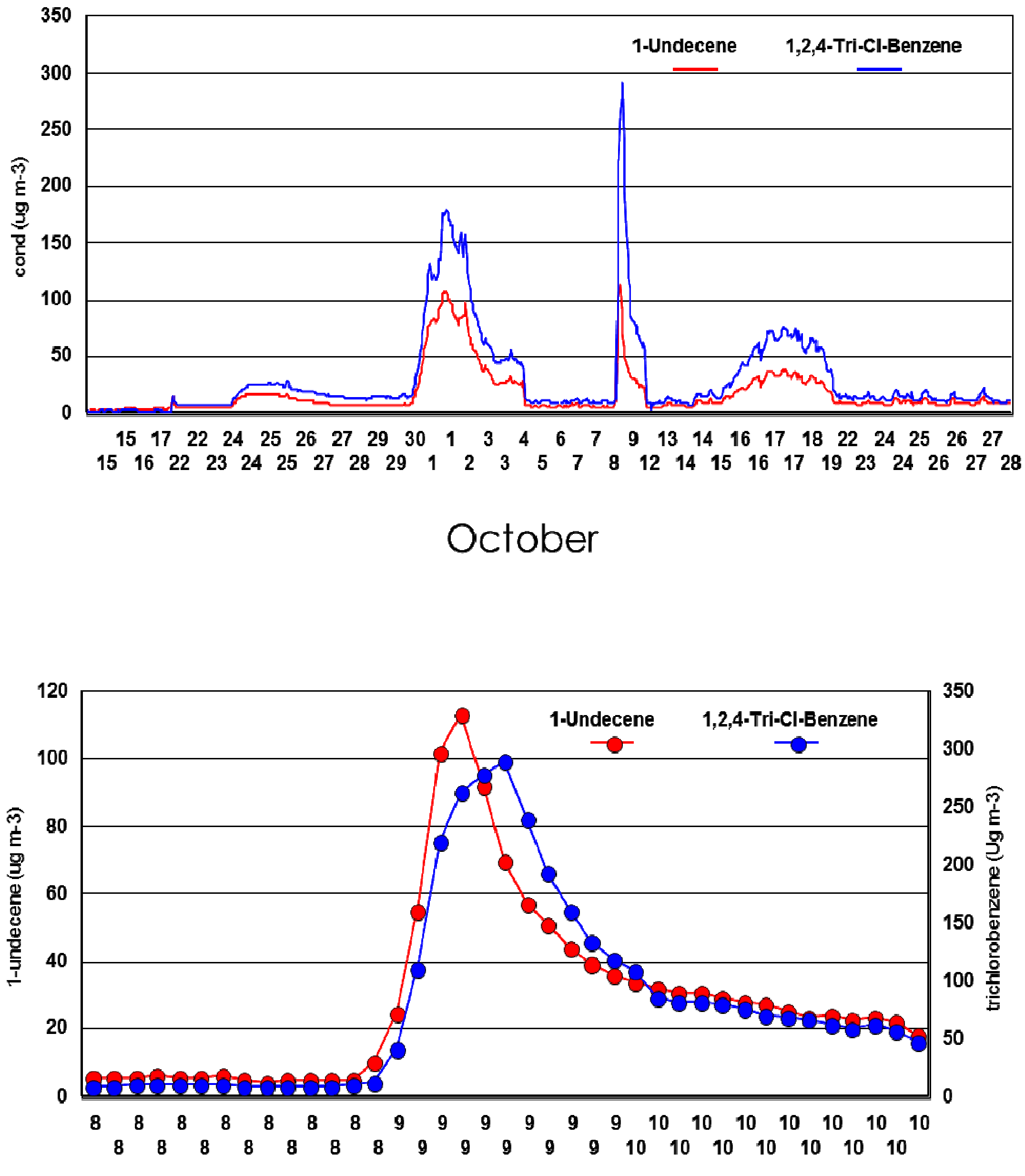


Figure 5-10 1-undecene and 1,2,4-trichlorobenzene concentrations (a) in campaign 1 and (b) between October 8 and October 11

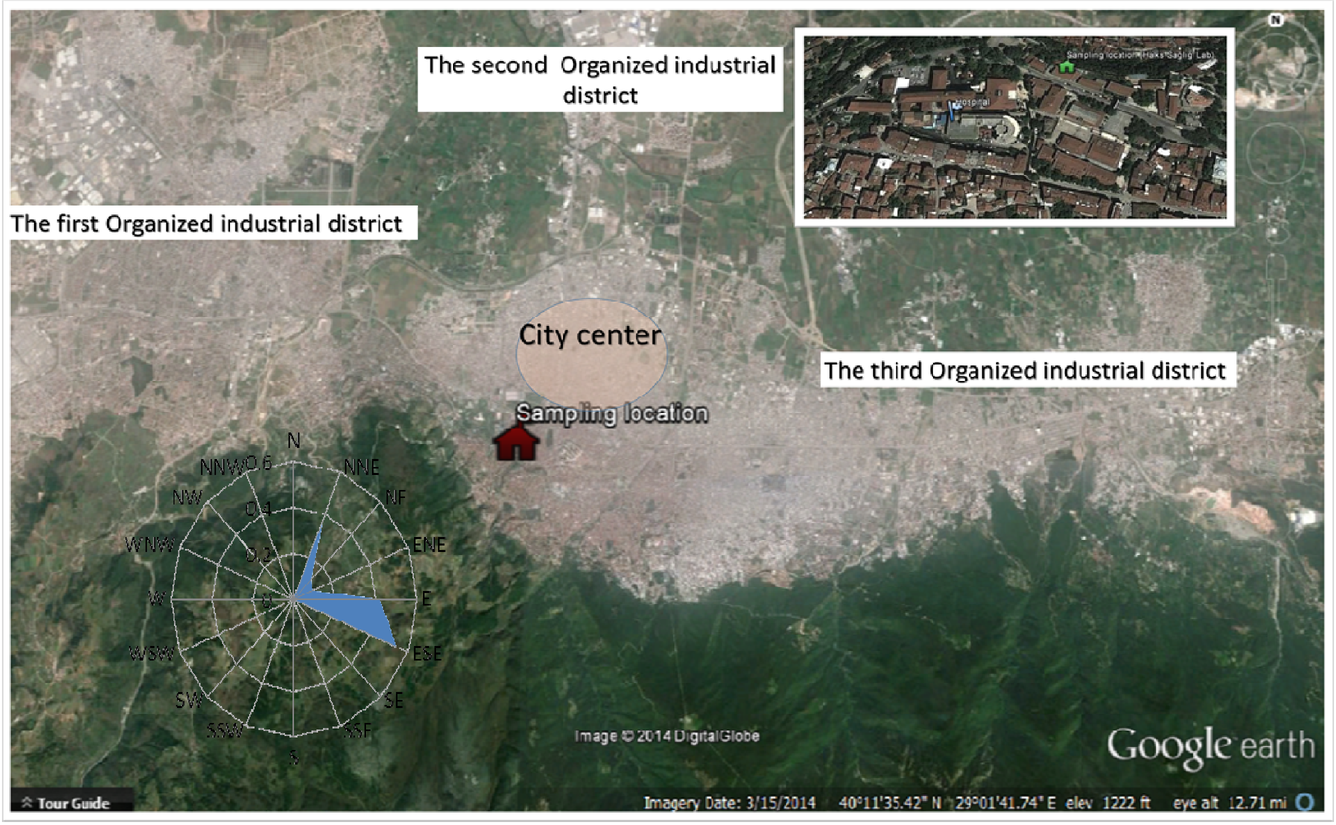


Figure 5-11 The pollution rose for the period between 8-10 October, 2005, which correspond to an episodic increase in Factor 3 g scores

Table 5-2 The distance of the sampling station to potential VOC sources

Potential sources	Approximate Distances
Ankara Highway	2 km
Yalova Highway	2 km
The nearest main avenue	1 km
Altıparmak Boulevard	1 km
Bursa State Hospital	60 m
The first Organized industrial district	10 km
The second Organized industrial district	9 km
The third Organized industrial district	12 km

Factor 3 profile is compared with a variety of profiles found from literature and from data bases to understand which of these three sources effectively generated factor 3.

Traffic-related source profiles and asphalt source profile did not correlate well with Factor 3. Consequently, different types of solvent profiles were examined and finally, domestic solvent and household products gave the best fit ($p<0.05$) with Factor 3. The source profiles for Factor 3 together with two other source profiles are given in Figure 5-11.

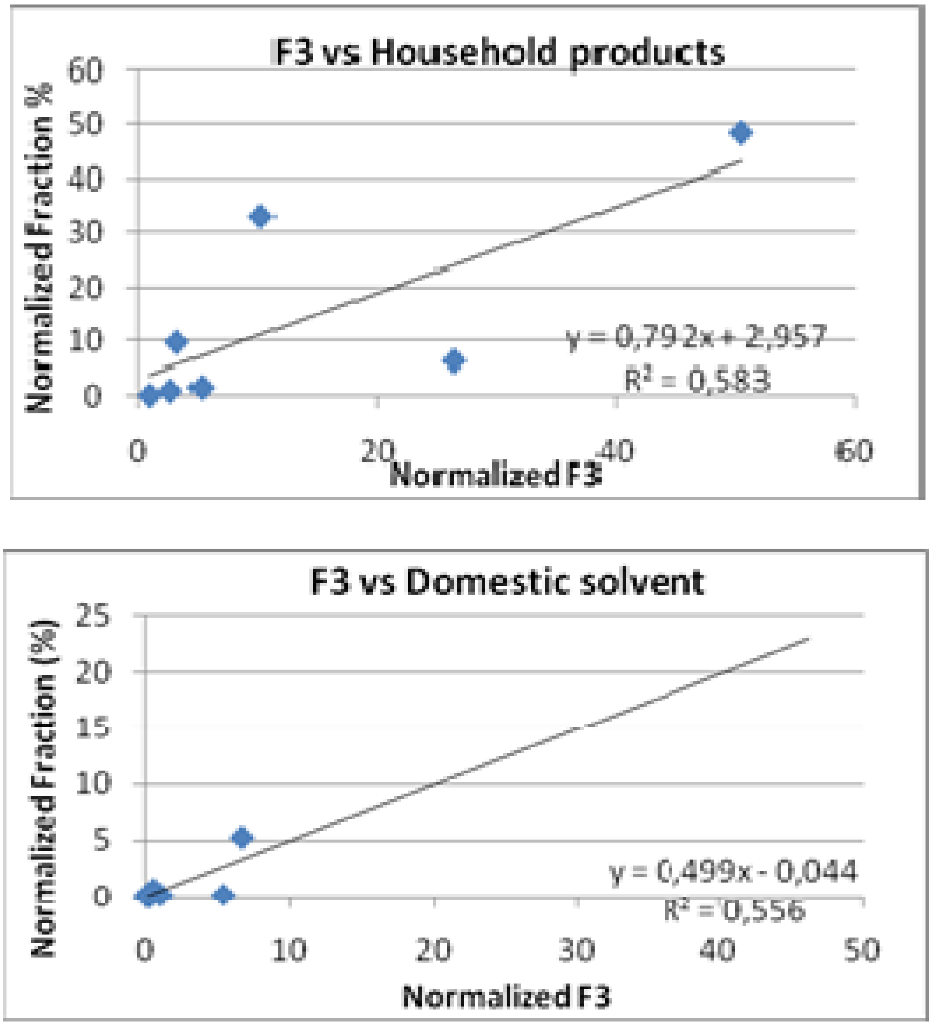


Figure 5-12 Correlation between F3 and solvent source profiles

Household products profile data were prepared based on the Atlantic consulting study and EPA species profiles. This profile was taken from the NAEI database and its profile number is 060408. Domestic solvent-general composite profile was obtained from Cal/EPA Organic Gas Speciation Database profile number 197. Consequently, the source of Factor 3 was identified as solvent-evaporation. Furthermore, source profile of Factor 3 was compared with the Bursa industrial source profile prepared by Civan in 2005. In this study, the identification, quantification and characterization of the VOCs in Bursa ambient air was achieved over seven campaigns performed in different microenvironments; industrial, residential, road and background. Passive sampling tubes were placed into the

Organized Industrial Zone for one week with the aim of providing an industrial source profile. Factor 3 was found highly correlated ($p<0.1$) with both industrial ($R^2=0.866$) and residential ($R^2=0.776$) source profiles of Bursa. Please note that residential solvent evaporation cannot account for one time episodic release of large amount of solvents to atmosphere. Among the three potential sources that can generate factor 3, **accidental release of solvents from one of the small scale commercial or production activities within the city** appears to be the most likely to generate this factor.

Source profile, EV and factor contribution plots for Factor 4 are given in Figure 5-46. BTEX compounds, acetylene, ethylene and isobutane+n-butane are the most abundant compounds in the source profile of the Factor 4. 1,3-Butadiene, ethylene are one of the typical product of the internal combustion engines (Borbon et al., 2002). Furthermore, BTEX compounds are assumed as an important indicator of the traffic (Hoque et al., 2008).

Source profile, EV and factor contribution plots for **Factor 4** are given in Figure 5-12. BTEX compounds, acetylene, ethylene and isobutane+n-butane are the most abundant compounds in the source profile of the Factor 4. All of these VOCs are well-documented tracers for gasoline exhaust emissions. Among these acetylene is particularly important, because it is a combustion product and does not occur in gasoline itself. Because of this feature it is used to differentiate between evaporative gasoline emissions and gasoline exhaust emissions. 1,3-butadiene and ethylene are also products of internal combustion engines (Borbon et al., 2002). Approximately 85-90% of benzene emissions originate from vehicle exhaust (Faiz et al., 1996). EV plot demonstrate that Factor 4 explains the 74% of the benzene and more than 20% of the concentrations of acetylene and 1,3-butadiene.

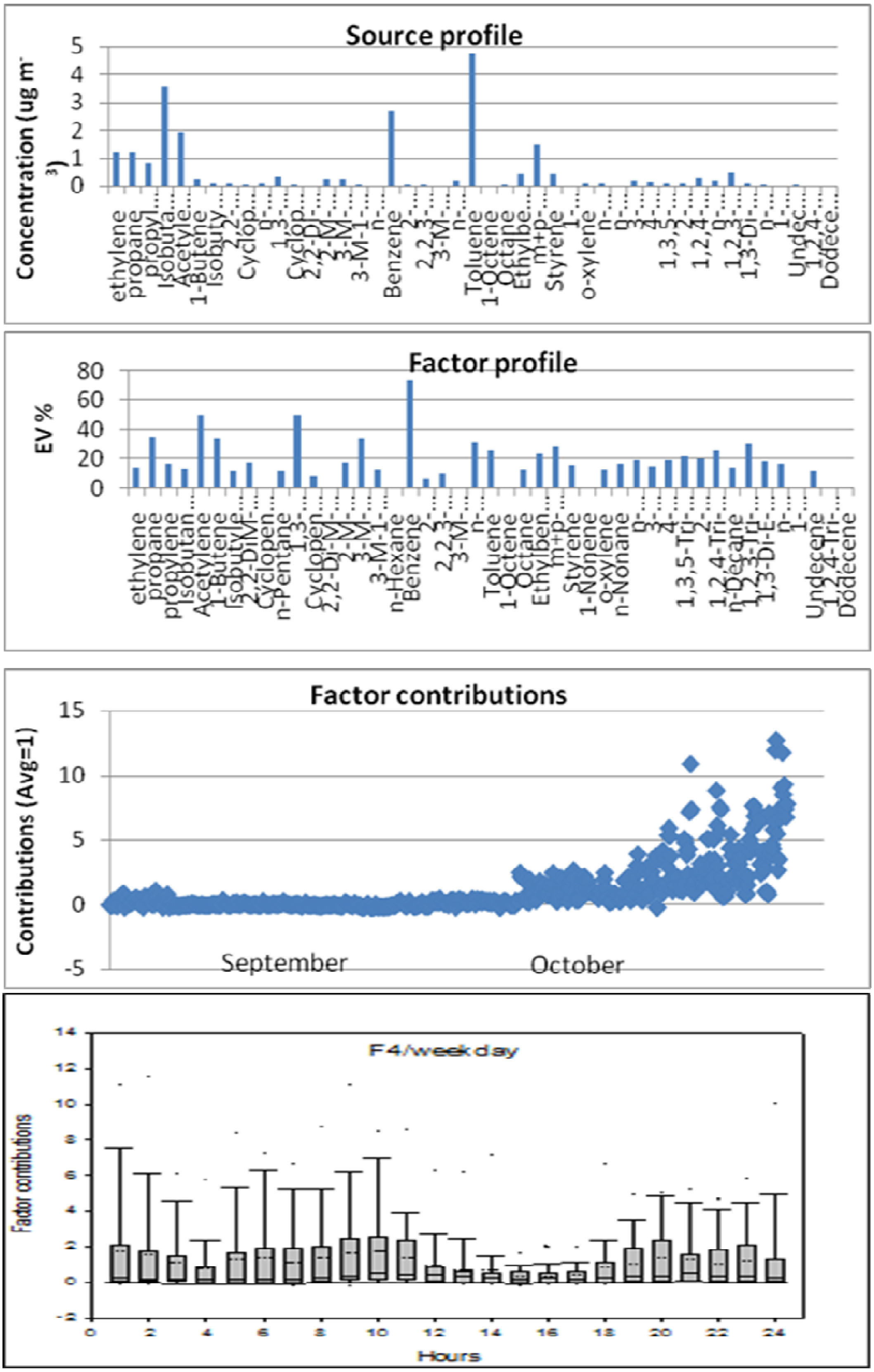


Figure 5-13 Factor loading, percentage of species accounted for by each factor, time-series and diurnal plots of factor 4 scores

Diurnal variation of G-scores depicts a typical traffic pattern with higher source strength during morning and afternoon rush hours. Time-series plot of G-scores shows that source strength is low in the beginning of Campaign 1 and suddenly increased in the middle of October. This is clearly due to restriction of traffic flow on the Altıparmak Boulevard due to asphalt pavement operations. This is demonstrated in Figure 5-13, where G-scores of Factor 4 and Factor 2, which is the factor representing asphalt pavement activities around our station.

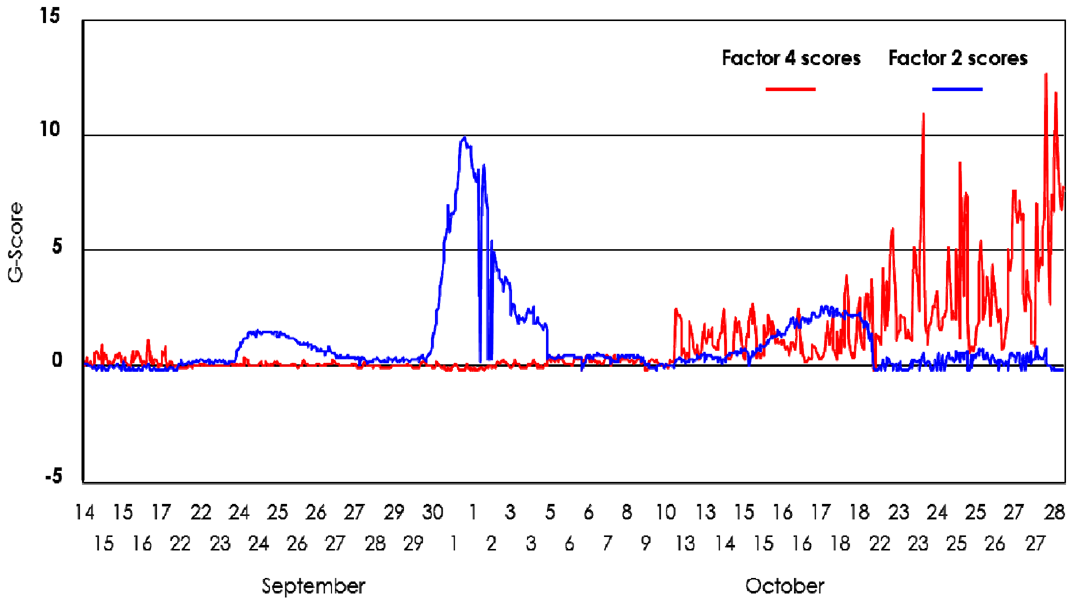


Figure 5-14 Temporal variation of factor 2 and factor 4 scores

Factor 4 profiles are compared with profiles reported in literature and generated for Ankara to confirm the gasoline exhaust source of Factor 4.

The selected profiles together with Factor 4 are given in Figure 5-14. Unleaded gasoline, leaded gasoline, diesel vapor and running vehicle exhaust profiles were generated by Kuntasal (2005) for Ankara. Running vehicle exhaust profile was generated in the Akay Tunnel in Ankara. Liquid gasoline and diesel samples purchased in Ankara were used for the preparation of the profiles.

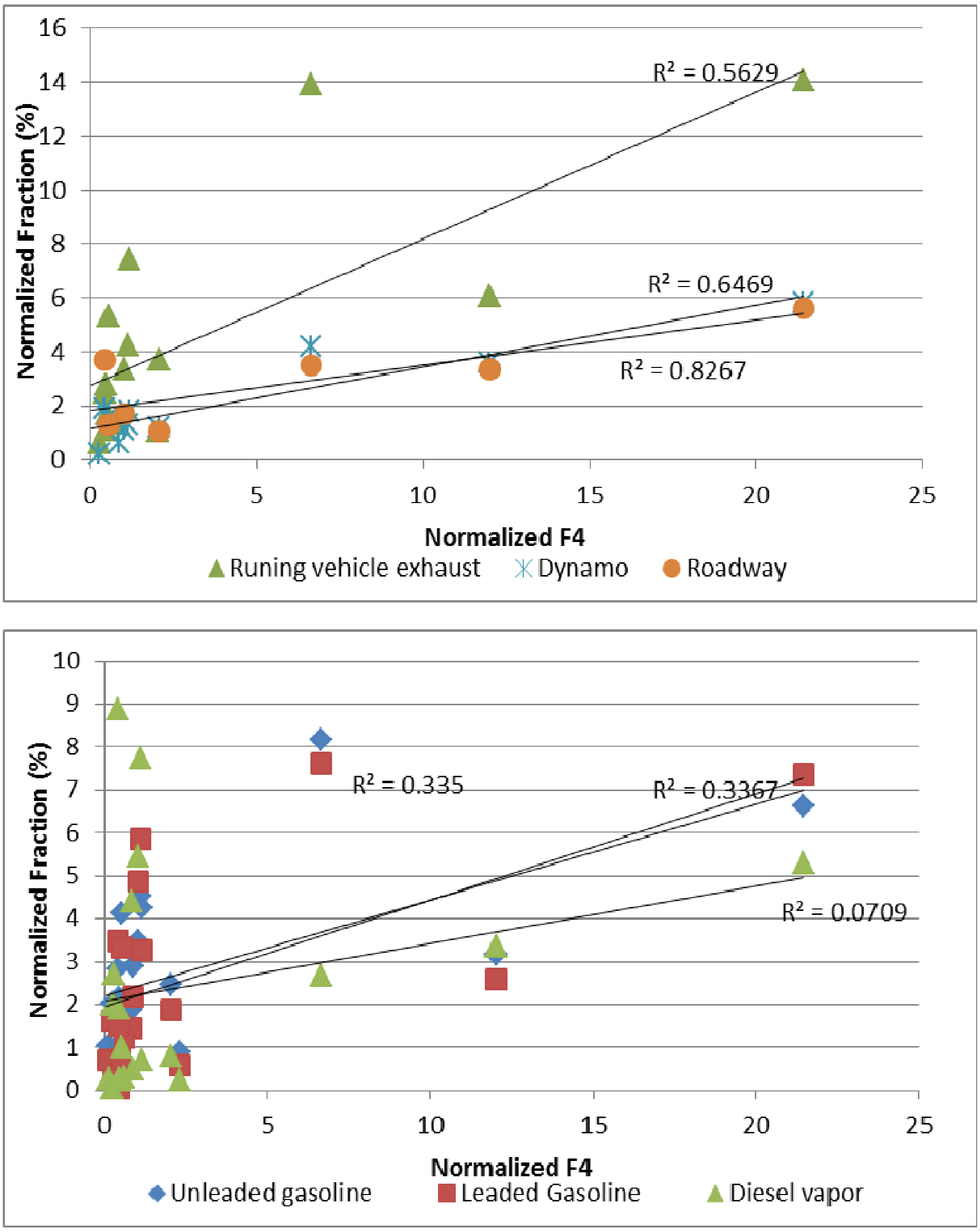


Figure 5-15 Comparison of the source profiles with Factor 4

Dynamometer source profile characterizes the composition of exhaust emissions from a non-catalyst, gasoline fueled, light duty vehicle (Harley et al., 1992). The roadway profile was prepared for Chicago (Doskey et al., 1992).

Running vehicle exhaust (r^2=0.5629), roadway (r^2=0.6469) and dynamo (r^2=0.826) profiles give good correlations with Factor 4 profile. Conversely, diesel vapor (r^2=0.070), unleaded gasoline (r^2=0.336), leaded gasoline (r^2=0.335) provide poor correlation. As it can be seen from Figure 5-14(b), the best fit was found with dynamo profile. As a result of all these discussions Factor 4 is assigned as **LDV exhaust**.

Diagnostic plots for **Factor 5** are given in Figure 5-15. The factor is heavily loaded by styrene and also has fair loadings of n-hexane, 3-m-hexane and dodecane. The factor accounts for approximately 60% of the styrene, 40% of the 3-m-hexane and 30% of the n-hexane concentrations.

A diurnal variation was not observed for this factor which suggests an evaporative source. Time series plot of factor 5 G-scores depicted an interesting pattern. Source strength for factor 5 is low in the first few days of the campaign 1. Then increased and remained high between September 17 and October 5. During this period source strength remained fairly constant. It decreased to a low level in October 5 and remain low until October 18. In the last 10 days of campaign 1, source strength increase and remained high. When the source strength is low G-scores are almost zero. But when it is high it remained constant all the way. This is a typical pattern for an industry, which operated on and off in the first campaign. Based on the VOCs associated with it and temporal variation in G-scores and lack of a significant diurnal variation, this factor is identified as "**industrial solvent evaporation**"

Although various solvent profiles from literature and data bases were compared with factor 5 profile, we were not able to find a statistically significant match with any of them. This may be due to solvent reformulation (i.e. change of the profile over time). Furthermore, reformulation of products which contain solvents will continue with time because regulations encourage manufacturers to reformulate in certain sectors, such as, industrial coatings, adhesives, and decorative paints. Therefore, depending on the technological changes and regulations, solvent profiles will show differences from one country to another.

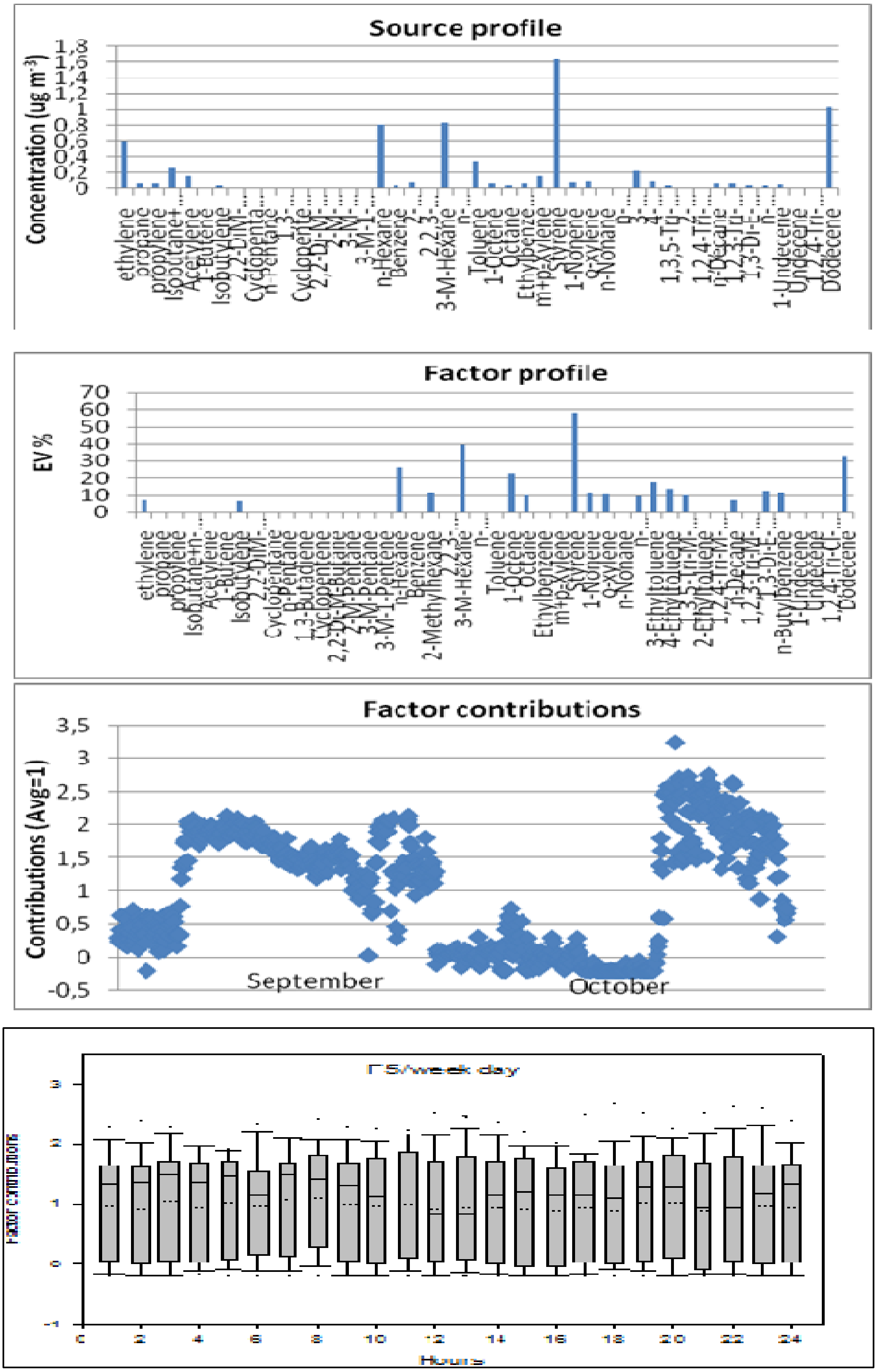


Figure 5-16 Factor loading, percentage of species accounted for by each factor, time-series and diurnal plots of factor 5 scores

Factor loadings, fraction of VOC concentrations accounted by the factor, time-series plots of G-scores and diurnal variations in G-scores for **factor 6** is given in Figure 5-16. The source profile plot shows that m,p-xylene, toluene and cyclopentane are the most abundant compounds in this factor. Factor 6 accounts for approximately 57% of the 2,2-di-m-butane, 49% of the cyclopentane, 44% of the cyclopentene and 37% of the n-pentane concentrations. Please note that n-butane, n-pentane and cyclopentane are accepted as indicators of evaporative sources such as LPG and gasoline evaporation (Guo et. al, 2004; Jorquera and Rappenglück, 2004). Diurnal variation in source strength depicted typical traffic pattern with a morning and afternoon rush hour peaks.

Factor 6 source profile is compared with the profiles generated by Kuntasal (2005) for Ankara. Various evaporative profiles were used in comparison. Regression lines are given in Figure 5-17. Among these Factor 6 is highly correlated with unleaded gasoline profile (R^2=0.738, $p<0.005$). Lack of combustion products, such as acetylene, presence of gasoline markers, such as n-pentane and cyclopentane and similarities in temporal variations in source strength with g-scores of factor 4 confirms that Factor 6 is associated with **gasoline evaporation** either from gas stations in the city or from vehicles themselves. Please not that source strength for this factor is low in September when traffic flow in Altıparmak Boulevard is restricted for asphalt pavement. Factor 6 scores increased when these traffic restrictions are removed.

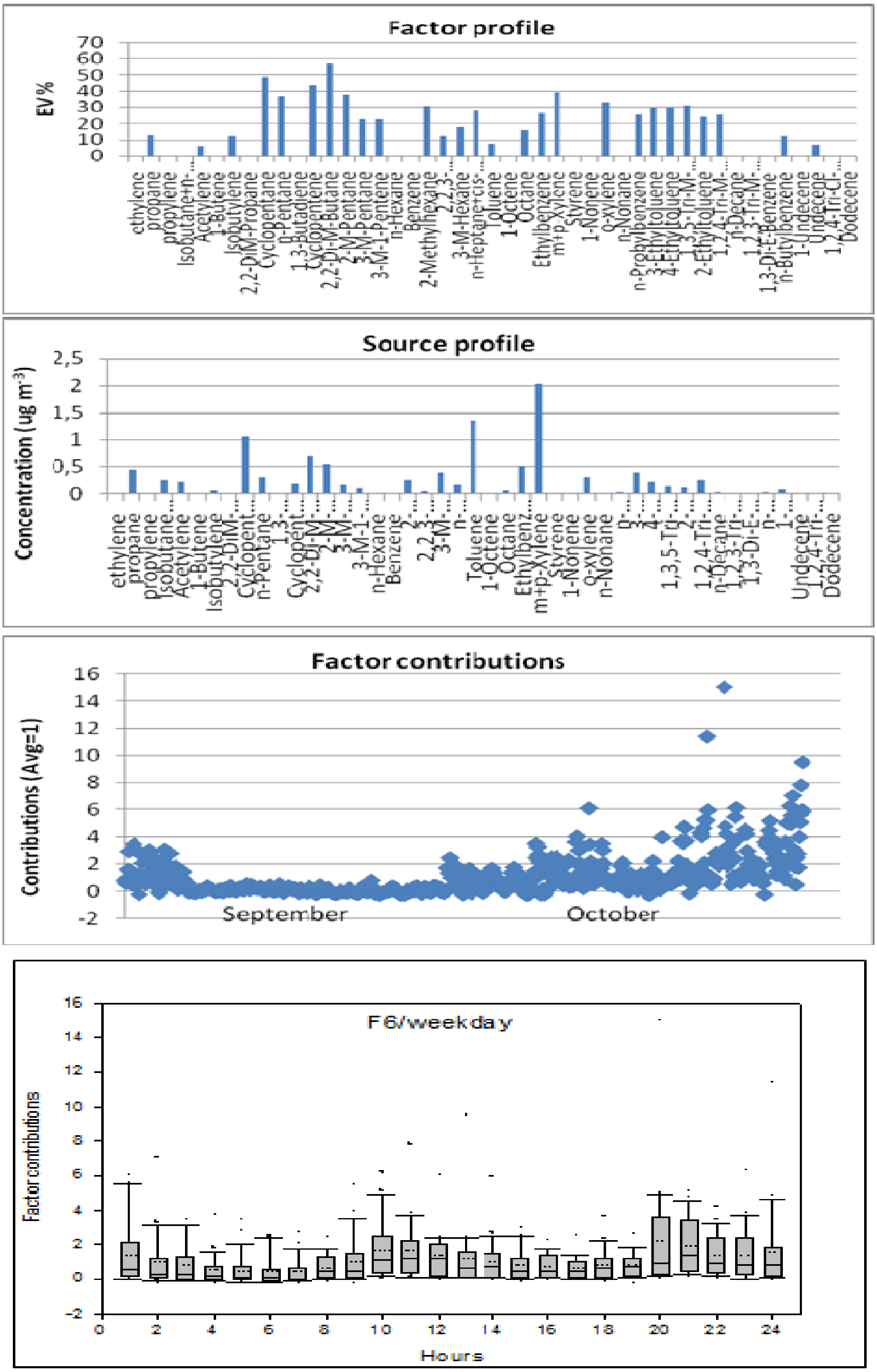


Figure 5-17 Factor loading, percentage of species accounted for by each factor, time-series and diurnal plots of factor 6 scores

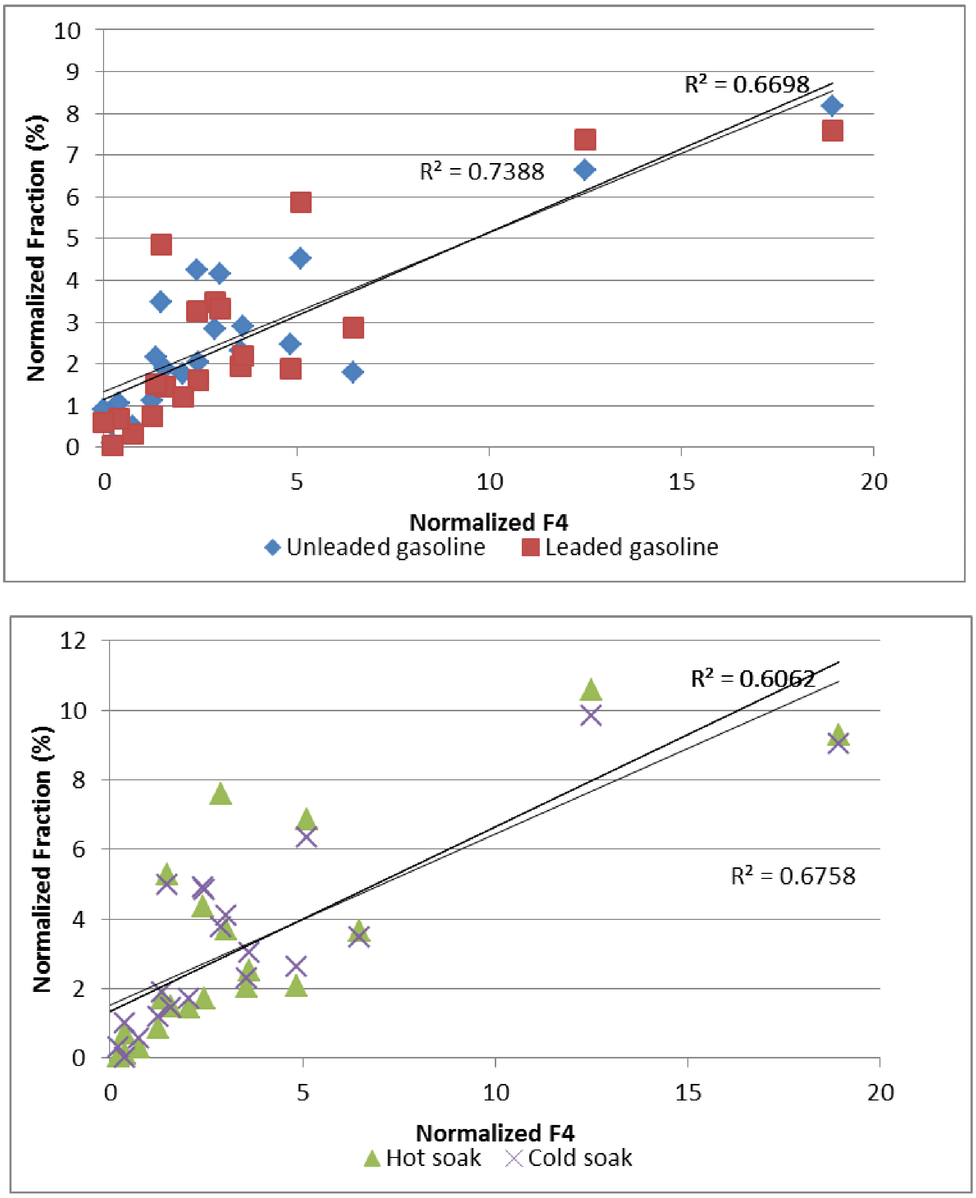


Figure 5-18 Comparison of source profiles with Factor 6

Source profile, EV and factor contribution plots for **Factor 7** are given in Figure 5-18. Ethylene, propane, propylene, isobutane+n-butane are the most abundant compounds in the source profile of Factor 7. The EV plot given in Figure 5-19 shows that Factor 7 explains 50% - 60% of the measured concentrations of ethylene, propylene and isobutene+n-butane and approximately 30%-40% of the concentrations of propane, acetylene, 1-butene, 2,2-di-m-butane. Therefore, light hydrocarbons were found highly loaded on this factor. Presence of propane, propene and isobutene strongly suggest that Factor 7 represents an LPG related source, because LPG is mainly composed of light hydrocarbons with carbon numbers between 2 and 4 (Kwangsam et al., 2004). It is also well-documented that propane, propene, isobutene and n-butane are main components of LPG (Kwangsam et al., 2004; Liu et al., 2005). Diurnal variation of G-scores depicts a typical traffic pattern with two rush hour maxima. Time series plot closely resembles that of that of factors 4 and 6, both of which are related to motor vehicle emissions. Factor 7 scores, like those of factor 4 and 6, are low in September due to traffic restrictions at Altıparmak Boulevard. G scores indicate that factor 7 is also a traffic related factor. Combining the presence of LPG markers in Factor 7 profile and close resemblance of temporal variations in G-scores with G-scores of gasoline exhaust factor we concluded that Factor 7 represents **LPG-fueled vehicles**

The total numbers of the motor vehicles in Bursa was 513,498 in 2009. LPG-fueled vehicles constitute 14% of the total number in Bursa (TurkSat, 2010). LPG used in the vehicles in our country is composed of 30% propane and 70% butane, so that all conditions will be provided for the proper mixture. In cold climate regions, the ratio of the propane in used LPG is increased. Accordingly, different propane to butane ratio is used in different countries. The source profile of Factor 7 was compared with various LPG profiles obtained from the literature for comparison. Factor 7 was found highly correlated ($p<0.1$) with an LPG source profile for Egypt. The source profile of Factor 7 was noticeably different than the source profiles for US, Seoul, Mexico, Germany and UK. Therefore, it seems that an LPG source profile is very sensitive to composition of the fuel (Doskey et al., 1999). The source profile for Factor 7, together with the LPG profile which was obtained from the study carried out in Cairo, is given in Figure 5-19. Consequently, this factor was attributed to LPG-fueled vehicles.

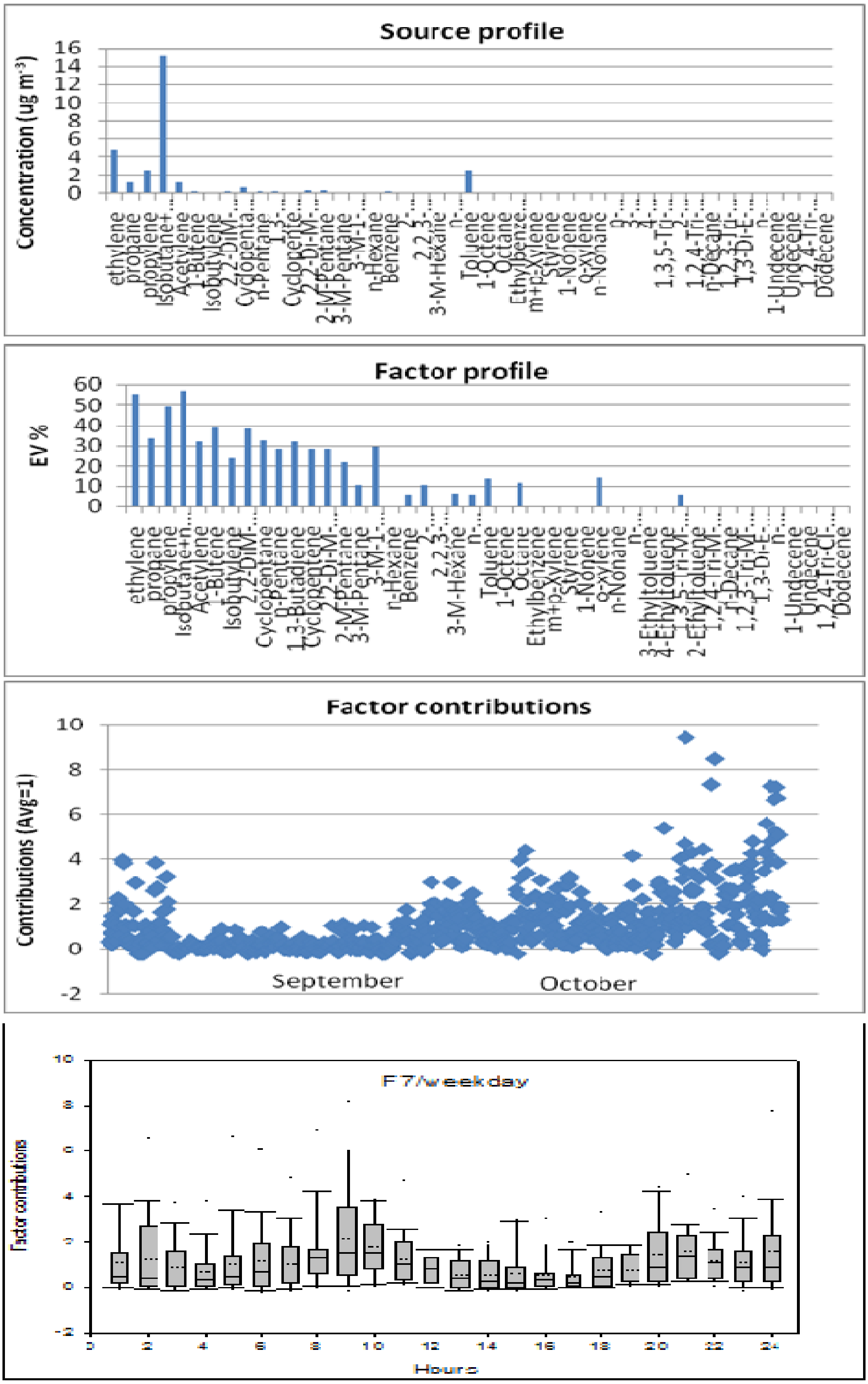


Figure 5-19 Factor loading, percentage of species accounted for by each factor, time-series and diurnal plots of factor 7 scores

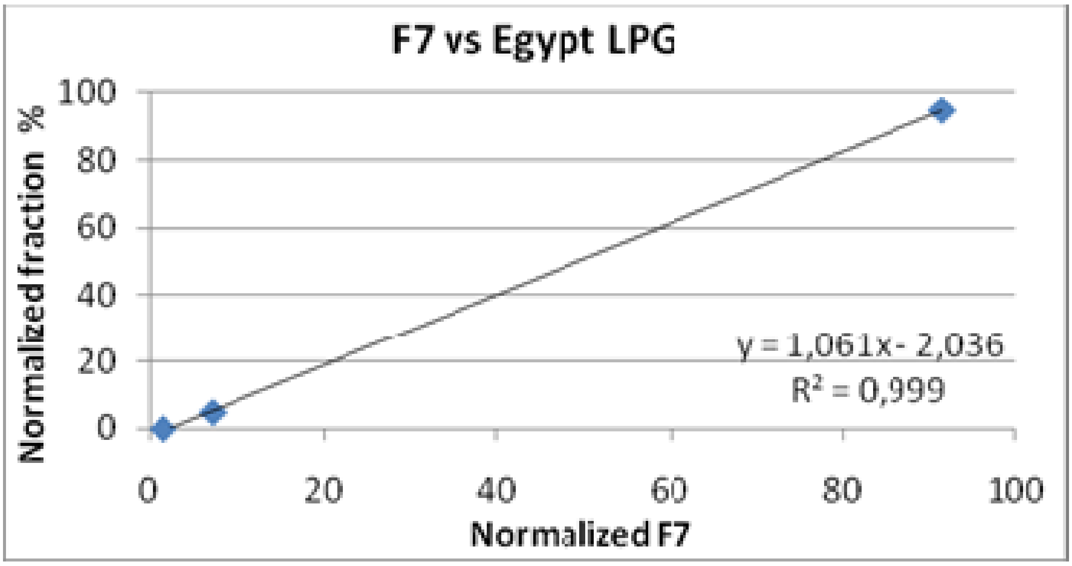


Figure 5-20 Correlation between F7 and LPG source profile

Diagnostic graphs for **factor 8** are given in Figure 5-20 Toluene is the most abundant compound in the source profile of the Factor 8. Although vehicle emissions are the main source of toluene to urban ambient air, an important amount toluene is also emitted to the atmosphere from solvent usage (Shin et al., 2011, EPA 2011). Toluene and xylene are frequently used as solvents for the production of paints. Solvents are one of the major elements of paint. These elements supply thinning of paints to maintain optimum viscosity for suitable manufacturing and application (Jafari et al., 2008).

The EV plot of this factor indicates that the EV values of Factor 8 for the heavy hydrocarbons are higher than the light hydrocarbons. Furthermore, Factor 8 explains approximately 40%-60% of the n-nonane, n-decane, undecane and 1,2,3-tri-m-benzene. Nonane and decane are released from different sources, namely evaporative sources, surface coatings and solvents besides diesel engine exhaust (Fujita, 2001; Watson et al., 2002; Srivastava et al., 2005). Besides, C9-C11 alkanes and toluene are also emitted to the atmosphere as a result of coating operations.

A diurnal variation was observed for Factor 8. The highest contributions were observed during the morning hours. Lower contributions were detected during night.

Traffic-related a diurnal variation with related rush hours was not observed. Furthermore, contribution of this source rose during the daytime, indicating evaporative sources. These findings are indicative of coating operations and industrial activities (Brown et al., 2007). Therefore, the source of Factor 8 was assumed to be related with coating operations. For the accurate identification of the source of the Factor 8, different source profiles obtained from the literature and profiles which were generated in the PhD thesis of the Civan (2010) for Bursa were used for the comparison.

Selected source profiles together with the source profile for Factor 8 are given in Figure 5--21. Paint solvent profile was generated for Seoul, South Korea by Na et al. (2004). Toluene is the major component (63%) of this profile.

Bursa industrial area source profile was obtained for Bursa by Civan (2010) in 2005. Toluene was the most abundant compound (35%) in this profile followed by m,p-xylene (14%). Paint solvent gives a very good correlation (R^2=0.983) with Factor 8. Furthermore, the correlation of Factor 8 with Bursa industrial area source profile is good (R^2=0.906). Consequently, F8 was found highly correlated ($p<0.1$) with paint solvent used in the industrial area of Bursa.

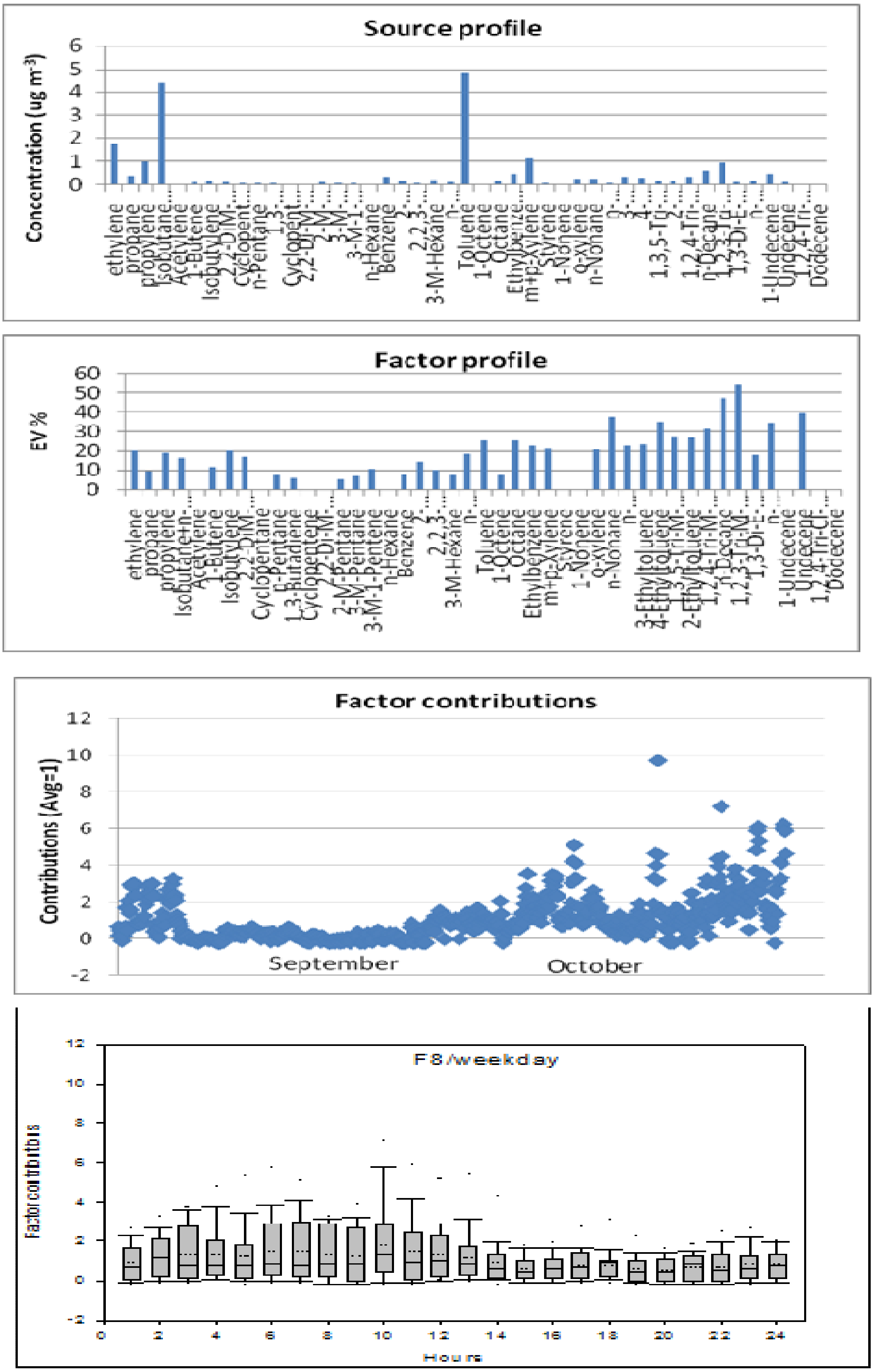


Figure 5-21 Factor loading, percentage of species accounted for by each factor, time-series and diurnal plots of factor 8 scores

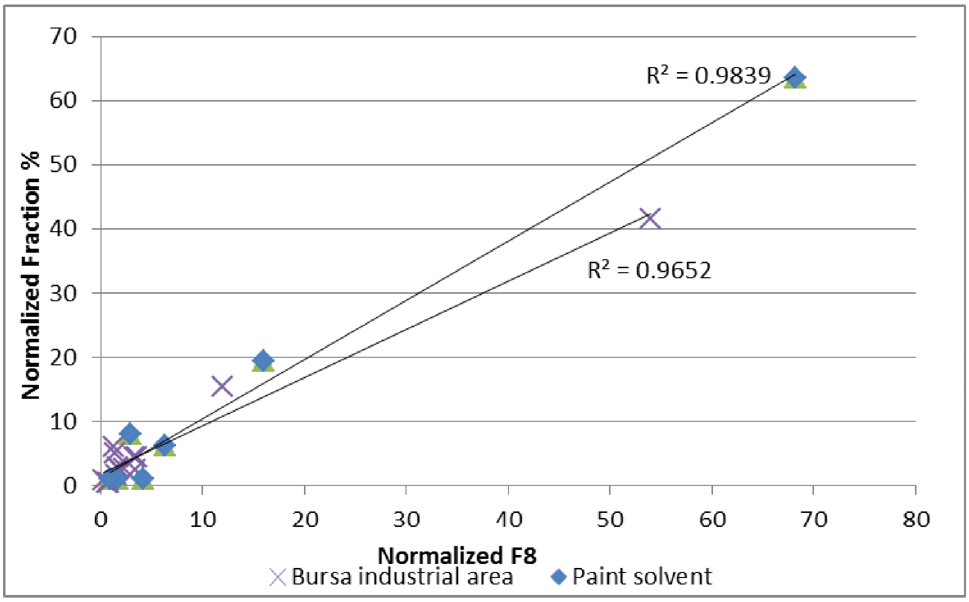


Figure 5-22 Correlation between F8 and paint source profiles

Vehicle refinishing paint source profile was also showed a good correlation ($p<0.1$) with Factor 8. This profile was acquired from NAEI database under industrial paints section with profile number 46. The main constituents of vehicle refinishing are toluene (17%), m,p-xylene (12%), and ethylbenzene (3.4%). Consequently, this factor was identified as a paint source. Therefore, utilization of the paint in industrial zones of Bursa is supposed to be the source of Factor 8.

5.2.4 PMF Results of the First Campaign

Linear regression was applied to compare the model results against measured concentrations. Results are given in Figure 5-22. Agreement between observed and measured ∑VOC concentrations is excellent (R^2=0.973, $p<0.001$), indicating that PMF analysis, is successful in explaining the measured levels of VOCs in Bursa atmosphere.

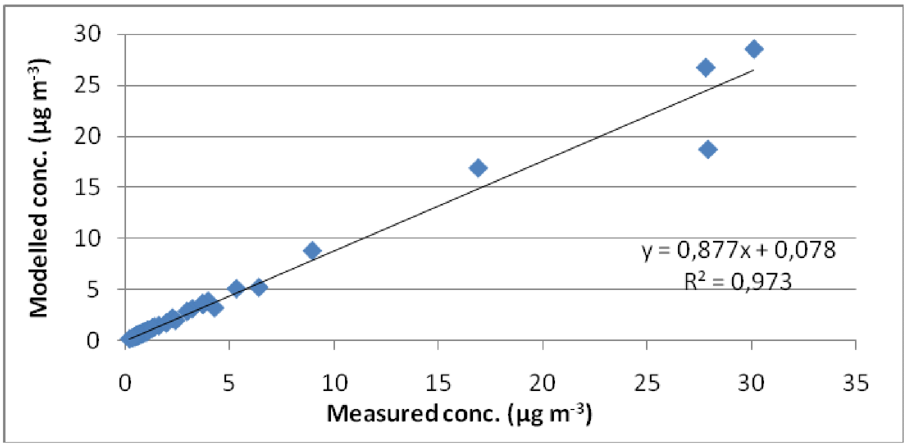


Figure 5-23 Modeled versus measured VOC concentrations

Contributions of each factor are given in Table 5-3. Traffic-related emissions collectively account for approximately 41 % of the ∑VOC concentrations in Bursa. Approximately 20% of this contribution comes from LPG-fueled vehicles, which is followed by emissions from gasoline exhaust (14%) and gasoline evaporation (7%). Such a high contribution by traffic-related sources is not unusual for this study given the urban location of the sampling station. Traffic contributions as high as 80% to ∑VOC concentrations are also reported in the literature for a number of urban stations (Brown et al., 2007; Warneke et al., 2011).

Solvent evaporation both from industries and from small scale manufacturing units accounts for approximately 21% of total VOC levels in the first campaign. Half of this source is due to evaporation in large industries and half was due to an accidental release from one of the smaller scale commercial or production facility operating within the city and outside the three organized industrial districts.

One of the single largest contributors to VOC levels in the first campaign is the asphalt pavement activities in the roads that are close to our station. Emissions from asphalt pavement activities accounted for 26% of the measured VOC levels.

Table 5-3 Source contribution of the obtained factors as a result of the PMF analysis

Factor	Source	% Contribution
1	Industrial process	5.49
2	Asphalt pavement operations	26.33
3	Solvent evaporation from small scale commercial activities	10.36
4	LDV exhaust	14.10
5	Industrial solvent evaporation	4.76
6	Gasoline evaporation	6.84
7	LPG fueled vehicles	19.83
8	Paint	12.30

5.2.5 Results of the Model for the Second Campaign

Eight physically meaningful factors were generated during the second sampling campaign. Source profiles, explained variation (EV) of the factors, diurnal and time variations of the source contributions obtained from the results of the model were examined to relate these factors to physical sources. As in the PMF for the first campaign, VOC profiles generated for each factor are compared with profiles obtained from literature and available databases to confirm the assigned source.

Composition of Factor 1 and temporal variations of factor 1 scores are given in Figure 5-23. The source profile of Factor 1 shows that ethylene, propane, propylene and isobutene+butane are the most abundant compounds. Approximately 50% of concentrations of ethylene, propane, propylene and isobutene+butane and 30% of the propane and t-2-butene are accounted for by this factor. Propane, propene, isobutene and n-butane are main components of LPG (Kwangsam et al., 2004; Liu et al., 2005). Furthermore, Source contribution plot for this factor shows a typical traffic pattern with two well-known rush-hour maxima.

Factor 1 represent emissions from LPG fueled vehicles. This is validated by comparing the factor 1 profile with other LPG profiles from literature. Correlation of Factor 1 profile with LPG profile generated in Egypt (Doskey et al., 1999) is given in Figure 5-24 High correlation ($p<0.05$) with $R^2=0.999$ between the two profiles confirms the LPG –Vehicle source for Factor 1 in the second campaign.

This factor is similar to the factor 7 in the PMF of the first campaign, which was also identified as LPG powered vehicle factor. This is demonstrated in Figure 5-25, where these two factors are regressed against each other. R^2 as high as 0.98 indicates a statistically significant correlation with 95% confidence. This suggests that emissions from LPG powered vehicles are perpetual source in Bursa atmosphere.

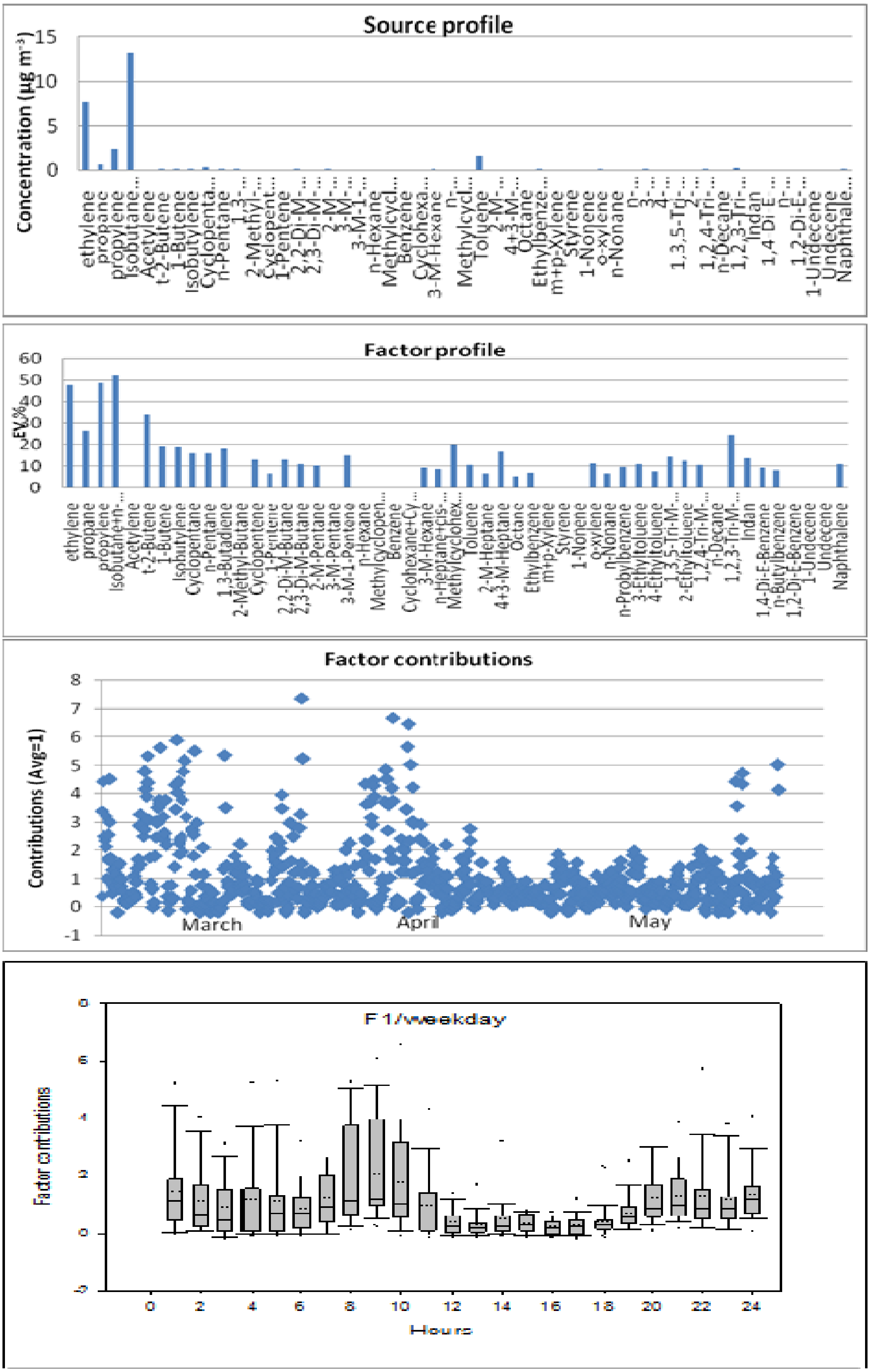


Figure 5-24 Factor loading, percentage of species accounted for by each factor, time-series and diurnal plots of factor 1 scores for campaign 2

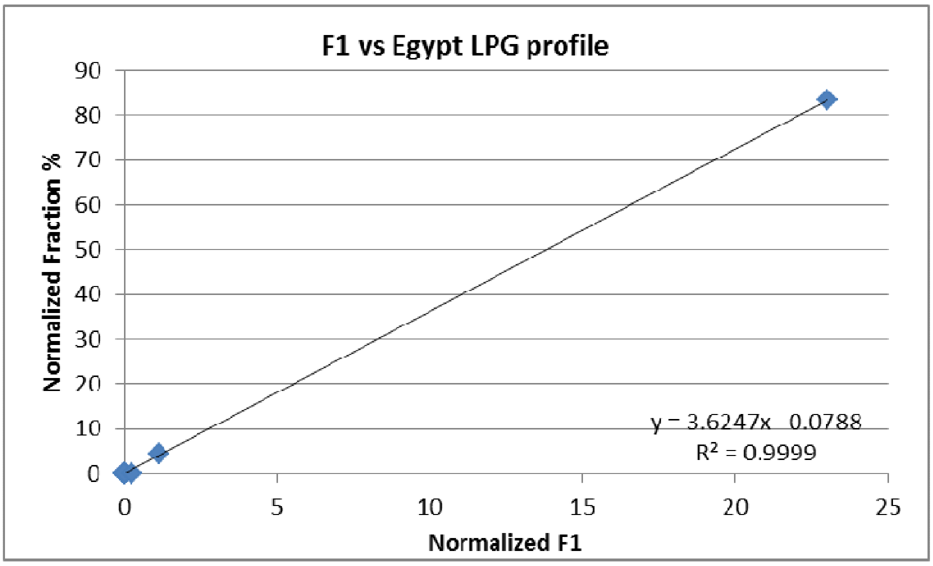


Figure 5-25 Correlation between F1 and Egypt LPG source profile

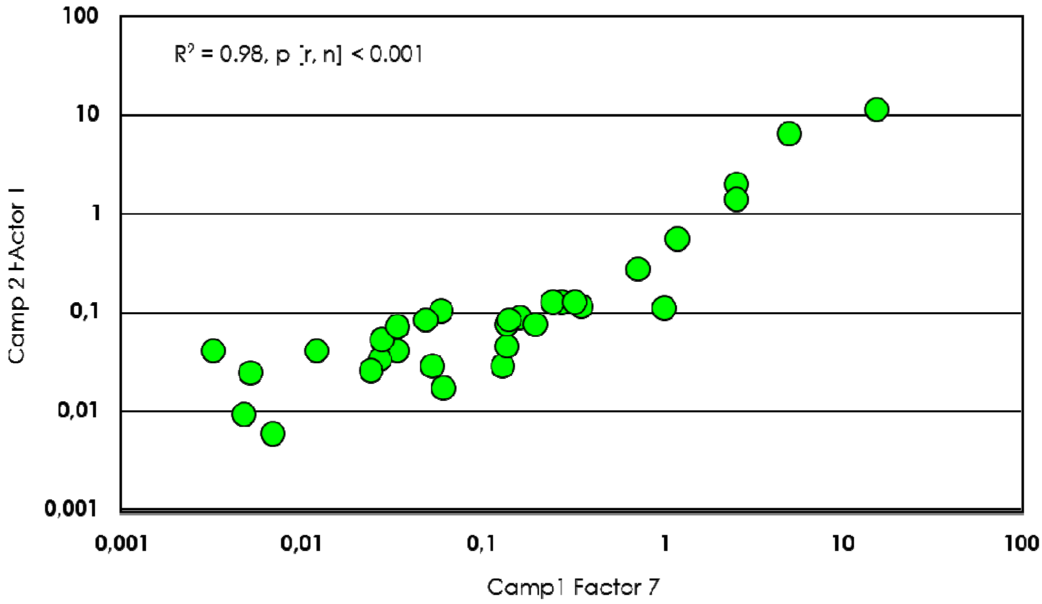


Figure 5-26 Correlation between factors identified as LPG-vehicle in the first (factor 7) and second (factor 1) campaigns

Factor loadings, contribution of the factor to VOCs and temporal variation of factor scores of Factor 2 are given in Figure 5-26. Toluene is the most abundant compound in the source profile of Factor 2. Absence of benzene and temporal variation of the factor contributions indicate that this factor is not a traffic-related source.

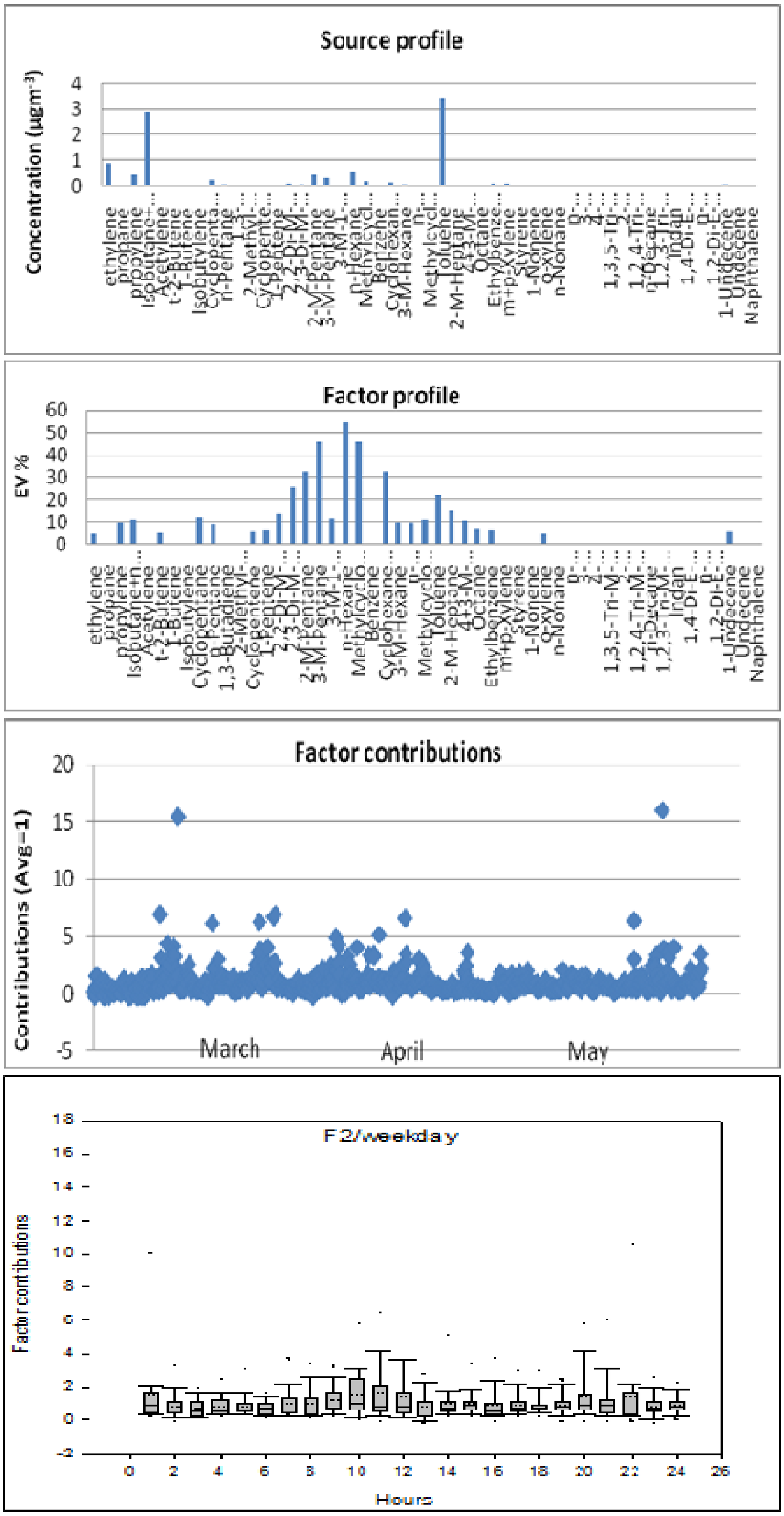


Figure 5-27 Factor loading, percentage of species accounted for by each factor, time-series and diurnal plots of factor 2 scores for campaign 2

The major source of toluene is anthropogenic activities such as combustion, fuel evaporation, solvent usage and industrial processes (White et al., 2009). 2,3-di-m-pentane, 2-m-pentane, 3-m-pentane, n-hexane, methylcyclohexane and toluene are heavily loaded in this factor. Factor 2 accounts for approximately 55% of the n-hexane and 22% of the toluene. n-hexane and toluene are found in many commercial products owing to their industrial use in the production of adhesives, glues, paints, cleaners, thinners, and plastics (Liu et al., 2008; Gomes et al., 2010). Furthermore, a slight diurnal variation in source contributions with high contributions in daytime and low contributions during nighttime was observed. This type of diurnal profile is consistent with both coating and solvent evaporation in industrial activities (Brown et al., 2007).

Factor 2 is similar to Factor 1 in the first campaign. The correlation between Factor 1 profile in the first campaign and Factor 2 profile in the second campaign is high ($R^2 = 0.92$ and $p<0.005$) Therefore, the source of Factor 2 was identified as an **industrial process** as in the factor 1 of the Campaign 1 PMF. Source profile, factor profile and temporal variation of **Factor 3** scores are given in Figure 5-27. Ethylene, propane and BTEX compounds were found as the most abundant compounds in the source profile of Factor 3. BTEX compounds are known indicators of traffic (Hoque et al., 2008). The EV plot of Factor 3 shows that 50% of the concentration of propane, 30% of the concentration of 1,3-butadiene and approximately 20% of the concentration of benzene and toluene are accounted by Factor 3.

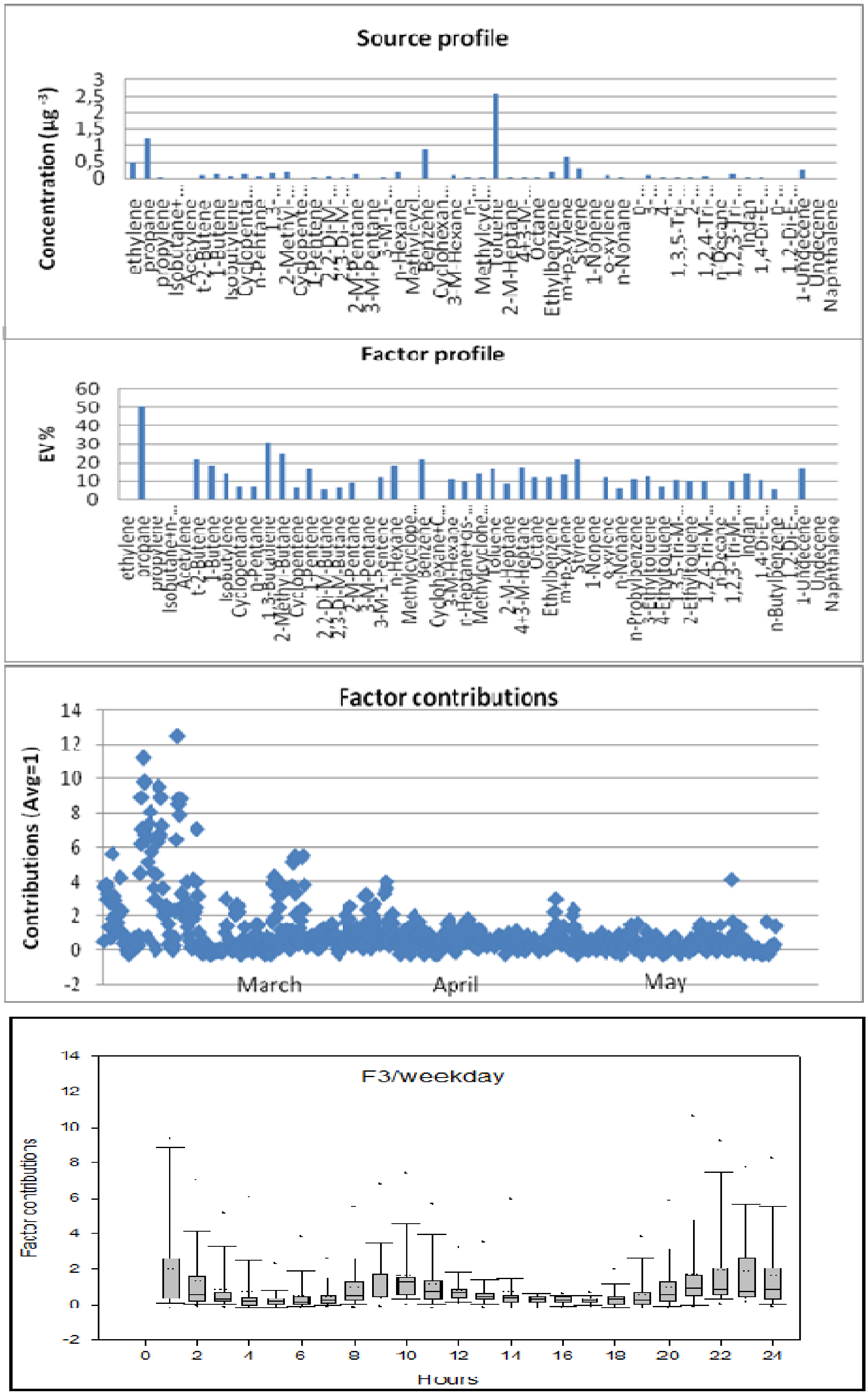


Figure 5-28 Factor loading, percentage of species accounted for by each factor, time-series and diurnal plots of factor 3 scores for campaign 2

Source of this factor is not very clear. The factor is loaded with traffic markers. Also diurnal variations of scores depict a clear traffic pattern with two rush hour maxima. These all indicate that Factor 3 is associated with some sort of vehicle emissions. Factor 3 profile correlate well with gasoline exhaust profile in Campaign 1 (F4) ($R^2 = 0.54$, $p<0.005$). However, factor 3 is not a LDV exhaust factor, because factor lacks acetylene. It looks more related gasoline evaporation, but it does not correlate well with the gasoline evaporation factor in Campaign 1. At this point physical source associated with factor 3 is not clear. It is related to light duty vehicle traffic and because of that it is identified as "**traffic**" factor, but more specific physical source cannot be assigned to factor 3. Diagnostic plots for factor 4 are given in Figure 5-28. 1-undece, undecane, n-decane and napthalahene are the most abundant compounds in the source profile of Factor 4. Factor accounts for fair amount of concentrations of heavy hydrocarbons. Diurnal variation of factor 4 scores showed higher values in the afternoon between 12:00 and 18:00. This pattern suggests an evaporative source for Factor 4.

To identify the source of Factor 4, different source profiles obtained from the literature were used. Results are presented in Figure 5-29. The best correlation ($R^2=0.565$) was found with a domestic solvent profile ($p<0.05$) obtained from Cal/EPA Organic Gas Speciation Database profile number 197. Factor 4 profile also showed statistically significant correlation with industrial source profile generated for Bursa by Civan (2010) ($R^2=0.612$; $p < 0.005$). Factor 4 is identified as **emissions from solvent evaporation from small scale industries within the city**.

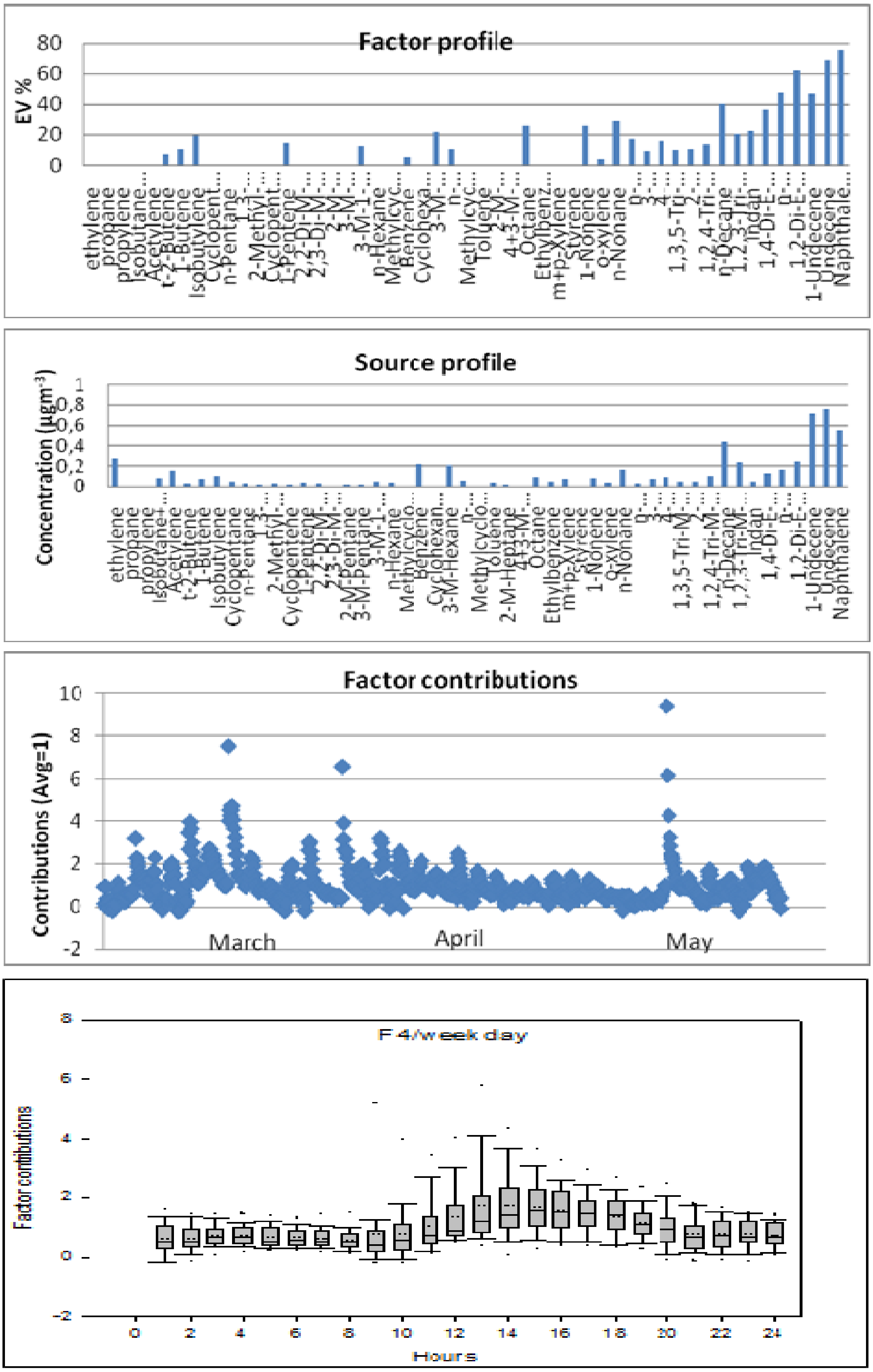


Figure 5-29 . Factor loading, percentage of species accounted for by each factor, time-series and diurnal plots of factor 4 scores for campaign 2

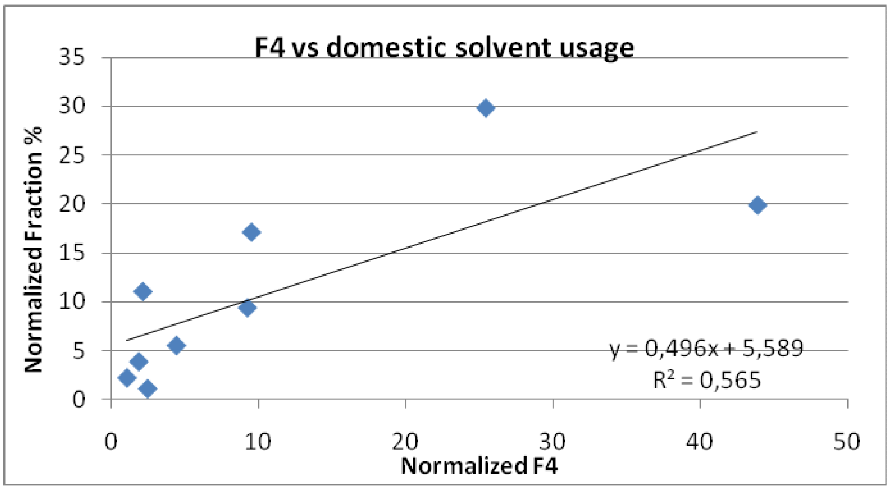


Figure 5-30 Correlation between F4 and domestic solvent source profile

Factor profile (loadings), fraction of VOCs accounted by Factor 5 and G-score plots of Factor 5 are given in Figure 5-30. Benzene, toluene, ethylene, acetylene and isobutene+-butane are the most heavily loaded VOCs in this factor. The factor accounts for approximately 60% of the benzene concentration and 80% of the concentration of acetylene. Factor scores do not show dramatic change from the beginning tot the end of the campaign 2. However diurnal variation of scores shows a typical traffic pattern with two rush hour maxima.

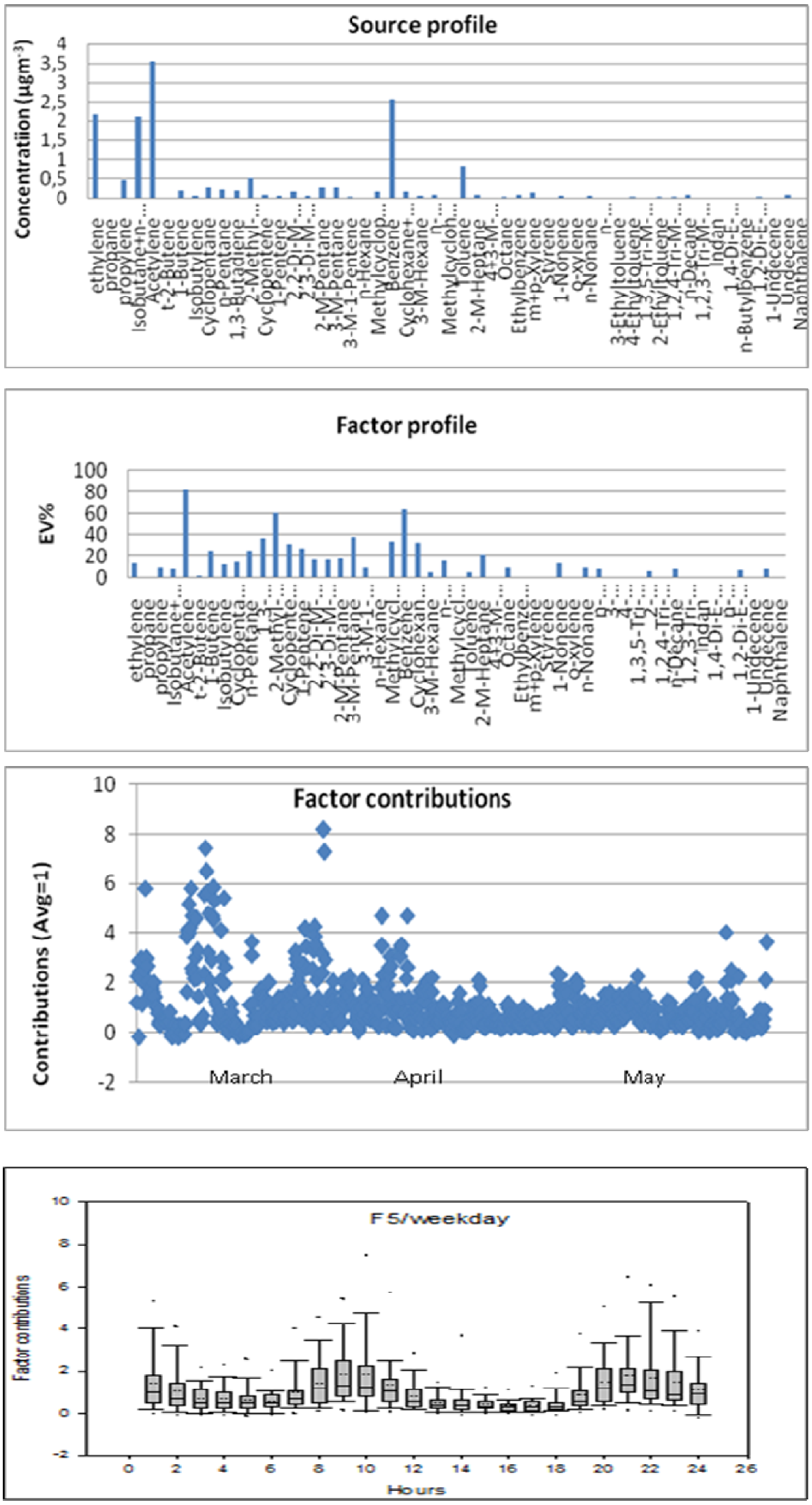


Figure 5-31 Factor loading, percentage of species accounted for by each factor, time-series and diurnal plots of factor 5 scores for campaign 2

Factor 5 represents emissions from **LDV exhaust**. The main difference between this factor and Factor 3, is that factor 5 is loaded with acetylene whereas acetylene is missing in factor 3.

Factor loadings, fractions of VOC concentrations accounted by factor 6, time-series plot of factor 6 scores and diurnal variation of scores are given in Figure 5-31. Toluene and isobutene+n-butane are the most heavily loaded VOCs in Factor 6.

Approximately 40% of concentrations of TEX compounds, n-nonane, n-decane and alkyled benzene are accounted for by Factor 6. Source contribution plots of Factor 6 signify that the contributions of the factor are maximum at noon. These observations suggest an evaporative source for factor 6. Composition of Factor 6 is very similar to the composition of Factor 8 in the PMF of the first campaign and thus represents a similar source, namely solvent evaporation resulting from both industrial and domestic activities. As in Factor 8 of the first campaign, factor profile correlated, with a statistical significance at 95% confidence level, with paint solvent source profile (R^2=0.977) generated by Na et al. (2004) for Seoul and industrial solvent coating-solvent based paint (R^2=0.9846) obtained from Cal/EPA database (profile number 783) and Bursa industrial source profile (R^2=0.844) generated by Civan (2010). These regressions between Factor 6 profile and solvent profiles are presented in Figure 1.

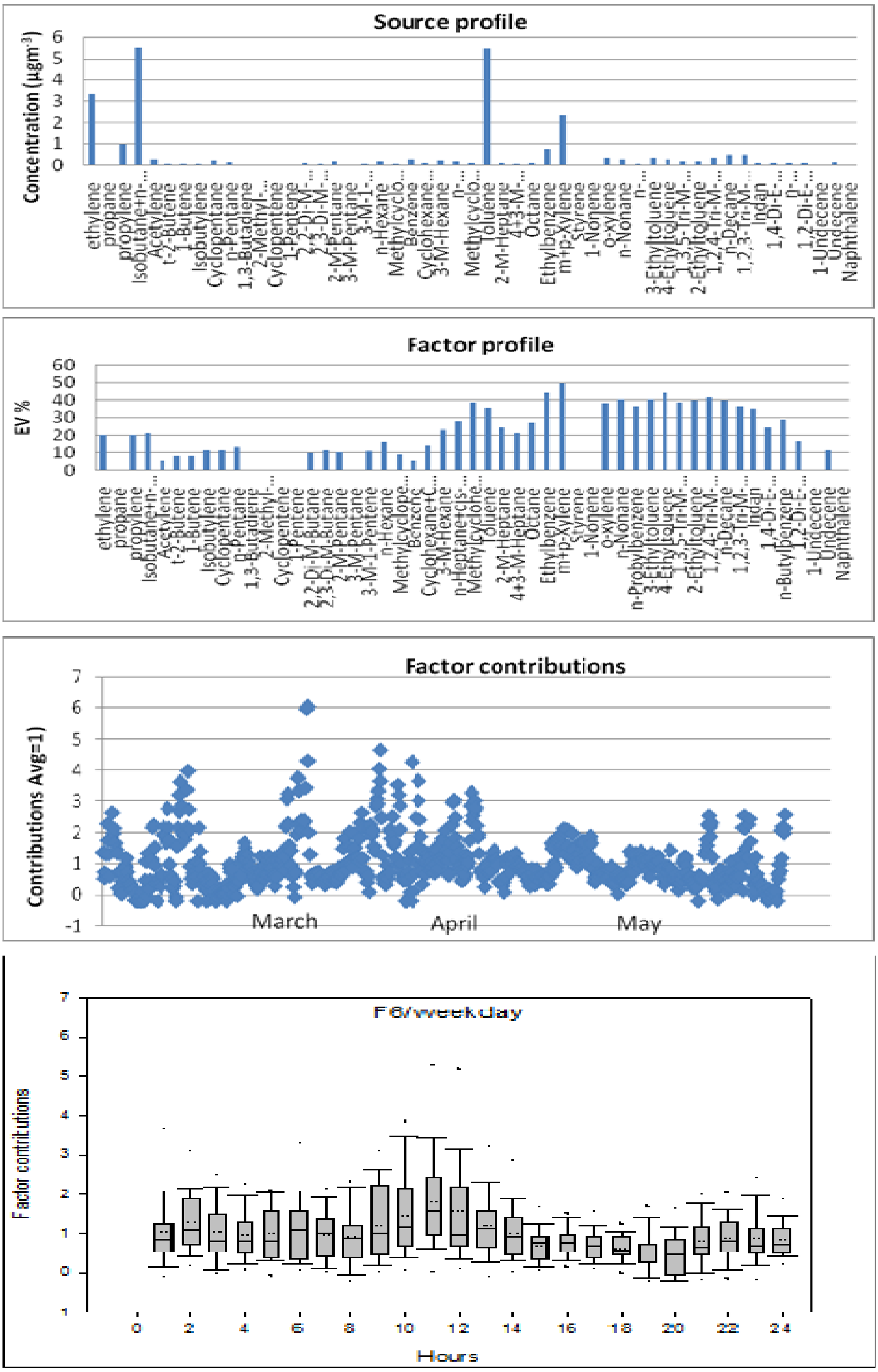


Figure 5-32 Factor loading, percentage of species accounted for by each factor, time-series and diurnal plots of factor 6 scores for campaign 2

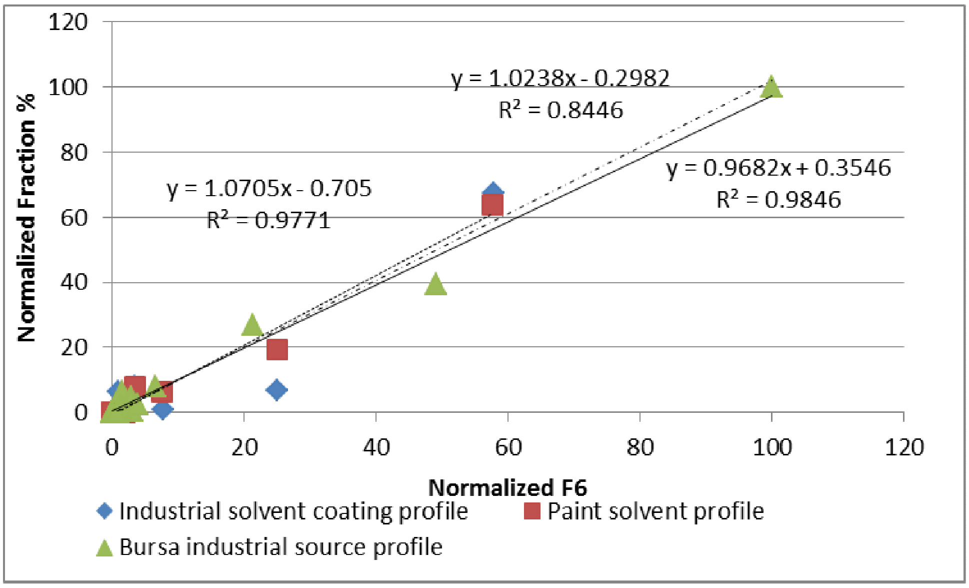


Figure 5-33 Correlation between F6 and paint source profiles

Diagnostic plots for Factor 7 are presented in Figure 5-33. The source profile plot of Factor 7 shows that m,p-xylene, cyclopentane an isobutane+n-butane are the most abundant compounds in this factor. Factor 7 accounts for 35% of the 2,2-di-m-butane, 30% of the cyclopentane and cyclopentene, 19% n-pentane concentrations.

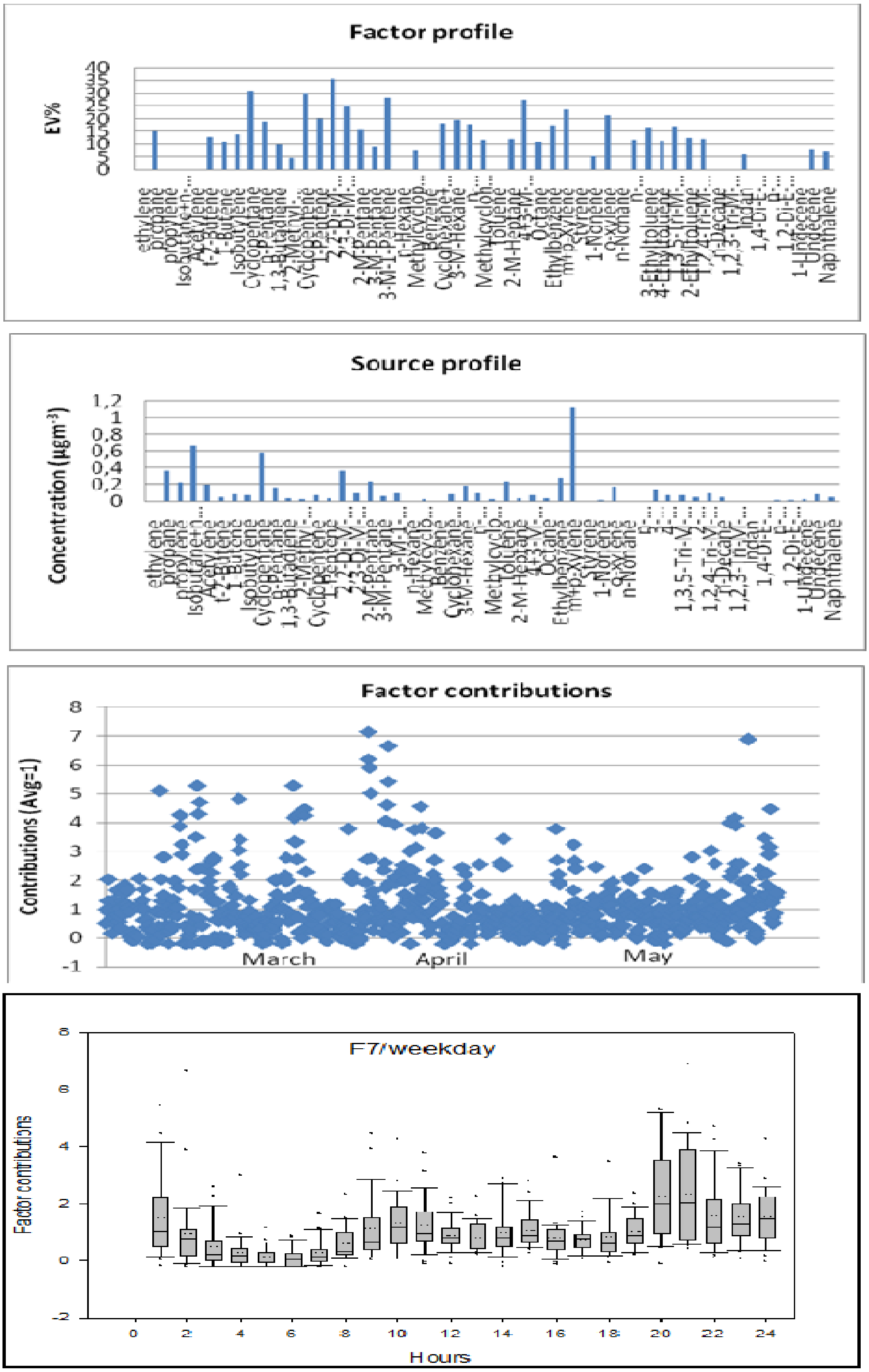


Figure 5-34 Factor loading, percentage of species accounted for by each factor, time-series and diurnal plots of factor 7 scores for campaign 2

Source contribution plots for Factor 7 show a diurnal pattern with high source strengths during morning and evening rush hours. Therefore, the source of Factor 7 was thought to be related with traffic.

The main point that differentiates this factor from the vehicle exhaust factor is the lack of acetylene in this factor. As pointed out before, acetylene is a combustion product and does not exist in liquid gasoline or evaporated gasoline. Because of this, acetylene is used to differentiate gasoline exhaust emissions from gasoline evaporation. Since there is no acetylene associated with factor 7, then this factor represent VOCs emitted from gasoline evaporation, either at gas stations or from the vehicle itself. In this sense Factor 7 is similar to factor 6 in the PMF of the first campaign.

To identify the source of the Factor 7 exactly, source profile of Factor 7 was compared with different source profiles obtained from the literature. Results are presented in Figure 5-34. The best fit was found with unleaded gasoline (R^2=0.498) source profile generated by Kuntasal in 2005 for Ankara. Accordingly, Factor 7 was also found correlated ($p<0.05$) with leaded gasoline profile (R^2=0.310), hot soak emission (R^2=0.277) and cold soak emissions (R^2=0.254) (Figure 46). Therefore, the source of Factor 7 was identified as gasoline evaporation.

Factor 7 profile also showed very high correlation with gasoline evaporation factor (Factor 6) in the PMF applied to Campaign 1 data ($R^2 = 0.94$, $p\ [r,n] < 0.005$), confirming gasoline evaporation source for factor 7.

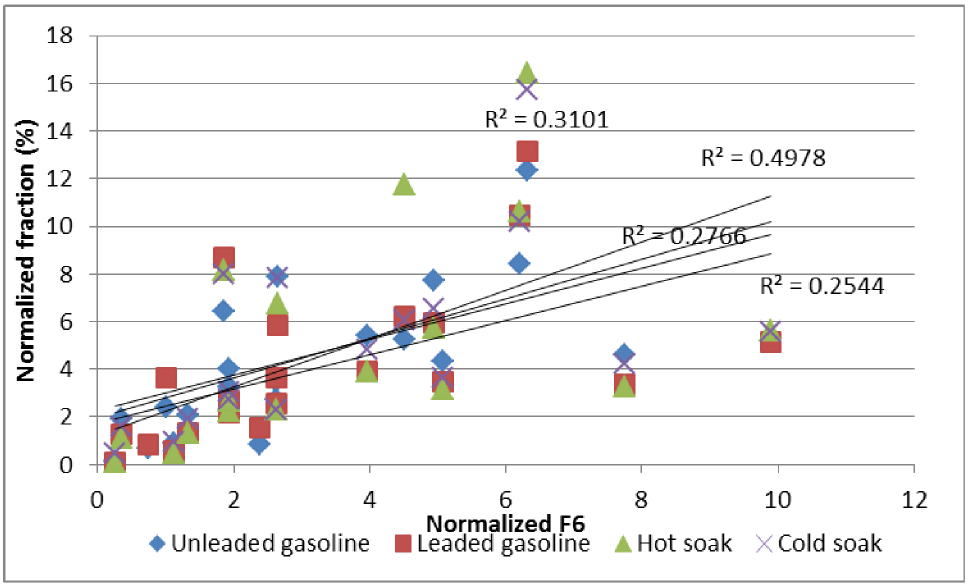


Figure 5-35 Correlation between gasoline profiles and Factor 7 source profile

Source profile, Fraction of concentration explained by the factor, and temporal variation of factor 8 scores are given in Figure 5-35. Ethylene, isobutane+n-butane, toluene and styrene were found the most abundant compounds in this factor. The factor accounts for approximately 74% of the variation of styrene. Temporal and diurnal variations of Factor 8 were found very similar to Factor 5 which was obtained in the first campaign. Variation of the factor contributions indicates an evaporative source. Moreover, Factor 8 did not show any diurnal variation, as with the first campaign, which is a pattern observed in industrial emissions.

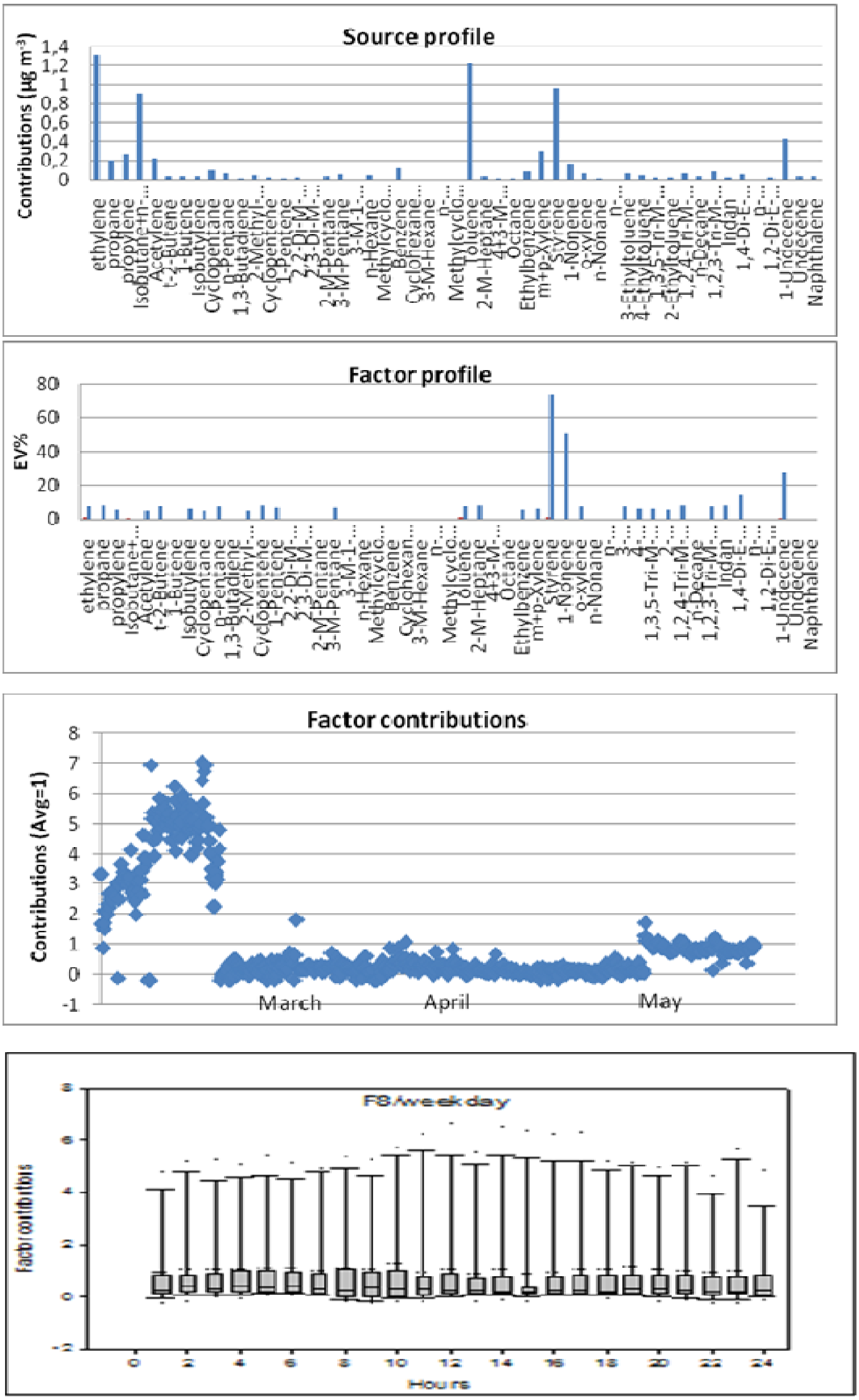


Figure 5-36 Diagnostic graphs for factor 8.

The correlation between factor 8 profile and other profile found in literature is depicted in Figure 5-36. Factor 8 correlates strongly (R^2 = 0,91, p [r,n]<0.005) the industrial source profile of Bursa generated by Civan (2005). Therefore, factor 8 is identified as a factor representing emissions from an industrial process. However, it is not possible to differentiate between different industrial processes that can account for this factor.

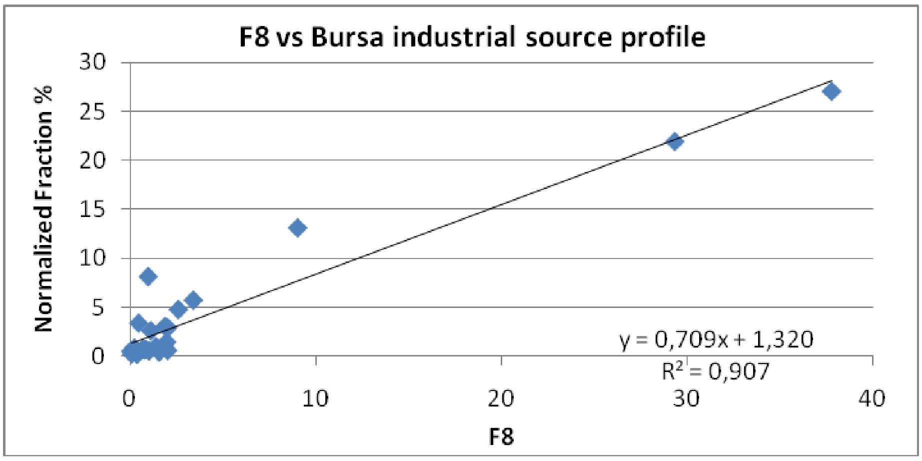


Figure 5-37 Correlation between Bursa industrial source profile and Factor 8 source profile

5.2.6 PMF Results of the Second Campaign

Linear regression between predicted and measured concentration of ∑VOC is depicted in Figure 5-37 was performed to compare modeled results and measured values. A very good correlation (R^2=0.991, p<0.001) was obtained between modeled and measured values, indicating that eight factors adequately explain measured concentrations of VOCs in Bursa atmosphere.

Contributions of each factor to ∑VOCs are given in Table 5-4. Traffic-related emissions accounts for approximately 50% of ∑VOC concentrations and various forms of solvent evaporation accounts for the other half. Emissions from LPG powered vehicles accounts for approximately half of the motor vehicle contribution to ∑VOC concentrations, which is followed by gasoline exhaust, which accounts for approximately 14% of traffic contribution to ∑VOC concentration in Bursa atmosphere.

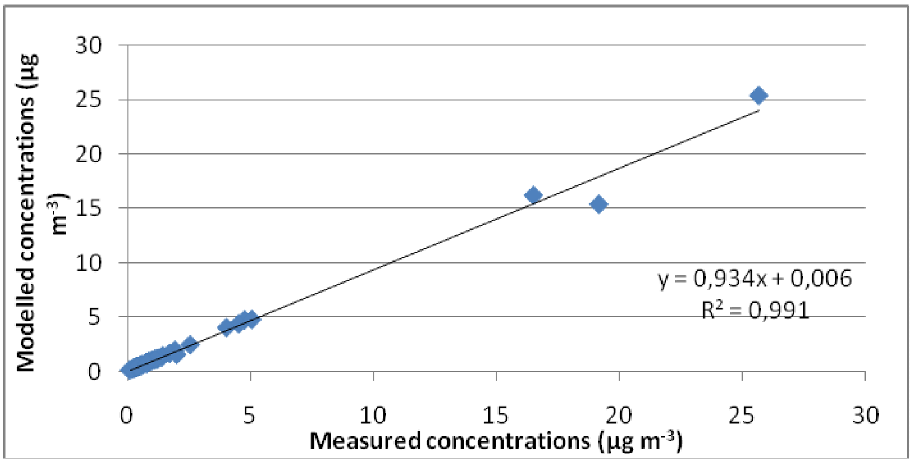


Figure 5-38 Modeled versus measured VOC concentrations for the second campaign

Contribution of traffic related contributions to ∑VOC concentrations in the second campaign is slightly lower than contribution of traffic related emissions to ∑VOC concentrations in the first campaign (41%). In both campaigns emissions from LPG powered vehicles are the highest contributor (19.8% in the first campaign and 26.5% in their second). Contribution of gasoline exhaust to total VOC concentration is approximately 14% and 22% in the first and second campaigns, respectively.

Contribution of solvent related emissions (from both industrial and commercial activities) on total VOC concentrations in the second campaign (45%) is higher than solvent contribution in the first campaign (33%). Contribution asphalt pavement activities to total VOC concentrations in the first campaign were significant (26%). This source is not included in the above calculation, because it is a traffic-related source, but it is also an evaporative source.

Table 5-4 Source contribution of the obtained factors as a result of the PMF analysis

Factor	Source	% Contribution
1	LPG fueled vehicles	26.56
2	Industrial process	10.17
3	Traffic	8.48
4	Solvent evaporation from small scale commercial activities	5.34
5	LDV exhaust	14.21
6	Paint	22.29
7	Gasoline evaporation	6.16
8	Industrial solvent evaporation	6.80

5.2.7 Comparison of the PMF Results

A total eight sources were obtained as a result of PMF analysis for both sampling campaigns. LPG fueled vehicles, industrial process, solvent evaporation from small scale commercial activities, LDV exhaust, paint, gasoline and industrial solvent evaporation are the seven common profiles observed in both sampling campaigns.

Traffic emissions are the major source in Bursa. However, the contribution of fall season traffic emissions was found to be smaller than the spring contribution owing to asphalting activities.

Asphalt pavement operations source is a unique factor which was obtained at the first campaign with a high share.

Five types of solvent related industrial/commercial sources were recognized for sampling campaigns, including, industrial process, paint and industrial/commercial solvent evaporation. The contribution of fall season industrial sources to total VOC load is about 25% smaller than spring campaign.

Two of the sources, namely “asphalt pavement activities” and “solvent release from small scale commercial activities” are transient source, which may not be found if PMF is applied at a different time interval. Maybe industrial solvent evaporation can also be included among these transient sources. However, remaining five sources are expected to be permanent features of Bursa atmosphere.

5.2.8 Implications of This Work

Data on levels and sources of volatile organic compounds in Turkish cities is very limited. Consequently, knowing the concentrations of VOCs by itself is useful information that can be used by decision makers. Very high resolution VOC data generated using an on-line GC system, identification of sources contributing to measured VOC concentrations can be used in variety of ways to develop actions to improve air quality in Bursa.

Source apportionment in this study generated source profiles for sources including, LPG fueled vehicle, gasoline evaporation, LDV exhaust, asphalt pavement activity and solvent related industrial/commercial activities. For some of these, such as light-duty vehicle source, source profiles are available to a certain extend and can be found in global data-banks, such as SPECIATE. However, VOC profiles for sources like, LPG-powered vehicle or emissions from asphalt pavement, or solvent emissions from industry are extremely scarce in global scale. Development of these profiles will be useful contribution to future source apportionment studies, particularly “Chemical Mass Balance” type of receptor modeling studies, where information of proposed source composition is essential.

Bursa is an industrial city. The contribution of the industrial/commercial activity related organic compounds to total VOC mass is nearly 40% in Bursa. Therefore, there is a solvent originated organic compound pollution problem in our industrialized cities. However, industries do not have any Toxic Organic Management Plan (TOMP) in Turkey. There must be some regulations for different types of industrial activities. These TOMPs must specify the types of toxic compounds used in the processes, storage and disposal methods of toxic compounds. Furthermore, there must be some limit values for the solvent emissions for each industry. Consequently, outcomes of this study can also be used as a tool for the preparation of Toxic Organic Management Plan, particularly to develop guidelines and standards, because results of this study provided preliminary data on organic compound emissions originated from industrial solvent consumption.

Health risk originating from current VOC concentration in Bursa was not a part of this work. However, public exposure to VOCs and health risks associated with current VOC levels can be performed by other researchers using data generated in this study. High resolution of data makes them ideal for health studies.

This thesis includes levels of measured organic compounds and their temporal variability in Bursa. Moreover, types of sources contributing to measured organic levels and ozone formation potentials of these organics in Bursa were also determined in the study. Therefore this thesis provides contribution to Bursa Metropolitan Municipality in terms to identify current pollution levels of the city. Municipality can take some precautions to decrease traffic density in Bursa city center. The capacity of the public transport system can be increased. Uncontrolled usage/storage of solvents during small scale commercial activities can be controlled by municipality.

CHAPTER 6

CONCLUSIONS AND RECCOMENDATIONS

6.1 Conclusions

The main objective of this study was to investigate sources and temporal variation of VOCs in Bursa urban atmosphere. For this purpose, organic compounds were measured on hourly basis in Bursa city center. The field study was performed between September 14 to November 6, 2005 and March 17 to May 10, 2006. About 62 and 64 compounds out of the 148 target compounds were detected in more than 50% of the samples collected for the first and second campaigns, respectively.

As a result of this study;

- The median total VOC concentrations were 115 and 86 µg m^{-3} for the first and second campaigns, respectively. In the first campaign, total VOC concentrations were higher than in the second campaign even though more stable weather conditions were present in the second campaign. The reason was asphalting operations going on during the first campaign which led significantly higher concentrations of organics; however, traffic-originated VOCs were higher than in the second campaign period than in the first campaign period. Therefore, data obtained during these campaigns highlights the importance of source strength and meteorology on VOC concentrations in the atmosphere.
- The concentration of measured organic compound showed great variations. The concentration of measured organic compounds ranged from 0.4 to 399 µg m^{-3}. There was a diurnal, weekday/weekend change of VOC concentrations on time basis and also on seasonal variations in Bursa atmosphere.
- Toluene was the most abundant single compound with a median concentration of 13.3 and 16.3 µg m^{-3} for the first and second campaigns,

respectively. In this study, median benzene concentrations of 1.51 and 2.79 μg m^{-3} were measured for the first and second campaigns, respectively. Measured benzene concentrations were found lower than the limit value which is 5 μg m^{-3}.

- Alkanes were the most abundant organic group in Bursa atmosphere followed by aromatics, alkenes and halogenated compounds. In this study, composition of the NMTVOCs was found consistent with the non-converter equipped cars for both campaigns.
- Measured average VOC concentrations were relatively similar or a little higher than those measured in developed cities such as Paris and Berlin. VOC levels in any city are a strong function of traffic activity and number of vehicles in that city. The number of vehicles in Paris and Berlin is four times higher than the number of cars in Bursa traffic. Similar VOC concentrations in Bursa with those cities probably indicate an uncontrolled emission in Bursa.
- It was concluded that the measured VOC concentrations in Bursa atmosphere were affected by the meteorological parameters.
- Although more stable weather conditions were observed during the period of second campaign, lower total VOC concentrations were measured in the second campaign than those measured in the first campaign. This was believed to be due to asphalting operations performed during the first campaign. Especially high heavy hydrocarbon concentrations such as dodecane and 1-undecene in the results showed that the asphalting operation was an important VOC source contributing to total VOC load of Bursa atmosphere. Consequently, data generated in this study clearly demonstrated that some of the heavy hydrocarbons can be used as good tracers of asphalt application in urban airshed.
- The results showed that only BTEX group contributes about 50% and 40% of the ozone formation potential in Bursa urban atmosphere for the first and second campaign period, respectively.
- PMF analysis results revealed that traffic related sources and industrial solvent evaporations were the most abundant VOC sources contributing to

total VOC load of ambient Bursa atmosphere. In both campaigns emissions from LPG powered vehicles were the highest contributor s (19.8% in the first campaign and 26.5% in the second).

- The largest contributor to VOC levels of ambient Bursa atmosphere in the first campaign was the asphalt pavement activities. Emissions from asphalt pavement activities accounted for 26% of the measured VOC concentrations. Therefore, asphalting activities can be a significant VOC source for the urban atmosphere in general, as most asphalt applications are done during summer season, when traffic activity is at minimum. VOC emissions are enhanced by warm temperatures however, the volatilization of asphalt compounds are at the maximum.

6.2 Recommendations for Future Work

- This study was performed in 2006 therefore the same study should be repeated to determine the current level of organic compounds in Bursa atmosphere. Moreover, the number of the sampling locations should be increased to provide spatial distribution of the variability in VOC data. A passive sampling work was performed in 2006, which generated information about spatial distribution of VOCs in bursa atmosphere. However, spatially distributed high-resolution VOC data allows to studies on transport and fate of VOCs in Bursa atmosphere, which cannot be done with weekly passive data
- As Bursa is an industrial city, it is recommended to a comprehensive source profile study especially including textile and automotive industries.
- This study was performed on fall and spring seasons. No samples were collected during winter and summer. Therefore, there need to be online VOC measurements on winter and summer seasons in order to examine the effect of the seasonality on VOC concentrations.
- In this study, PMF analysis was applied to data set to estimate sources of ambient VOCs at Bursa atmosphere. However, due to inadequacy of PMF analysis, diesel exhaust and gasoline exhaust source profiles could not be

separated from each other. Therefore, CMB analysis should be applied to data set to estimate potential sources of organic compounds. CMB analysis needs source profiles. Consequently, the source profiles obtained from this study and the previous study which was performed by Civan (2010) would be very helpful for the future CMB analysis.

- There is no hourly traffic count information for Bursa city center. So, the findings obtained from this study could not be correlated with the traffic count. Traffic is the major source of the measured organic compounds in Bursa atmosphere. Therefore, there has to be traffic counts on hourly basis for a significant correlation of organic compounds with traffic.
- A health risk assessment study was not performed based on the measurement results of this study. It is recommended to a health risk assessment study using the hourly VOC measurement results of this study.

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PUBLICATIONS

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APPENDIX A

POLLUTION ROSES OF THE MEASURED ORGANIC COMPOUNDS

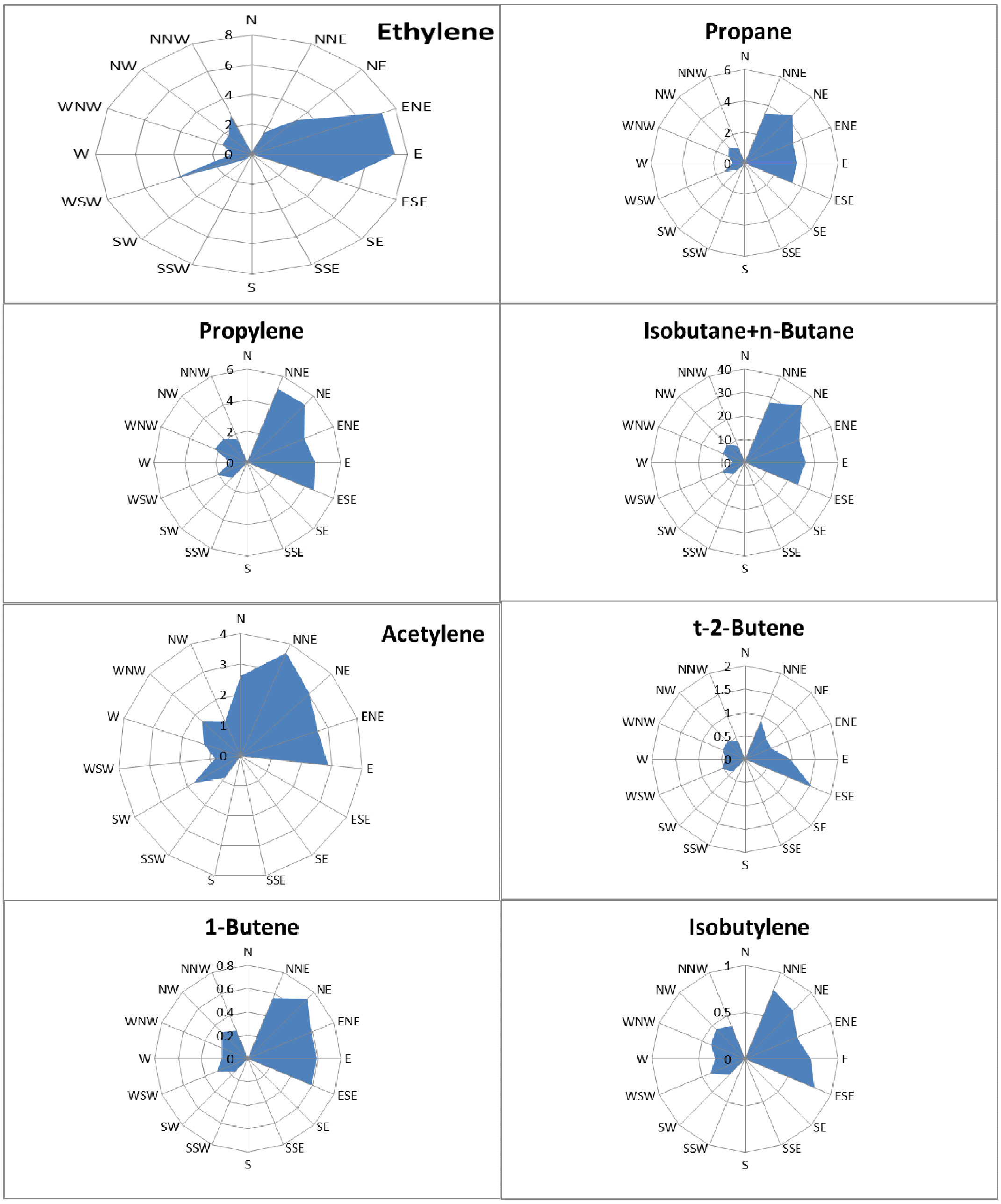


Figure A-1 Pollution roses of the second campaign (µg/m^3)

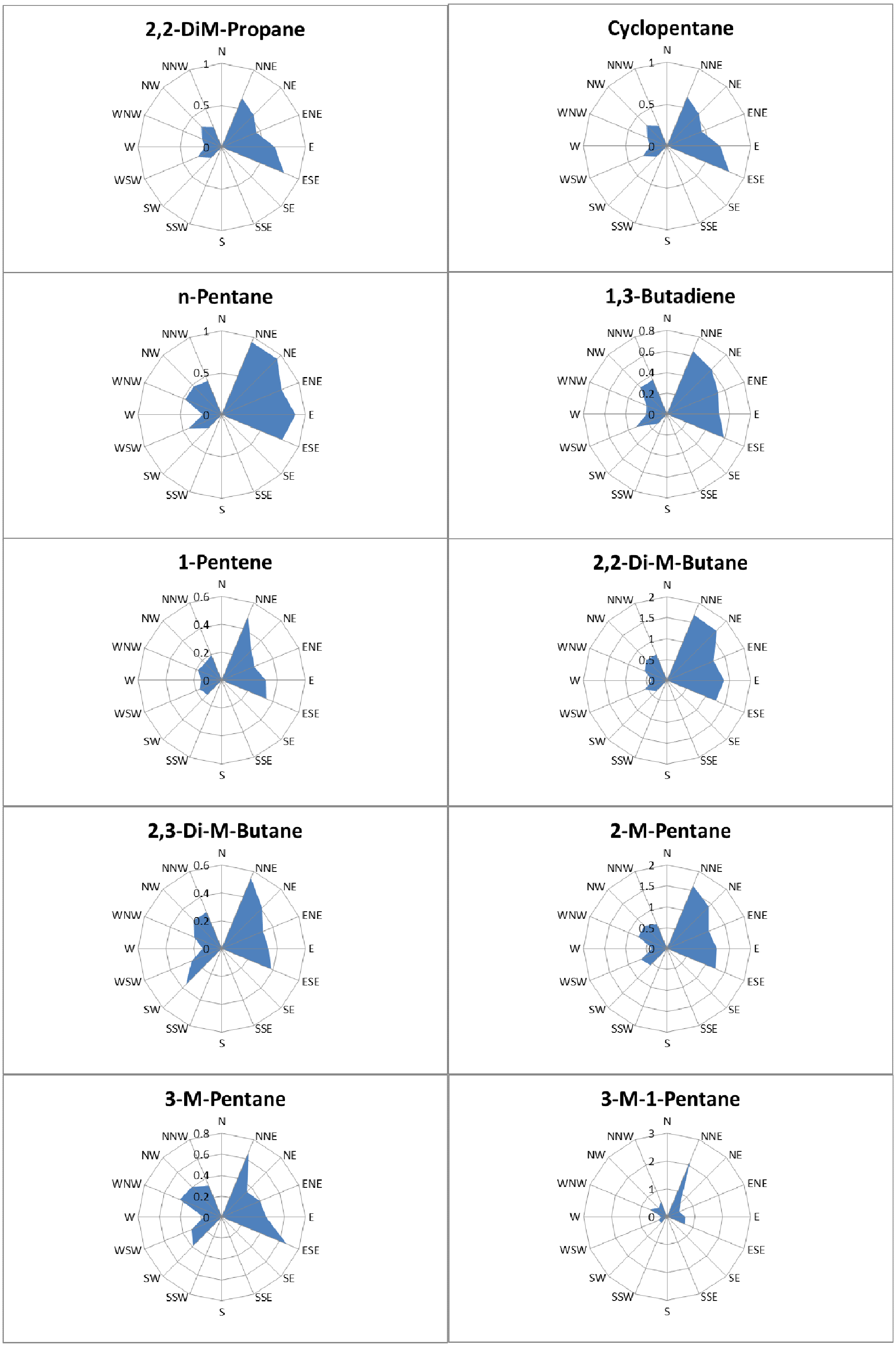
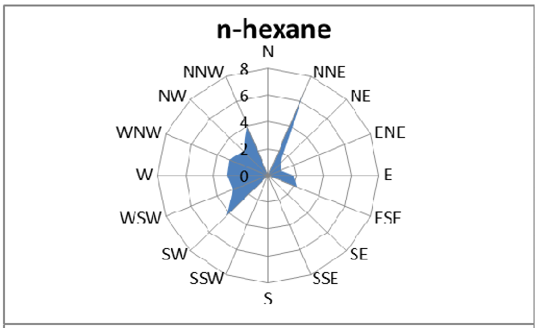
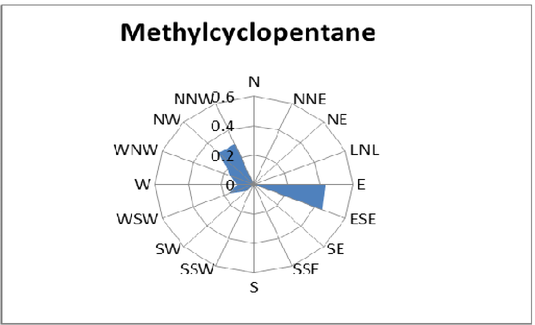


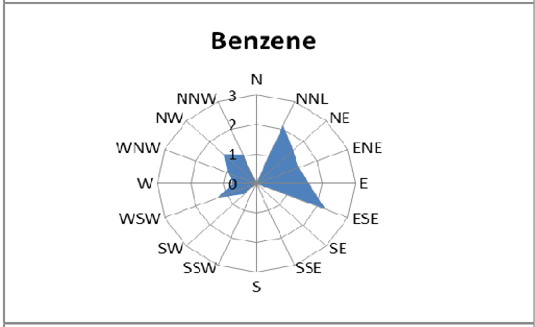
Figure A-1 (Continued)



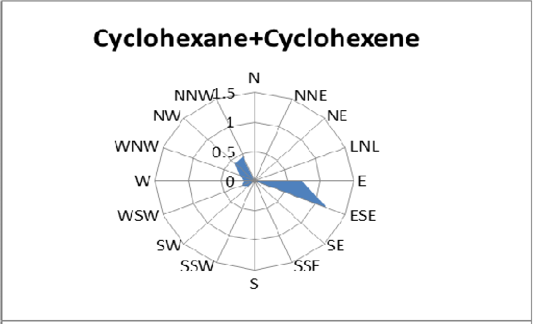
n-hexane



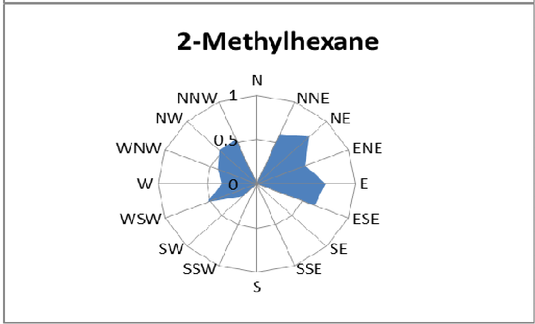
Methylcyclopentane



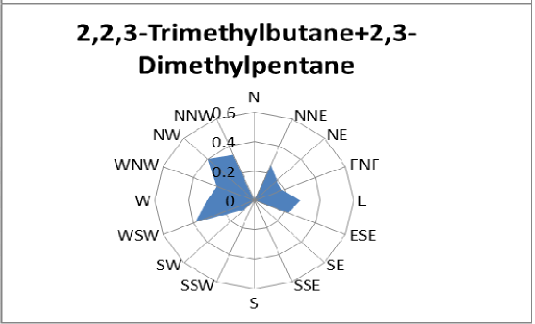
Benzene



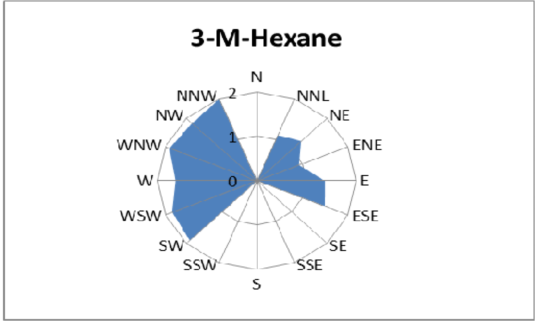
Cyclohexane+Cyclohexene



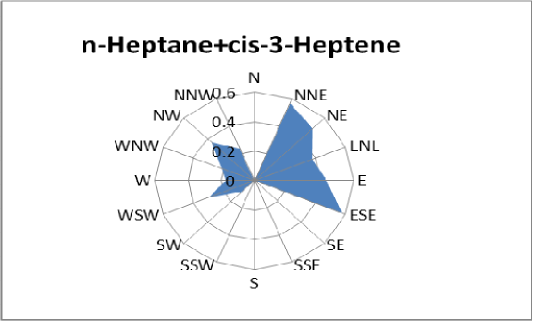
2-Methylhexane



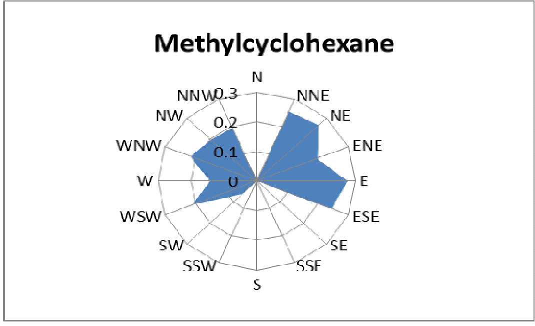
2,2,3-Trimethylbutane+2,3-Dimethylpentane



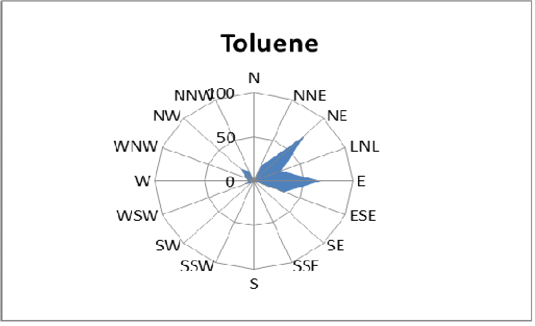
3-M-Hexane



n-Heptane+cis-3-Heptene



Methylcyclohexane



Toluene

Figure A-1 (Continued)

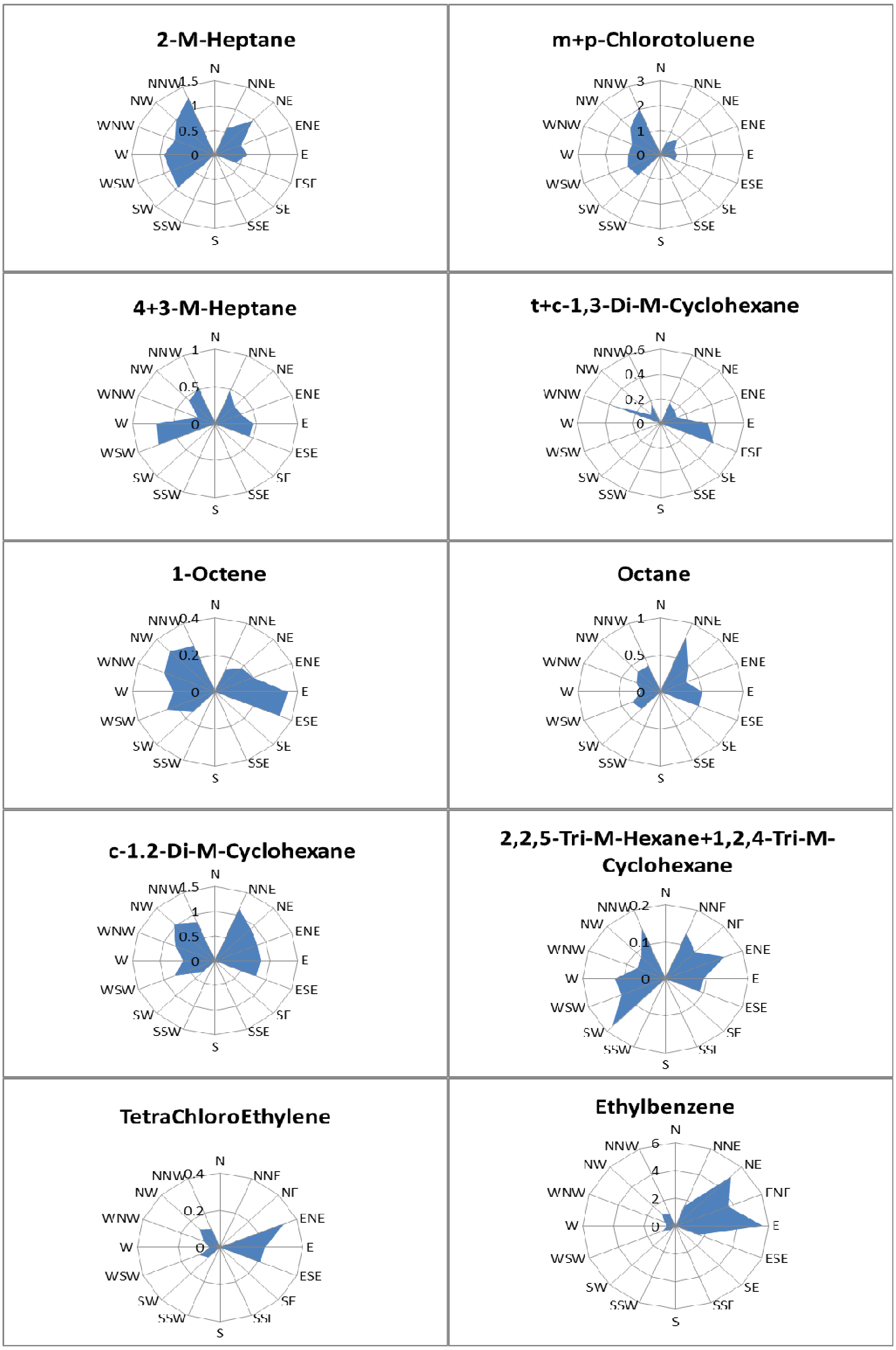


Figure A-1 (Continued)

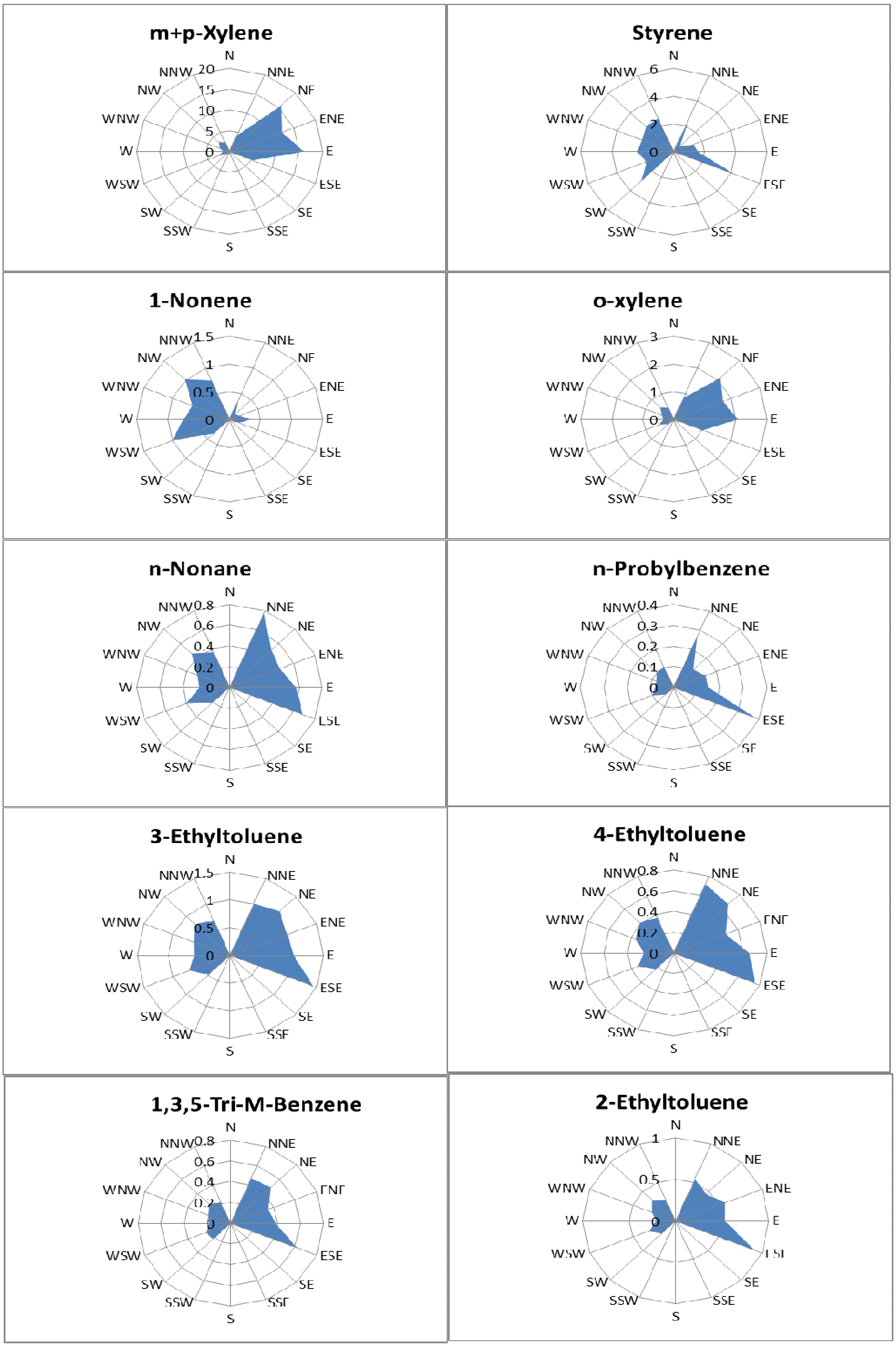


Figure A-1 (Continued)

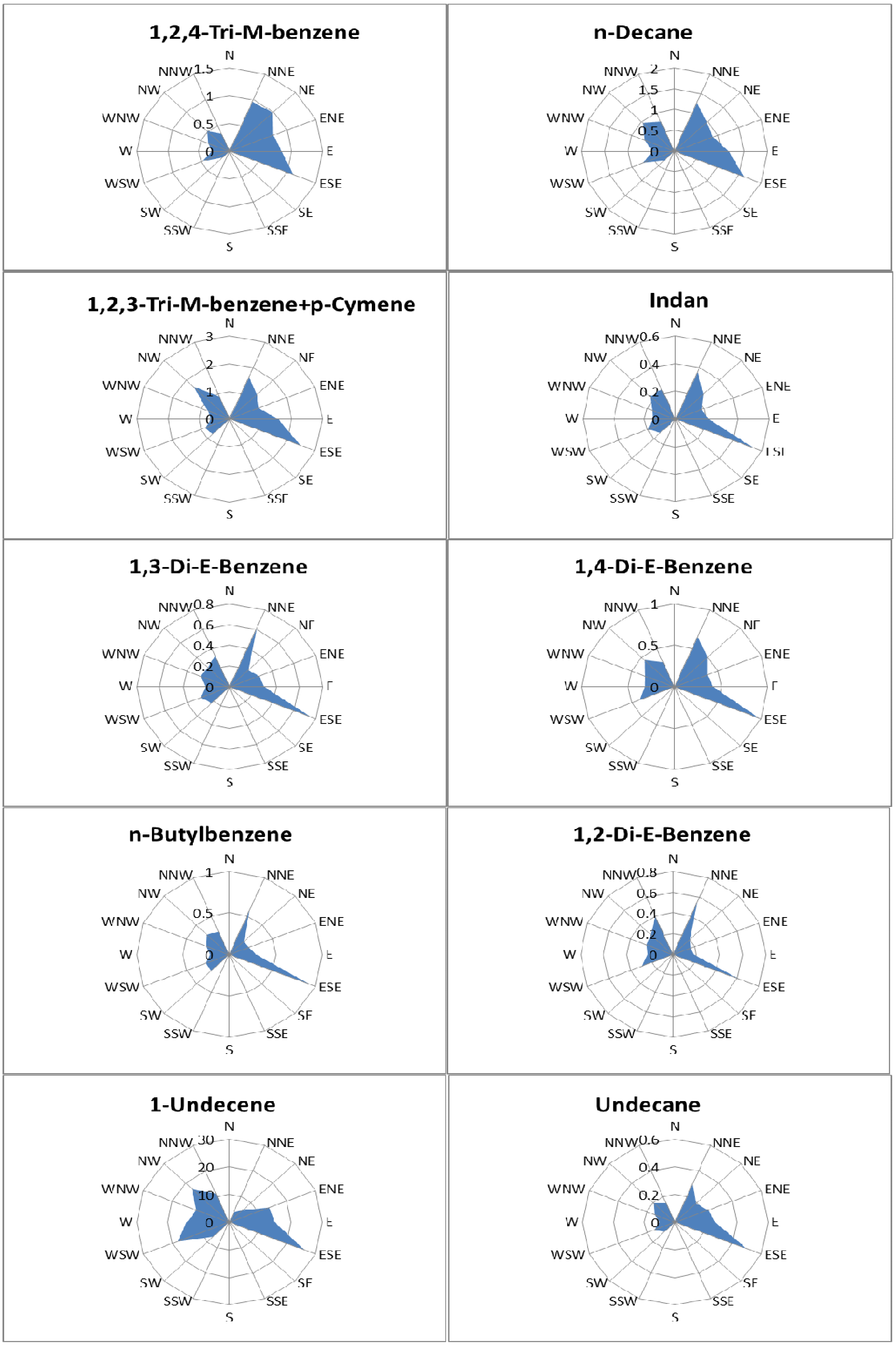
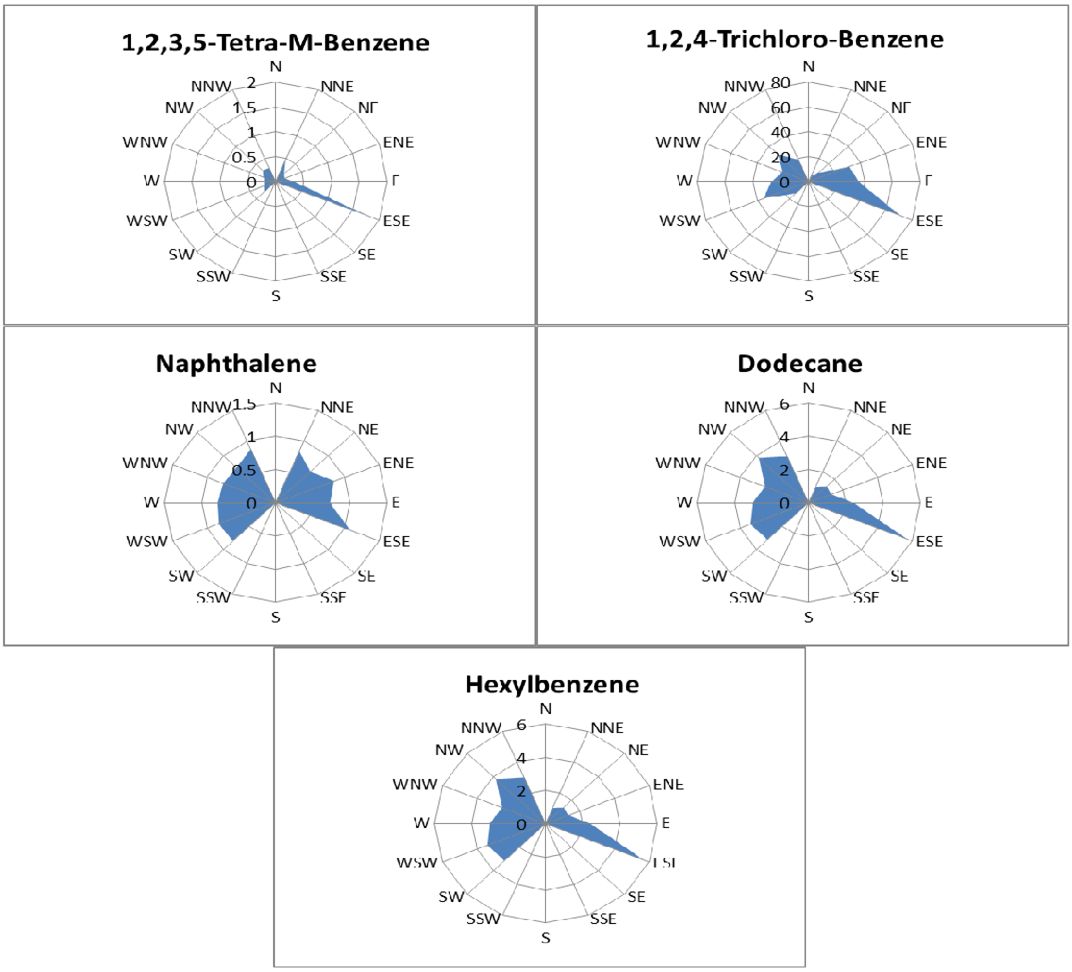


Figure A-1 (Continued)



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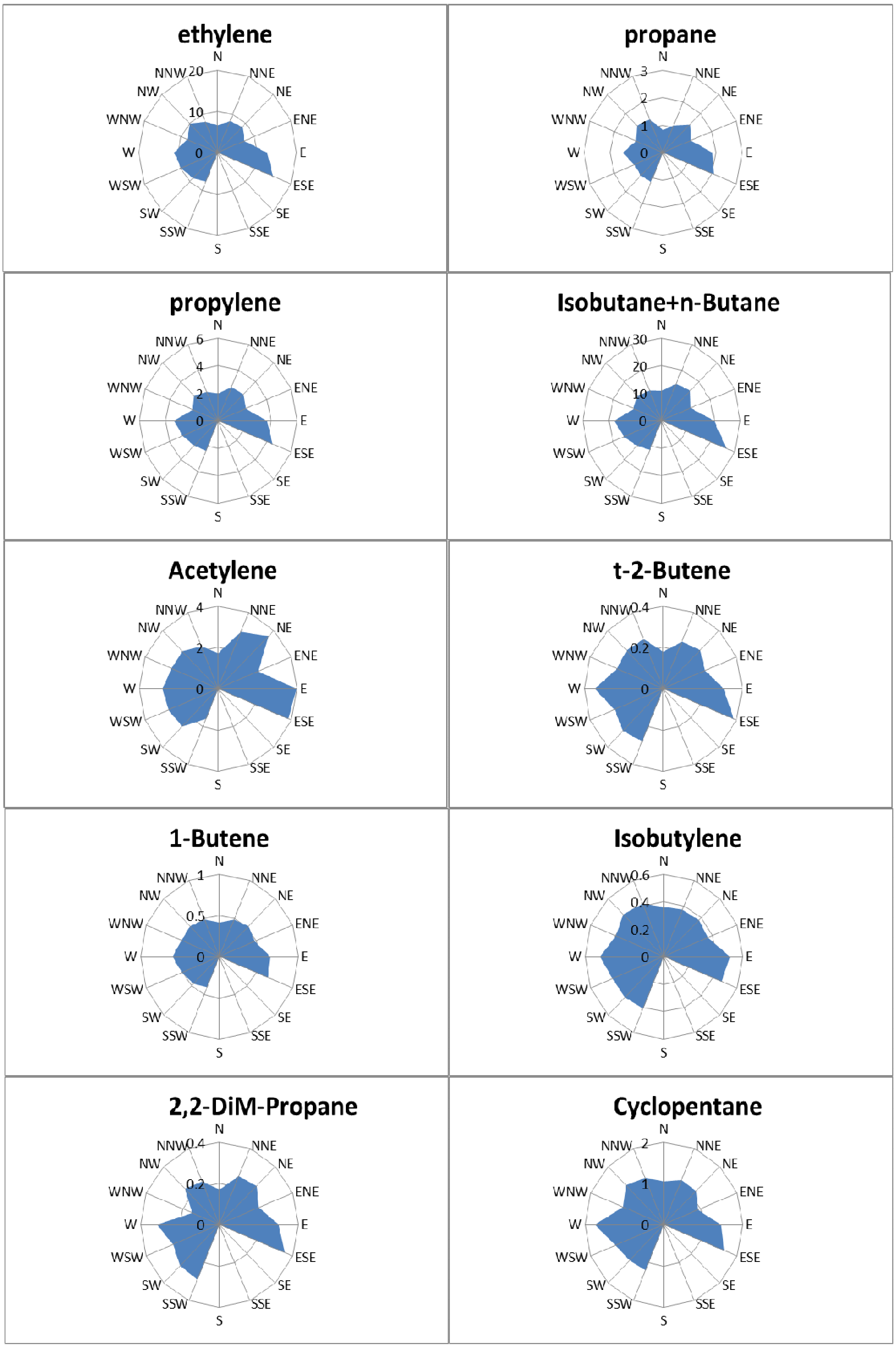


Figure A-2 Pollution roses of the second campaign (μg/m^3)

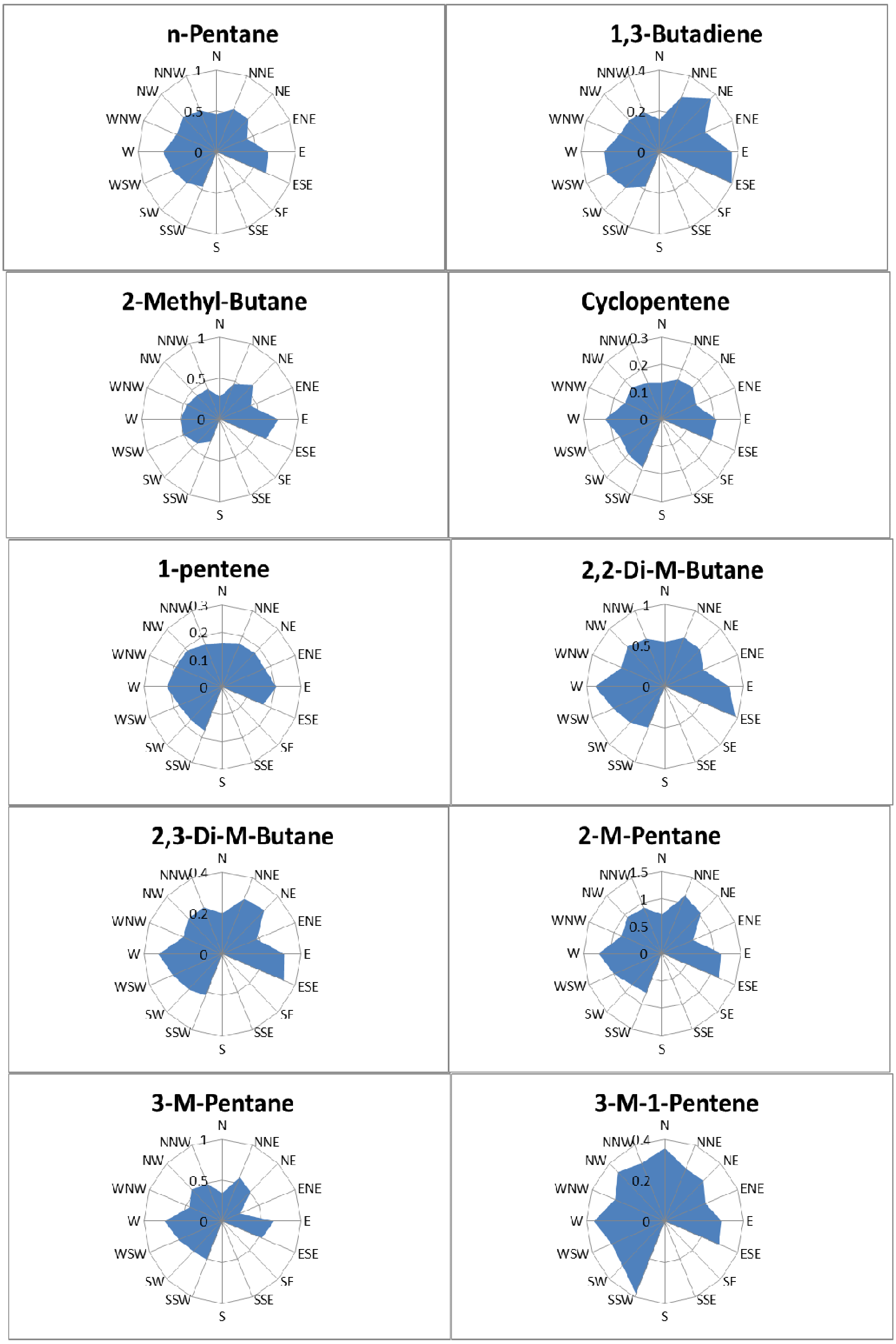
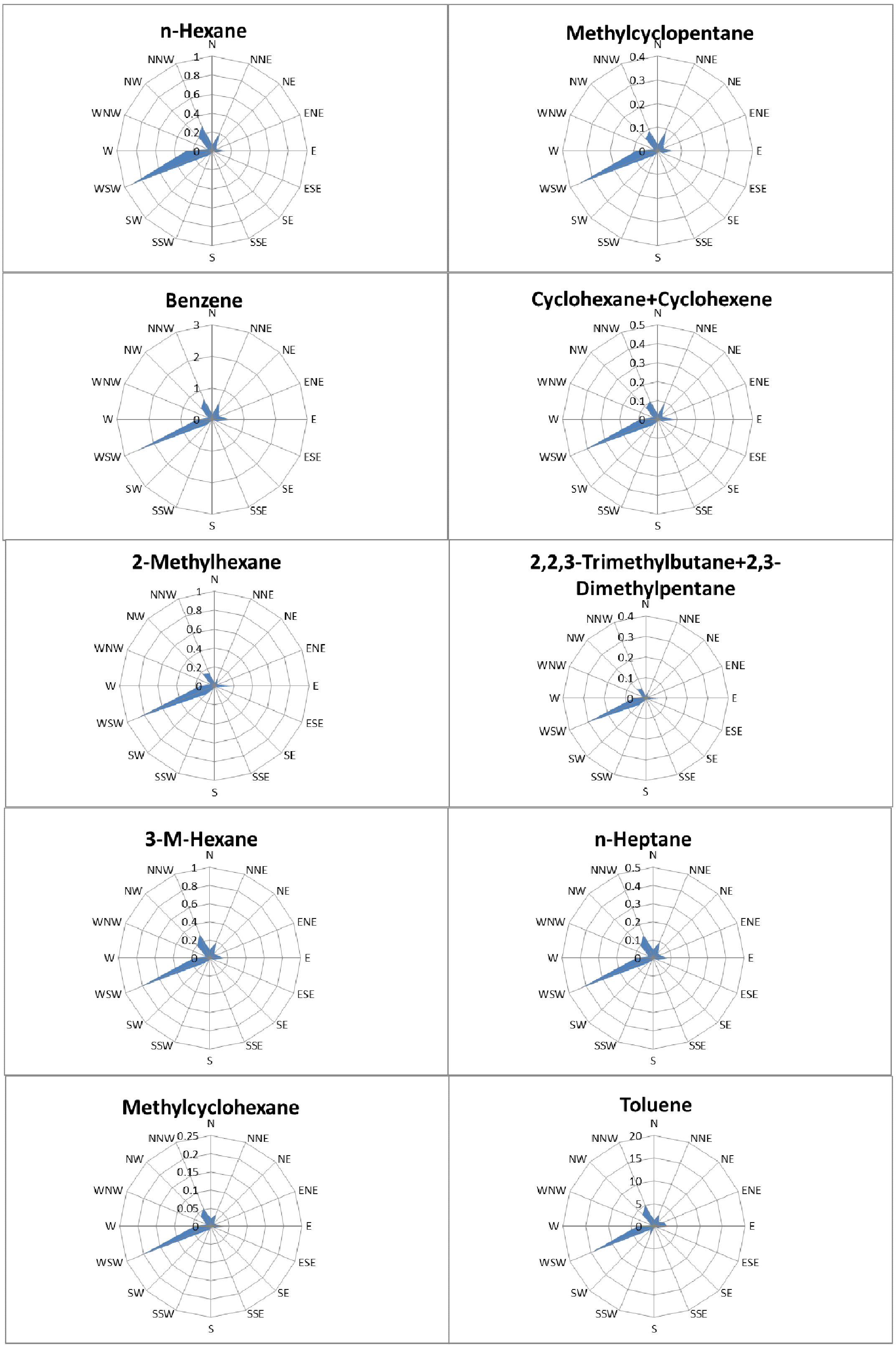


Figure A-2 (Continued)



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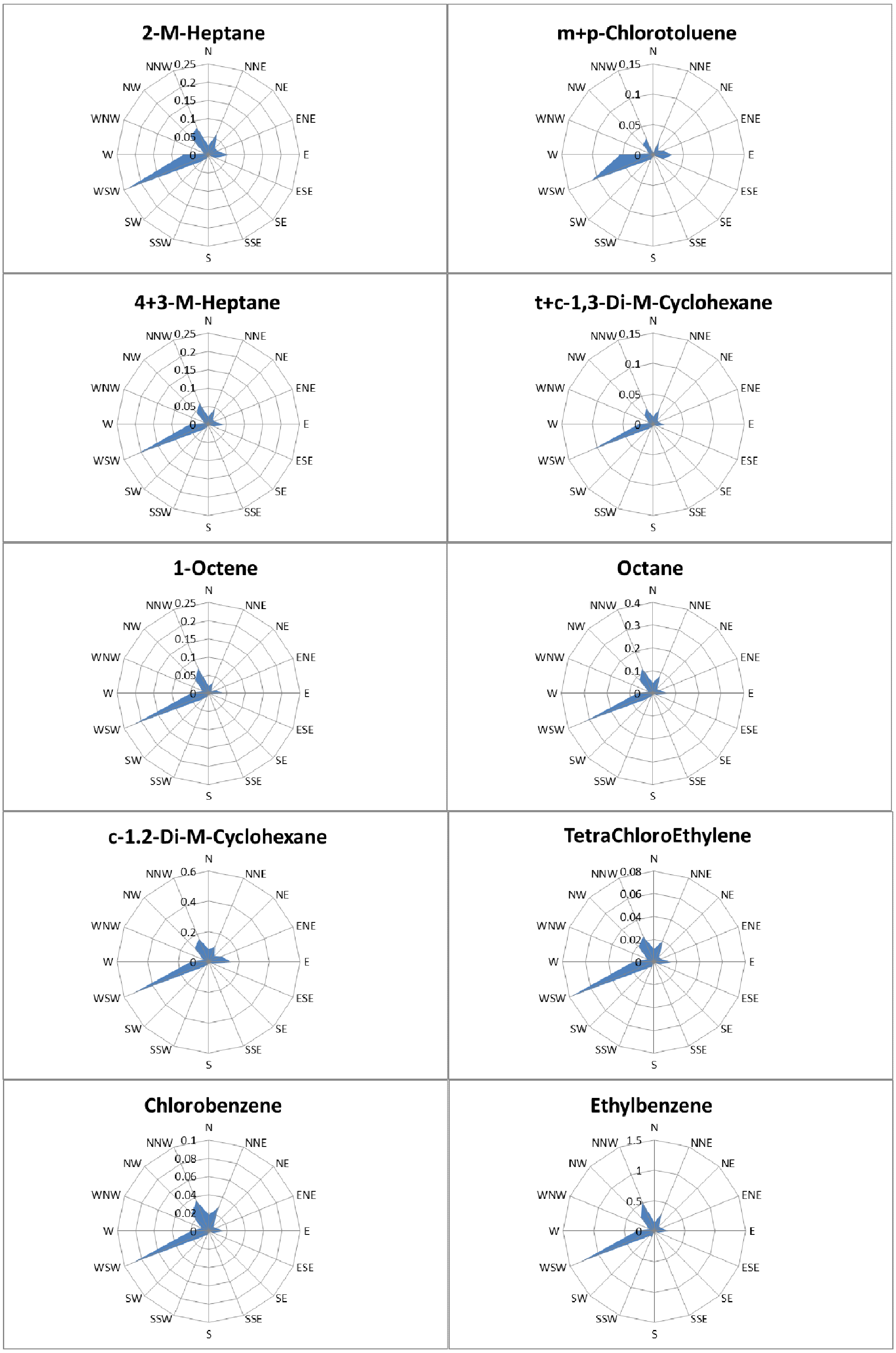
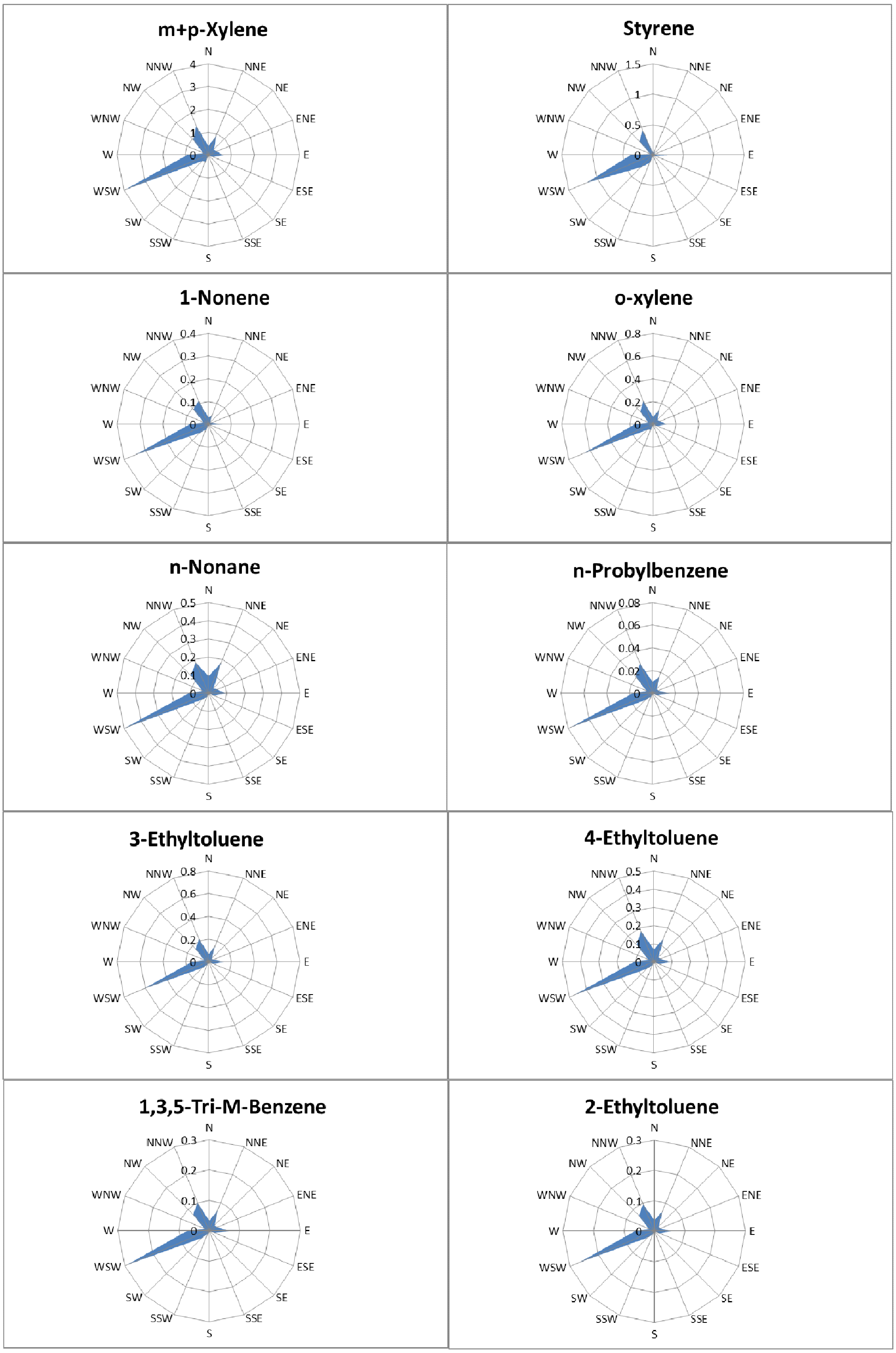


Figure A-2 (Continued)


m+p-Xylene

Styrene

1-Nonene

o-xylene

n-Nonane

n-Probylbenzene

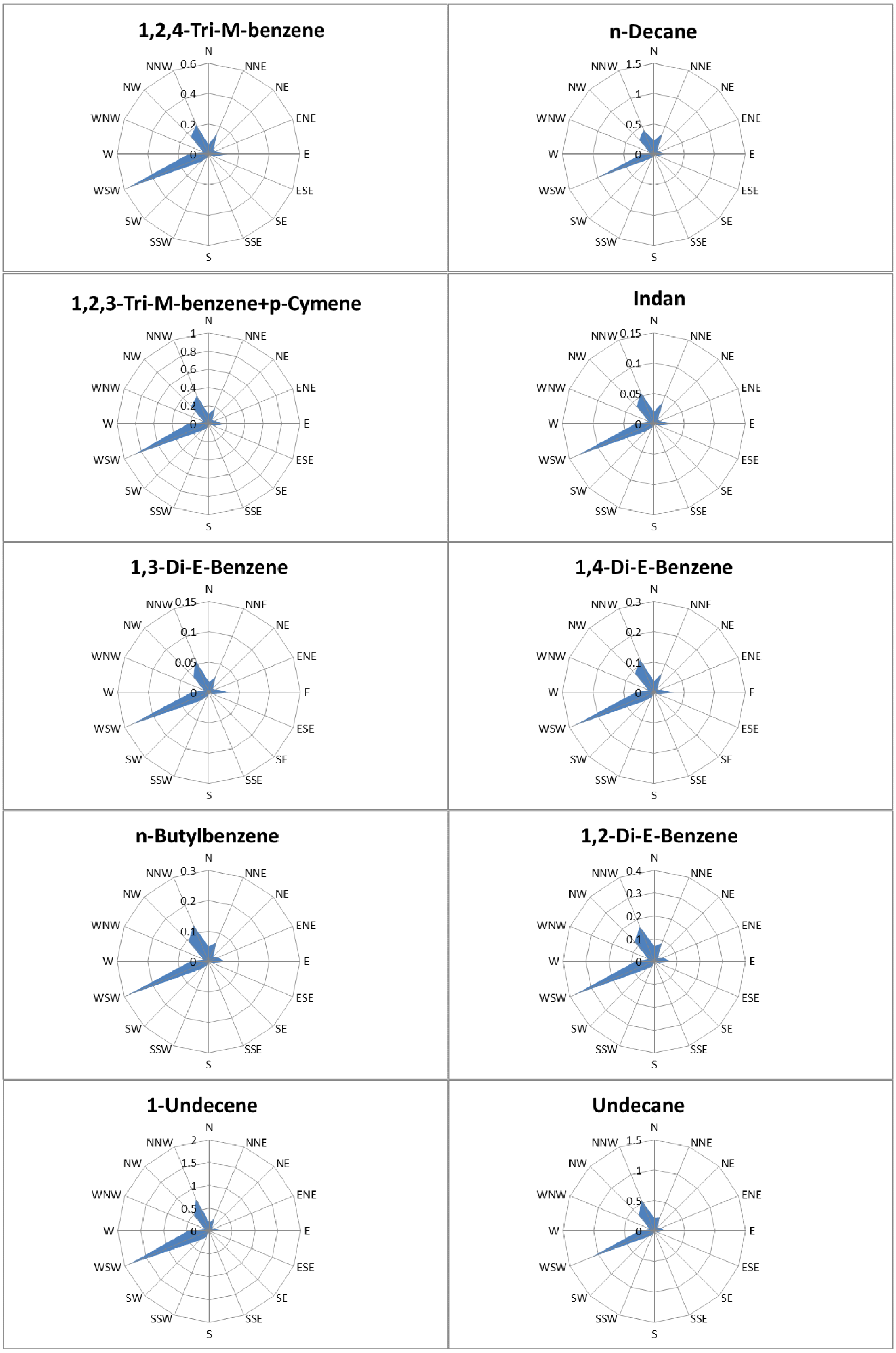
3-Ethyltoluene

4-Ethyltoluene

1,3,5-Tri-M-Benzene

2-Ethyltoluene

Figure A-2 (Continued)



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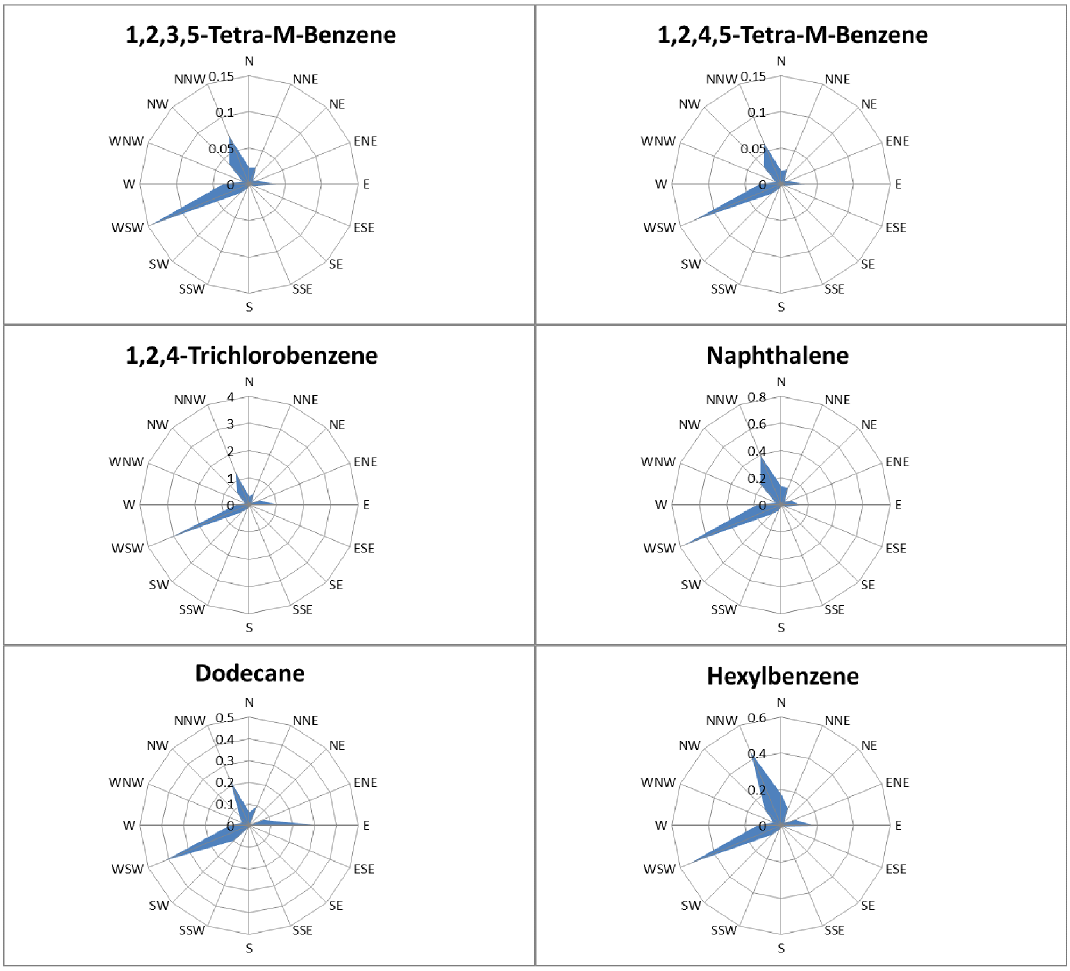

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