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POTENTIAL SOURCES AND MEASURED AMBIENT CONCENTRATIONS OF VOCs IN THE ATMOSPHERE OF BALIKESIR

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Highlights

• Sources and spatial distribution of VOCs were investigated in a mid-sized city
• Agricultural activities were found to be important VOC source for the city
• High VOC levels detected due to recreational and agricultural activities

Resumen

La evaluación de compuestos orgánicos volátiles (COV) se ha convertido en un importante campo de interés en la contaminación atmosférica. Este estudio cuantifica y caracteriza los niveles ambientales y la distribución espacial de los COV en las zonas urbanas y rurales de la ciudad de Balikesir. Para estas evaluaciones, el muestreo pasivo de COV se realizó en aproximadamente 50 lugares en y alrededor de la ciudad de Balikesir y se analizó con el sistema GC-FID y 25 COV fueron monitoreados regularmente. Los períodos de muestreo fueron en marzo de 2010 y en agosto de 2010, que se llevaron a cabo durante períodos de 7 días.

En el estudio, se encontró que las concentraciones medias de $\Sigma$COV eran de 67 μg m$^{-3}$ y 51 μg m$^{-3}$ para las temporadas de invierno y verano, respectivamente. Las concentraciones medias de benceno, tolueno, etilbenceno, m,p-xileno y o-xileno fueron 2.6, 11, 1.30, 1.80 y 0.73 μg m$^{-3}$, respectivamente. Aunque hubo algunos cambios entre las concentraciones de grupos de COV entre las campañas de verano e invierno, las diferencias no fueron dramáticas. Las proporciones de invierno a verano de los compuestos objetivo variaron de 0.2 (1,2,4 trimetilbenceno) a 9 (hexano).

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La mayoría de los compuestos objetivo tienen concentraciones más altas en invierno. Solo unos pocos COV, incluidos el n-propilbenceno, el 1,2,4-trimetilbenceno, el 1-undeceno y el 1,2,4-triclorobenceno tienen concentraciones más altas en verano. La distribución espacial de COV demostró que las carreteras son puntos calientes para las concentraciones de COV medidas. Las fuentes que contribuyen a la carga total de VOC en la atmósfera de Balikesir son la planta de tratamiento de agua potable, las emisiones de solventes industriales de las aplicaciones de pesticidas e insecticidas en la agricultura y las emisiones del tráfico.

**Abstract**

The assessment of volatile organic compounds (VOCs) has become an important field of interest in atmospheric pollution. This study quantifies and characterizes the ambient levels and spatial distribution of VOCs in urban and rural areas of Balikesir city, Turkey. For these assessments, passive sampling of VOCs performed at approximately 50 locations in and around the city of Balikesir and analyzed with GC-FID system and 25 VOCs were regularly monitored. The sampling periods were in March of 2010 and in August of 2010 which were held for 7-day periods.

In the study, mean \( \sum \) VOC concentrations were found to be as high 67 µg m\(^{-3}\) and 51 µg m\(^{-3}\) for the winter and summer seasons, respectively. Median concentrations of benzene, toluene, ethylbenzene, m,p-xylene and o-xylene were 2.6, 11, 1.30, 1.80 and 0.73 µg m\(^{-3}\), respectively. Although there were some changes between concentrations of VOC groups between the summer and winter campaigns, differences were not dramatic. Winter-to-summer ratios of the target compounds ranged from 0.2 (1,2,4-trimethylbenzene) to 9 (hexane). Most of the target compounds have higher concentrations in winter. Only few VOCs, including n-propylbenzene, 1,2,4- trimethylbenzene, 1-undecene and 1,2,4- trichlorobenzene have higher concentrations in summer. Spatial distribution of VOCs demonstrated that the roads are hot spots for measured VOC concentrations. Drinking water treatment plant, industrial solvent emissions from pesticide and insecticide applications in agriculture and emissions from traffic were the sources that contribute to total VOC load in the Balikesir atmosphere.

**Keywords:** Source Apportionment, VOCs, PMF, Urban atmosphere
1. Introduction

VOCs have become significant pollutants in the urban atmosphere due to effects both on human health and atmospheric chemistry (Kim et al. 2012). Furthermore, VOC levels were also found to be strongly related with photochemical smog and ground level ozone concentrations (Guo, et al. 2011). Therefore, necessary efforts should be made to identify the both levels and sources of VOCs in urban atmosphere and obligatory precautions against VOCs should be taken.

Like many other developing countries, air pollution is considered as a serious problem in many cities in Turkey. Although the Ministry of Environment and Forestry has established air quality stations which monitor criteria pollutants (i.e. PM, CO, NO\textsubscript{x}, SO\textsubscript{2} and O\textsubscript{3}) in 81 provinces of Turkey, there are only a small number of studies about organic compounds conducted in Turkey (Muezzinoglu et al., 2001; Cetin et al., 2003; Elbir et al., 2007; Im et al., 2008; Özden et al., 2008; Pekey and Arslanbaş, 2008; Civan et al., 2011; Demir et al., 2011; Pekey and Yılmaz, 2011; Kara and Aydın, 2013; Kuntasal et al., 2013; Demirel et al., 2014; Öztürk et al., 2015; Artun et al. 2017; Yurdakul et al., 2017). Furthermore, these studies mainly focused on highly populated and industrialized cities and they are so limited. Therefore, the levels, sources, seasonal and diurnal variations and ozone formation potentials of the VOCs in smaller cities of Turkey are still lacking.

The main purpose of the study is to investigate the ambient VOC levels in Balikesir both in rural areas including a dam where the city’s drinking water is supplied and urban areas in different seasons, to find out sources of these pollutants and to understand the factors affecting the spatial distribution of VOCs.

2. Materials and Methods

2.1. Study Site

Balikesir is a mid-sized city, which is located in the north-western part of Turkey (39.55 N 27.73 E). The location of the city is depicted in Figure 1. It has a population of 1,150,000. Approximately
700,000 of the population are urbanized. The city is very close to popular summer resort areas in Turkey. The highway that connects Istanbul to Izmir, which has heavy traffic, particularly during summer, passes through Balikesir.

Although there are some small scale industrial activities, such as metal casting and production of electrical utensils, Balikesir cannot be considered as a heavily industrialized city. The main income is from agriculture and agriculture-based industries. Because of its geographical location, Balikesir has a climate that ranges between Mediterranean climate with very hot summers and relatively mild winters and the climate of the Anatolian plateau with very cold winters and mild summer conditions. Annual precipitation is 545 mm and annual average temperature is 14.5 °C (Tağıl, 2007).

Locations for sampling stations were selected using a grid system, which covers urban and rural areas. The latter includes the İkizcetepeler reservoir, which provides drinking water for the city. At first, stations were situated at the corners of the grid system, but then, by visual inspection, stations at some of the grid corners were moved to more important locations to increase density of stations at the urban area, industrial area and around the reservoir. Final positions of sampling locations are given in Figure 1. These 50 stations were grouped as residential, traffic and background. There are 14 “Residential” stations, which are located in the urban area, but not very close to major roads. “Traffic” stations are the ones that are in the immediate vicinity of the roads in the city and around İzmir highway outside the city. There were 13 traffic stations. Five of these stations were at the urban area and 8 were in the proximity of the İzmir highway. “Background” stations included 23 stations that were located outside the city. Eight of these stations were situated around İkizcetepeler Dam Lake. The remaining 15 background stations were located between the city and the lake.

2.2 Sampling

Samples were collected using stainless steel passive sampling tubes with 0.5 cm internal diameter, 9 cm long (Gradko ltd.), which were filled with 60/80 mesh Tenax TA adsorbent (Supelco). Sampling tubes were conditioned in a conditioning oven at 300 °C for four hours. During the conditioning, high purity nitrogen was passed through the tubes, at a flowrate of 100 ml/min.
Extensive measures were taken to avoid contamination during storage of tubes before sampling. Both ends of tubes were sealed using stainless steel screw caps and tubes were stored in sealed test tubes containing silica-gel and activated charcoal. Test tubes containing sampling tubes were stored at -10°C until sampling. At the start of the sampling, the top screw cap was replaced with a diffusion cap. Passive sampling tubes were exposed for one week, because our earlier studies demonstrated that sample losses start to be significant for exposures longer than one week (Civan et al., 2011). Two sampling campaigns were conducted; first one between March 10 – 17, 2010 and the second one between August 13 – 20, 2010 to cover both winter and summer conditions. During the study, 103 tubes were deployed in total (50 tubes for the winter and 53 tubes for the summer sampling) and 100 of them collected back. Temperature varied between 2°C and 14°C during winter campaign, with an average value of 8°C. There was no precipitation during this time. Minimum and maximum temperatures were 19°C and 33°C during the summer campaign with an average value of 25°C. No precipitation was recorded during the summer campaign.

2.3 Analysis of the Collected Samples

Passive samples were analyzed using a Gas Chromatography equipped with a Flame Ionization Detector (FID) (HP – Agilent, Technologies Inc., USA, model 6990). Samples were introduced to GC-FID system using a thermal-desorber unit (Markes International Limited, UK), which was equipped with a Deans Switch. Compounds lighter than hexane go through the alumina plot capillary column (J&W, Polo Alto, CA, USA) and compounds with molecular weights higher than that of hexane were directed to the DB1 column (J&W, Polo Alto, CA, USA). The system works by desorbing analytes at approximately 300°C and collecting them in a cold trap at -15°C. Operating parameters of the GC-FID system, such as, desorption temperature, desorption time, cold trap temperature and time, flow rates through columns and column temperatures were optimized before the campaigns.

External standard method was used for quantification of target compounds and system was calibrated with a standard gas mixture containing 148 VOCs with carbon numbers between 2 and 12, which was obtained from the Environment Technology Center, Environment Canada (Ottawa, Canada). Concentrations of the compounds in the standard mixture were varying between 2 and
Although there were 148 VOCs in the calibration mixture, 25 VOCs were regularly detected in collected samples. Only a small group of VOCs were detected in passive samples, partly because concentrations of some target VOCs were low in the atmosphere, but more importantly, because VOCs with carbon number <5 were not efficiently collected by the adsorbent used in samplers (Tenax). Retention time of VOCs was identified both by using homemade mixtures of smaller number of VOCs, such as aromatics, olefins, paraffin and BTEX liquid mixtures, and standard gas mixture.

The stability of the calibration curve was checked at every analysis day by injecting one of the midpoint standards. The precision of the measurements was monitored by replicate measurements of low-level standards. Relative standard deviations for all VOCs measured in this study were < 10%.

In addition to precision tests and calibration checks, laboratory and field blanks and desorption efficiency were routinely monitored as a part of the QA/QC program. Breakthrough test was also performed at the beginning of the study. Furthermore, the relative standard deviation among the co-located 7 passive sampling tubes was always found to be less than 5% for most of the target compounds.

The field blank tubes were filled and conditioned with the same procedures used in filling and conditioning sampling tubes. Masses of VOCs measured in all field blanks were < 10% of average masses of VOCs collected on sample tubes. For example, 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 89% to 100% with an average value of 96%.

Method detection limit (MDL) for each VOC was the concentration corresponding to 3σ obtained from seven replicate measurements of a blank tube. Detection limits of individual VOCs varied between 0.04 µg m\(^{-3}\) for naphthalene and 0.26 µg m\(^{-3}\) for 1,2,4-trimethylbenzene. 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. Detection limits and performance parameters of the 25 target VOCs are given in Table 1.
3. Results and Discussion

3.1 Data

A statistical summary of the 25 target VOCs, which were measured in about > 70% of the samples are given in Table 2. As in most studies, toluene is the most abundant VOC in the atmosphere of Balikesir. Its concentration varied between 86 µg m\(^{-3}\), which was measured at the urban center and 1.4 µg m\(^{-3}\) at a background station.

Approximately 46% of ΣVOC concentration was accounted for by aromatics and 33%, 12% and 10% of total VOC concentration were accounted for by halogenated compounds, alkanes and alkenes, respectively, in the summer season. In the winter campaign, contributions of aromatics, halogenated compounds, alkanes and alkenes were 53%, 18%, 17% and 11%, respectively. Although there were some changes between concentrations of VOC groups between the summer and winter campaigns, differences were not dramatic. The only exception to this was observed in the summer and winter concentrations of halogenated compounds. Both percent contribution of halogenated VOCs to VOC profile and their absolute concentrations increased by approximately a factor of 2 in the summer campaign. This seasonal variation is not entirely surprising, because halogenated hydrocarbons are widely used as degreaser and solvent in industry (Toyoda et al., 2016) and high concentrations of halogenated hydrocarbons observed in the summer campaign were probably due to enhanced evaporation from their sources at higher ambient temperatures.

3.2 Comparison with the literature

Concentrations of BTEX compounds measured in this work and in passive sampling campaigns in other cities in Turkey and Europe are given in Table 3. Comparison was limited to BTEX compounds, because VOCs other than BTEX are not reported as frequently in the literature.

BTEX concentrations measured in this study are comparable to the corresponding concentrations measured in European cities, but lower than average concentrations reported for other Turkish cities. In most VOC studies average concentrations strongly depend on distances of sampling
stations to VOC sources, particularly to roads. Since average BTEX concentrations that are given in Table 3 are all generated from passive sampling campaigns and include data from 9 – 50 different locations in those cities, average concentrations reported for studies are expected to be representative for cities. Similarities in concentrations measured in Turkish cities with those reported in various European and North American cities were also reported in earlier studies with active sampling (Civan et al., 2011; Kuntasal et al., 2013; Civan et al., 2015; Pekey et al., 2015; Yurdakul et al., 2017). Lower concentrations of BTEX compounds measured in this work, than corresponding concentrations reported for other Turkish cities like Ankara and Bursa, is due to fairly large number of background stations used in this work.

3.3 Seasonal Variations of VOCs

As mentioned above, passive sampling campaigns in this study were performed in March and August. The March campaign was considered as winter while the August campaign was considered as summer, because of two reasons; (1) in most Turkish cities the heating season officially ends on 15 April and starts on 15 October. The use of heating units is not allowed between these two dates. This was a rule stemming from the 70s and 80s when most cities in the country suffered from very heavy air pollution from coal combustion due to space heating. (2) In most parts of Turkey 20% of the annual rainfall occurs between April and October and 80% occurs between October and April. With such distribution of precipitation and timing of heating emissions, selection of the period between April and October as summer and the rest of the year as winter was appropriate to highlight the role of precipitation and heating-related emissions on measured concentrations of VOCs. Mean $\Sigma$VOC concentrations were 67 $\mu$g $m^{-3}$ and 51 $\mu$g $m^{-3}$ for the winter and summer seasons, respectively. Since Balikesir is not an industrial city, light and heavy-duty traffic is the dominating source for VOCs. In cities in central Anatolia, traffic emissions can be lower in summer due to migration of the population to coastal areas. In Ankara, for example, the number of vehicles on the roads decreases by 30% in June, July and August (Kuntasal et al. 2013). However; since Balikesir is on the highway that connect the Marmara region (which includes Istanbul with a population of approximately 20 million), traffic related emissions are expected to increase during summer. Thus, temporal variability in traffic related emissions cannot explain observed high VOC concentrations in winter months. Another reason can be more extensive photochemical destruction.
of VOCs in the summer (Kuntasal, 2005). However, it should be noted that some of the VOCs, particularly the ones that are intermediates in oxidation mechanism, are also produced faster in summer. The most likely source for observed high winter concentrations is the seasonal variation in meteorology, particularly variations in mixing height. Mixing height depicts a well-defined seasonal variation, with approximately a factor of two-to-three higher values in summer (Civan, 2010). Since mixing height defines the volume in which pollutants are dispersed, higher mixing height results in a larger volume, which in turn results in dilution of VOCs and lower concentrations in summer. In addition to mixing height, wind speed, wind direction, temperature and atmospheric stability also control dispersion and reactivity of the organics in the atmosphere (Jones et al., 1998). In this study, during both sampling campaigns, northerly winds were frequently seen. The prevailing wind directions for the first and second sampling campaigns were N (52%) and N (60%), respectively. Therefore, northerly winds were found to be very effective for the ventilation of the Balikesir. Average wind speeds for the first and second campaigns were 2.33 m s\(^{-1}\) and 3.85 m s\(^{-1}\), respectively. Lower concentrations with increasing wind speed are frequently observed (Wang et al., 2009; Ojiodu and Uwadia, 2013). Accordingly, higher wind speeds during August produced stronger ventilation in Balikesir and decreased the concentrations of target VOCs as reported for other cities (Filella and Penuelas, 2006).

Different winter-to-summer concentration ratios of VOCs also indicate that meteorology is not the only factor. Winter-to-summer ratios of the measured organics vary between 9 for hexane and 0.2 for 1,2,4-trimethylbenzene (Figure 2). Most of the 25 target VOCs measured have higher concentrations in winter. Only few VOCs, including n-propylbenzene, 1,2,4- trimethylbenzene, 1-undecene and 1,2,4- trichlorobenzene have higher concentrations in summer. VOCs with winter-to-summer ratios close to or smaller than unity are the ones with higher source strength in summer. A likely source with higher source strength in summer is solvent use, because many VOCs are used as solvents or in the production of solvents. Enhanced evaporation of solvents in summer reduces the winter-to-summer concentration ratios of VOCs, which are at least partly from solvent use.

Toluene to benzene (T/B) and xylene to ethylbenzene (X/E) are widely used in the literature to identify emission sources of organics and photochemical age of the air parcels, respectively (Al-Harbi, 2019). For the traffic emissions, T/B ratio is between 1.5 and 3, however the ratio increases
with contributions from non-traffic sources (Miller et al., 2011). In winter and summer seasons, mean T/B ratios were found to be $3.497\pm 4.357$ and $7.819\pm 9.088$, respectively. Calculated T/B ratios suggest that there were persistent local emissions of toluene. Furthermore, mean T/B ratio in the summer season is a factor of two higher than mean T/B ratio in the winter season. Therefore, there is a significant contribution by non-traffic sources on measured VOC levels in Balikesir during the summer, whereas vehicular emissions are a more important contribution in winter. The calculated mean X/E ratios were $3.351\pm 0.707$ and $2.790\pm 5.151$ for the winter and summer seasons, respectively. Lower ratios of X/E are found at a receptor which is far from the sampling location (Zahng et al., 2008). Therefore, mean X/E ratios indicate fresh emissions from traffic in Balikesir.

### 3.4 Spatial Distribution of VOCs

The spatial distribution of VOC concentrations can provide preliminary information on their sources. Therefore, distribution maps were prepared for measured VOCs to identified sources of VOCs in Balikesir. Maps for BTEX compounds for the summer and winter campaigns are given in Figures 3 and 4, respectively.

Distribution maps were prepared by interpolation, using GIS software (MapInfo, version 10.0). Maps for other VOCs were prepared, but not included in the figures, because their distributions were not very different from those shown for BTEX. The most obvious feature, which was observed in all distribution maps, is higher concentrations of VOCs in stations located within the city. This is not surprising due to strong traffic and non-traffic VOC sources in the urban area. High VOC concentrations were observed at the industrial area, which is located in the northeast corner of the city. Another interesting point in the BTEX distributions shown in Figures 3 and 4 are the high concentrations of BTEX concentrations in stations around the Ikizcetepeler reservoir. Probably due to traffic activity on the Istanbul – Izmir highway, high BTEX concentrations were obtained around the reservoir.

During the experimental design, locations of sampling points were carefully selected, to be in one of three microenvironments, namely residential, traffic and background. Median concentrations of measured VOCs in these three microenvironments were calculated and given in Table 4.
Differentiation of traffic and non-traffic sources is difficult in the city because light-duty traffic activity occurs in all parts of the city, including residential areas. Traffic microenvironment in this study refers to VOC concentrations measured along the Istanbul – Izmir highway. Background stations are the ones that are not in close proximity to the city or the highway. For most of the VOCs highest median concentrations are observed in residential stations, which are followed by traffic stations. The lowest concentrations were measured at background stations for all VOCs without any exception. This pattern is consistent with the VOC distributions depicted in Figures 3 and 4, and demonstrate that urban emissions from traffic and non-traffic sources dominate measured VOC concentrations in the study area.

It is interesting to note that concentrations of a few heavy VOCs, including nonane, 1,2,4 trimethylbenzene and 1,2,4 trichlorobenzene are higher in traffic stations around the highway than in residential stations. Nonane is an accepted tracer for diesel exhaust (Cai et al., 2010; Wu et al., 2016), while 1,2,4-trimethylbenzene is primarily used as a gasoline additive. It is also used as a solvent during other industrial activities such as production of paints, pesticides, cleaners and printing inks (Parao, 2012). The highway that connects Istanbul and Izmir has a dense activity of both heavy (trucks and buses) and light-duty vehicles. Since heavy duty vehicles have limited access to roads in the city, higher concentrations of VOCs emitted from diesel engines are expected at the sampling points around the highway. Industrial or fossil fuel combustions are the main sources of 1,2,4-trichlorobenzene in the atmosphere (Qadoumi, 2016). On the other hand, 1,2,4-trichlorobenzene is also used as herbicide intermediate and insecticide (Ramamoorthy and Ramamoorthy, 1997; Sullivan and Krieger, 2001). Probably, due to agricultural activities around the Istanbul-Izmir highway, high 1,2,4-trichlorobenzene concentrations were detected during the study. VOCs other than nonane, 1-decene, 1,2,4 trimethylbenzene and 1,2,4 trichlorobenzene, are also emitted from diesel or gasoline exhaust, but their non-traffic sources at the urban area dominates resulting in higher concentrations in the residential group.

3.5 PMF Results

Positive Matrix Factorization (EPA PMF v.5.0) was applied to identify the possible sources of measured VOC concentrations in Balikesir. Methodology developed by Pollisar et al., (2001) was
used to generate uncertainties of each datum. Briefly, when a data point is above the detection limit concentration value, it is directly used and its uncertainty is set equal to the summation of the detection limit for each compound and a certain ratio of concentration of that compound. This ratio was selected as a 0.05 for this study. In the study, the data below the detection limit were replaced with half of the detection limit and their uncertainties were replaced with 5/6 of their detection limits. On the other hand, missing values were replaced with geometric mean of the data and their uncertainties were replaced with 5/6 of the detection limits (Polissar et al. 2001).

To determine the exact number of sources, three main criteria were applied (Zhao et al., 2004). In the first step, numbers of factors where Q values did not change significantly were determined. In the second step, various F-peak values between -2 and +2 were also tried. FPEAK affect autocorrelation between factors. Accordingly, by using different FPEAK values, oblique edges were examined and given that Q value did not change significantly, optimum FPEAK value was selected as -0.1. In the third step, scaled residuals were investigated and more than the 99% of the scaled residuals of the target compounds were found to be within ±2 around the mean value. Finally, interpretability of the retained factor compositions were also investigated (Xie and Berkowitz, 2006). Additionally, 5% extra modeling uncertainty was selected and the models run 20 times with the five factors and all runs were converged. The Q(robust) was within 1.03 % of the Q(true). Therefore, outliers did not significantly affect the Q value. Finally, 5 factors were obtained as a result of the PMF analysis. The factor loadings and fractions of VOC concentrations accounted for by each factor are given in Figures 5 and Figure 6, respectively.

Factor 1 is dominated by bromoform. It accounts for approximately 80% of the measured bromoform concentration. We measured relatively high bromoform concentrations at sampling locations close to the Balikesir drinking water treatment plant. Since bromoform is a marker for water chlorination (Carpenter et al., 2005; Carpenter et al., 2007), factor 1, which accounts for 12.60% of the total VOC concentration was attributed to emissions from the Balikesir water treatment plant.

Factor 2 accounted >80% of the concentration of 1,2,4-trichlorobenzene and about 30% of the concentration of 1-octene, octane, nonane and tert-butylbenzene. Contribution of this factor was
high in agricultural fields both around the lake and the Izmir highway. 1,2,4-trichlorobenzene is used as a herbicide intermediate and insecticide (Ramamoorthy and Ramamoorthy, 1997; Sullivan and Krieger, 2001). Diesel contains nonane and octane (Wang 2014). Therefore, Factor 2 which explains 22.17% of the total VOC load, was identified as herbicide and/or insecticide usage in agricultural activities mixed with diesel exhaust.

Factor 3 explains >50% of the toluene concentration. The factor also accounts for approximately 40% of the n-propylbenzene concentration, >30% of concentrations of ethylbenzene and m,p-xylene. Toluene, ethylbenzene and m,p-xylene which are known as TEX group are good markers for solvent usage, paints and industrial coatings (Yuan et al., 2009; Guo et al., 2011; Zhang et al., 2013; Sarkar et al., 2014). High factor 3 scores were found around a small industrial zone located in the northeastern part of the city. Factor 3, which explains 15.33% of the total VOC concentration, was associated with solvent use related with industrial activities.

Factor 4 was identified as mixed traffic exhaust, because it included both aromatic hydrocarbons including benzene, toluene, ethylbenzene, xylene, naphthalene, which are good markers for light-duty vehicle emissions (Guo et al., 2011; Wu et al., 2016), and heavy alkanes/alkenes, such as n-hexane, methylcyclopentane, 2-methylhexane, 3-methylhexane, methylcyclohexane, nonane, 1,2,3-trimethylbenzene, n-decane, undecane and dodecane, which are indicators for diesel exhaust (Yuan et al., 2009; Wu et al., 2016). Furthermore, the highest factor 4 scores were observed in the city center and around the Balikesir - Izmir highway in the lake area. The factor accounted for approximately 36% of the total VOC concentration.

The last factor, which explained about 14% of the total variance, accounted for >80% of the 3,6-dimethyloctane concentration and >20% of the concentrations of 1-nonane, 3-ethyltoluene and tert-butylbenzene. The highest factor 5 scores were found around roads and at residential areas. We believe that factor 5 represents mixed urban emissions (or urban plume).

4. Conclusion
The ambient levels and spatial distributions of 25 target VOCs were measured in an urban area at 50 stations during two sampling campaigns performed in March and August 2010.

In the study, the most abundant specie was found to be toluene with an average concentration of 15.8 µg m\(^{-3}\) in winter and 6.00 µg m\(^{-3}\) in summer which was measured in 100% of the sampling points. The only other compound found in all the sampling stations was benzene, which had a concentration of 4.50 µg m\(^{-3}\) in winter and 0.79 µg m\(^{-3}\) in summer. The BTEX compounds in addition to 1,2,4- trichlorobenzene were accounted for around 57% of the total amount of VOCs in winter but in summer the ratio decreases to 52%.

To identify the sources of VOCs in the atmosphere of Balikesir, PMF analysis was also performed. Traffic was found to be the most dominant source accounting for 36.22% of the system variance. On the other hand, the contribution of the industrial activities to the total VOC load of the city was also found to be significant (29%). Therefore, it can be concluded that even industrial activities in a small city can be important to the total VOC load of the urban atmosphere. Furthermore, since factors associated with agriculture and traffic have higher scores at sampling points located around the lake, one can argue these sources can have an effect on water quality in the lake. Consequently, the activities (i.e. traffic, agricultural and recreational activities) around the reservoirs should be carefully examined in terms of VOC pollution and necessary precautions should be taken in order to protect water quality.

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Figure captions

Figure 1. Location of the sampling points (the location of the Balikesir is shown on the upper left corner)
Figure 2. W/S ratios of the most abundant 25 compounds
Figure 3. Pollution maps of the BTEX group for the summer season (µg m⁻³)
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Table captions

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Table 4. Median and mean concentrations of measured VOCs at residential, traffic impacted and background stations (µg m⁻³)
Table 1. Detection limits and performance parameters of the 25 target VOCs

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>MDL (µg m$^{-3}$)</th>
<th>Linearity (%)</th>
<th>Precision (%)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-hexane</td>
<td>0.13</td>
<td>0.997</td>
<td>10.77</td>
<td>92</td>
</tr>
<tr>
<td>Methylcyclopentane</td>
<td>0.11</td>
<td>0.996</td>
<td>4.74</td>
<td>90</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.09</td>
<td>0.994</td>
<td>4.05</td>
<td>91</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.13</td>
<td>0.997</td>
<td>7.01</td>
<td>94</td>
</tr>
<tr>
<td>2-methylhexane</td>
<td>0.13</td>
<td>0.990</td>
<td>12.38</td>
<td>96</td>
</tr>
<tr>
<td>3-methylhexane</td>
<td>0.09</td>
<td>0.994</td>
<td>5.16</td>
<td>99</td>
</tr>
<tr>
<td>c-3-heptene</td>
<td>0.13</td>
<td>0.994</td>
<td>3.44</td>
<td>91</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
<td>0.04</td>
<td>0.994</td>
<td>4.69</td>
<td>97</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.24</td>
<td>0.993</td>
<td>4.57</td>
<td>91</td>
</tr>
<tr>
<td>Octane</td>
<td>0.16</td>
<td>0.996</td>
<td>9.74</td>
<td>97</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.16</td>
<td>0.993</td>
<td>5.91</td>
<td>99</td>
</tr>
<tr>
<td>m,p-xylene</td>
<td>0.11</td>
<td>0.992</td>
<td>11.58</td>
<td>91</td>
</tr>
<tr>
<td>Styrene</td>
<td>0.10</td>
<td>0.998</td>
<td>13.18</td>
<td>95</td>
</tr>
<tr>
<td>o-xylene</td>
<td>0.17</td>
<td>0.992</td>
<td>8.07</td>
<td>91</td>
</tr>
<tr>
<td>Nonane</td>
<td>0.04</td>
<td>0.989</td>
<td>11.34</td>
<td>100</td>
</tr>
<tr>
<td>n-propylbenzene</td>
<td>0.09</td>
<td>0.990</td>
<td>6.16</td>
<td>97</td>
</tr>
<tr>
<td>Camphene</td>
<td>0.12</td>
<td>0.997</td>
<td>3.85</td>
<td>93</td>
</tr>
<tr>
<td>1-decene</td>
<td>0.09</td>
<td>0.993</td>
<td>6.77</td>
<td>99</td>
</tr>
<tr>
<td>1,2,4-trimethylbenzene</td>
<td>0.26</td>
<td>0.992</td>
<td>7.39</td>
<td>100</td>
</tr>
<tr>
<td>Benzylchloride</td>
<td>0.21</td>
<td>0.993</td>
<td>4.95</td>
<td>91</td>
</tr>
<tr>
<td>n-decane</td>
<td>0.13</td>
<td>0.990</td>
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<tr>
<td>1,2,3-trimethylbenzene</td>
<td>0.13</td>
<td>0.990</td>
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<td>89</td>
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<tr>
<td>1-undecane</td>
<td>0.09</td>
<td>0.991</td>
<td>7.99</td>
<td>91</td>
</tr>
<tr>
<td>1,2,4-trichlorobenzene</td>
<td>0.21</td>
<td>0.998</td>
<td>9.14</td>
<td>93</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.04</td>
<td>0.996</td>
<td>17.98</td>
<td>95</td>
</tr>
</tbody>
</table>
Table 2. Statistical summary of the most abundant species (µg m\(^{-3}\))

<table>
<thead>
<tr>
<th>Compound Name</th>
<th>Winter Period</th>
<th>Summer Period</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Range</td>
</tr>
<tr>
<td>n-hexane</td>
<td>1.64</td>
<td>0.21 - 14.44</td>
</tr>
<tr>
<td>Methylcyclopentane</td>
<td>1.11</td>
<td>0.23 - 3.68</td>
</tr>
<tr>
<td>Benzene</td>
<td>4.50</td>
<td>1.72 - 14.77</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>1.57</td>
<td>0.48 - 3.57</td>
</tr>
<tr>
<td>2-Methylhexane</td>
<td>2.12</td>
<td>1.09 - 4.89</td>
</tr>
<tr>
<td>3-Methylhexane</td>
<td>1.12</td>
<td>0.30 - 2.57</td>
</tr>
<tr>
<td>c-3-Heptene</td>
<td>0.22</td>
<td>0.06 - 0.64</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
<td>0.18</td>
<td>0.07 - 0.45</td>
</tr>
<tr>
<td>Toluene</td>
<td>15.77</td>
<td>2.96 - 85.90</td>
</tr>
<tr>
<td>Octane</td>
<td>0.94</td>
<td>0.21 - 4.70</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>1.32</td>
<td>0.26 - 8.18</td>
</tr>
<tr>
<td>m,p-xylene</td>
<td>5.05</td>
<td>0.66 - 37.94</td>
</tr>
<tr>
<td>Styrene</td>
<td>2.48</td>
<td>0.45 - 8.40</td>
</tr>
<tr>
<td>o-xylene</td>
<td>0.89</td>
<td>0.15 - 3.33</td>
</tr>
<tr>
<td>Nonane</td>
<td>0.97</td>
<td>0.27 - 3.12</td>
</tr>
<tr>
<td>n-propylbenzene</td>
<td>1.25</td>
<td>0.16 - 7.38</td>
</tr>
<tr>
<td>Camphene</td>
<td>3.66</td>
<td>0.10 - 13.95</td>
</tr>
<tr>
<td>1-decene</td>
<td>2.74</td>
<td>0.46 - 7.80</td>
</tr>
<tr>
<td>1,2,4- trimethylbenzene</td>
<td>0.57</td>
<td>0.21 - 1.45</td>
</tr>
<tr>
<td>n-decane</td>
<td>0.43</td>
<td>0.07 - 1.53</td>
</tr>
<tr>
<td>Benzylchloride</td>
<td>1.33</td>
<td>0.31 - 11.61</td>
</tr>
<tr>
<td>1,2,3-trimethybenzene</td>
<td>0.56</td>
<td>0.18 - 2.43</td>
</tr>
<tr>
<td>1-undecene</td>
<td>3.65</td>
<td>1.10 - 10.61</td>
</tr>
<tr>
<td>1,2,4- trichlorobenzene</td>
<td>11.33</td>
<td>1.35 - 74.05</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>1.66</td>
<td>0.39 - 6.42</td>
</tr>
</tbody>
</table>
Table 3. Literature comparison of the average BTEX concentrations (µg m$^{-3}$)

<table>
<thead>
<tr>
<th></th>
<th>This study</th>
<th>Bursa$^1$ Turkey</th>
<th>İzmir$^2$ Turkey</th>
<th>Kocaeli$^3$ Turkey</th>
<th>Ioannina Greece$^4$</th>
<th>Dunkerque France$^5$</th>
<th>Navarre Spain$^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>2.6</td>
<td>5.2</td>
<td>6.8</td>
<td>2.3</td>
<td>12</td>
<td>2.8</td>
<td>1.9</td>
</tr>
<tr>
<td>Toluene</td>
<td>11</td>
<td>24</td>
<td>14</td>
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<td>41</td>
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<td>Ethylbenzene</td>
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<td>3.6</td>
<td>2.6</td>
<td>9.7</td>
<td>-</td>
<td>2.2</td>
<td>1.4</td>
</tr>
<tr>
<td>m,p-xylene</td>
<td>3.8</td>
<td>9.9</td>
<td>-</td>
<td>37</td>
<td>-</td>
<td>3.4</td>
<td>4.6</td>
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<tr>
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<td>1.4</td>
<td>-</td>
<td>12</td>
<td>-</td>
<td>2.6</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 4. Median and mean concentrations of measured VOCs at residential, traffic impacted and background stations (µg m\(^{-3}\))

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Residential</th>
<th>Traffic</th>
<th>Background</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mean</td>
<td>median</td>
<td>mean</td>
</tr>
<tr>
<td>n-hexane</td>
<td>1.63</td>
<td>0.85</td>
<td>0.87</td>
</tr>
<tr>
<td>methylecyclopentane</td>
<td>1.14</td>
<td>1.09</td>
<td>0.68</td>
</tr>
<tr>
<td>Benzene</td>
<td>4.98</td>
<td>4.64</td>
<td>2.11</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>1.11</td>
<td>1.01</td>
<td>0.97</td>
</tr>
<tr>
<td>2-m-hexane</td>
<td>1.95</td>
<td>1.73</td>
<td>1.15</td>
</tr>
<tr>
<td>3-m-hexane</td>
<td>1.01</td>
<td>0.94</td>
<td>0.58</td>
</tr>
<tr>
<td>c-3-heptane</td>
<td>0.24</td>
<td>0.21</td>
<td>0.14</td>
</tr>
<tr>
<td>methylecyclohexane</td>
<td>0.22</td>
<td>0.18</td>
<td>0.13</td>
</tr>
<tr>
<td>Toluene</td>
<td>17.1</td>
<td>17.8</td>
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</tr>
<tr>
<td>Octane</td>
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<td>0.48</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>1.56</td>
<td>1.28</td>
<td>0.99</td>
</tr>
<tr>
<td>m,p-xylene</td>
<td>6.27</td>
<td>5.22</td>
<td>3.92</td>
</tr>
<tr>
<td>Styrene</td>
<td>2.35</td>
<td>1.95</td>
<td>1.53</td>
</tr>
<tr>
<td>o-xylene</td>
<td>1.22</td>
<td>1.09</td>
<td>0.69</td>
</tr>
<tr>
<td>Nonane</td>
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<td>0.96</td>
<td>1.03</td>
</tr>
<tr>
<td>n-propylbenzene</td>
<td>1.99</td>
<td>1.69</td>
<td>2.27</td>
</tr>
<tr>
<td>Camphene</td>
<td>4.04</td>
<td>3.09</td>
<td>2.33</td>
</tr>
<tr>
<td>1-decene</td>
<td>2.40</td>
<td>2.13</td>
<td>2.13</td>
</tr>
<tr>
<td>1,2,4-trimethylbenzene</td>
<td>0.70</td>
<td>0.63</td>
<td>1.22</td>
</tr>
<tr>
<td>n-decane</td>
<td>0.45</td>
<td>0.39</td>
<td>0.19</td>
</tr>
<tr>
<td>benzylchloride</td>
<td>1.14</td>
<td>1.15</td>
<td>0.61</td>
</tr>
<tr>
<td>1,2,3-trimethylbenzene</td>
<td>0.45</td>
<td>0.42</td>
<td>0.21</td>
</tr>
<tr>
<td>1-undecene</td>
<td>3.87</td>
<td>2.94</td>
<td>3.15</td>
</tr>
<tr>
<td>1,2,4-trichlorobenzene</td>
<td>10.7</td>
<td>6.54</td>
<td>19.1</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>1.57</td>
<td>1.35</td>
<td>0.71</td>
</tr>
</tbody>
</table>
Figure 1. Location of the sampling points (the location of the Balikesir is shown on the upper left corner)
Figure 2. W/S ratios of the most abundant 25 compounds
Figure 3. Pollution maps of the BTEX group for the summer season (μg m$^{-3}$)
Figure 4. Pollution maps of the BTEX group for the winter season (μg m⁻³)
Figure 5. Factor loadings
Figure 6. Explained variances

Fraction of variance explained

n-hexane
Methyleclopentane
Benzene
Cyclohexane
2-methylhexane
3-methylhexane
1-heptene
c-3-Heptene
c-1,3-Dichloropropene
Methyleclopentane
toluene
1-octene
Octane
Ethylbenzene
m,p-xylene
Bromoform
1-nonane
nonane
3,6-dimethyloctane
n-propylbenzene
3-ethyltoluene
Camphene
4-ethyltoluene
2-ethyltoluene
tert-butylbenzene
n-decane
1,2,3-trimethylbenzene
indan
undecane
1,2,4-trichlorobenzene
naphthalene
dodecane

Fraction of variance explained

n-hexane
Methyleclopentane
Benzene
Cyclohexane
2-methylhexane
3-methylhexane
1-heptene
c-3-Heptene
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Methyleclopentane
Toluene
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Octane
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Bromoform
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Camphene
4-ethyltoluene
2-ethyltoluene
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undecane
1,2,4-trichlorobenzene
naphthalene
dodecane

Fraction of variance explained

n-hexane
Methyleclopentane
Benzene
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2-methylhexane
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Fraction of variance explained

n-hexane
Methyleclopentane
Benzene
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3-ethyltoluene
Camphene
4-ethyltoluene
2-ethyltoluene
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indan
undecane
1,2,4-trichlorobenzene
naphthalene
dodecane

Fraction of variance explained

n-hexane
Methyleclopentane
Benzene
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2-methylhexane
3-methylhexane
1-heptene
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c-1,3-Dichloropropene
Methyleclopentane
Toluene
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Octane
Ethylbenzene
m,p-xylene
Bromoform
1-nonane
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3,6-dimethyloctane
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3-ethyltoluene
Camphene
4-ethyltoluene
2-ethyltoluene
tert-butylbenzene
n-decane
1,2,3-trimethylbenzene
indan
undecane
1,2,4-trichlorobenzene
naphthalene
dodecane

Fraction of variance explained

n-hexane
Methyleclopentane
Benzene
Cyclohexane
2-methylhexane
3-methylhexane
1-heptene
c-3-Heptene
c-1,3-Dichloropropene
Methyleclopentane
Toluene
1-octene
Octane
Ethylbenzene
m,p-xylene
Bromoform
1-nonane
nonane
3,6-dimethyloctane
n-propylbenzene
3-ethyltoluene
Camphene
4-ethyltoluene
2-ethyltoluene
tert-butylbenzene
n-decane
1,2,3-trimethylbenzene
indan
undecane
1,2,4-trichlorobenzene
naphthalene
dodecane

Fraction of variance explained

n-hexane
Methyleclopentane
Benzene
Cyclohexane
2-methylhexane
3-methylhexane
1-heptene
c-3-Heptene
c-1,3-Dichloropropene
Methyleclopentane
Toluene
1-octene
Octane
Ethylbenzene
m,p-xylene
Bromoform
1-nonane
nonane
3,6-dimethyloctane
n-propylbenzene
3-ethyltoluene
Camphene
4-ethyltoluene
2-ethyltoluene
tert-butylbenzene
n-decane
1,2,3-trimethylbenzene
indan
undecane
1,2,4-trichlorobenzene
naphthalene
dodecane

Fraction of variance explained

n-hexane
Methyleclopentane
Benzene
Cyclohexane
2-methylhexane
3-methylhexane
1-heptene
c-3-Heptene
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Methyleclopentane
Toluene
1-octene
Octane
Ethylbenzene
m,p-xylene
Bromoform
1-nonane
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3,6-dimethyloctane
n-propylbenzene
3-ethyltoluene
Camphene
4-ethyltoluene
2-ethyltoluene
tert-butylbenzene
n-decane
1,2,3-trimethylbenzene
indan
undecane
1,2,4-trichlorobenzene
naphthalene
dodecane