Volatile organic compounds in suburban Ankara atmosphere, Turkey: Sources and variability

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ABSTRACT

In this study, concentrations of approximately 30 VOCs were measured, between January and June 2008 at a university campus in Ankara. Concentrations of measured VOCs are lower than corresponding concentrations reported for other cities in literature. Average concentrations of the measured VOCs ranged from 0.04 to 7.89 $\mu g\ m^{-3}$. Benzene (2.18 $\mu g\ m^{-3}$), toluene (7.89 $\mu g\ m^{-3}$), ethylbenzene (0.85 $\mu g\ m^{-3}$) and xylenes (2.62 $\mu g\ m^{-3}$) (BTEX) were found as a major organics in suburban Ankara atmosphere. The measured VOCs also show well defined diurnal and weekday–weekend cycles. Toluene-to-benzene ratio (T/B) suggested that non-traffic sources can be important during summer months. The m,p-xylene-to-ethylbenzene ratio (X/E) pointed to transport of organic compounds from high-emission districts of the city. Positive matrix factorization applied to data revealed four sources, including gasoline exhaust, solvent evaporation, diesel emissions and a local laboratory source, contributing to VOC concentrations. Strengths of these sources, particularly solvent source, on total VOC concentrations showed seasonal differences. Source contributions on light and heavy VOCs were also different.

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1. Introduction

Different definitions of VOCs are available because VOC family consists of many organic compounds which have very different properties. According to the EC Directive 1999/13/EC, VOC is defined as an organic compound whose vapor pressure is 0.01 kPa or higher at 20 °C. Pure hydrocarbons (alkanes, alkenes, alkynes and aromatics) are important VOC classes. Other VOC groups include aldehydes, alcohols, ketones, chlorinated alkanes and alkenes, chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). As soon as VOCs are released into the atmosphere, they will be portioned or evaporated into air. Since, and most of the oxidative degradation processes of the VOCs take part into the atmosphere, their atmospheric photochemistry or photodegradation routes of VOCs are very important as the products of these chemical

processes are generally oxidants including ozone (Mackay et al., 1992).

Fates of the organic compounds will be affected by the chemical and physical properties of individual compounds. Likely reactive routes available for VOCs include OH-initiated photochemical oxidation (Derwent, 1995; Stevens, 2008), photolysis in the troposphere and stratosphere, reaction with other reactive species, such as, chlorine atoms, nitrate radicals and ozone (Derwent, 1995). Lifetime of VOCs is determined by their reactivities against HO radical (Atkinson, 2000). Since VOCs that have high-molecular weight can be adsorbed on atmospheric particles, dry and wet depositions are also important scavenging mechanisms for VOCs (Karl et al., 2010). Tropospheric chemistry between NO_x and VOCs is the main mechanism for the production of the photochemical ozone (Sillman, 2000; Barna et al., 2001), although there are some uncertainties about the mechanism (Atkinson, 2000).

It is not easy to define a general source for VOCs as there are numerous compounds in this group, which can be emitted from very different sources. However, biogenic sources (Guenther et al., 2006; Williams and Koppmann, 2007), gasoline powered (Hellen et al., 2003; Demir et al., 2011) and diesel powered

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(Demir et al., 2011) motor vehicles, fuel storage and fuel combustion (Lanz et al., 2008), biomass burning (Yokelson et al., 2008), natural gas (Latella et al., 2005), LPG (Lai et al., 2005), industrial processes and solvents (Lai et al., 2005; Lanz et al., 2008) are well documented sources of VOCs.

Furthermore, since some VOCs exist in the fuel formulations, they can be released into the atmosphere through evaporation during storage and filling operations and from gasoline stations (Schifter et al., 2002). Other VOCs occur in the atmosphere through secondary production (Vehicle emissions, air quality, 1998). Although, relative significance of this source on atmospheric VOC concentrations varies from one location to the other (Na et al., 2003), light and heavy duty traffic is a common source observed in almost all source apportionment studies (Jouquera and Rappenglück, 2004; Song et al., 2008; Yuan et al., 2009).

The existence of numerous compounds and fingerprints in the VOC group make them very attractive source markers in receptor modeling studies (Scheff et al., 1989). Although their reactivity in the atmosphere is a drawback (Scheff and Wadden, 1993), uncertainties which are coming from the modeling are considered to not cause significant inaccuracies (Yarwood et al., 2005). Different forms of receptor modeling approaches, such as, principle component analysis (PCA) (Ho et al., 2002; Wahab et al., 2005), absolute principal component analysis (APCA), (Guo et al., 2004a, 2004b), chemical mass balance (CMB) (Hellen et al., 2003; Lai et al., 2005) and positive matrix factorization (PMF), (Lanz et al., 2008; Yuan et al., 2009), UNMIX (Song et al., 2008) were successfully applied to VOC data. All of these studies clearly demonstrated that, contributions of sources that are difficult to quantify with trace element data, such as gasoline exhaust, diesel exhaust, evaporative emissions, paint, ink use, LPG and natural gas can be successfully quantified when VOCs are used as source fingerprints (Wiswanath, 1994).

The use of VOCs in receptor modeling studies is limited in Turkish cities. Elbir et al. (2007) applied PMF to VOC data generated in Izmir. Paint application/production (34%), diesel vehicle exhaust (40%) and gasoline vehicle exhaust (26%) were found as main VOC sources in suburban atmosphere by PMF (Elbir et al., 2007). Kuntasal (2005) also identified the ambient sources of the VOCs in a suburban area in Ankara. Diesel exhaust (39.18), solvent usage (14.77), residential heating (25.23) and vehicle exhaust/gasoline evaporation (20.82) were found as major sources in suburban Ankara atmosphere.

In the present study results obtained from six-month-long (from January 2008 to June 2008) active measurements at a suburban university campus where 20,000 students come and go every day are discussed. University campuses are rather dense population centers where a large number of students spend a significant fraction of their time and some, living in the dormitories, spend almost all of their time for the four years they stay in the university. Consequently knowing the levels of air pollutants, including VOCs is essential at least to get an idea about the levels these students are exposed to and to decide whether a comprehensive indoor/outdoor study is a necessity. With this purpose, ambient air samples were collected, twice a day. Thirty four VOCs were identified and quantified. The discussion in this manuscript focuses on temporal variation and sources of these 34 VOCs.

2. Material and methods

2.1. Sampling site

The VOC samples were collected at Ankara, Turkey, between January 8 and June 16, 2008. Ankara, which is the capital of the country, has a population of approximately 3,000,000. The city is located on the Anatolian Plateau and has an altitude of approximately 1000 m. Samples were collected at the Environmental Engineering department of the Middle East Technical University (METU), which is located at one of the suburbs of the city. The sampling location is depicted in Fig. 1. Ankara is not a heavily industrialized city and most important VOC sources are expected to be traffic and solvent evaporation. Since the METU campus is at the outskirts of the city there is not an important VOC source at the immediate vicinity of the station. The nearest road is 100 m to the sampling point, but it does not carry heavy traffic as the Environmental Engineering Department is located at the peripheral of the university campus. The distance of the station to Eskişehir highway, which is a busy road joining downtown Ankara to its suburbs, is approximately 2700 m. Other roads with heavy traffic are even further away.

2.2. Sample collection

Sampling and analysis of VOCs was based on USEPA method TO-17. Volatile organic compounds were collected onto Chromosorb 106 adsorbent (60–80 mesh) packed into 8.89 cm long stainless steel tubes having a 6.35 mm outer diameter. Approximately 350 mg adsorbent was used for each sampling tube. In conditioning process, the tubes were placed in the conditioning oven and it was set to 250 °C. During this time, high-purity nitrogen passed through tubes with an air flow speed of 100 ml min^{-1}. The conditioning process lasts 4 h. After the process is over, adsorbent tubes are taken to protective glass tubes and kept in a refrigerator until they are placed in the field. Air was pulled through sampling tubes using a pump (SKC, model Universal) at a constant flow rate of 16 ml min^{-1}. The air flow was kept constant with AALBORG, model GFC171 mass flow controller (MFC). Two samplings were performed to detect daytime–nighttime differences and to avoid leaking of VOCs from sampling tubes. Tubes were changed at approximately 8:30 am and 5:30 pm. This schedule was based on the traffic activity in the university. Since classes start at 8:40 am and end at 5:30 pm, most of the activity in the campus is covered in day-time sampling. Night-time sampling, on the other hand corresponds to a relatively calm period in the university.

2.3. Analysis of samples

VOCs collected on adsorbent tubes were analyzed using an Agilent 6990 Gas Chromatography (GC)-Flame Ionization Detector equipped with a Deans Switch device used to obtain better resolution of the peaks with two different types of column that were coupled with Unity Thermal Desorption System. Heavy hydrocarbons were eluted from the HP Al/S capillary column (50 m × 0.32 mm × 8 μm). In the system, samples were desorbed in the thermal Desorber at 200 °C. Desorbed VOCs were first captured in a carbonized molecular

Fig. 1. Sampling point in the METU, Dept of Environmental Engineering.

sieve filled cold trap at −15 °C, which is then quickly (in 6–8 s) heated to 300 °C to introduce analytes to the GC.

The instrument was calibrated using a standard gas mixture specially prepared at ambient levels of 148 C_2–C_{12} VOCs, obtained from Environment Technology Center, Environment Canada (Ottawa, Canada). Concentrations of the compounds in the standard mixture were varying between 2 and 20 µg m^{-3}. The retention time of the compounds was identified both with separated mix liquid VOC mixtures (aromatic, olefin, paraffin and BTEX liquid mixtures) and standard gas mixture. Although there were large numbers of VOCs in the standard, 34 of these were regularly detected in samples. The peaks identified by the FID system were also confirmed by analyzing some of the samples and standards with a GC-MS system (HP – AgilentTechnologies, Palo Alto, CA, USA – model 6890 GC and model 5973MS). Five-point calibration curves were prepared for each organic compound and slopes of these curves were used in quantification. The stability of the calibration was checked at every analysis day by injecting one of the mid-point standards.

Precision of measurements was monitored by replicate measurements of low-level standards. Relative standard deviations for all VOCs measured in this study was <10%. In addition to precision tests and calibration checks, laboratory and field blanks and desorption efficiency of the samples were routinely measured as parts of the QA/QC program in the study. Breakthrough test was performed at the beginning of the study.

Although USEPA method TO-17, was followed in the analytical part of this study, some minor modifications were

done on the method. The most significant modification was to use two sampling tubes in series in sampling instead of one tube recommended in the method. The use of two successive tubes was to ensure that no VOCs leaked. Although the breakthrough tests showed that one tube would be enough, two tubes in series were used throughout the sampling. Both tubes were analyzed and if any VOC detected in the second tube, data from both tubes were excluded from the data set. This happened in only one of the sampling periods. In all remaining sampling periods no VOCs above the blank level was detected in the second tube.

The field blank tubes were filled and conditioned with exactly the same procedures used in filling sampling tubes. They were carried to the sampling point and loaded onto pumps, but pumps were not operated. Blank tubes were then removed from the sampling system and treated like a regular sample tube. The VOC masses measured on field blanks were <10% of average masses of VOCs collected on sample tubes. For example the average benzene concentration in samples was 2.2 µg m^{-3}. The highest benzene blank value was 0,012 µg m^{-3}. More or less a similar difference was observed in the other VOCs as well. Desorption efficiency of the analysts ranged from 92% to 99% with an average of 96%.

Detection limits of individual VOCs varied between 0.01 µg m^{-3} for m + p-chlorotoluene and 0.18 µg m^{-3} for cyclohexane + cyclohexene. Method detection limit (MDL) for each VOC was the concentration corresponding to 3σ obtained from seven replicate measurements of a blank tube. Detection limit values of all VOCs, are orders of magnitude smaller than concentrations found

in samples, indicating that VOC concentrations close to detection limit values are not a serious source of uncertainty in this study.

Another part of our QA/QC program was the data validation. A three step data validation procedure was used. (1) Time-series plots were prepared for each VOC and outliers were flagged, (2) scatterplot matrix was investigated and outliers in the scatterplots were also flagged. Finally time (3) series plots of VOC ratios were prepared and outliers were again flagged. For each flagged data, chromatogram and calculations were inspected for a possible fitting and calculation error. If no error is found, flagged data was accepted as real.

3. Results and discussion

Mean and median concentrations of measured VOCs are given in Table 1. Median concentrations are included in the table, because the chi-square test indicated that most of the 34 VOCs measured in this study are long-normally distributed with 0.95 or higher confidence. Although arithmetic mean does not properly represent log-normally distributed data, it is also included in the table to facilitate comparison with literature, where arithmetic mean values are reported very frequently.

Table 1
Average and median concentrations of VOCs measured in this study.

	$X \pm \sigma$ μg m^{-3}	Median μg m^{-3}	N
methylcyclopentane + 2,4-dimethylpentane	0.24 ± 0.23	0.16	207
Benzene	2.18 ± 2.25	1.20	208
cyclohexane + cyclohexene	0.23 ± 2.30	0.15	184
2-methylhexane	0.24 ± 0.22	0.17	189
2,2,3-trimethylbutane + 2,3-dimethylpentane	0.11 ± 0.18	0.08	187
3-m-hexane	0.42 ± 0.31	0.29	189
1-heptene	0.06 ± 0.32	0.03	190
2,2,4-tri-m-pentane	0.09 ± 0.11	0.05	204
n-heptane + cis-3-heptene	0.31 ± 0.29	0.19	207
methylcyclohexane	0.09 ± 0.31	0.05	182
toluene	7.89 ± 9.64	3.60	209
2-m-heptane	0.23 ± 9.40	0.14	204
m + p-chlorotoluene	0.22 ± 0.25	0.13	200
o-cl-toluene + di-br-cl-methane	0.28 ± 0.24	0.19	82
4 + 3-m-heptane	0.12 ± 0.21	0.07	192
t + c-1,3-di-m-cyclohexane	0.14 ± 0.15	0.10	113
octane	0.15 ± 0.17	0.09	206
2,2,5-tri-m-hexane + 1,2,4-tri-m-cyclohexane	0.06 ± 0.15	0.03	194
ethylbenzene	0.85 ± 0.91	0.45	209
m + p-xylene	2.21 ± 2.50	1.13	209
styrene	0.41 ± 2.48	0.14	208
1-nonene	0.16 ± 0.48	0.08	201
o-xylene	0.41 ± 0.47	0.21	209
n-nonane	0.17 ± 0.46	0.09	208
isopropylbenzene	0.06 ± 0.19	0.02	141
n-probylbenzene	0.04 ± 0.07	0.02	194
3-ethyltoluene	0.22 ± 0.27	0.12	205
4-ethyltoluene	0.31 ± 0.44	0.13	206
1,3,5-tri-m-benzene	0.17 ± 0.40	0.08	205
2-ethyltoluene	0.13 ± 0.22	0.06	201
1,2,4-tri-m-benzene	0.27 ± 0.35	0.11	206
n-decane	0.22 ± 0.38	0.11	204
iso-butylbenzene	0.10 ± 0.27	0.04	168
1,2-di-cl-benzene	0.26 ± 0.35	0.09	159

Concentrations of VOCs, which are shown in Table 1, vary between 0.06 μg m^{-3} for isopropylbenzene, and 7.9 μg m^{-3} for toluene. Concentrations other than these two generally vary between 0.1 μg m^{-3} and 1.0 μg m^{-3}.

VOC data reported in literature for different parts of the world are given in Table 2, together with data generated in this study. The comparison is limited to a small number VOCs owing to lack of data in literature for compounds other than BTX. It is clear from Table 2 that VOC concentrations measured in this study are generally smaller than concentrations reported for other cities around the world. It is well documented that traffic is not the only, but the most important source of VOCs in urban atmosphere. Because of this, one has to be careful in comparing data from different studies as the location of sampling point can strongly affect VOC concentrations measured. There are two main reasons for lower VOC concentrations measured in this study compared to other urban areas in Table 2. One of these is the relatively long distance between our station and roads with heavy traffic and industrial areas. As pointed out in the experimental section, the station where samples were collected is approximately 3 km to major arteries with heavy traffic. In another study, Kuntasal (2005) reported factors of two-to-three higher VOC concentrations at a location in downtown Ankara which is strongly affected from traffic, confirming that low VOC concentrations measured in this study is at least partly due to distance from sources.

The second reason for the large variation in VOC concentrations reported for different sites is different traffic load at different sampling locations. Although there are adequate rules and regulations to control traffic emissions in Ankara, these rules and standards are not strongly enforced. Because of the lack of enforcement, one would expect to have higher concentrations of organic compounds in Ankara atmosphere, than concentrations measured in better regulated cities. However, Kuntasal (2005) demonstrated that VOC concentrations measured using identical sampling and analytical techniques at comparable locations at Ottawa, Canada were similar to the VOC concentrations measured at Ankara. Traffic counts in both cities indicated that the number of vehicles in traffic at Ottawa was approximately a factor of four higher than vehicles in traffic at Ankara. This also contributes to the observed lower VOC concentrations at Ankara atmosphere compared to those measured in other cities around the world.

Percent contribution of each organic compound to total VOC mass, which is also referred to as "VOCs profile" or "VOC finger print" are given Fig. 2. Measured concentrations of 34 VOCs were summed up and the contribution of each VOC was calculated for each sample and finally averaged over the sampling period.

BTX compounds totally accounted for approximately 70% of the VOC mass. Among these toluene has the highest contribution (41%), which is followed by Benzene (11%) and m,p-xylene (11%). Contributions of o-xylene (4.5%) and ethylbenzene (2.2%) were smaller. The contribution of other VOCs' total mass is smaller than 2% each. This pattern is generally similar in most parts of the world. However, ratios of some compounds may differ and can make this pattern a fingerprint for a given urban environment. Ratios of selected VOCs will be discussed later in the manuscript.

Table 2
Comparison of the selected VOCs with the literature (μg m⁻³).

Compound	This work	Ankara[a] downtown winter	Ankara[a] downtown summer	Ottowa[a] winter	Ottowa[a] summer	Toronto[b], Canada	Hong Kong[c], China	Lillie[d], France	Athens[e], Greece	Izmir[f] suburban summer Turkey	Izmir[f] urban winter Turkey	Izmir[f] urban summer Turkey
Methylcyclopentane	0.24	1.45	0.78	1.29	1.26	3.30						
3-Methylhexane	0.42	1.74	1.29	1.33	1.30	16.10						
Benzene	2.18	7.24	4.59	2.61	2.18	12.80	26.70	2.49	37.38	0.85	10.40	3.31
Toluene	7.89	14.73	10.46	7.22	7.23	69.50	77.20	8.75	79.91	4.65	13.50	15.39
Ethylbenzene	0.85	2.94	3.23	1.33	1.48	6.10	3.10	1.13	17.37	0.38	1.60	3.65
m/p-Xylene	2.21	13.06	8.60	3.16	3.24	25.10	12.10	3.08	49.08			
o-Xylene	0.41	5.01	3.01	1.42	1.19	7.40	4.60	1.09	23.89			
1,2,4-Trimethylbenzene	0.27	6.58	3.55	1.85	2.03	10.60				0.08	0.43	0.80
Toluene/Benzene	3.61	2.03	2.28	2.77	3.31	5.43	2.90	3.51	2.14	5.81	1.30	4.65

[a] Kuntasal, 2005.
[b] Kendall, 1993.
[c] Chan et al., 2002.
[d] Borbon et al., 2002.
[e] Rappengluck et al., 1998.
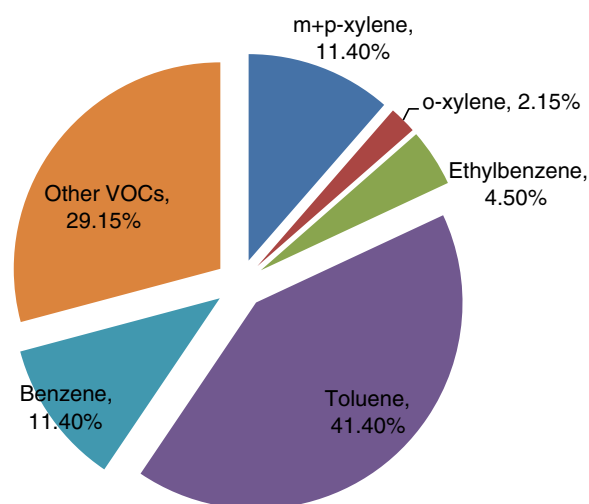[f] Elbir et al., 2007.

Fig. 2. Percent contributions of VOCs tot total VOC mass (VOC profile). Each white slice corresponds to one of the VOCs measured in this study. Only BTX compounds, which have the highest contributions to total VOC concentrations, are shown. Each white slice is a separate hydrocarbon.

3.1. Temporal variation in VOC concentrations at Ankara atmosphere

Concentrations of VOCs measured in this study showed strong episodic changes and well defined seasonal variations. Short- and long-term variations in concentrations of selected VOCs are depicted in Fig. 3. Most of the other VOCs showed similar seasonal pattern.

Observed episodic changes in VOC concentrations (short-term variations) are fairly typical in urban atmosphere and generally attributed to changes in ventilation conditions driven by diurnal and seasonal variations (Srivastava et al., 2010) in the city, variations in emissions and surroundings of sampling sites (Wang and Zhao, 2008). The main source that strongly affects variability in VOC concentrations in Ankara atmosphere, as will be discussed later in the manuscript, is traffic. Since VOCs emitted from traffic varies, but not episodically, observed episodic variations in concentrations of measured organic compounds must be explained with ventilation conditions.

Wind speed and mixing height are two parameters that govern horizontal and vertical ventilations of the atmosphere. Short- and long-term variations in these two parameters and ventilation coefficient, which is the product of the two in Ankara atmosphere, were thoroughly discussed by Genc et al. (2010). Although meteorological data were not from the same year, authors clearly demonstrated existence of short term episodic changes in wind speed, mixing height and ventilation coefficient, which are also likely sources of episodic changes in VOC concentrations observed in this study. Although episodic variations in VOC concentrations seem to be stronger in winter, coefficient of variation, which is also plotted in the figure, does not support this suggestion, because it does not change significantly from one month to another.

Measured VOC concentrations also showed clear seasonal variations with minimum concentrations during summer months. There are probably two reasons that can account for observed seasonal variation in concentrations of VOCs. One of
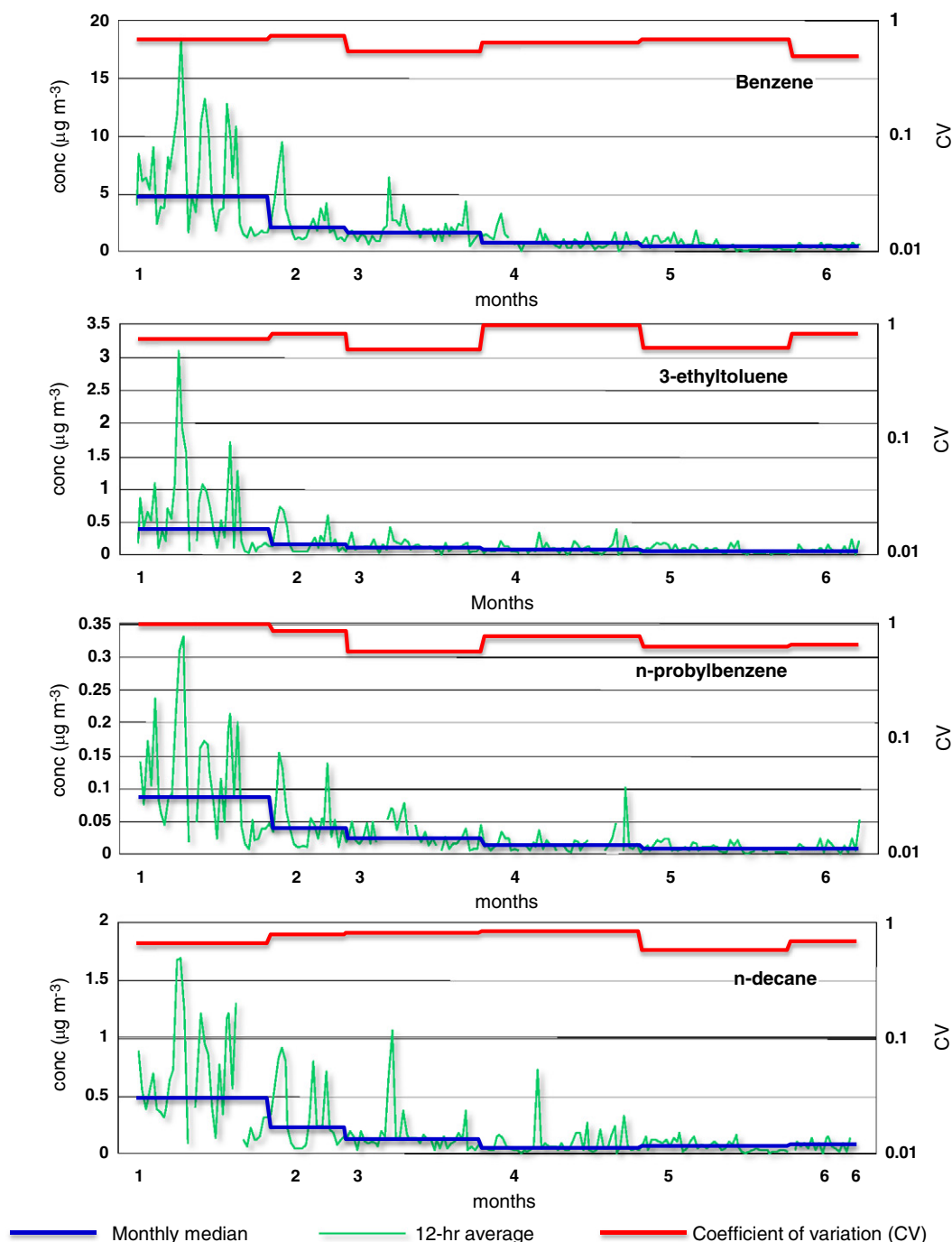
Fig. 3. Short-, long-term variations and variability in the concentrations of selected four VOCs. Coefficient of variation (CV) is the ratio of standard deviation to mean value.

them is the seasonal variation in the reactivities of VOCs. Volatile organic compounds are removed from the atmosphere by deposition and photochemical reactions. They are oxidized into simpler molecules such as CO and CO_2 or intermediate VOCs in the atmosphere as a result of the chain reactions which are mainly driven by OH radicals in the presence of sunlight. These photochemical reactions also

include reactions with ozone and reactions with nitrate radicals during the night (Gouw and Warneke, 2007). Therefore, photochemical reactions play a controlling role for the ozone formation and sometimes can also affect diurnal temporal variability of VOC concentrations (Filella and Penuelas, 2006). Chemical removal of the VOCs, due to OH driven reactions, is more significant during summer than

in winter owing to more vigorous photochemical activity resulting from enhanced solar flux, temperature and higher OH radical concentrations in summer (Lee et al., 2002).

Another reason for low summer concentrations of VOCs is the higher mixing height in summer months. Genc et al. (2010) demonstrated that both the mixing height and ventilation coefficient (which is the product of mixing height and wind speed) in Ankara are a factor of four-to-five higher in the summer season, which results in dilution of pollutants over a deeper mixing depth in summer (Chou et al., 2007). The role of mixing height on seasonal variations in concentration of pollutants are reported in other studies as well (Harrison, 2001; Yang et al., 2005; Pandey et al., 2008; Lü et al., 2009; Parra et al., 2009).

If the meteorology was the only reason for the observed decrease in VOC concentrations in the summer season, concentrations of all measured VOCs are expected to decrease by the same amount in summer. Summer-to-winter concentration ratios of VOCs are given in Fig. 4. All ratios are > 1.0, but they are not equal to each other, indicating that meteorological parameters are not the only factors that determine the concentrations of VOCs in this study. Traffic activity also contributes to observed seasonal variation in VOC concentrations. Kuntasal (2005), counting vehicles at a main artery in Ankara, demonstrated that the number of cars in traffic decrease from approximately 900 vehicles h^{-1} in winter to approximately 500 vehicles h^{-1} in summer. The decrease was explained by migration of people to coastal areas in summer.

Measured VOCs can be classified into two groups depending on their seasonal behavior. The first group whose winter-to-summer ratios are between 2.0 and 5.0 includes iso-butylbenzene, 1,2,4-tri-m-benzene, 2,2,5-tri-m-hexane, ethylbenzene, 2,2,4-tri-m-pentane, 3-m-hexane, 4 + 3-m-heptane, o-cl-toluene, 1,3,5-tri-m-benzene, 1,2-di-cl-benzene, methylcyclohexane, t + c-1,3-di-m-cyclohexane, n-heptane + cis-3-heptene, cyclohexane + cyclohexene, 1,2-di-cl-benzene,

isopropylbenzene, n-nonane, octane, o-xylene, benzene, n-decane and 1-heptene. It should be noted that this group includes all BTX compounds, except toluene. It is well documented that main sources of benzene, ethylbenzene and xylenes in urban atmosphere is gasoline powered vehicles (Kuntasal, 2005; Elbir et al., 2007). Therefore, this observation suggests that the winter to summer ratios of the VOCs which are strongly affected from traffic emissions should have between 2.0 and 5.0.

The second group consisted of 3-ethyl toluene, 2-m-heptane, toluene, 2,2,3-trimethylbutane, 2-methylhexane, m + p-chlorotoluene, and methylcyclopentane. These VOCs have winter-to-summer ratios <2.0. Both traffic source and meteorology favors lower concentrations of VOCs during summer season. The VOCs can have relatively lower winter-to-summer ratios, if they have additional sources in summer. The most likely source, which strength increases in summer is the evaporation of solvents in ink, paint and other applications (Ho et al., 2004). It should also be noted that toluene, which has well documented evaporative sources (Ho et al., 2004; Qin et al., 2007) is in this group.

Weekday-to-weekend concentration ratios of the VOCs are given in Table 3. Ratios vary between 2.0 for o-xylene and 0.5 for isopropylbenzene. It is well known that, the emissions of the various pollutants in atmosphere show higher concentrations in weekday than the weekend (Shan et al., 2008). Most of the traffic markers, such as o-xylene, m,p-xylene, trimethylbenzene, ethylbenzene, and benzene have ratios at the high end of this range, due to a higher number of vehicles on the roads during the week. For some of the VOCs traffic is not the only source, their concentrations in the atmosphere are also contributed by non-traffic sources. Their concentrations do not change significantly between weekdays (WD) and weekends (WE), thus these VOCs have smaller WD-to-WE ratio compared for which traffic is the only source. Consequently, the measured VOCs
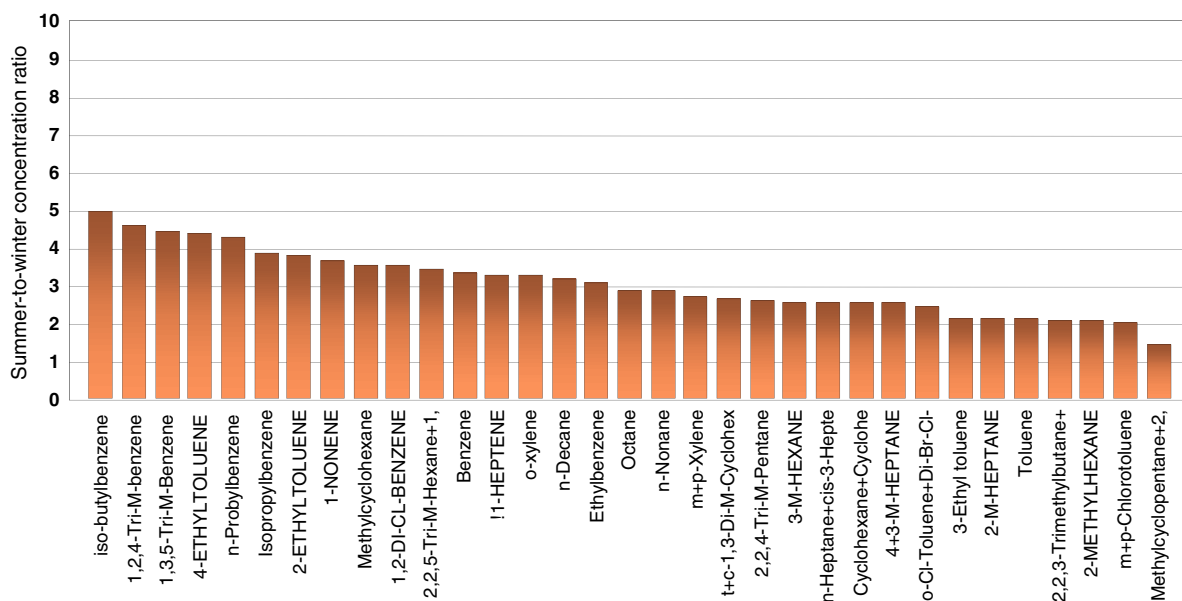

Fig. 4. Summer-to-winter concentration ratios of VOCs.

Table 3
Weekday/weekend ratios of the collected samples.

Compound names	Weekday/weekend ratios
Methylcyclopentane + 2,4-dimethylpentane	1.14 ± 0.67
Benzene	1.75 ± 1.26
Cyclohexane + cyclohexene	1.14 ± 0.77
2-Methylhexane	1.55 ± 1.11
2,2,3-trimethylbutane + 2,3-dimethylpentane	1.45 ± 0.97
3-M-hexane	1.30 ± 0.89
1-Heptene	1.22 ± 1.35
2,2,4-Tri-M-pentane	1.45 ± 0.96
n-heptane + cis-3-heptene	1.51 ± 0.95
Methylcyclohexane	1.06 ± 0.78
Toluene	1.21 ± 0.99
2-M-heptane	1.20 ± 0.74
m + p-chlorotoluene	1.21 ± 0.86
o-Cl-toluene + Di − Br − Cl-methane	1.51 ± 1.08
4 + 3-M-heptane	1.49 ± 1.13
t + c-1,3-Di − M-cyclohexane	1.56 ± 1.83
Octane	1.10 ± 0.76
2,2,5-Tri-M-hexane + 1,2,4-Tri-M-cyclohexane	0.80 ± 0.75
Ethylbenzene	1.52 ± 1.12
m + p-Xylene	1.79 ± 1.37
Styrene	0.76 ± 0.50
1-Nonene	1.20 ± 0.86
o-xylene	2.05 ± 1.53
n-Nonane	0.91 ± 0.82
Isopropylbenzene	0.42 ± 0.36
n-Probylbenzene	1.30 ± 0.91
3-Ethyltoluene	1.67 ± 1.47
4-Ethyltoluene	1.60 ± 1.20
1,3,5-Tri-M-benzene	1.82 ± 1.49
2-Ethyltoluene	1.50 ± 2.19
1,2,4-Tri-M-benzene	1.56 ± 2.25
n-Decane	0.83 ± 0.97
iso-butylbenzene	1.10 ± 1.11
1,2-Di − Cl-Benzene	0.81 ± 1.00

can be classified into three groups. The first group is the VOCs that have WD/WE ratios are between 1.5 and 2.0. This group includes compounds such as o-xylene, m, p-xylene 1,3,5-Tri-M-benzene, benzene, ethybenzene and 1,2,4-Tri-M-benzene. These are well documented traffic markers. Higher weekday concentrations of these compounds are due to higher number of vehicles on roads in the weekday than the weekend. Filella and Penuelas (2006) and Qin et al. (2007), also explained higher weekday concentrations of the same group of VOCs with the traffic load. The second group includes VOCs such as toluene, m,p-chlorotoluene, 1-nonene, octane and isobutybenzene. These VOCs have comparable concentrations in weekdays and weekends (WD/WE ratio is approximately 1). Toluene, nonen and octan are known solvent markers (Liu et al., 2005; Yuan et al., 2010). Similarity of their WE and WD concentrations can be explained by their evaporative sources. Source strengths of such evaporative sources do not change between WD and WE. The last group consisted of n-nonane, n-decane, 1,2-Di-Cl-benzene, 2,2,5-Tri-M-hexane, styrene and isopropylbenzene whose WD-to-WE ratios are < 1.0. This is an interesting group. These compounds are strongly associated with diesel emissions in PMF results, which will be discussed later in the manuscript. Higher WE concentrations of these compounds can be explained by the restricted entrance of heavy duty vehicles to the city during weekdays. Although a number of light-duty vehicles on the roads are higher during weekdays, there is higher number of heavy duty vehicles in the

city at the weekend, because their entry to the city is limited to certain hours in the morning and at night during weekdays. This may reflect in higher concentrations of VOCs associated with diesel emissions at the weekend.

3.2. VOC ratios

Since different organic compounds have different sources and reactivities in the atmosphere, some of their ratios are frequently used to get preliminary information on their sources and transport. Two frequently used ratios are toluene-to-benzene ratio (T/B) and m,p-xylene-to-ethylbenzene (X/E) ratio. Toluene-to-benzene concentration ratio provides information on the relative abundances of traffic and non-traffic sources (Suthawaree et al., 2012). Benzene is a marker of vehicle exhaust (Hong et al., 2006). Although light duty motor vehicles are also an important source for toluene, it is also emitted to atmosphere from other sources, particularly from evaporation of solvents used in ink, paint etc. (Yuan et al., 2010). Benzene, on the other hand, due to its mutagenic nature is not used in solvent formulations (Zalel and Broday, 2008). Therefore, the T/B ratio is used as an indicator of the non-traffic source contributions to measured VOC concentrations (Lee et al., 2002; Elbir et al., 2007). Low T/B ratios (<2.0) are used as indicator of strong influence of motor vehicle emissions on measured VOC concentrations, whereas ratios > 2.0 are suggested to indicate contribution from non-traffic sources (particularly solvent evaporation) (Gelencsér et al., 1997; Heeb et al., 2000; Oguz et al., 2003; Elbir et al., 2007).

Average T/B ratio in this study is 4.3 ± 3.4, indicating contribution of non-vehicle sources on measured concentrations of VOCs. However, T/B ratio changes seasonally. Variation of T/B ratio in the course of this study is depicted in Fig. 5a. Toluene-to-benzene ratio in Ankara is approximately 2 at the beginning of the study in January and gradually increases towards summer season. The winter average ratio is 2.7 ± 1.2 and summer average ratio is 5.8 ± 4.1. In an earlier study at Ankara T/B ratio was found to be 1.9, 2.1 and 2.2 at a gas station, tunnel and in an underground garage, respectively (Kuntasal, 2005). When compared with these reported values, low T/B ratios measured in this study during winter season indicate that traffic is the main source for VOC concentrations at the university during winter months. However, solvent evaporation becomes a significant source in summer with increasing temperatures and with reduced traffic when the semester ends. These two factors result in the higher T/B ratios in the summer season.

Since m,p-xylene and ethylbenzene have different reactivities against OH radical, m,p-xylene-to-ethylbenzene ratio (X/E ratio) is used as indicator for the age of the VOCs in the atmosphere (Elbir et al., 2007; Guo et al., 2004a, 2004b). The ratio becomes smaller as the VOCs get older in the atmosphere, because m,p-xylene is more reactive than ethylbenzene. The atmospheric life times of the m,p-xylene and ethylbenzene are 3 h and 8 h, respectively. This means that as the air mass containing VOCs travels, m,p-xylene will react more rapidly than the ethylbenzene and at the specific distance from the source the ratio will decrease. Kuntasal (2005) found X/E ratio as 3.8, 3.8 and 4.4 in fresh emissions at a gas station, in a tunnel and in an underground garage, respectively. The variation of the X/E ratio in the course of
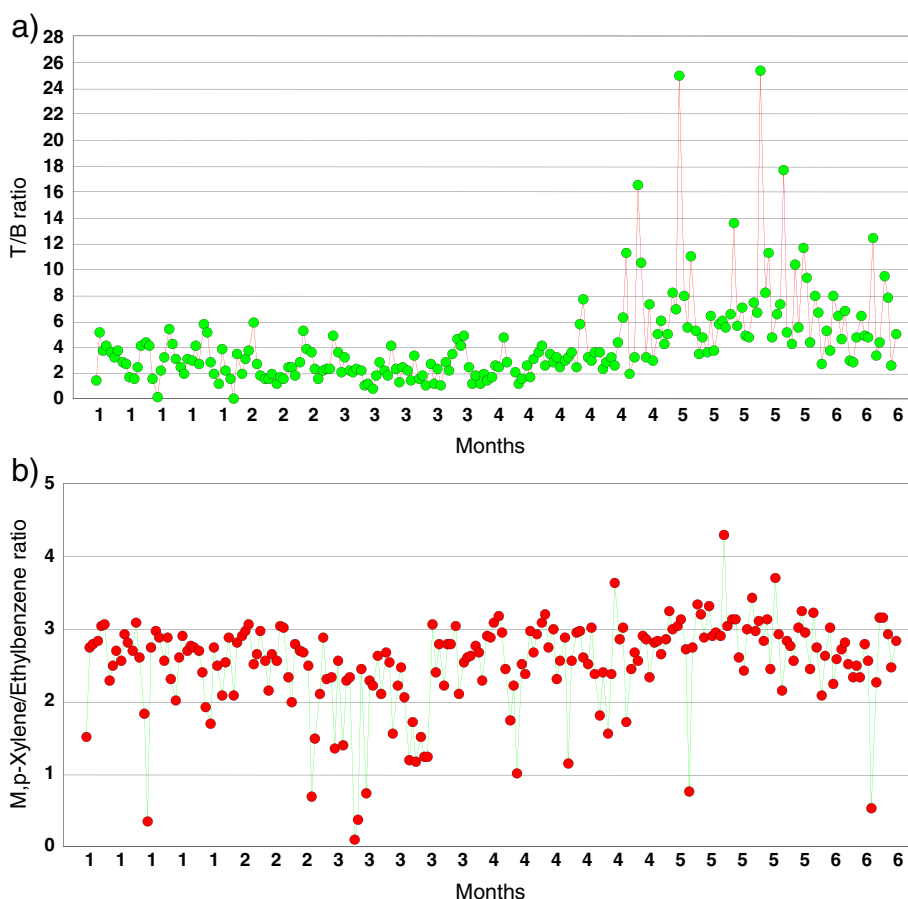
Fig. 5. Variations of toluene-to-benzene and m,p-xylene-to-ethylbenzene ratios during the course of the study.

this study is depicted in Fig. 5b. The average ratio is 2.5 ± 0.6 and it does not show a significant difference between the summer and winter season, indicating that a significant fraction of VOCs measured in the university campus is not emitted in situ.

The wind rose prepared using hourly meteorological data from the nearest Met station is depicted in Fig. 1 Prevailing wind direction is NNE. Wind sectors SSW and N are the other sectors were winds blow frequently. City center is located between north and east relative to the sampling point in the campus. In an earlier study Genc et al. (2010) demonstrated that districts such as Kızılay, Dikmen and Çankaya are the main areas affecting air quality in the METU campus. These are also the sectors from where winds blow most frequently. Consequently these districts are likely source areas for VOCs measured in the campus.

3.3. PMF results

Sources contributing to observed concentrations of VOCs were estimated using positive matrix factorization (PMF), which is a multivariate statistical tool, frequently used in source apportionment studies (Pandolfi et al., 2011). The software PMF 2 was used in Robust mode (Kuntasal, 2005; Richard et al., 2011). In this study error model developed by Polissar et al., (1998) was used to generate uncertainties associated with data and values below detection limit were

replaced by half of the detection limit values and their uncertainties were set at 5/6 of the detection limit values. Missing values were replaced by the geometric mean of the measured values and their uncertainties were set as four times the geometric mean values.

Parameters F peak, seed and alpha were optimized to obtain closest Q calculated to the theoretical Q value. Scaled residuals for most of the VOCs were symmetrically distributed and had values ± 2. To obtain global minimum, pseudo-random seeds are used. Alpha is the parameter that defines the outliers. F-peak on the other hand is a parameter to minimize rotational ambiguity and to generate more realistic solutions (Paatero et al., 2002). The values of the parameters F-peak, seed and alpha, used in this work were 0.6, 6 and 4.0 for, respectively.

Factor loadings and explained variances of VOCs are depicted in Figs. 6 and 7, respectively. Factor 1 is enriched with light VOCs. 20%–60% of the variances of light VOCs are explained with this factor. Factor 1 is a typical gasoline exhaust factor. The presence of well documented gasoline exhaust markers, like benzene, ethyl benzene and xylenes (Elbir et al., 2007; Suthawaree et al., 2012) in this factor further confirms that factor 1 represents gasoline exhaust source. Moreover, good agreement between compositions of light duty vehicle exhaust profiles (USEPA SPECIATE profiles 2536 and 2538) and Factor 1 loadings also suggests that this factor represent gasoline powered vehicle emissions.
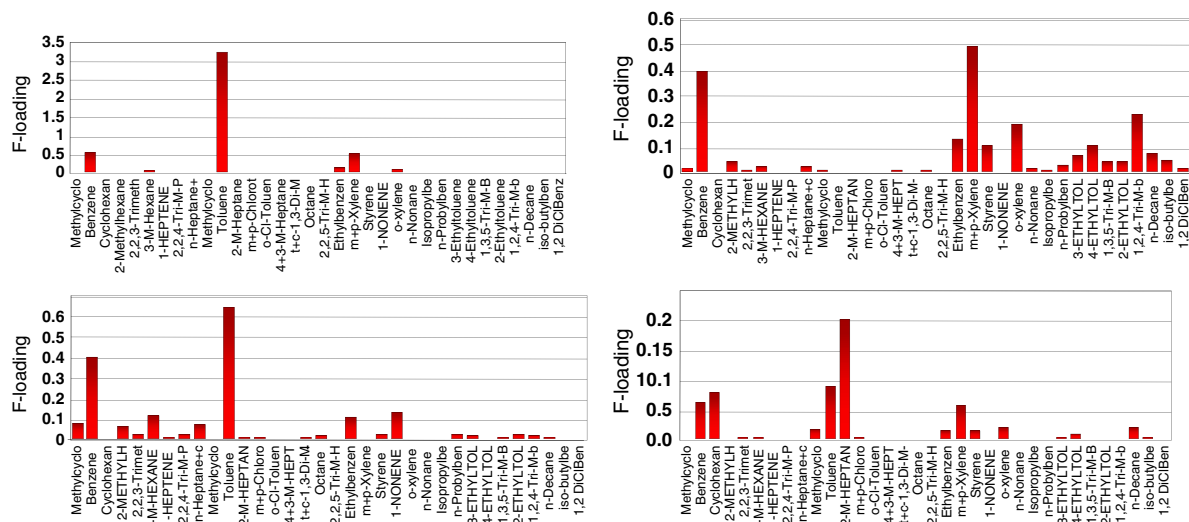
Fig. 6. Factor loadings.

Factor 2 is a mixed factor that explained significant fractions of variances light hydrocarbons, particularly toluene and some of the heavy hydrocarbons like 1-nonene. Toluene, in addition to traffic, is a good marker for solvent originated an industrial source (Yuan et al., 2010; Suthawaree et al., 2012). Furthermore, the composition of Factor 2 loadings were compared with compositions of two solvent evaporation profiles obtained from EPA, SPECIATE data-base and a linear regression test indicated that composition of factor 2 is similar to SPECIATE profiles 1003 and 1018, with 95% and 99% confidence, respectively. Based on these arguments Factor 2 was identified as "solvent evaporation".

Factor 3 explains large fractions of variances of heavy hydrocarbons. It is a typical diesel factor. Although heavy
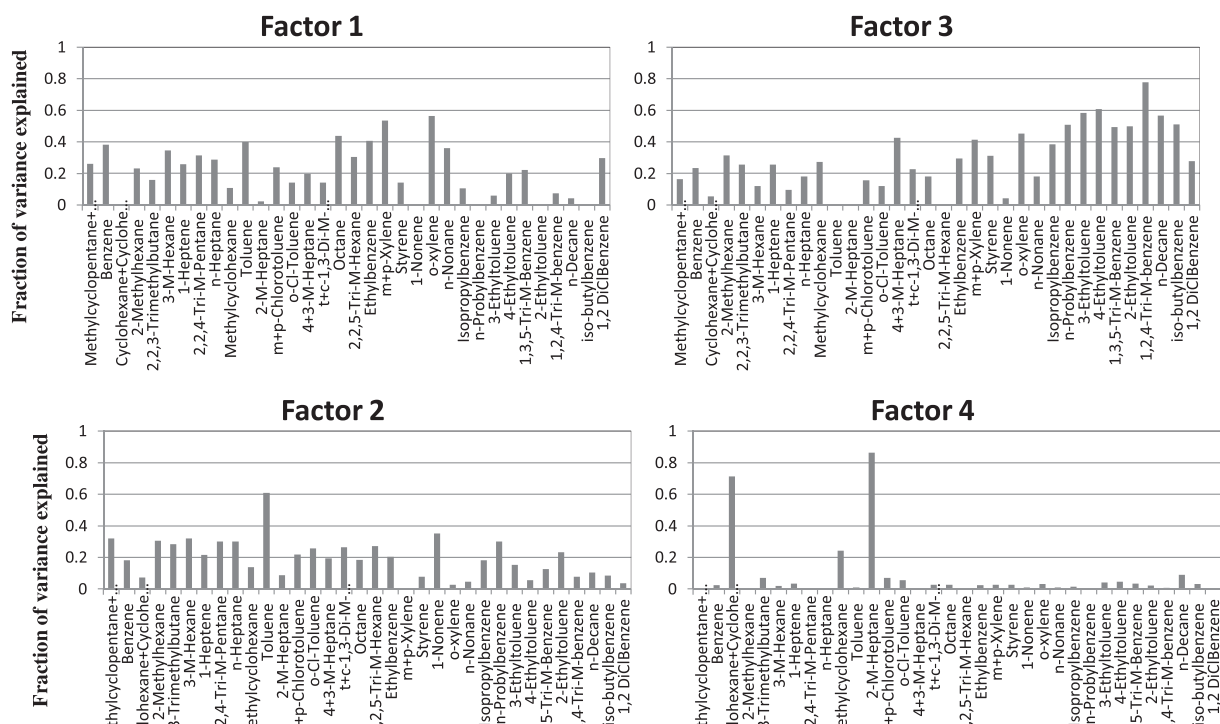

Fig. 7. Explained variances.

hydrocarbons are also emitted from certain industries and from asphalt production or application (Liu et al., 2005; Yuan et al., 2010), none of these activities are significant sources in this study. There is no industrial activity around university that can emit heavy VOCs to atmosphere. Also no asphalting activity occurred during the study. Consequently, most likely source for Factor 3 is emissions from diesel traffic. Composition of Factor 3 profile was compared with two diesel emission profiles obtained from SPECIATE data-base (profiles 2520 and 2526). Linear-regression fit indicated that the composition of Factor 3 can be explained with these two profiles with >95% confidence. Based on these discussions factor 3 is identified as diesel emission factor.

Factor 4 explains large fractions of variances of specific compounds such as cyclohexane, 2-methylheptane, and methylcyclohexane. These compounds are solvents commonly used in laboratories in Environmental Engineering Department. Furthermore, high concentrations of these compounds were found in indoor passive sampling studies performed in Environmental Engineering Department (Yurdakul, unpublished data) and at Hacettepe University, Chemical Engineering Department (Akal, unpublished data). Therefore, this factor represents emissions from laboratories in the vicinity of the sampling point.

Correlation between measured total VOC concentration and total VOC concentrations predicted in the PMF model are depicted in Fig. 8. Excellent correlation between observed and predicted $\sum$VOC concentrations signifies the success of the PMF model used in explaining sources of VOCs in Ankara.

Contributions of each of the four factors to total VOC concentrations measured in this study are given in Fig. 9. In addition to average contributions of four factors to total VOC concentrations, contributions at different periods of the year and contributions to light and heavy hydrocarbons are separately calculated and depicted in the same figure. On the average, 48% of the measured average $\sum$VOC concentrations are accounted for by light duty vehicle exhaust emissions. This is not surprising, because there is very limited industrial activity in Ankara and traffic is the most important source for most of the VOCs.

Contribution of emissions from solvent evaporation is 28%. Contributions of diesel traffic and local laboratory emissions to $\sum$VOC concentrations are 21% and 3%, respectively.

Source contributions at winter and summer are given in Fig. 9b and c, respectively. Winter in this manuscript refers to January and February and summer refers to March, April and May. Although the winter period corresponds to true winter months, summer refers to spring season rather than true summer. Contribution of gasoline exhaust emissions (factor 1) to total VOC concentrations is not significantly different between summer and winter periods. Slightly higher contributions in winter can be explained by variations in meteorology, particularly the mixing height. The most substantial seasonal variation, in source contributions is observed for solvent evaporative emissions (factor 2). Contribution of this source on total VOC concentrations in winter is approximately 14%, but increases to 40% in summer. This difference between winter and summer seasons signify the importance of temperature change on evaporation from surfaces. Since the summer in this study includes the March–May period, contribution of solvent evaporation to total VOC concentrations is expected to be even higher in July and August, when temperatures are higher.

Contribution of diesel emissions (factor 3) to total VOC concentrations is decreased from 28% in winter to 16% in summer. The magnitude of this decrease between summer and winter is comparable with the decrease observed in gasoline exhaust emissions (factor 1) and is probably due to seasonal variations in meteorology. Contribution of local laboratory source (factor 4) does not show any seasonal variation.

Contributions of these four sources on concentrations of light and heavy VOCs are depicted in Fig. 9d and e, respectively. The division between light and heavy hydrocarbons was based on association of VOCs with diesel source in our previous studies. Heavy VOCs are the ones that are heavier than o-xylene. In other words o-xylene was the last light VOC in our list. The highest contribution to light VOCs is from gasoline exhaust (factor 1), followed by contribution from solvent evaporation (factor 2), diesel emissions (factor 3) and local laboratory source (factor 4).
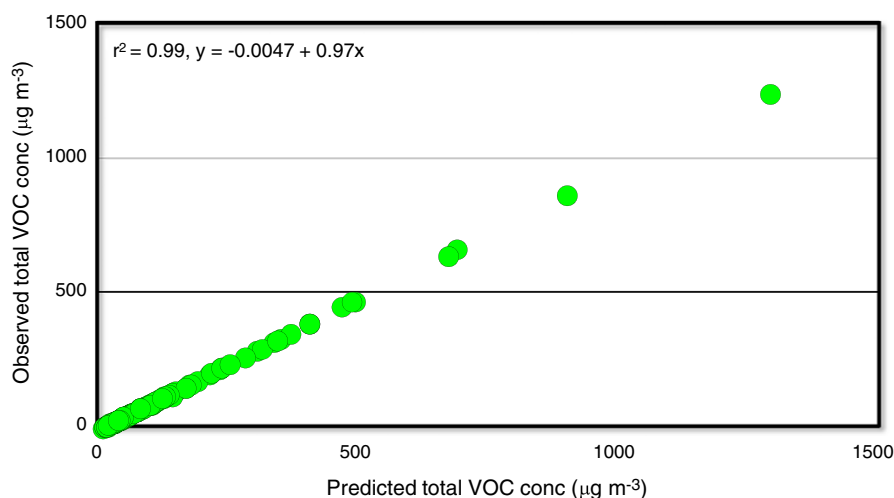

Fig. 8. Agreement between measured total VOC concentration and total VOC concentrations predicted in PMF.
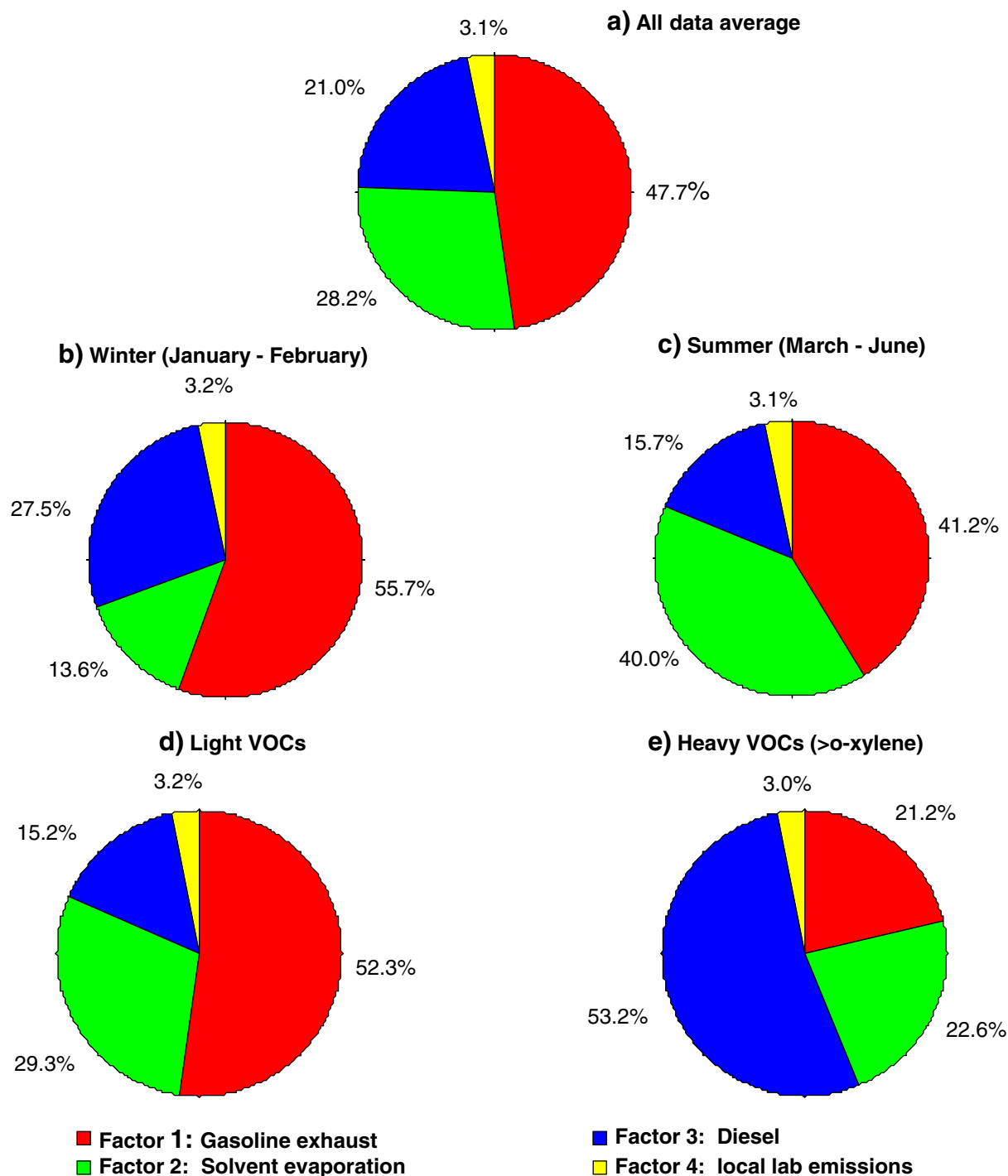
Fig. 9. Contribution of sources on measured VOC concentrations. (a) Average of all data, (b) winter season (January and February), (c) summer (March–June), (d) light hydrocarbons (molecular weight up to o-xylene) and (e) heavy VOCs (molecular weight > o-xylene).

The highest contribution on total heavy VOC concentration is from diesel source, which accounted for 53% of total heavy VOC concentration. Both solvent evaporation source and gasoline exhaust sources have approximately 20% contribution to heavy VOC concentrations.

4. Conclusion

The measured average VOC concentrations in the METU campus were found to be lower than data reported for other cities in the literature. This is due to smaller number of cars in

traffic compared to the number of vehicles in other crowded cities of the world and partly due to location of the station.

Summer–winter, weekday–weekend and day–night comparisons demonstrated that VOCs can be grouped under two classes based on their temporal behavior. The first group contains BTX compounds except for toluene and other VOCs originating from the traffic. Concentrations of the VOCs in this group were found to be higher in winter (compared to summer), during weekdays (compared to weekend) and during day-time (compared to night). The second group includes, VOCs which did not show a statistically significant difference between their summer and winter, weekday-weekend and day-night concentrations. This non-traffic pattern suggested that these VOCs were emitted from the evaporative sources in Ankara.

The PMF revealed 4 sources that contribute to VOC concentrations measured in the METU campus. These four sources were gasoline evaporation, exhaust emissions, solvent evaporation, diesel emissions and emissions from laboratories in the immediate vicinity of the sampling point. Gasoline exhaust had the highest contribution to $\sum$ VOCs. On the average it accounts for approximately 50% of the measured $\sum$ VOC concentrations. This source has dominating influence on concentrations of light VOCs, but its contribution to heavy VOCs is only 20%. Evaporative emissions from solvents and diesel emissions account for 20% of the measured VOC concentrations, on the average. However, contribution of solvent evaporation to total VOC concentrations increases to 40% in March and April. Contribution of diesel source is high on concentrations of heavy VOCs (53%), but its contribution to light VOCs is only 15%.

Concentrations of VOCs measured in this study indicated that the exposure of METU students to high VOC levels is not a likely situation. Three factors contribute to this conclusion. (1) The traffic source is far from the part of the university where students reside and (2) local sources within the university have insignificant contribution to measured VOC levels. Although a laboratory source is identified in the PMF exercise, its contribution to measured outdoor VOC levels is not very high. A passive sampling study within the buildings is needed, particularly in departments where laboratory activity is extensive, like Chemistry department.

Acknowledgements

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