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Temporal variations of VOC concentrations in Bursa atmosphere



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ABSTRACT

The levels and sources of VOCs in the atmosphere of Bursa have been investigated by measuring C₂–C₁₂ VOCs which include alkanes, alkenes, alkynes, aromatics and halogenated hydrocarbons in two different campaigns. The first campaign was carried out between September 14 and November 6, 2005, and the second one between March 17 and May 10, 2006. The concentrations of 112 VOCs were detected in the collected samples. The median total concentrations of VOCs were 115 and 86 $\mu\text{g m}^{-3}$ for the first and second campaigns, respectively. Alkanes ($\bar{x} = 51.50 \mu\text{g m}^{-3}$) are the most abundant group in the Bursa airshed, which is followed by aromatics ($\bar{x} = 49.38 \mu\text{g m}^{-3}$), alkenes ($\bar{x} = 36.86 \mu\text{g m}^{-3}$) and halogenated compounds ($\bar{x} = 13.07 \mu\text{g m}^{-3}$). In the present study, the VOCs showed well defined diurnal, weekday/weekend and seasonal variations. Diurnal variation of most of the measured organic compounds followed traffic rush-hours. On the other hand, some VOCs such as 1-octene, 1-nonene, 1-undecene, n-nonane, n-decane, 1,2,3-trimethylbenzene, undecane and dodecane have displayed unusual profiles that do not follow the traffic pattern during the first campaign due to asphalting operations. Moreover, the average T/B ratio obtained in the first campaign was found to be significantly higher than the second one. This relatively high difference between T/B ratios is an indication of the availability of different sources rather than the traffic. Therefore, it can be suggested that there were additional VOC sources than traffic in Bursa city center.

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1. Introduction

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 (Saeaw and Thepanondh, 2015). In addition to their adverse effects on humans, VOCs have a profound influence on the formation of tropospheric ozone and other oxidants (Rappenglück et al., 1998; Rappenglück and Fabian, 1999a; Yassaa et al., 2011; Saeaw and Thepanondh, 2015; Sahu and Saxena, 2015). Solar radiation is a key element in the atmospheric

photochemistry of VOCs and NO_x because tropospheric ozone and PAN will be produced when NO_x and VOCs combine in the presence of sunlight (Rappenglück et al., 1998; Sahu and Saxena, 2015). The issues of decreasing tropospheric ozone concentrations and controlling VOCs concentrations are particularly important in air pollution management throughout the world (Iqbal et al., 2014). Towards this aim, the VOCs measurements in the ambient atmosphere are essential in cities with a high population and a dense vehicle fleet (Khoder, 2007).

The ambient levels of VOCs are affected from various factors such as meteorological conditions and availability of different sources in any urban or industrially impacted urban areas. For example, more rainy days in summertime lead to decrease the concentrations of organics compared to dry winter days (Lee et al., 2002). Higher hydroxyl (OH) concentrations in summer will be more effective for removal of VOCs by chemical reaction. Indeed, higher temperatures and more sunlight will speed most of the chemical reactions (Lee et al., 2002). Furthermore, higher NMHC concentrations are observed at higher altitudes as owing to low OH accessibility in higher altitudes (Sharma et al., 2000). Seasonal

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variations of atmospheric VOCs are also affected by other meteorological conditions, including wind direction, wind pattern, precipitation, boundary layer dynamics and transport and/or dilution from the surrounding region (Rappenglück and Fabian, 1999a; Cai et al., 2010; Park et al., 2013; Menchaca-Torre et al., 2015; Valach et al., 2015; Baudic et al., 2016). Calm conditions, shallow boundary layer, stagnant wind patterns and high atmospheric stability prevent the dilution of the organics and pollutants accumulate in the atmosphere (Rappenglück et al., 2000; Dumanoglu et al., 2014; Barletta et al., 2016; Baudic et al., 2016). Variability of sources also influences on the observed seasonal variation in atmosphere (Hoque et al., 2008; Kuntasal et al., 2013; Park et al., 2013; Valach et al., 2015; Singh et al., 2016). Seasonal variations of organic compounds, with a maximum in winter and minimum in summer, have been reported in many studies (Ho et al., 2004; Na et al., 2005; Kerbachi et al., 2006; Guo et al., 2007; Qin et al., 2007; Hoque et al., 2008; Chang et al., 2009; Russo et al., 2010; Stock et al., 2010; Kuntasal et al., 2013; Singh et al., 2016). On the contrary, different seasonal patterns have been also 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 because elevated temperature causes increased VOC concentrations due to increased vapor pressure of the both solvents and monomers in paints, adhesives, coatings, etc (Thad, 2000; Ho et al., 2004; Na et al., 2005; Elbir et al., 2007; Li and Wang, 2012; Dumanoglu et al., 2014).

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 (Cai et al., 2010; Zou et al., 2015). VOC concentrations also show variation through the day depend on the emissions, transport and dilution, and chemical removal (Rappenglück and Fabian, 1999a; Derwent et al., 2000; Leuchner and Rappenglück, 2010). 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; Valach et al., 2015). The two peaks are usually observed at 9:00 a.m. and between 15:00–20:00 p.m. during the morning and afternoon rush hours (Cai et al., 2010; Li and Wang, 2012; Olumayede and Okuo, 2012; Valach et al., 2015). 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 (Lai et al., 2004; Kelessis et al., 2006; Yurdakul et al., 2013). In addition to traffic 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.

Bursa is the fourth largest city of Turkey with a population of about 3 million. Bursa, covering an area of 10,819 km², 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 also 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 was about 400,000 in Bursa in 2006 however this number was increased to 800,000 in 2016 (TSI, 2016a). Therefore, between 2006 and 2016 there was nearly 100% of increase in the number of

vehicles registered to traffic in Bursa. Same situation is also true for the population because the population of Bursa reached to about 1.5 million in 2006 and according to the Turkish Statistical Institute reached to about 3 million in 2016 (TSI, 2016b). Although, both Bursa's population and the total number of road motor vehicles registered to the traffic in Bursa have been doubled in the last 10 years, there was no significant changes in the practices, used fuel quality/type and national regulations, etc. Accordingly, the concentration of VOCs in the Bursa atmosphere probably increased even more in the last decade.

The objective of this study is to determine the level of pollution in Bursa in terms of wide range of organic pollutants, ranging from C₂ to C₁₂, and to identify the factors and sources affecting temporal variations of the measured species. A significant contribution of the study is the investigation of extensive asphalt pavement activities in the city during the study, which allowed us to observe how asphalt paving modified the VOC composition of the atmosphere. The asphalt profile generated is included in the follow-up paper where source apportionment by a receptor modeling, PMF, will be discussed. Finally, the ozone formation potential of individual VOCs species was calculated to estimate effect of each species on the ozone level in urban atmosphere.

2. Material and methods

2.1. Sampling

Two sampling campaigns were performed during the study. The first campaign was carried out between September 14 and November 6, 2005, and the second one between March 17 and May 10, 2006. The numbers of hourly measurements in fall and spring campaigns were 841 and 856, respectively. The online GC-FID system was placed in a shelter which was 3 m far away from the surrounding buildings and trees (in the middle of the garden). Furthermore, system was 1.5 m high from the surface.

2.2. Site description

The measurements were performed at the back of Bursa Hygiene Center (40.19°N, 29.05°E), which is located approximately at the city center. The location of the Hygiene Center in Bursa is given in Fig. 1. Detailed figure which shows the three industrial zones, city center and sampling location is also given in Fig. S1. Altıparmak Boulevard with four lanes of two-way traffic is a major thoroughfare in the Bursa. The boulevard with heavy traffic is the nearest main avenue and located approximately 250 m to the north of the sampling point. Intercity roads that connect Bursa to Ankara and Yalova, which are the two highways with the heaviest traffic load in the city, are approximately 1 and 1.5 km away from the Hygiene Center, respectively. Other roads with heavy traffic are further away.

Bursa, which is located in the northwestern part of the country, is the fourth largest city in Turkey with its population of 2.5 million people. There are approximately 8000 small- and large-scale facilities producing textile. Cotton weaving, artificial and synthetic yarn production, woven fabric and home textile are the leading subsectors in the textile industry. The city accounts for >75% of the annual yarn production in Turkey. Bursa is also the center of automotive industry in the country, accounting for approximately 60% of the annual automotive production in Turkey.

There was an intense asphalt pavement activity in Altıparmak Boulevard and in Hasta Yurdu Road (about 50 m to the south of the sampling point) which connected with Altıparmak Boulevard between September 20 and October 25 during the first campaign. This provided an ideal opportunity to characterize an asphalt profile and

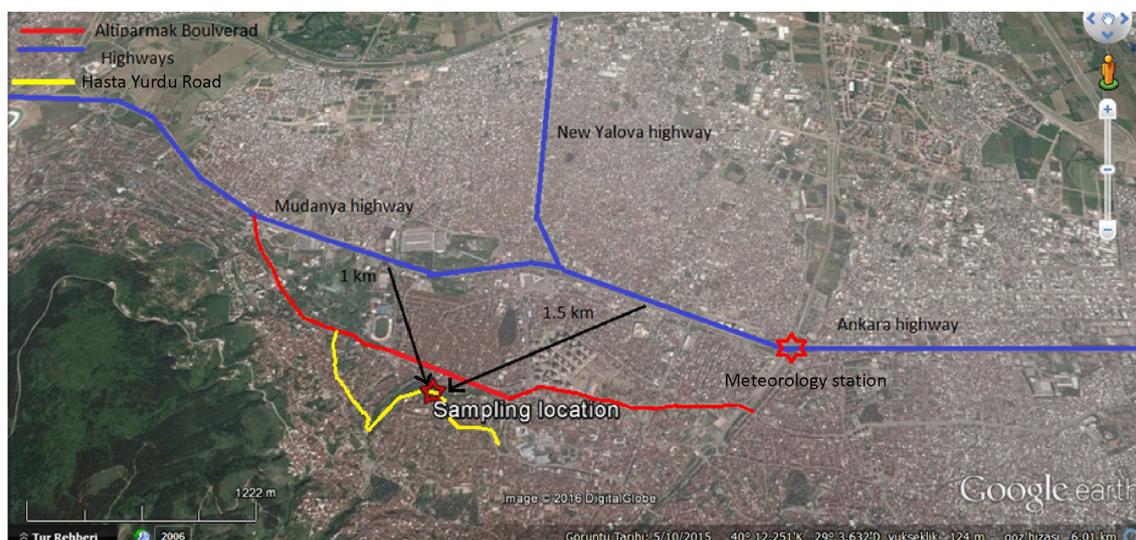


Fig. 1. Location of the sampling site.

to observe how the concentrations of asphalt markers varied in the days following the asphalt pavement. The effect of asphaltting operations on the measured VOCs concentrations will be discussed in the following sections.

2.3. Analysis

The VOCs were measured *in situ* and continuously using an online GC-FID system. The measurements were performed on an hourly basis and approximately 112 VOCs were measured. The target compounds are given in Tables S1 and S2. The online measurement system consisted of an Agilent Model 6890 gas chromatograph equipped with two flame ionization detectors (FID) coupled to a Unity model thermal desorption and a Markes Air Server sampling system. For each measurement, 450 mL of sample was pulled directly from the air over 45 min onto a multilayer sorbent packed (12 cm × 2 mm i.d.) “Ozone Precursor/Freons” trap at a 10 mL min⁻¹ 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 °C. After samples were collected on the trap, the trap was rapidly heated at rates approaching 100 °C/sec from -15 °C to 300 °C and samples were sent to the inlet of GC equipped with Deans switch device for analysis. Once the trap finished its 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/Al₂O₃, sodium sulfate-deactivated, 19091P-S15 model) alumina PLOT column excellent use with light hydrocarbons (C₁ to C₈) and two FID detectors. In the present study, light compounds (molecular weight smaller than 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. In the study, the GC oven program begins with initial temperature of 40 °C (10 min), followed by 10 °C min⁻¹ ramp rate to a final temperature of 195 °C and followed to hold 10 min at final temperature.

Nitrogen was used as a carrier gas for the GC system. Dry air and

hydrogen were used for the ignition 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.

2.4. QA/QC

For the optimization of the thermal desorption system, different parameters were examined based on the recommended operational values by the producer. Accordingly, 300 °C was used as a desorption temperature.

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 in the literature. In the study, the lowest temperature (-15 °C) which gives the highest compound recovery was selected as a desorption temperature. In addition to the effect of temperature, desorption time of the cold trap was also investigated for the selected target compounds. 1 min was found to be insufficient for the recovery of the compounds on the cold trap; after 3 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. 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 was calibrated using a calibration gas mixture with 148 VOCs, which was obtained from Environment and Climate Change Canada, Analysis and Air Quality Division (AAQD). This gas mixture included VOCs with carbon numbers between 2 and 12. A 6-point calibration curve was prepared before each campaign. Mid-point calibrations were also performed once every two days to check the calibration and the deviations of the compounds were detected lower than 20% therefore the previous full calibrations were used for the calculation of VOCs. Due to the Unity Thermal Desorption system being directly connected with GC-FID system, gas standards could be directly analyzed and very high Pearson correlation

coefficients (99.999) between mass of each compound and their area response were obtained for each compound during the calibration process.

The precision of the system was determined by five replicate measurements of the calibration gas. The Relative Standard Deviation values were lower than 15% for most of the VOCs. The detection limits of individual VOCs varied between $0.021 \mu\text{g m}^{-3}$ for n-propylbenzene and $0.29 \mu\text{g m}^{-3}$ for dodecane. Other optimized operational properties of the unity and the GC-FID system was presented elsewhere (Yurdakul et al., 2013).

2.5. Meteorology of the study area

In the study, meteorological variables were taken from station of the municipality located about 2 km away North East of the sampling location. Long-term wind speed and direction measured at the same station between 1975 and 2005 were obtained to examine how typical the wind pattern measured during our study was for the region. It is clear that the variation of wind speed and direction measured during the sampling period were very similar with the long-term data obtained from the Bursa meteorological station.

Winds were rather slow during both measurement campaigns. The average wind speed for the first and second campaigns was 1.3 and 1.8 m/s, respectively. These were lower than the annual average wind speed for the city, which is 3 m s^{-1} (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 recorded. The total precipitation was 68 mm and 25 mm for first and second campaigns, respectively. The average temperatures were $15.8 \pm 5^\circ\text{C}$ and $13.5 \pm 5.2^\circ\text{C}$ for the first and second campaigns, respectively. Although, average temperatures were similar in September and May, the highest temperatures (30°C) were recorded in September. On the other hand, the lowest temperatures were observed in March (-0.9°C).

Wind roses for Bursa are given in Fig. 2 for both sampling campaigns. Although the prevailing wind direction was ENE, WSW and ESE winds were also relatively frequent during the first campaign. On the other hand, winds from WSW were dominant during the second campaign.

The average mixing heights, which were calculated using the

meteorological pre-processor PCRAMMET (USEPA), were $816 \pm 393 \text{ m}$ and $769 \pm 480 \text{ m}$ for the first and second campaigns, respectively. After the sunrise, the mixing height increased rapidly and reached its maximum depth of 900 m and 1000 m by the mid-afternoon of both sampling campaigns. After the sunset, the depth of the mixing height was $<820 \text{ m}$ during the first and $<600 \text{ m}$ during the second campaigns.

3. Results and discussion

3.1. Descriptive statistics

The mean, median, minimum and maximum levels of the 30 most abundant VOCs for each sub-groups (alkanes, alkenes, etc.) measured during each sampling period are given in Table 1. These VOCs formed basis for most of the discussions in the manuscript, due to regularly detected in more than 90% of hourly measurement data ($n > 700$). During the study, 112 VOCs were detected with different frequencies. Seventy of these VOCs were detected with a frequency of $>70\%$, 60 VOCs were detected with a frequency of $>90\%$ and 80 VOCs were detected with a frequency of $>50\%$. Ten of the VOCs were detected in only one or two samples and was not included in the statistical treatment of data.

The median total concentrations of VOCs ($\sum_{112}\text{VOCs}$) were 115 and $86 \mu\text{g m}^{-3}$ for the first and second campaigns, respectively. Higher $\sum_{112}\text{VOCs}$ concentration in the first campaign was likely due to affecting from emission of asphalted operations, which will be discussed later in the manuscript. Higher concentrations of solvent-originated compounds (i.e., toluene, m,p-xylene, 1,2,4-trichlorobenzene and styrene) were recorded during the first campaign due to slightly higher temperatures. However, traffic-originated VOCs, such as benzene, acetylene and 1,3-butadiene, were higher in the second campaign than in the first one. This pattern indicates that the VOC concentration in the atmosphere of Bursa is determined by a combined influence of the emission strength and meteorology.

Toluene was the most abundant single compound with a median concentration varying from 16.3 to $13.3 \mu\text{g m}^{-3}$ for the first and second campaigns, respectively. High toluene concentrations have been frequently observed in urban studies (Bauri et al., 2015;

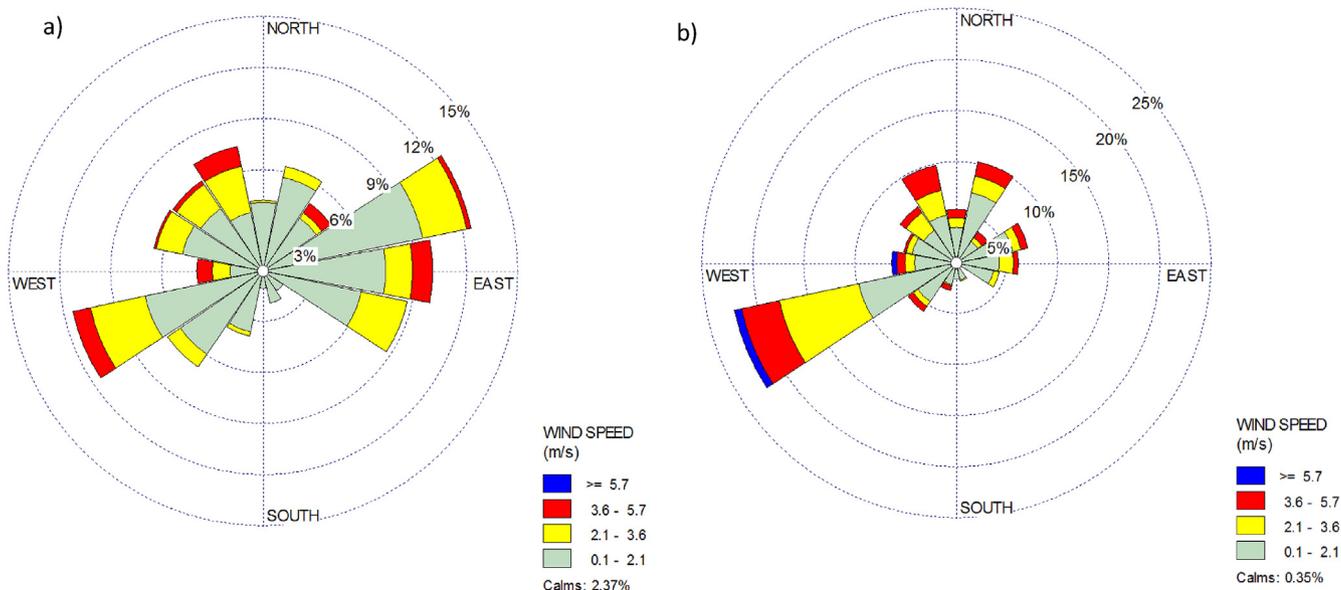


Fig. 2. Wind roses a) for the first and b) second campaigns.

Table 1
Descriptive statistics of the selected data ($\mu\text{g m}^{-3}$).

Compound name	1st Campaign			2nd Campaign		
	Mean \pm SD	Med.	Range	Mean \pm SD	Med.	Range
Ethylene	8.96 \pm 9.19	6.17	0.21–58.90	16.5 \pm 14.0	11.9	1.40–92.90
Propane	3.71 \pm 4.42	2.11	0.14–33.00	2.56 \pm 2.94	1.48	0.14–20.97
Acetylene	3.96 \pm 5.11	2.09	0.14–35.80	4.54 \pm 4.60	3.02	0.13–33.60
Cyclopentane	2.23 \pm 2.36	1.48	0.07–20.70	1.96 \pm 1.56	1.46	0.17–11.80
2-Methylpentane	1.59 \pm 2.00	0.92	0.03–21.90	1.45 \pm 1.28	1.06	0.11–3.08
n-Hexane	3.20 \pm 2.43	2.73	0.31–14.00	1.13 \pm 0.99	0.82	0.12–12.90
Benzene	3.68 \pm 5.27	1.52	0.12–40.10	4.03 \pm 3.78	2.79	0.32–28.86
Toluene	27.90 \pm 48.70	16.3	2.10–949	19.2 \pm 21.90	13.34	2.35–399
m,p-Chlorotoluene	1.12 \pm 1.06	0.78	0.13–7.20	0.38 \pm 0.25	0.31	0.08–2.01
Ethylbenzene	2.39 \pm 3.97	1.57	0.15–79.00	1.73 \pm 1.30	1.35	0.24–17.25
m,p-Xylene	6.38 \pm 11.80	3.89	0.13–226	5.07 \pm 3.88	3.94	0.80–60.33
Styrene	2.94 \pm 2.08	2.90	0.18–13.20	1.43 \pm 2.29	0.54	0.10–23.62
1-Nonene	0.97 \pm 1.17	0.50	0.08–7.20	0.36 \pm 0.29	0.24	0.04–1.77
o-Xylene	1.09 \pm 1.40	0.68	0.05–24.30	0.87 \pm 0.62	0.68	0.17–8.67
3-Ethyltoluene	1.37 \pm 1.18	0.95	0.25–8.15	0.88 \pm 0.58	0.69	0.02–4.21
4-Ethyltoluene	0.81 \pm 0.79	0.54	0.09–4.73	0.64 \pm 0.38	0.52	0.15–2.92
1,2,4-Trimethylbenzene	1.03 \pm 1.10	0.70	0.07–6.80	0.82 \pm 0.52	0.65	0.16–3.57
n-Decane	1.27 \pm 10.00	1.01	0.17–7.80	1.21 \pm 0.72	1.01	0.34–6.41
Dodecane	4.23 \pm 4.99	2.71	0.17–27.10	1.28 \pm 2.27	0.34	0.09–18.32
Hexylbenzene	1.81 \pm 1.60	1.39	0.17–10.20	0.85 \pm 2.85	0.35	0.06–29.68
Percent contributions of the organic groups to ΣVOC concentrations (%)						
Alkanes		31.45			37.36	
Alkenes		22.05			23.22	
Alkynes		1.82			3.40	
Aromatics		31.48			34.25	
Halogenated compounds		13.16			1.77	

Sahu and Saxena, 2015). In this study, benzene concentrations of 1.52 and 2.79 $\mu\text{g m}^{-3}$ were measured for the first and the second campaigns, respectively. Annual average benzene standard in the EU directive (Air Quality Directive, 2008/50/EC) and the Turkish Air Quality Regulation (Air Quality Assessment and Management Directive, June 6, 2008) is 5 $\mu\text{g m}^{-3}$. Therefore, the mean benzene concentrations were lower than the standard in both campaigns.

The separately investigation of alkanes, alkenes, alkynes, aromatics and halogenated compounds which are sub groups of VOCs can be informative, because each class has different oxidation pathways, rates, products and different contributions to ozone and aerosol production (Cai et al., 2010). The fractional contribution of five VOC groups to $\Sigma_{112}\text{VOCs}$ concentrations in both campaigns are presented in Table 1. The contributions of VOC groups to $\Sigma_{112}\text{VOCs}$ concentrations were fairly similar in the first and second campaigns, except for the halogenated VOCs. The percent contribution of halogenated compounds to $\Sigma_{112}\text{VOCs}$ concentration was a factor of seven higher in the first campaign, compared to the corresponding concentrations measured in the second campaign. This was due to an episodic increase in the concentrations of 1,2,4-trichlorobenzene (TCB) during the asphalt pavement operations (Santagata et al., 2012). The average TCB concentration outside the asphaltting period was approximately 13 $\mu\text{g m}^{-3}$, but its hourly concentration during the asphaltting activities increased up to the level of 178 $\mu\text{g m}^{-3}$ (the average concentration during the asphaltting period was 89 $\mu\text{g m}^{-3}$). Since there were only three halogenated VOCs measured in this study, dramatic increases in the concentrations of one of them resulted in a significantly higher average of the halogenated VOC concentration in the first campaign.

Alkanes ($x^- = 51.50 \mu\text{g m}^{-3}$) are the most abundant group in the Bursa atmosphere, which is followed by aromatics ($x^- = 49.38 \mu\text{g m}^{-3}$), alkenes ($x^- = 36.86 \mu\text{g m}^{-3}$) and halogenated compounds ($x^- = 13.07 \mu\text{g m}^{-3}$). A higher concentration of alkanes in both campaigns is at least partly due to their slower oxidation rate relative to other VOC groups (Fanizza et al., 2014). Alkanes

(34%), alkenes (23%) and aromatics (33%) have comparable contributions to $\Sigma_{112}\text{VOCs}$ concentration. These contributions are fairly similar to their contributions to ΣVOCs emissions from non-converter-equipped cars (39.1% for alkanes, 21.8% for alkenes and 35.3% for aromatics (Kuntasal, 2005)).

As can be seen from Table 2, average concentrations of the VOCs included in the table cover wide ranges. This is expected because VOC concentrations measured in any cities depends on a variety of factors, including differences in weather conditions, the major source types (i.e. vehicle emissions, fuel type and industrial sources), a typical traffic conditions, quality of the gasoline, percentage of catalyst-equipped cars, location of the sampling point (i.e. urban/suburban or rural area), duration of the sampling, and the economic development level of the cities (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 Table 2, 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 asphaltting operations were performed during the first campaign, higher non-methane total volatile organic compounds (NMTVOC) concentrations were recorded in the present study. Since the traffic emissions were moved away from the sampling point due to changing of traffic route as a result of asphaltting activities, VOCs emitted from gasoline exhaust were measured low level at our station. Therefore, the reasons for such a difference in measured concentrations of

Table 2
Comparison of the measured concentrations of the selected VOCs with literature (mean concentrations, $\mu\text{g m}^{-3}$).

Compound	This study		Ankara Turkey ^a	İzmir Turkey ^b W/S	Bursa Turkey ^c W/S	Canada ^d	Hong Kong China ^e W/S	Hyogo Japan ^f	Pathumwan Thailand ^g	Kolkata, India ^h	Rio de Janeiro Brazil ⁱ	Mexico city Mexico ^j	London UK ^k	Paris France ^k	Berlin Germany ^k	Pamplona Spain ^k
	1 st	2 nd														
n-Pentane	0.87	0.90			0.97/0.34	3.0–21.2		1.3–3.2			ND-15.1					
1,3-Butadiene	0.74	0.51			0.39/0.16	0.19–0.36		0.06–0.15								
2-Methylpentane	1.59	1.46	1.76–3.72			2.42–6.75					0.8–7.8					
3-Methylpentane	0.83	0.79				1.48–3.78					<DL-1.6					
n-Hexane	3.20	1.13	3.62–11.9		0.66/0.46	1.55–6.32		2.3–8.8			2.8–6.0					
Benzene	3.68	4.03	7.32–21	10.4/3.31	8.21/2.26	2.03	5.01/2.97	1.3–2.0	26.5–72.4	24.9–79.2	1.5–6.6	32.03	2.7	4.0	6.9	2.84
Heptane	0.69	0.56			0.85/0.61	0.86–2.30		0.98–2.2			<DL-3.1					
Cyclohexane	0.45	0.26			0.33/0.16	0.53–2.54		0.71–1.7			ND-1.9					
Toluene	27.86	19.15	7.05–23.9	13.5/15.4	23.41/25.2	4.54–5.38	26.4/26.2	8.7–18	28.7–122.2	27.6–103	10.8–16	34.4	7.2	15.0	13.8	13.26
Octane	0.56	0.40	0.53–1.14	0.04/0.07	0.65/0.32	0.37–0.91		0.34–1.5								
Ethylbenzene	2.39	1.73	1.36–4.21	1.60/3.65	3.37/3.77	0.91–1.4	2.61/3.18	2.9–8.1	2.05–5.93	4.5–36.2	2.4–11.2	16.12	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	3.2–6.4		11.2–35.9	6.3–11.2	14	3.7	7.0	7.5	3.38
o-Xylene	1.09	0.87	1.49–5.75		1.52/1.33	1.15–1.70	2.03/3.06	1.2–2.6		8.1–14.7	5–8.2		1.5	4.0	2.9	2.63
1,2,4-tri-M-benzene	1.03	0.82	1.67–4.25	0.43/0.8	3.21/0.57	1–1.62	2.15/2.59	2–3			7.2–8.4					

1st: 1st campaign.

2nd: 2nd campaign.

W: winter; S: summer; ND: Not Detected; DL: Detection Limit.

^a Kuntasal, 2005 (four sites, urban).

^b Elbir et al., 2007 (suburban and urban).

^c Civan, 2010 (urban).

^d Ayers, 2002 (three sites, urban).

^e Ho et al., 2004 (urban).

^f Okada et al., 2012 (eight sites, urban and industrial).

^g Tunsaringkarn et al., 2015 (urban and roadside).

^h Dutta et al., 2009; (3 sites, urban).

ⁱ Martins et al., 2010 (at three different times, residential and commercial urban).

^j Ceron-Breton et al., 2013 (urban).

^k Parra et al., 2009 (urban).

organics in Bursa atmosphere may be explained by differences in sampling methodology, source strength and meteorology.

The concentrations of VOCs measured in this study show a general agreement with the concentrations reported for European, North American (Parra et al., 2009; Zabiegala et al., 2010; Fanizza et al., 2014; Franco et al., 2015) and other Turkish (Elbir et al., 2007; Yurdakul et al., 2013) cities. However, the VOC levels measured in this study is significantly lower than those VOCs concentrations reported for cities in South America and Asia. VOCs in urban areas are not only impacted by traffic. 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 Bursa traffic (Kuntasal et al., 2013). Similar VOC concentrations in Bursa with those cities probably indicate uncontrolled emissions in Bursa.

3.2. Effect of meteorology on the measured VOCs concentrations

High temperatures and high solar flux promote the photochemical removal of VOCs and thus facilitate faster removal from the atmosphere (Ho et al., 2004; Parra et al., 2009). 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. VOCs can be divided into three groups based on their dependence on temperature. Most of the measured VOCs in this study depicted a statistically significant ($p < 0.05$, r ranges from -0.17 to -0.39) decrease with increasing temperatures. Concentration of benzene 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.

On the contrary, hexane ($r = 0.32$), 2,2,3-trimethylbutane ($r = 0.14$), m,p-chlorotoluene ($r = 0.13$), 1,2,4-trichlorobenzene ($r = 0.13$), 1,2-diethylbenzene ($r = 0.35$), undecane ($r = 0.52$) and n-decane ($r = 0.34$) were found to be positively correlated with temperature ($p < 0.05$). 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 such as painting, heating etc. (Baudic et al., 2016; Wang et al., 2014). Therefore, these compounds may have been released from evaporative sources which were closely located to the sampling location.

In the third group, namely; 3-m-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 ($p > 0.05$, r ranges from -0.006 to -0.070) relationship with temperature. 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 group.

An inverse relationship ($p < 0.05$) was detected between wind speed and nearly all of the measured VOC concentrations 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

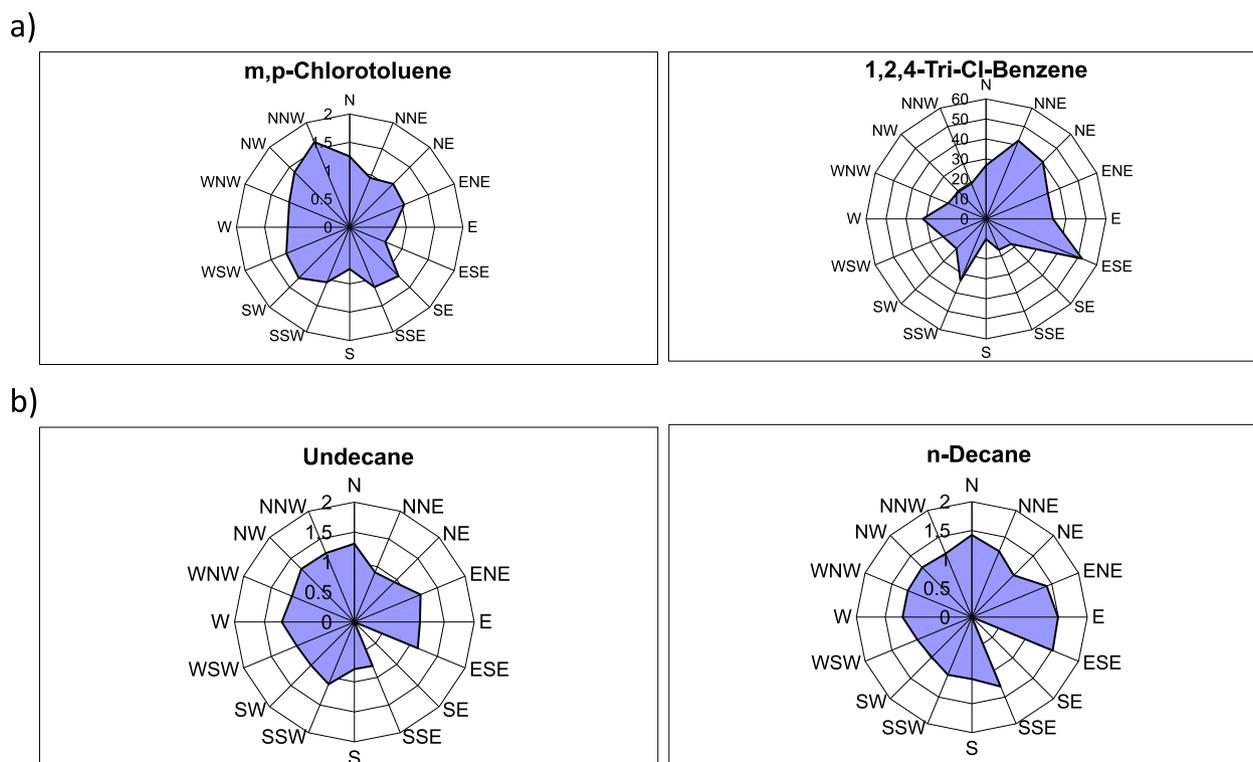


Fig. 3. Pollution roses for a) the first campaign and b) the second campaign ($\mu\text{g m}^{-3}$).

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.

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 (Jia and Batterman, 2010; Fanizza et al., 2014). Relative contributions of meteorology and photochemistry on the apparent dependence of concentration on temperature are difficult to assess. With few exceptions concentrations of VOCs decreased with increasing mixing height with a 95% or better statistical significance in the study. 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. Therefore, we probably could not detect the effect of mixing height

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. This interpretation was also verified by prepared pollution roses of the target compounds (Fig. 3) and screening for various wind speeds. ENE and WSW sectors were the prevailing wind directions during the first campaign however higher concentrations at the ESE sector for 1,2,4-trichlorobenzene and NNW for the m,p-chlorotoluene indicated sources other than traffic since northerly and northeasterly winds were responsible for the urban plume for Bursa. Though WSW sector was the prevailing wind direction in the second campaign, higher concentrations were observed at other sectors for undecane and n-decane. Furthermore, wind directional frequencies were also indicate that the calms conditions had a great contribution on the measured concentrations of these target compounds at the sampling station for both sampling campaigns.

3.3. Temporal variations of VOC concentrations

Hourly and monthly average concentrations of measured $\sum_{112}\text{VOCs}$ are given in Fig. 4. A gradual increase towards autumn and a subsequent decrease toward spring is obvious in both figures. Such a dependence of measured VOC concentrations on local meteorology is frequently reported in the literature (for example Tiwari et al., 2010; Menchaca-Torre et al., 2015; Schafer et al., 2016).

The assimilative capacity of the atmosphere was the lowest in

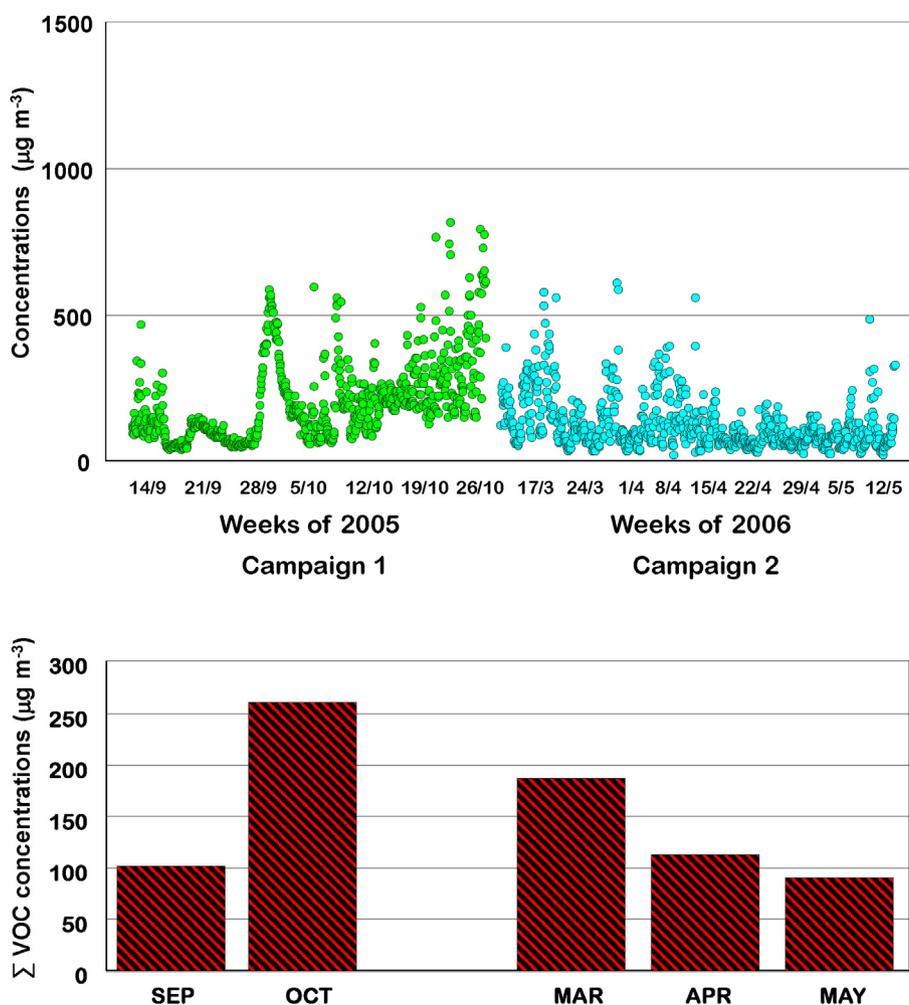


Fig. 4. Hourly and monthly variation of $\sum_{112}\text{VOC}$ concentrations in both campaigns.

March, as discussed in the text. However, the highest $\sum_{112}\text{VOCs}$ concentrations were observed not in March, but in October. This is due to the unusual $\sum_{112}\text{VOCs}$ peak that appeared in the early October and the significantly increased concentrations of most VOCs. The peak was owing to asphalt pavement activities around the station. The contribution of asphalt activities on VOC levels at the station will be discussed later in the manuscript.

Campaign 2 – to – Campaign 1 concentration ratios of the selected VOCs are given in Fig. 5. Most of the VOCs (83 of 107 VOCs) included in the figure had higher concentrations in Campaign 1. 21 VOCs had comparable concentrations in both campaigns. Well-defined gasoline exhaust markers, like benzene or acetylene, were included in this group. Only three VOCs had higher concentrations in campaign 2. A higher concentration of most VOCs in campaign 1 is at least partly due to the emissions from hot asphalt paved between September 20 and October 25.

The diurnal variations of $\sum\text{VOC}$ concentrations are given in Fig. 6 for both campaigns. High concentrations were observed at midnight (1:00–3:00), morning (8:00–11:00) and evening (19:00–21:00) hours in both campaigns. The high concentration at morning and evening hours is a typical traffic pattern reported frequently in the literature (Fares et al., 2013; Li et al., 2014; Patokoski et al., 2014; Liu et al., 2016). Whereas the slower removal mechanisms at night, which contribute to a longer residence time, lower boundary layer, lower wind velocity and slower dilution/dispersion processes occurring, may effect on the observed high level at midnight (Menchaca-Torre et al., 2015; Baudic et al., 2016). The relations between VOC concentrations and both the expected emission patterns and meteorology imply that although the diurnal pattern in VOC concentrations is determined by diurnal variations in their emission strength, the pattern is modified by both the local meteorology and photochemical activity.

The total VOC concentrations depict a clear traffic pattern, because light and heavy duty traffic is a source for most, if not all, of the VOCs. However, this does not mean that all the VOCs display the same diurnal pattern. VOCs that have significant non-traffic sources, like naphthalene and styrene, depicted different patterns. Industrial emissions are accepted as a major source of the styrene in urban atmosphere (Guo et al., 2004). Industry, open burning, tail-pipe emissions, and cigarettes are the main sources of the naphthalene in the atmosphere (Jia and Batterman, 2010).

Most of the VOCs have fairly similar diurnal variations in both campaigns, suggesting that their sources were similar in both

campaigns. However, there were few VOCs, including 1-octene, 1-nonene, 1-undecene, n-nonane, n-decane, 1,2,3-trimethylbenzene, undecane and dodecane, which showed different diurnal patterns in campaigns 1 and 2. These compounds depicted a bimodal traffic pattern during the second campaign. However, their concentrations were higher throughout the day in the first campaign. This is attributed to the asphalt operations in the proximity of our station during campaign 1, but not during the second one. The non-traffic pattern observed in the concentrations of these heavy hydrocarbons is due to their emissions from hot asphalt paved during day time.

The diurnal variation of the alkane, alkene, aromatic and halogenated VOC concentrations for the first and second campaigns are given in Fig. 7. The concentrations of all VOCs sub groups, except for halogenated VOCs, depicted a well-defined traffic pattern in both campaigns. This is because traffic is an important source of VOCs with the highest concentrations in each group and also traffic emissions contribute to the measured concentrations of VOCs, like toluene, xylenes, trimethylbenzene, dimethylbutane, and isopentane, emitted from non-traffic sources such as solvent use, dry cleaning, and painting. The halogenated VOCs did show a traffic pattern in campaign 2, but they did not show any significant diurnal variation in campaign 1 due to the strong influence of asphalt emissions on trichlorobenzene concentrations as discussed previously in the manuscript.

3.4. Weekday vs. weekend variation

Weekday-to-weekend (WD/WE) concentration ratios of the measured VOCs in both campaigns are given in Fig. 8. Most of the VOCs showed statistically significant differences between their weekday and weekend average concentrations at a 95% confidence level ($p < 0.05$). From 2,3-dimethylbutane to indane in the figure, the WD/WE ratios of VOCs are >1.0 in both campaigns. Higher concentrations of these 34 VOCs in weekdays are due to more vigorous traffic activity in weekdays and faster destruction of VOCs on weekends compared to weekdays (Warneke et al., 2013).

However, the figure is more complicated for the remaining VOCs. For all of these 25 VOCs, the WD/WE ratio is <1.0 in the first campaign, but their WD/WE ratio, with few exceptions, is >1.0 in the second campaign. Probably emitting these VOCs from different sources is the main reason of this difference during the sampling campaigns. For example, most of these compounds, such as octane,

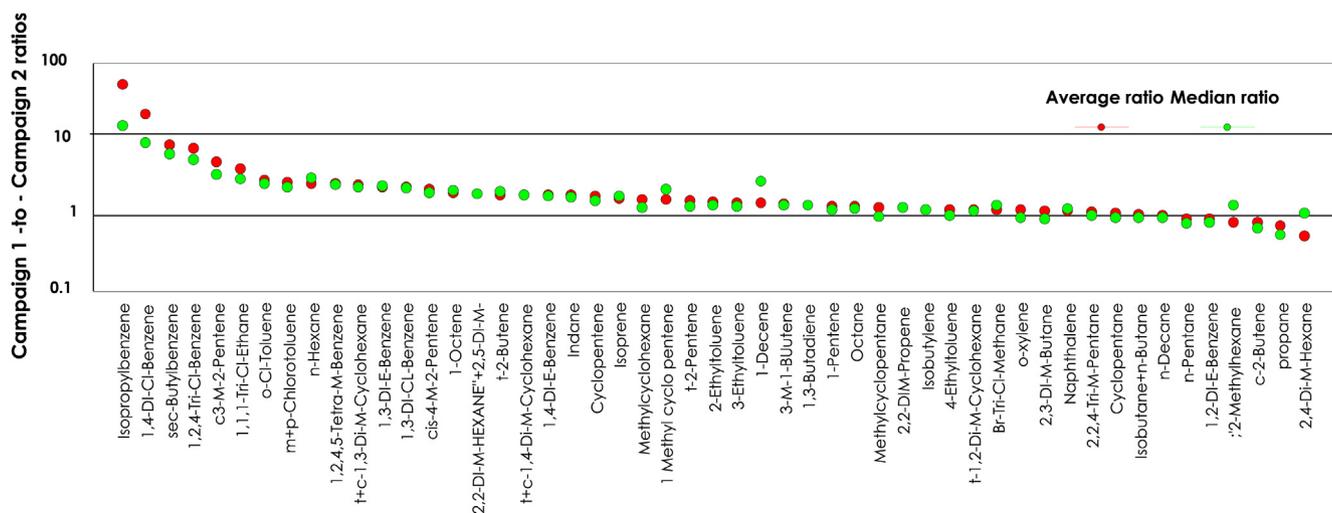


Fig. 5. Campaign 1-to-campaign 2 concentration ratios of selected VOCs.

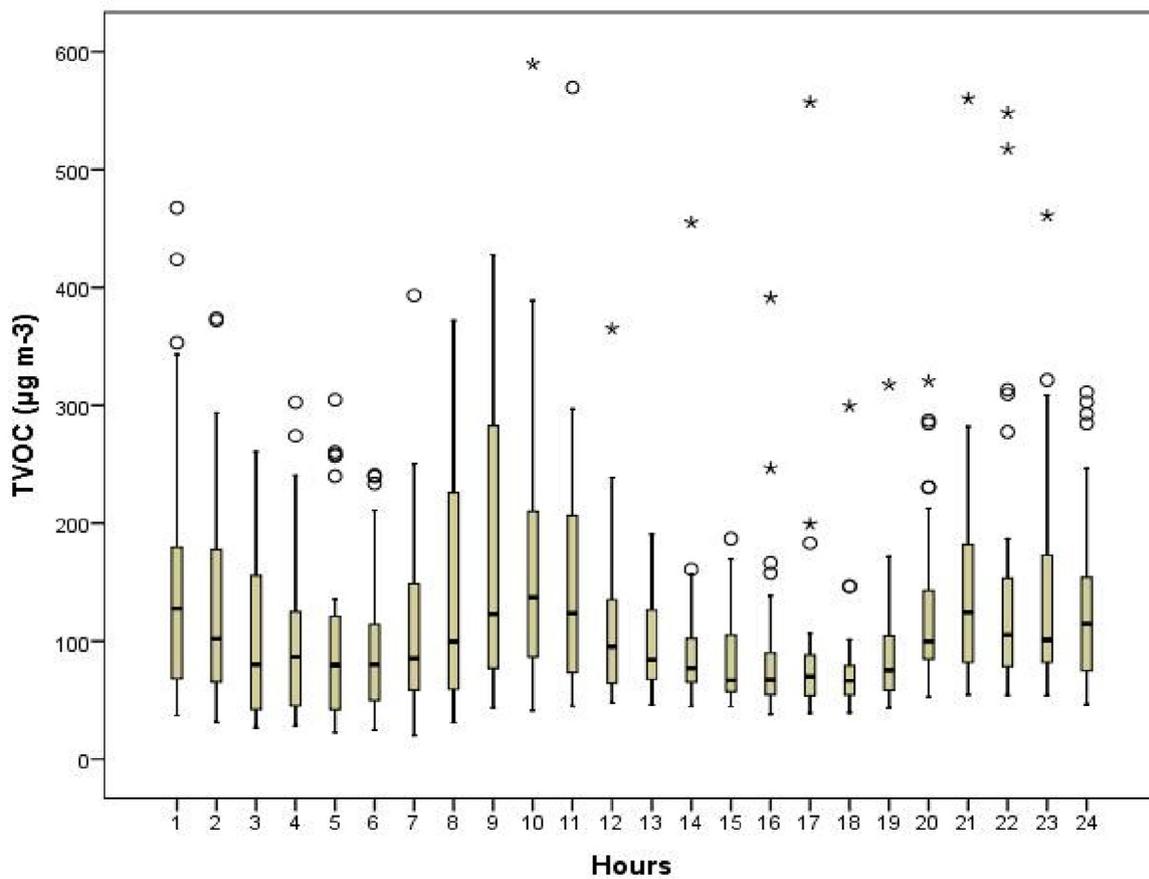
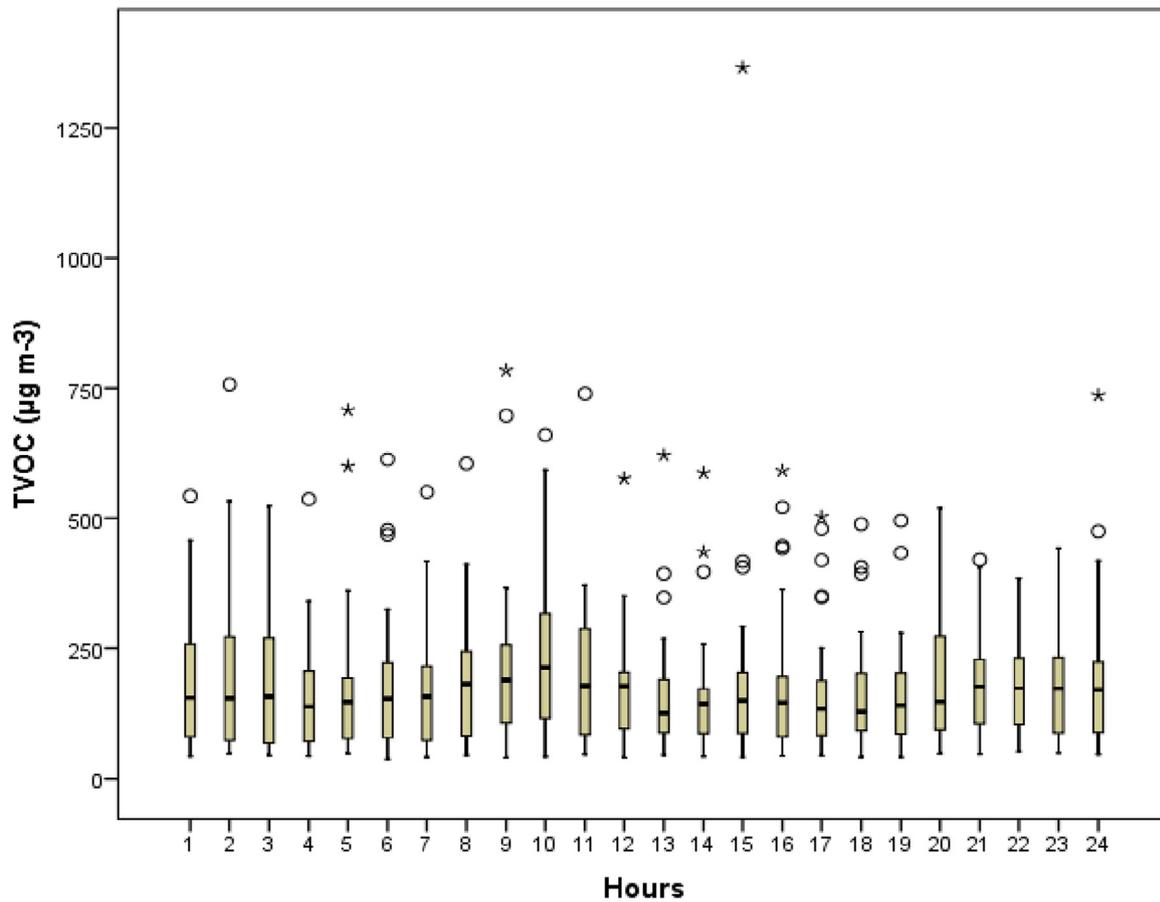


Fig. 6. Diurnal variation of the Σ VOC concentrations in the first and second campaign (Extreme values and outliers marked with star and round dot, respectively).

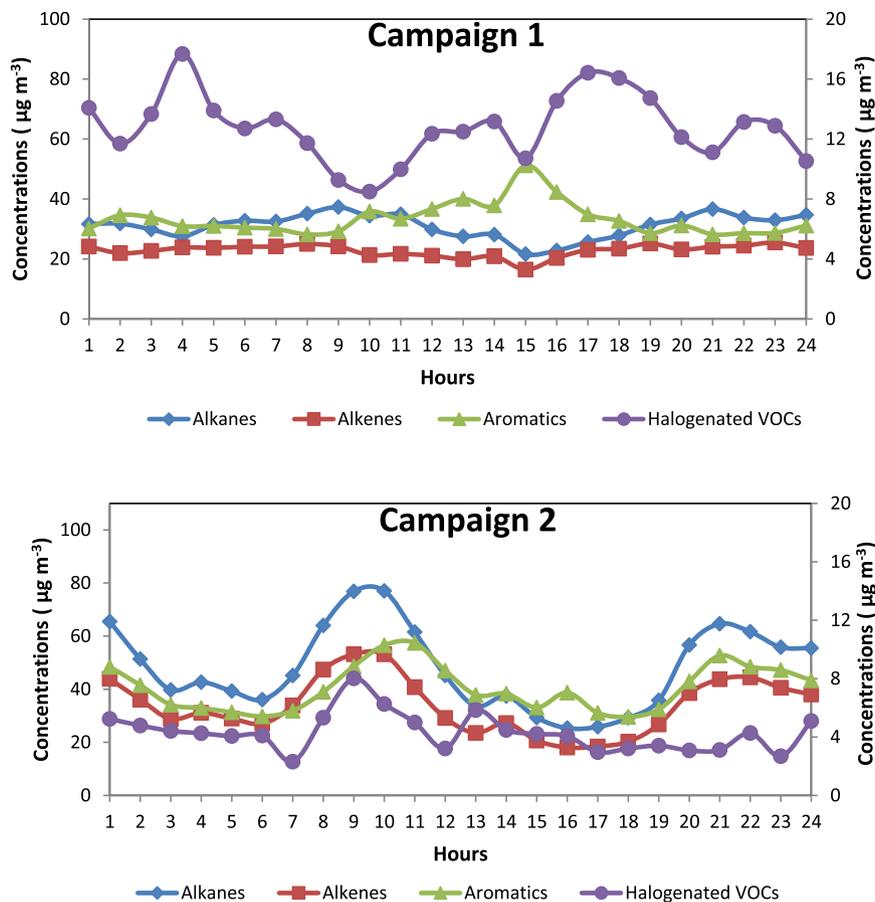


Fig. 7. Diurnal variation in concentrations of alkane, alkene, aromatic and halogenated VOC groups in the first and second campaigns.

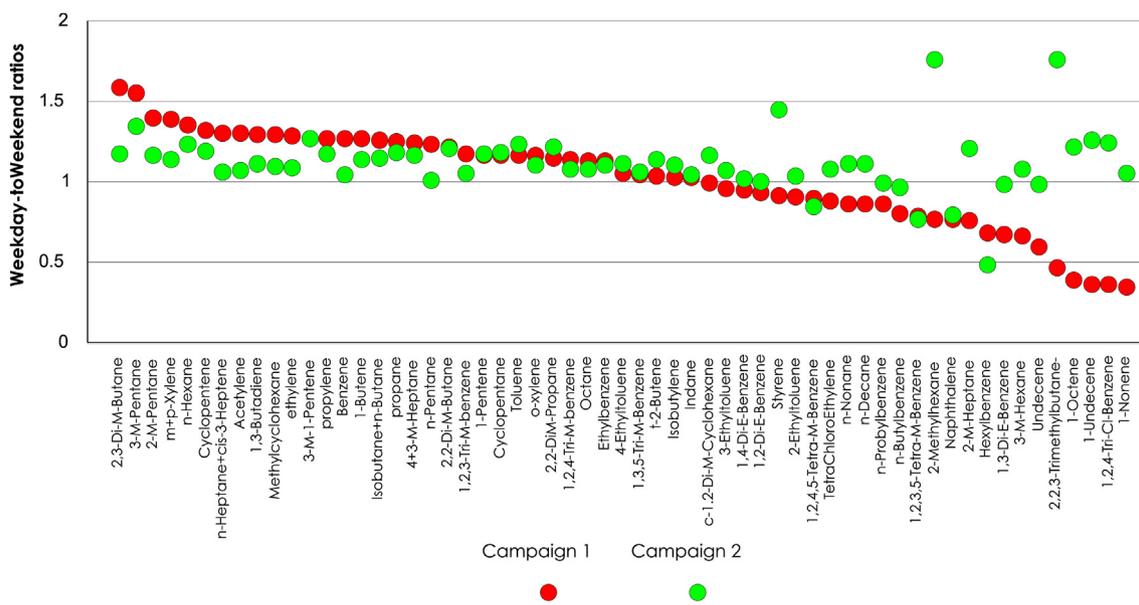


Fig. 8. Weekday-to-weekend concentration ratios of VOCs in campaign 1 and 2.

nonane, 1-nonene, undecane, and decane, are heavy hydrocarbons and their main source in the first campaign is the asphalt pavement around the station. We started to see higher concentrations of

asphalt-related VOCs in September 30. Their concentrations increased until October 1, 17:00 h and then the concentrations gradually decreased until October 4, 09:00 h. In this period, October

1 was Saturday and October 2 was Sunday. The second episode was observed between October 16 and 22, which also included a weekend. This pattern resulted in higher weekend concentrations of asphalt-related VOCs and WD/WE ratios <1.0 for these species.

The asphaltting activities were not observed in the second campaign and most of the heavy hydrocarbons measured in this campaign had WD/WE ratios >1.0. Therefore, heavy VOCs in the second period can be associated with diesel exhaust emissions due to heavier diesel traffic during weekdays (Song et al., 2007; Liu et al., 2008; Yuan et al., 2009; Demir et al., 2011; Wang, 2014).

Hydrocarbons, which have WD/WE ratios around unity in both campaigns, including n-pentane, 1,2-diethylbenzene, n-propylbenzene, 1,3-diethylbenzene, n-butylbenzene, 1,2,4,5-tetramethylbenzene, naphthalene, 1,2,3,5-tetramethylbenzene and hexylbenzene, should have sources that do not decrease in weekends. With the exception of naphthalene, these are VOCs associated with industrial solvent, paint, polymers and automotive applications in addition to vehicle emissions (NTP, 2014; Wang et al., 2014; EPA, 2015). Naphthalene, on the other hand, is used in moth balls, deodorizers and fumigants in addition to vehicle emissions, industry and open burning (Jia and Batterman, 2010; Batterman et al., 2012; Chauhan et al., 2014; Wheeler et al., 2014).

3.5. Effect of asphalt pavement activities on VOC concentrations

Time series plots of the some heavy hydrocarbons showed two very strong episodes on October 2 and October 10. These episodes are depicted in Fig. 9 for the selected VOCs. The first episode started on September 30 and lasted for five days. The second episode started on October 15 and lasted for a week. None of the light hydrocarbons and not all of the heavy ones showed this pattern. There was an intense asphalt pavement activity in Altiparmak Boulevard and in Hasta Yurdu road around the station between September 20 and October 25. The roads were begin to be paved approximately 500 m at the north-east direction from the sampling point and continued in front of the building in which the sampler was located.

The asphalt pavement activities were finished to the south west of the sampling point on October. Furthermore, asphaltting was performed during the weekend. These episodes in heavy VOCs are due to asphaltting operations that took place around our station. Heavy hydrocarbons are good markers of emissions from heavy duty vehicles (Qiao et al., 2012; Pekey et al., 2013). However, diesel engine 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., 2008; Naveed et al., 2014).

The average concentrations of VOCs calculated during episode days and during non-episode days of the first campaign are given in Fig. 10. Among the measured VOCs, hexylbenzene, dodecane, 1,2,4-trichlorobenzene, undecane, 1-undecene, sec-butylbenzene, isobutylbenzene, 1,4-dichlorobenzene, 3,6-dimethyloctane, isopropylbenzene, 1-nonene, chlorobenzene and 1-octene have higher average concentrations in the episode period than their corresponding concentrations in the remainder of the first campaign.

The total contribution of asphalt-related VOCs to the concentration of \sum_{112} VOCs was approximately 19% in the absence of asphalt pavement activities and approximately 60% during asphaltting periods. Such a large difference in the VOC profiles in the absence and presence of asphaltting activities around the station implies that asphaltting activities can be a significant source for some of the VOCs in urban atmosphere and can dominate the VOC profile if it is in close proximity to the station.

Interestingly, the concentrations of light hydrocarbons decreased after September 21 for approximately 10 days. This can be clearly seen in Fig. 10. Lower concentrations of light hydrocarbons during asphalt pavement activities are due to traffic limitations, as traffic route was changed and the roads connecting to Hasta Yurdu were closed off to traffic during asphaltting operations.

The ratios of VOCs with different sources can provide valuable information on the relative contributions of these sources. Therefore, toluene-to-benzene (T/B ratio) and m,p-xylene-to-ethylbenzene (X/E ratio) ratios, which are two BTEX ratios widely used in the literature were also investigated in the study (Amodio

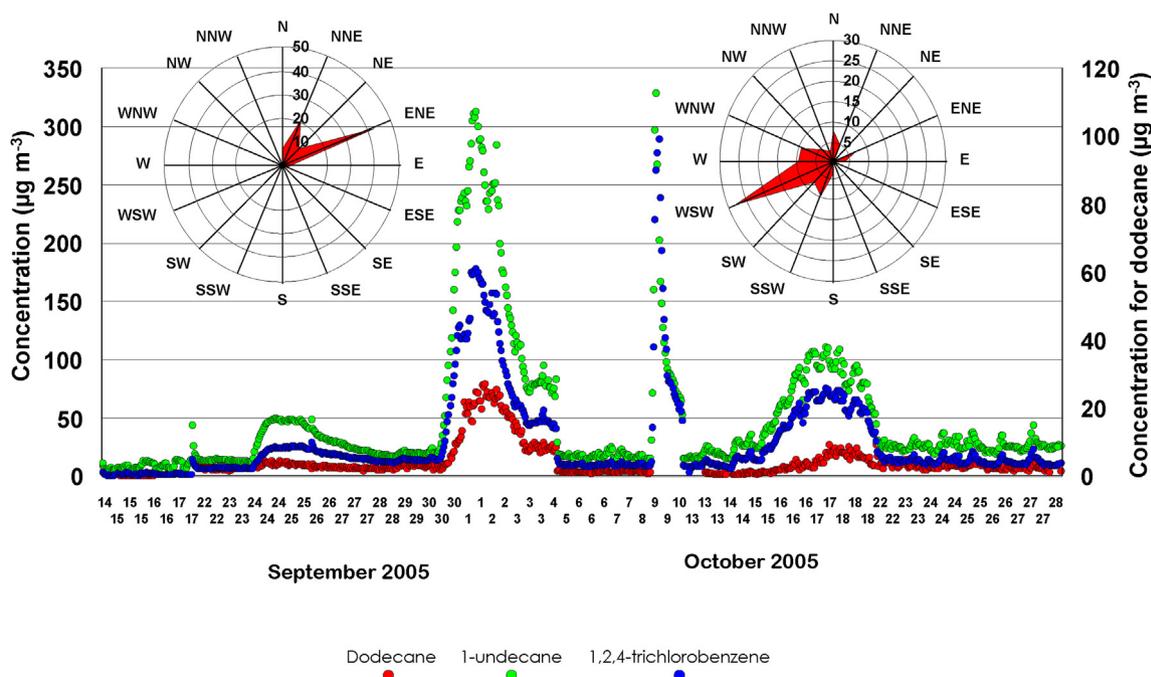


Fig. 9. Hourly temporal variations of selected heavy VOCs during first campaign and wind roses (in %) during asphalt episodes which were observed during the September and October, respectively.

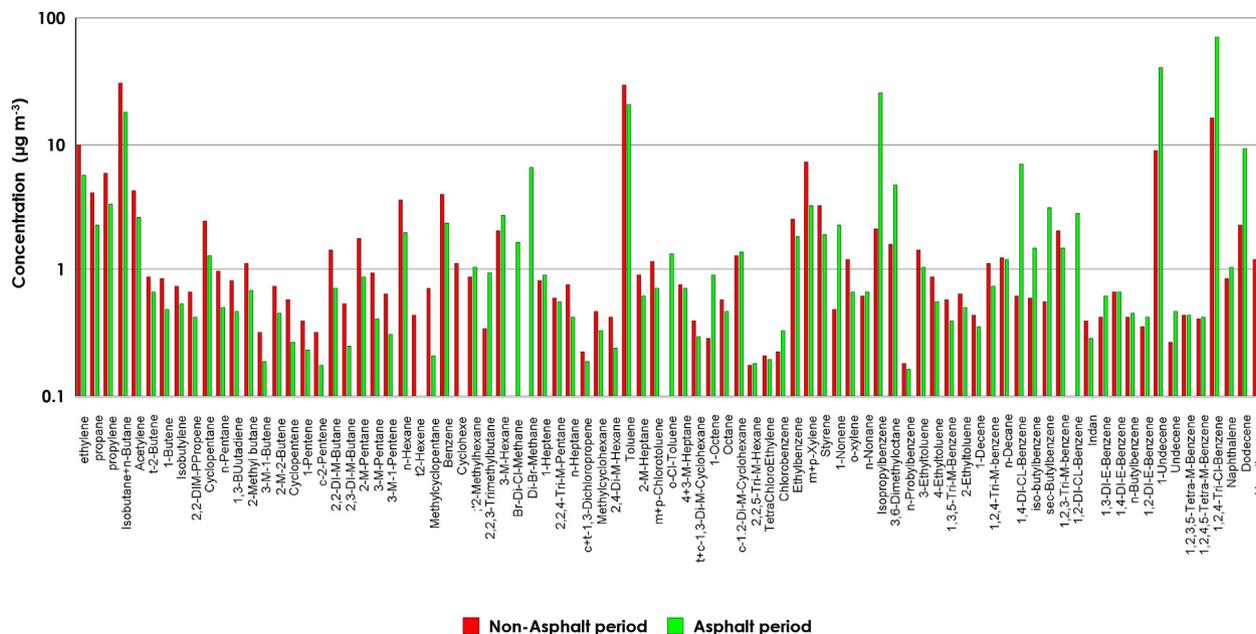


Fig. 10. Average concentrations of VOCs during asphalt and non-asphalt periods in Campaign 1.

et al., 2013; Singh et al., 2016). Light-duty gasoline exhaust is a dominating source of benzene in an urban atmosphere. Although light-duty vehicle exhaust is also an important source of toluene, solvent evaporation and evaporation from painted surfaces also emit significant quantities of toluene to atmosphere. A low T/B ratio (~ 2) indicates traffic emissions and higher T/B ratios designate a strong contribution of non-traffic sources to the VOC composition of the atmosphere (Suthawaree et al., 2012; Jia et al., 2016). The X/E ratio, on the other hand, is used as an indicator of aging of VOCs if they originate from the same sources before they are intercepted at the receptor (Rappenglück et al., 2000). The ratio is fairly constant in different sources, but it starts to decrease in time as VOCs stay in the atmosphere, due to faster reactivity of m,p-xylene with OH radical (Huang et al., 2015). Typical X/E ratios measured in the urban atmosphere are around 3 (Monod et al., 2001; Hsieh et al., 2011; Amodio et al., 2013). Therefore, the ratios substantially less than 3 indicate the transport of VOCs from distant sources.

Diurnal variations of T/B and X/E ratios are given in Fig. 11. X/E ratios did not show any variation during the day. Its value is constant at around 3 in both seasons. The stability of X/E ratio demonstrates that there is no significant variation in the age of air parcels arriving to our station, which is expected in an urban atmosphere, where the emission strengths of sources for xylenes and ethylbenzene largely exceed their photochemical removal. There may be episodic changes in transport distances, as discussed earlier in the manuscript, 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. Probably due to higher contribution of non-traffic sources and limitation of traffic activity for asphaltting operations are the reasons of observed high T/B ratios during the first campaign. 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 increasing temperature. Furthermore,

higher T/B ratios during the night and lower values during the day might be due to high solar radiation and highly availability of OH radicals during the day time (Rappenglück and Fabian, 1999b).

The median values of T/B in the first and second campaigns were 16 and 4, respectively. The corresponding median values of X/E ratio were 2.5 in the first and 2.9 in the second campaign. Xylene-to-ethylbenzene ratios between 2.5 and 2.9 are typical for urban areas and indicate that VOCs are transported to the receptor from sources within the city. The toluene-to-benzene ratio of 4 measured in the second campaign is also typical for the receptors that are not in the immediate vicinity of traffic activities. Ratios around 4 were observed in fair number of cities in Turkey (Elbir et al., 2007; Kuntasal et al., 2013; Yurdakul et al., 2013). However, the median value of 16 observed in the first campaign is unrealistically high to be explained by solvent sources of toluene. Temporal variation of T/B and X/E ratios during the first campaign is depicted in Fig. 12, together with temporal variations in concentrations of benzene, toluene, ethylbenzene and m,p-xylene in the same period. It is clear from the figure that asphaltting activities have a profound influence on BTEX ratios. The toluene-to-benzene ratio episodically increased between September 30 and October 4, which exactly matches with the first asphaltting episode discussed previously. The X/B ratio displayed a sharp decrease in the same period. The increase in the T/B ratio and decrease in the X/E ratio during the asphaltting activities is not a coincidence and suggests that emissions from asphalt also affected the BTEX composition of the atmosphere. The variation of benzene and toluene concentrations during the campaign 1 is depicted in Fig. 12b. Although benzene concentrations did not change significantly between September 30 and October 4, the concentration of toluene increased up to $77 \mu\text{g m}^{-3}$ in the same period (The average toluene concentration before the episode was $10 \mu\text{g m}^{-3}$ and the average toluene concentration during the episode was $48 \mu\text{g m}^{-3}$). This pattern demonstrated that toluene was emitted from hot asphalt and affected both its concentration and the T/B ratio measured at our station.

Temporal variations in ethylbenzene and m,p-xylene concentrations during campaign 1 are given in Fig. 12c. The concentration of ethylbenzene also increased between September 30 and October

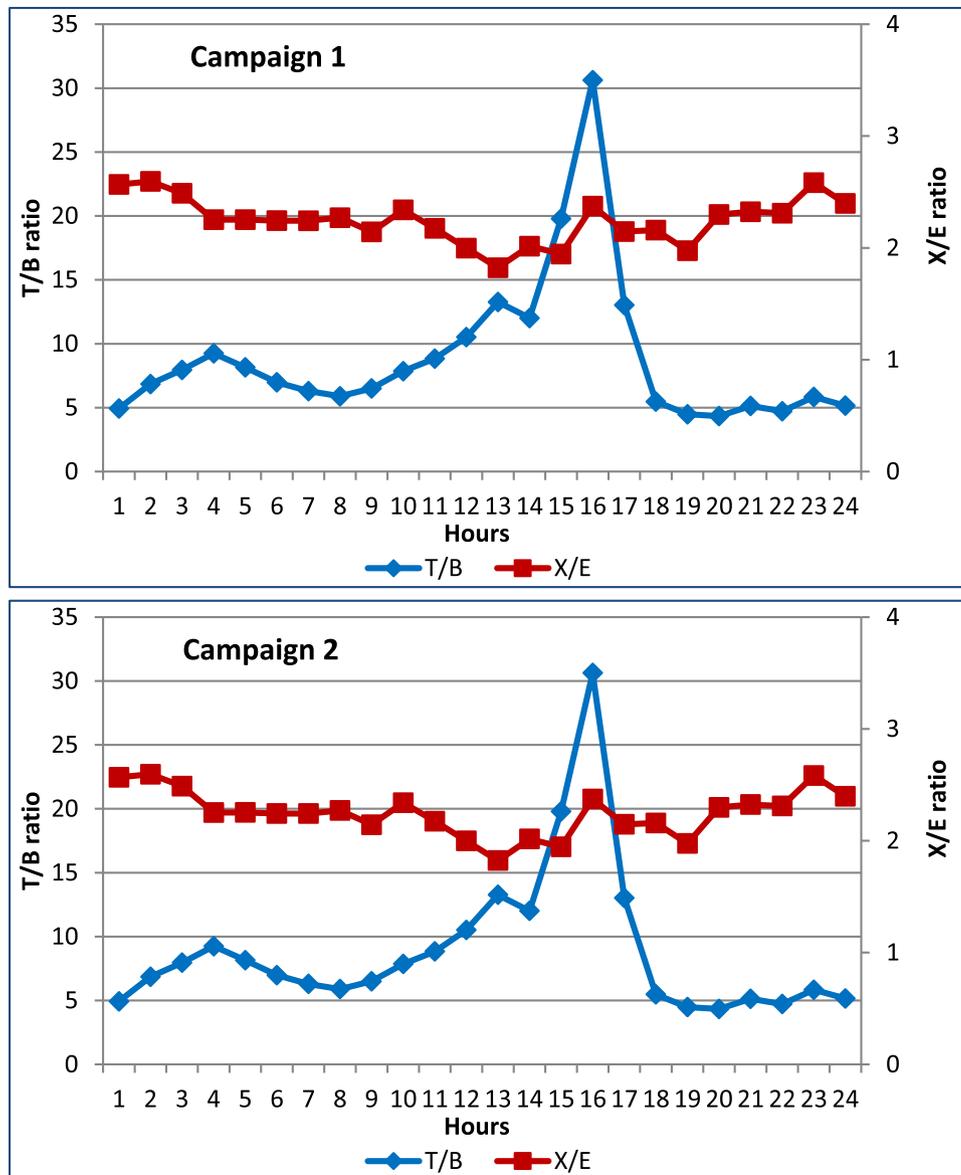


Fig. 11. Diurnal variation of the VOC ratios for both campaigns.

4, explaining the decrease in the X/E ratio in that period. During the same period, m,p-xylene concentration decreased slightly, and this enhanced the drop in X/E ratio. The decrease in xylene concentration is probably due to the shift of the wind to the north (Fig. 12a), where the bulk of the city lies, implying longer transport distances between the station and VOC sources.

Another point worth noting is that neither the BTEX ratios, nor the BTEX concentrations show unusual patterns during the second asphalt episode, which took place between October 16 and October 22. The reason is not clear, but may suggest that a different asphalt formulation was used during asphaltting between October 16 and 22.

3.6. VOC reactivity and ozone formation potential

VOCs can be ranked according to their ozone formation potential (ozone reactivity) by using Carter's "maximum incremental reactivity" (MIR) (Carter, 2010). Carter's MIR refers to the amount (in grams) of ozone formed per gram of VOC added to an initial

VOC–NO_x mixture. The ozone formation potential of VOCs measured in this study was calculated using MIR coefficients reported in the literature (Carter, 2010). The ozone formation potential is calculated as product of the concentration of each VOC and the MIR. Therefore ozone formation potential of the each compound was calculated as (Olumayede, 2014),

$$\text{OFP}_{(i)} = \text{concentration}_{(i)} \times \text{MIR}_{(i)} \quad (1)$$

where, $\text{OFP}_{(i)}$ is the ozone formation potential of compound i , $\text{MIR}_{(i)}$ is the maximum incremental reactivity coefficient of the compound i .

The ozone forming potential of the measured VOCs are presented in Fig. 13 for both campaigns. Day and nighttime values were used for the calculation. Based on the MIR scale, toluene (21.53%) and ethylene (28.64%) are the dominant VOCs for ozone formation for the first and second campaigns, respectively. Since solvent use and vehicle exhaust are the main sources of toluene in the Bursa atmosphere, a more effective control of its emissions from solvents

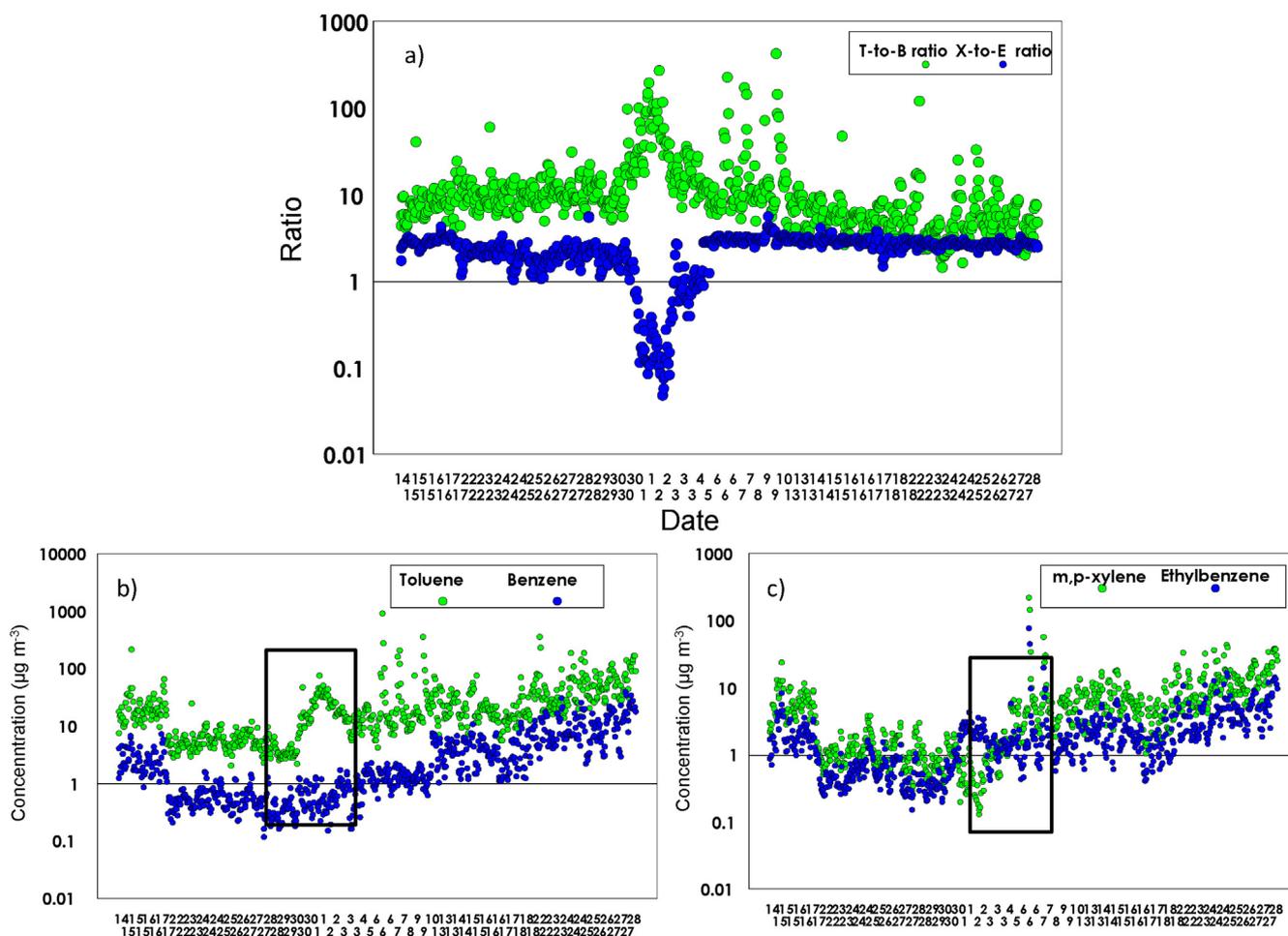


Fig. 12. Temporal variation of a) BTEX ratios, b) benzene and toluene and c) m,p-xylene and ethylbenzene for the first campaign.

will result in more effective reductions in ozone concentrations in the Bursa atmosphere. The BTEX group alone brought about approximately 24% and 37% of the total ozone formation potential for the first and second campaigns, respectively.

Although the ozone formation potentials of 1,3-butadiene, 1,3,5-tri-*M*-Benzene and *t*-2-butene are very high, the contribution of these VOCs to the ozone levels in Bursa was <5% due to their low concentrations. Therefore, due to either low atmospheric concentrations or low MIR values of the VOCs, low ozone production were obtained for some of the VOCs such as acetylene, ethylbenzene and benzene. The difference in ozone formation potentials of VOCs in the first and second campaigns and the species that have the highest contribution to ozone formation display no difference. However, there are also some differences between the first and second campaigns in terms of ozone formation potential. Ozone formation potentials of the dodecane (1.16%) and 1-undecane (6.07%) in the first campaign were found to be significantly higher than those calculated in the second campaign. These compounds are found to be related with asphaltting in the first campaign. Therefore, it can be said that asphaltting activities had also effect on the ozone levels in the Bursa city center.

4. Conclusion

The concentration of measured organic compounds in Bursa atmosphere showed great variations. There was a diurnal,

weekday/weekend change of VOCs concentrations on time basis and also on seasonal variations in Bursa atmosphere.

The median total VOCs concentrations were 115 and 86 $\mu\text{g m}^{-3}$ for the first and second campaigns, respectively. In the first campaign, total VOCs concentrations were higher than in the second campaign even though more stable weather conditions were present in the second campaign. The reason was asphaltting 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.

Data generated in this study clearly demonstrated that some of the heavy hydrocarbons such as dodecane and 1-undecene can be used as good tracers of asphalt application in urban airshed. 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. Furthermore, the calculation of ozone formation potential suggested that BTEX group and ethylene had significant impacts on the O_3 concentrations. These finding indicated that a more effective control of its emissions from solvents usage and vehicle exhaust, could result in a reduction in ozone concentrations in the Bursa atmosphere.

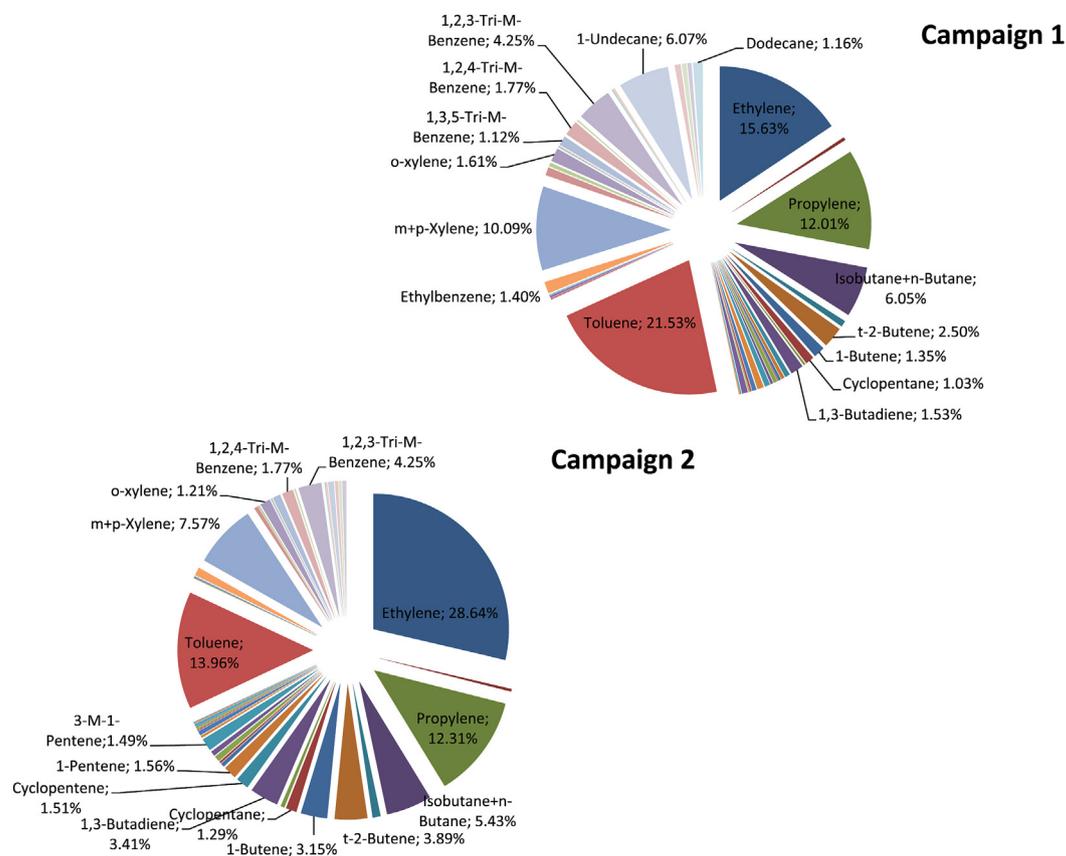


Fig. 13. Ozone formation potentials of the measured VOCs in both campaigns contributions <1% (10% and 28% for the first and second campaigns, respectively) are not shown in the figure.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.apr.2017.09.004>.

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