Temporal variations of BTX compounds in Bursa/Turkey atmosphere

Sema Yurdakul*

Environmental Engineering Department,
Middle East Technical University,
06800, Ankara, Turkey
E-mail: ysema@metu.edu.tr
*Corresponding author

Mihriban Civan

Environmental Engineering Department,
Kocaeli University,
41380, Ankara, Turkey
E-mail: mihriban.civan@kocaeli.edu.tr

Öznur Oğuz Kuntasal

The United Nations Development Programme,
06610, Ankara, Turkey
E-mail: oznur.oguzkuntasal@undp.org

Gürdal Tuncel

Environmental Engineering Department,
Middle East Technical University,
06800, Ankara, Turkey
E-mail: tuncel@metu.edu.tr

Abstract: Ambient concentrations of C2-C12 volatile organic compounds (VOCs) were measured at Bursa, which is the fourth largest city of Turkey. Two measurement campaigns were carried out between September 14 to November 6, 2005 and March 17 to May 10, 2006. Fifty one VOCs were regularly determined in each chromatogram. However, only BTX compounds are discussed in this study. Concentrations of BTX compounds showed well-defined diurnal cycles. Concentrations increased starting at 06:00 am in the morning, reaching to a maximum somewhere between 9:00 to 11:00 am. Then concentration decreased, until the evening rush hour, owing to increasing mixing height during day time. Then concentrations of BTX increased in the afternoon rush hour which extended to 08:00 pm. BTX concentrations remained low throughout the night. High binary correlations between BTX compounds suggest a common source, which are traffic emissions. However, other non-traffic sources were also found to be effective, for benzene in the November to March campaign.

Biographical notes: Sema Yurdakul graduated from Kocaeli University, Environmental Engineering Department in 2000. She received her Master of Business Administration in 2003 from the same university,. After that, she received her second MSc degree from Middle East Technical University, Environmental Engineering Department in 2006. Currently, she is working in the same department as a Teaching Assistant and attending her PhD education. Her fields of interest are VOCs, secondary organic pollutants, biomass combustion, and thermal kinetics of wood-based products.

Mihriban Civan graduated from the Dokuz Eylül University, Environmental Engineering Department in 1999. She received her PhD from Middle East Technical University in 2010. Currently, she is working as an Assistant Professor in the Kocaeli University, Environmental Engineering Department. Her fields of interest are ambient and indoor sampling of VOCs, inorganic pollutants in atmosphere and odour measurements.

Öznur Oğuz Kuntasal graduated from the Middle East Technical University, Environmental Engineering Department in 1997. She received her PhD from Middle East Technical University in 2005.

Gürdal Tuncel graduated from the Middle East Technical University, Chemistry Department in 1977. He received his MSc degree from the Middle East Technical University, Marine Sciences Institute and a PhD from University of Maryland in 1984. He joined Middle East Technical University, Environmental Engineering Department in 1987. Currently, he is working as a Professor in the same department. His fields of interest includes aerosol and precipitation chemistry, long range transport of pollutants, the use of trace elements and organic compounds as tracers of atmospheric transport, and environmental analytical chemistry, including, developing contamination free aerosol and precipitation sampling techniques, improving sample handling procedures for determination of trace elements in precipitation and aerosols and standardisation of available analytical techniques for routine analysis of large number of environmental samples.

1   Introduction

Volatile organic compounds (VOCs) are organic compounds having a vapour pressure greater than 0.1 torr at 25ºC and 1 atm (USEPA, 1997). Their volatility depends on the carbon number, heavy hydrocarbons being less volatile than the light ones (Environ Yukon, 2011). Hydrocarbons containing carbon and hydrogen elements such as alkanes, alkenes, alkynes and aromatics are important VOCs. When VOCs are released to environment, some fractions of them, depending on their volatility, and thus molecular weight ends up in the atmosphere. Atmospheric concentrations of VOCs are controlled

by variety of natural and anthropogenic sources, including combustion, vehicles, furnaces, industrial production processes and biological processes (Parra et al., 2006).

Atmospheric burden of these compounds attracted a substantial attention in last two decades, because:

1 many of them are toxic and mutagenic, or suspected mutagenic compounds (Sun et al., 2010; Whaysner et al., 2004), (analytical tools, like GCMS and online systems developed significantly in this time period

2 there are many of them and at least some of them are good candidates to be used as marker species in receptor modelling applications (EPA, 2005).

In urban areas, nearly 60% of the non-methane VOC mass consists of BTX compounds namely Benzene, Toluene, Ethylbenzene and Xylene. This group is demonstrated to be good markers of traffic emissions and can be used in quantification of vehicle-related air pollution (Hoque et al., 2008). Temporal variability of BTX compounds at Bursa, which is an industrial town at Northwestern Turkey is discussed. Bursa is an industrial city, which hosts variety of industries, particularly textile and automotive industries. With 2.6 million inhabitants, it is also the fourth largest city in the country. Concentrations of BTX compounds were measured in two field campaigns, one in autumn (September to November) and the other one in spring (from March to May). Hourly measurements of BTX concentrations were performed using an online GC-FID system, fairly large data set were generated. The hourly data for approximately 60 VOC compounds are now being evaluated, particularly for source apportionment. Only temporal variability of BTX compounds is discussed in this manuscript.

2   Material and methods

2.1   Station

Ambient concentrations of C2-C12 VOCs were measured hourly in Bursa atmosphere. For this purpose, an online GC-FID system was placed to the Bursa Hygiene Center (40.19ºN, 29.05ºE), which is located at the city centre of the Bursa and onsite measurements were done. The nearest main avenue is approximately 1 km to the north of the station; it carries heavy traffic of the city centre. The distance of the station to Ankara and Yalova highways, which are very busy roads joining downtown Bursa to its neighbour cities, is approximately 2 km. Other roads with heavy traffic are further away. The location of the station in Bursa is given in Figure 1.

Hourly measurements were performed in two campaigns. The first campaign which is named as the Fall campaign was carried out between September 14 and November 6, 2005, and the second campaign, which is named as Spring campaign was performed between March 17 and May 10 2006. A total of 1667 chromatograms were generated during the study.

Figure 1 Location of the sampling point (see online version for colours)
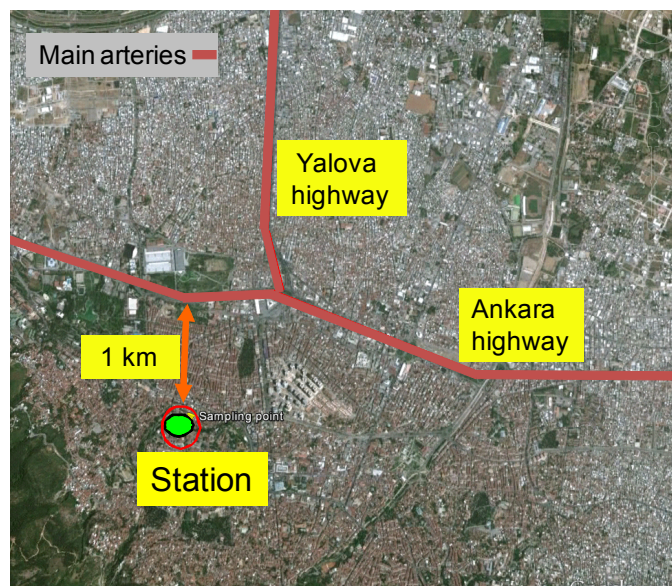

2.2 Analytical system

The VOCs were measured in-situ using an online GC system The air samples was continuously measured with air server-unity thermal desorption (AS/TD) (Markes International Ltd., UK). Air samples were collected at 10 mL min^{-1} flow onto the ozone precursor cold trap during 45 minutes. The trap is cooled by a Peltier system suitable for field monitoring since there is no need for liquid N_2 or carbondioxide gas (Roukos et al., 2009). Once all the air sample had been collected and focused in the cold trap, the target analytes were then thermally desorbed in the reverse direction to sample flow and injected through a transfer line into the column head and analysed by GC system (Model 3800 GC, Varian, USA) equipped with two flame ionisation detectors (FIDs). The GC/FID system has two columns, namely DB-1 (% 100 Dimethylpolysiloxane, Operating temperature range; 60 to 325ºC) (60 × 0.32 × 1 µm) capillary column appropriate for hydrocarbons and HP-Al/S (HP-PLOT/Al$_2$O$_3$, sodium sulphate-deactivated, operating temperature; –60 to 200ºC) (50 × 0.32 × 8 µm) alumina PLOT column for light hydrocarbons (C1 to C8) and two FID detectors. Thermal desorption provides higher sensitivity than chemical desorption and minimise artefacts, losses and carry-over effects. US EPA TO-17 method was used for the analysis.

During the first 45 minutes of each measurement cycle, 450 ml air sample was pulled in, at a flow rate of 10 mL min^{-1}, on to directly a multilayer sorbent-packed, cold trap (12 cm × 2 mm i.d.) at –15ºC (Markes). Sampling rate was controlled by a mass flow controller (MFC). A Peltier electrical cold element is used to cool the trap to –15ºC. During the desorption process, cold trap is suddenly heated 300ºC, at rate of 100ºC sec^{-1} and gas phase analytes are introduced to the inlet of GC equipped with Dean Switch system. Dean Switch system is used to obtain better resolution of the peaks with two

different types of column. Lighter compounds whose molecular weights are lighter than hexane go through the Alumina Plot capillary column and heavier compounds whose molecular weights are heavier than hexane go through DB1 capillary column with the help of Dean Switch system. After desorption, the trap was cooled, equilibrated in terms of temperature and a new sampling cycle started.

Various parameters of the online GC system, including desorption temperature, desorption rate, trap temperature (both maximum and minimum) were examined. The minimum trap temperature allows quantitative retention of compounds as volatile as ethane. The minimum operating temperature for the cold trap is given as 15ºC for ozone precursor cold trap in the operation manual of the tube. The effect of cold trap temperature for analyte recovery was also investigated and results are illustrated in Figure 2 for selected compounds. Cryfocusing of the analytes provide rapid injection and thus narrow bands resulting in good resolution (Camel and Caude, 1995). The aliquots of 300 ml calibration gas were collected on cold trap with different temperature ranged from −5ºC to −15ºC and then analysed at GC-FID. As a result of these analyses, peak areas have been normalised to the maximum value for each individual compound. As can be shown in Figure 2, coldtrap temperature has significant influence on analyte recovery obtaining higher recovery at lower temperatures. Therefore, a cold trap temperature of −15ºC was chosen as the optimum. The results were presented only for selected target analytes but the similar patterns and conclusions were acceptable for all other target analytes. The desorption temperature adopted was 300ºC, which was also the desorption temperature recommended by the manufacturer. Three minutes was selected as the optimum time for the complete collection of target compounds on the cold trap. The time period recommended by the manufacturer is 1 min.

Figure 2   Effect of the minimum cold trap collection temperature (see online version for colours)
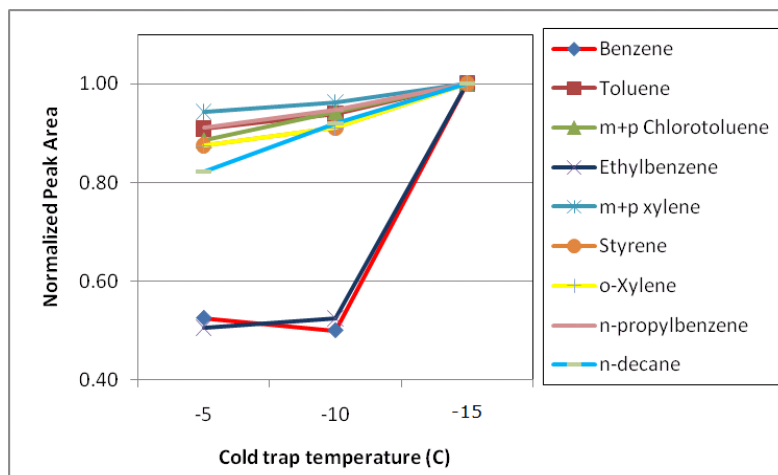
Parameters used in the GC system, such as starting temperature, ramp values, holding temperature, and carrier gas flow rate through the column have strong influence on retention time and resolution of analyte peaks in the chromatogram, they are optimised using a standard calibration mixture. The following GC parameters were found to be optimum and used in the study.

Carrier gas	N_2
Inlet temperature	300ºC
Detector temperatures	300ºC
Temperature programme	40ºC hold for 10 min, 10ºC min^{-1} ramp to 195ºC and hold 10 min.

The analytical system was calibrated using a calibration VOC mixture, which was provided by the Environment Canada, analysis and air quality division (AAQD). The calibration mixture consisted of 148 aliphatic, aromatic and halogenated hydrocarbons which have carbon numbers varying between 2 and 12 at concentration range between 2 and 20 ppb.

As unity thermal desorption system which is containing cold trap was directly connected to the GC-FID system, thus gas standards could be directly analysed and very high (99.999) correlations between mass of the analytes and their area responses were obtained for each compound during the calibration process. The measurement system was calibrated between each campaign and calibration checks, where a single mid-point standard were analysed daily.

2.3 Meteorology of the study area

Bursa was located in the Marmara Region and it has a fairly temperate climate. Bursa province has a type of transit climate between the Mediterranean climate and Black Sea climate regimes. According to the Köppen climate classification which is the based on the hottest and coldest months Bursa has a borderline 'Mediterranean/humid subtropical' Climate (Kottek et al., 2006). The average temperature in the January, which is the coldest month in Bursa province, is 5.5ºC and the average temperature in the July, which is the hottest month in Bursa, is 24.6ºC. The average lowest and highest temperatures as recorded are 1.7ºC in February and 30.6ºC in June and August. The annual average of the central county is 14.4ºC (DMİ, 2010). The prevailing wind direction is the NE (49.3%). Local conditions are very effective on the wind properties of the Bursa. The city is located at the slopes of the Uludağ Mountain. This topography has a strong influence on the wind pattern in Bursa. Northern winds are very effective for the ventilation of the city (Öztürk, 2010).

The most important feature of the meteorology during measurement campaigns was slow winds. Average wind speed for the first and second campaigns was 1.3 and 1.8 m s^{-1}, respectively. The highest wind speeds were recorded in April and the lowest in March. During the sampling campaigns precipitation was also low. Total precipitation was found as a 68 mm and 25 mm respectively. The highest temperatures (30ºC) were recorded in April, while on most of the midday temperatures in September were higher than in September. In September and May temperature averages were found very similar. The lowest temperatures were observed in March (–0.9ºC). Average mixing height was measured as 816 and 769 m.

Effects of meteorological parameters such as temperature, mixing height and wind speed on the measured VOC concentrations were also examined during the study. Effect of temperature on selected BTX compounds during the second campaign is depicted in Figure 3. During the study, most of the organic compounds including benzene were found inversely proportional ($p < .05$) with temperature for both campaigns. However,

TEX compounds are not affected from the temperature ($p > .05$). The major source of the benzene in the atmosphere is traffic (Skov et al., 2001). However, evaporative sources can account for increase in the TEX concentrations. Probably, due to shortage of nearby major benzene source other than traffic, oxidation rate of benzene became important factor for the variation of benzene concentrations in Bursa atmosphere (Yuval and Broday, 2008). Due to dilution effect of the wind speed, inverse relation was detected for most of the observed VOCs ($p < .05$). On the other hand, just for TEX group, chlorobenzene and m, p-chlorotoluene any correlation could not be observed in the first campaign. Similar results were also obtained in the second campaign because inverse relation ($p < .05$) was detected between wind speed and most of the measured VOCs (94%) including BTX (Figure 4).

Figure 3   Effect of temperature on selected BTX compounds during the second campaign
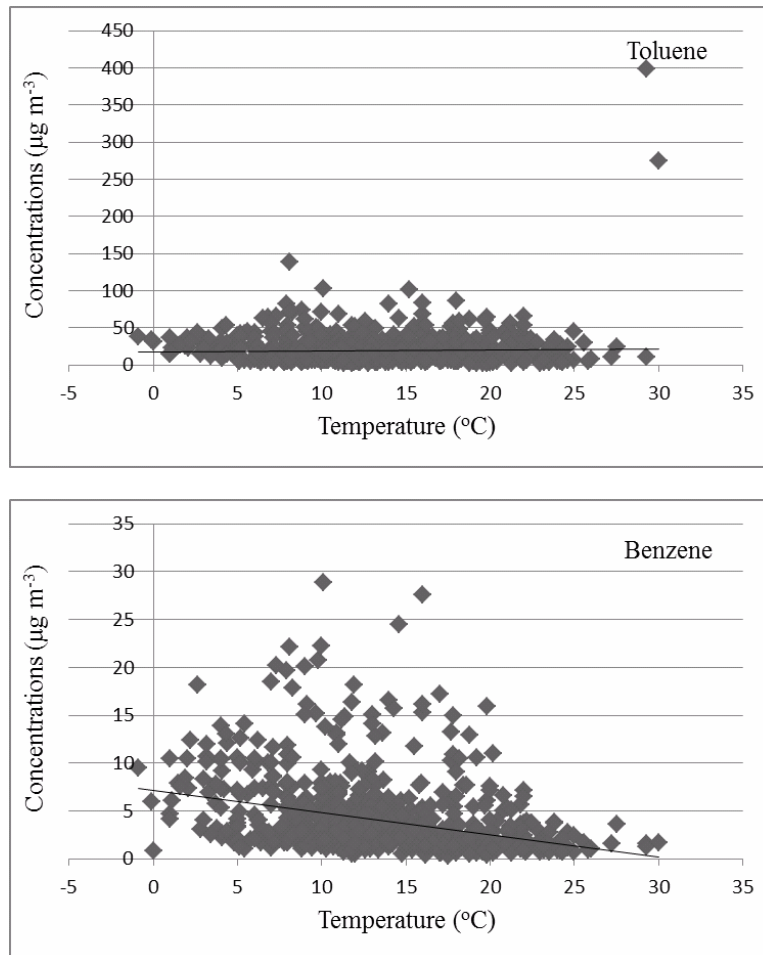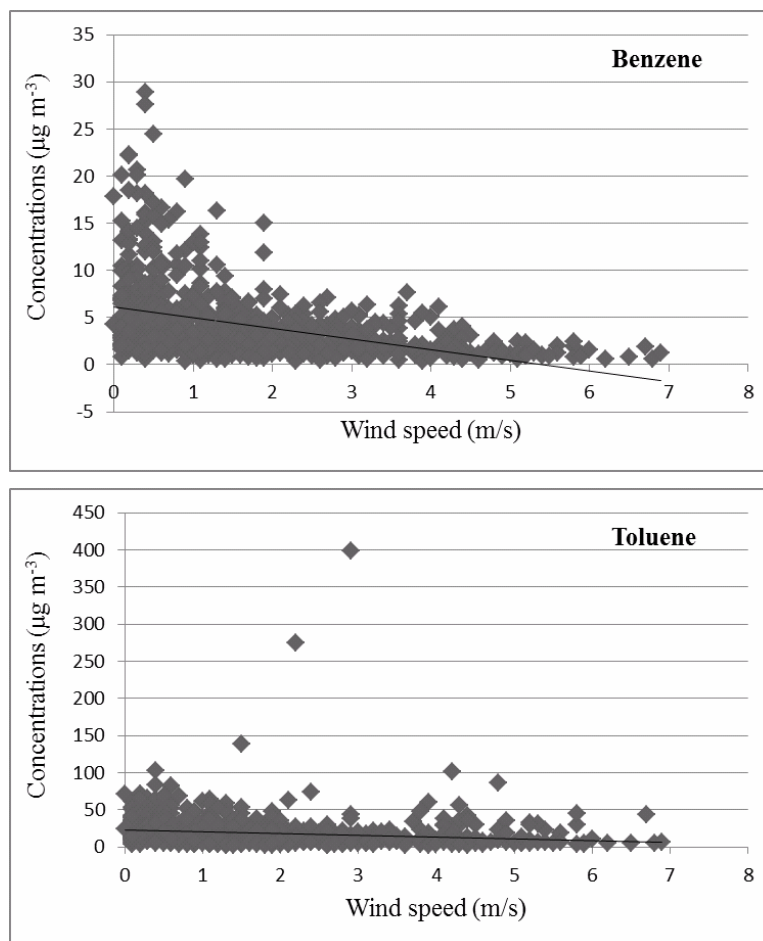
Figure 4 Effect of wind speed on selected BTX compounds during the second campaign

Mixing height defined as a depth pollutants released into the atmosphere is well mixed and it determines the vertical range of the dispersion which occurs due to the release of the pollutants below that height (Nath and Patil, 2006). The variation of the mixing height during the day because of the solar heating and atmospheric cooling can cause deep results on the ground level concentrations of the pollutants (Harrison, 2001). Therefore, high mixing height seems to cause low pollutant concentrations; however low mixing height will cause high pollutant concentrations (Chou et al., 2007). In this study, as mixing height increased, measured pollutant concentrations decreased ($p < .05$) nearly most of the measured VOCs due to effect of dispersion during the first campaign. Just for TEX compounds, m, p-chlorotoluene and 1,2,4-trichlorobenzene any correlation could not be observed. On the contrary, inverse correlations ($p < .05$) were obtained between mixing height and BTX compounds during the second campaign. Changes in the source strength and the distance between the sources and sampling location are the possible reasons of this variance especially for the solvent originated VOCs.

In the present study, stability classes were calculated, on hourly bases using a meteorological pre-processor, namely, PCRAMMET Unstable atmospheric conditions have been observed during the noon time for both sampling campaigns. However, during the night time no unstable conditions have been observed. For the second campaign, duration of the unstable conditions was more frequent compared to the first campaign. Meteorological features prevailing during measurement campaigns suggested that, the assimilative capacity of the Bursa is highest in the spring season than the fall season. However, dispersion conditions over the city were poor during both campaigns.

2.4   QA/QC

Blank levels of the sampling system were determined by analysing the carrier gas passing through cold trap in GC. No blank correction was performed, because blank values were insignificant for all VOCs measured in this study. Detection limits of individual VOCs varied between 0.01 $\mu g\ m^{-3}$ for m + p-Chlorotoluene and 0.18 $\mu g\ m^{-3}$ for Cyclohexane + Cyclohexene.

The precision of the method was determined by five replicate measurements. For the determination of the precision 100 ml gas was injected from the canister contains AAQD standard to the system five times and relative standard deviations (RSDs) were calculated for each compounds. RSD values were found lower than the 15%.

Before each sampling campaigns, six points calibration curves were prepared. During each sampling period to check whether there is problem in the GC or not, mid point calibrations were also performed. For mid point calibrations 300 ml calibration gas was used. Peak areas from the mid point calibrations were compared with the six-point calibration results The EPA method 8,000 b require that a new calibration must be prepared if there is difference between the areas is higher than 20%. However, differences between the calibrations were always lower than 20%.

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

In this study, for the QA/QC of the data firstly univariate outliers were determined for each compound by using SPSS 15.0 software. By this method, outliers which are very different from the rest of the data set were identified by conversion of all the scores for a variable to standard scores. In the current study, all data set were examined for two campaigns and the sample whose standard score is ±2.5 or beyond was flagged as an outlier. In here an outlier was assumed as an unusually extreme value for a variable, given the statistical model in use. The outliers detected with SPSS software were also compared with the results of the time series, scatter plots, finger plots and diurnal profiles of the compounds. The same outliers (constitute 10% of the data set) were also identified as a result of these procedures. After identification of these anomalies, chromatograms which contain these anomalies were re-evaluated to control any misidentification or quantification of the peaks. If any problems could not be observed as a result of these re-examination and any problems could not be found during the collection of these samples or during the analyses, these anomalies were attributed to changes in the source strength of the compounds or meteorological activities and these samples were not removed from the data set.

3   Results and discussion

Summary statistics of the data sets generated in the first and second campaigns are given in Table 1. Concentrations of BTX compounds at Bursa varied between 1.2 μg m^{-3} for o-xylene and 25 μg m^{-3} for toluene in fall campaign and 0.87 and 19 μg m^{-3} in spring campaign. Toluene has the highest concentrations among all BTX compounds, which is followed by m,p-xylene, benzene, ethylbenzene and o-xylene. This ordering of concentrations were the same in both campaigns. The only standard for BTX compounds in Turkish Air Quality regulation is 5.0 μg m^{-3} for benzene. Other BTX compounds are not regulated. Benzene concentrations measured in this study were 3.68 ± 5.27 μg m^{-3} in the fall campaign and 4.0 ± 3.78 μg m^{-3} in spring campaign. These values are close, but below the standard currently effective in Turkey. Since there is no regulatory standard for other BTX compounds, their average concentrations are compared with corresponding values reported for other cities in the world. This comparison is given in Table 2. BTX concentrations measured in this study are comparable with corresponding concentrations reported for other cities around the world. Benzene concentration measured in this study is 3.9 μg m^{-3}. This value is comparable to average benzene concentration reported for Beijing, China, lower than benzene concentration reported for a urban site that is under strong influence of traffic emissions in Izmir, Turkey and higher than remaining averages given in Table 2. Toluene concentration measured in this study is 25 μg m^{-3}, which is the highest in the table. Toluene is the only BTX compound that has significant non-traffic sources. Its concentrations in the atmosphere are contributed by solvent evaporation (Velasco et al., 2009). Bursa is an industrial city, where solvents are widely used in variety of processes. High toluene concentrations measured at Bursa can be due to such strong solvent source in the city. Another reason for observed high toluene levels might be the close proximity of the sampling site to a hospital because toluene is widely used in different parts of hospitals and there are numerous studies in the literature focusing on hospital staff who are unintentionally exposed to toluene in hospitals (Pierce et al., 1997; Lü et al., 2010; Ekpanyasku, 2010). Concentrations of ethylbenzene, m,p-xylene and o-xylene are comparable to corresponding concentrations measured at the urban site in Izmir and higher than average concentrations reported for other cities.

   This comparison gives the impression that Bursa is a polluted city compared to other cities in the table. However, it should be noted that BTX concentrations show large variations from city to another, because measured concentrations depends strongly on relative proximity of stations to busy roads. Consequently, although observed differences are indication that Bursa can be heavily polluted with BTX compounds, comparison only cannot be taken as conclusive evidence.

   BTX concentrations show well defined short and long-term temporal patterns. Concentration of BTX compounds measured during fall and spring campaigns are depicted in Figure 5. Episodic variations are clear in the figure. These episodes are due to changes in meteorology, particularly wind direction. The station is located to the south of the city, on the slopes of the mountain. Most of the roads with heavy traffic are located to the north of the station. Effect of the wind direction is also clearly seen from the pollutant roses prepared for BTX compounds during the study (Figure 6). Consequently, emissions are intercepted and high concentrations are recorded whenever winds blow from northern directions such as N, ENE, NNW and NE sectors.

Table 1   Summary statistics of BTX concentrations in Bursa atmosphere (concentrations are in µg m^{-3})

	Benzene	*Toluene*	*Ethylbenzene*	*m+p-xylene*	*o-xylene*
			Fall		
Average	3.68 ± 5.27	23.28 ± 23.03	2.24 ± 2.39	5.74 ± 6.50	1.09 ± 1.45
Median	1.52	15.95	1.57	3.84	0.68
Geomean	1.71	15.56	1.46	3.11	0.72
Range	0.12 – 40	2.10 – 146	0.15 – 20	0.13 – 39	0.05 – 24
N	765	753	764	760	767
			Spring		
Average	4.03 ± 3.78	18.42 ± 15.30	1.74 ± 1.31	5.01 ± 3.40	0.87 ± 0.62
Median	2.80	13.34	1.35	3.95	0.68
Geomean	2.95	14.02	1.41	4.16	0.73
Range	0.33 – 29	2.36 – 139	0.24 – 17	0.80 – 28	0.17 – 9
N	844	842	844	842	844
			All data		
Average	3.87 ± 4.55	20.72 ± 19.49	1.97 ± 1.92	5.36 ± 5.13	0.98 ± 1.10
Median	2.23	14.70	1.43	3.92	0.68
Geomean	2.28	14.72	1.44	3.63	0.72
Range	0.12 – 40	2.10 – 146	0.15 – 20	0.13 – 39	0.05 – 24
N	1,609	1,595	1,608	1,602	1,611

Table 2   BTX concentrations reported for different cities around the world

|	*This work*	*Dukerque (France) Badol et al. (2008)*	*Beijing, China Song et al. (2008)*	*Dallas USA Qin et al. (2007)*	*Beijing, China Guo et al. (2006)*	*Spain Durana et al. (2006)*	*Izmir Turkey (suburban) Elbir et al. (2007)*	*Izmir (Turkey) (Urban) Elbir et al. (2007)*	*Istabul (Turkey) Demir et al. (2011)*
Benzene	3.9	0.53	5.43	1.62	0.86	1.0	0.85	10.40	1.86
Toluene	25	1.05	11.14	5.80	5.6	2.50	4.65	13.50	24.7
Ethybenzene	2.4	0.17	4.08	0.76	0.87	0.40	0.38	1.60	0.76
m,p-xylene	6.7	0.53	8.54	2.60	0.97	1.50	0.59	2.87	2.46
o-xylene	1.2	0.20	3.91	0.94	0.37	0.40	0.74	3.58	0.77

Figure 5   Time series plots of BTX compounds (see online version for colours)
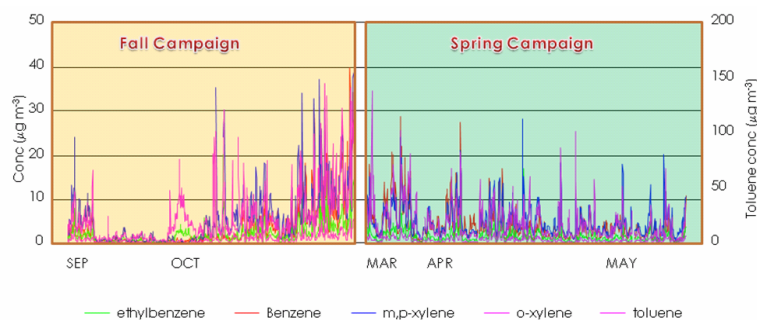
Figure 6 Selected pollutant roses (on each sector average concentration are given as µg m^{-3})
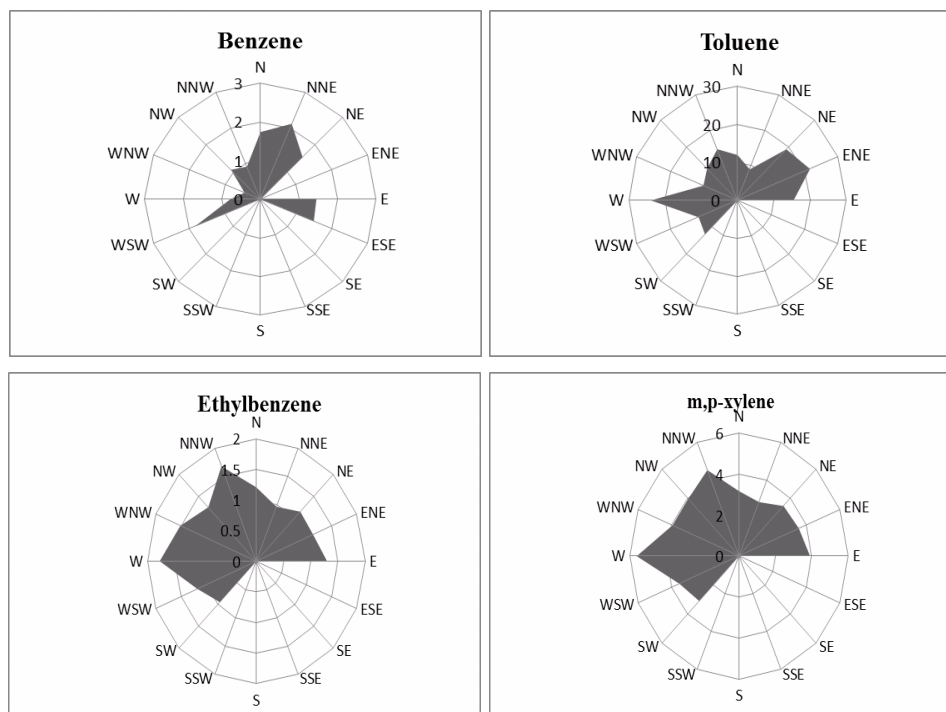

Average diurnal variations in BTX concentrations are given in Figure 7. Concentrations of benzene, ethylbenzene, m,p-xylene and o-xylene depicted very similar diurnal patterns. Their concentrations starts to increase early in the morning with the start of traffic activity, reaches to a maximum at approximately 9:00 to 10:00 am, then decrease to a minimum at 2:00 to 3:00 pm. Concentrations then increased with the afternoon rush hour, reaching to maximum at 7:00 pm. Traffic count did not perform during the study. Moreover, continuous traffic count records are not available in Bursa. However, traffic counts performed in Ankara (the second biggest city of Turkey) city centre in 2003 indicated that a well-defined similar diurnal pattern both in summer and in winter. The number of vehicles reaches to a maximum number during afternoon and decrease to a minimum number at noon hours. High number of vehicles passing through the tunnel during morning and afternoon are owing to traffic rush hours in the city (Kuntasal, 2005). The two peak patterns in the diurnal variation of BTX indicate that the major sources of these organics are traffic emissions. Furthermore, similar diurnal variations in BTX concentrations related with traffic activity were also observed in literature (Ho et al., 2004; Velasco et al., 2007; Olumayede and Okuo, 2012). Therefore, in the present study, the diurnal variations of BTX compounds displayed two peak patterns with one at 9:00 in the morning and another one at 19:00 in the evening, both are conforming to traffic rush hours in Bursa city centre. However, Toluene concentrations showed a slightly different pattern. Morning rush-hour peak is observed in toluene concentrations, as in the other BTX compounds. However, afternoon rush-hour peak was not observed. A second, fairly strong maximum occurred at 3:00 pm, but concentrations did not increase after that hour. This different behaviour of toluene is probably due to its sources other than traffic.

Figure 7   Average diurnal variations of BTX concentrations (see online version for colours)
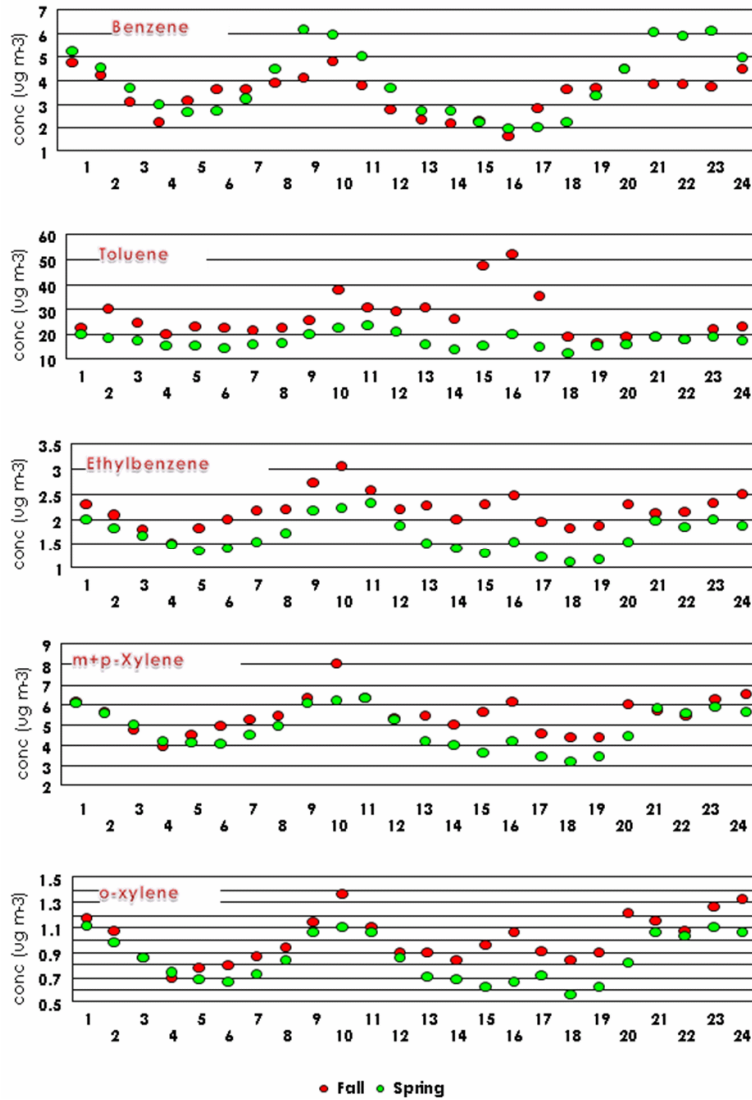
Weekday and weekend average concentrations of BTX compounds are given in Figure 8. Weekday concentrations of all BTX compounds are slightly higher than their corresponding weekend concentrations. Although differences are small they are statistically significant at 95% confidence level. Higher weekday concentrations of BTX compounds are frequently reported in literature and generally attributed to higher traffic intensity during weekdays (Fernandez et al., 2004; Mohan and Ethirajan, 2012). Observed weekday-weekend concentration pattern in this study is not any different from differences observed in other studies and can also be explained by higher traffic intensity, consequently higher VOC emissions during weekdays. However, the difference observed between weekday and weekend concentrations of BTXs are smaller than the difference observed in other Turkish cities, like Ankara (Kuntasal, 2005) or İzmir (Elbir et al.,

2007), which can be due to closer proximity of the sampling stations at Ankara and Izmir to main arteries in these cities. In Bursa, the sampling point was relatively far from main traffic activity in the city, which probably smeared out the differences between weekday and weekend concentrations.

Figure 8   Weekend-weekday differences in concentrations of BTX compounds at Bursa atmosphere (see online version for colours)
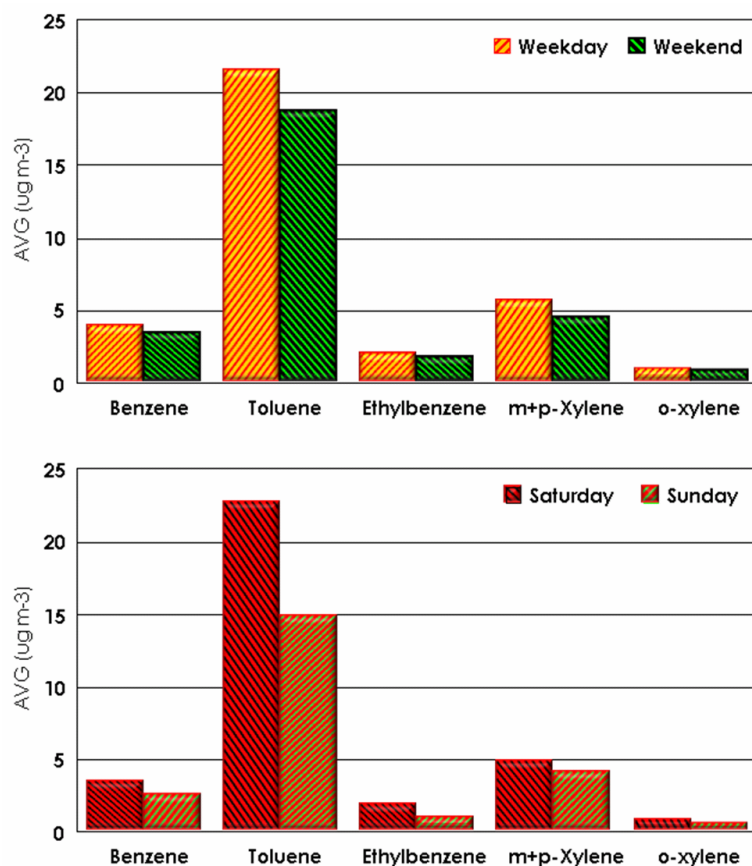
Concentrations of BTX compounds showed well defined monthly pattern as well. Monthly average concentrations of benzene, toluene, ethylbenzene and xylenes are depicted in Figure 9. Measurement periods in this study were from September 14th to October 28th and from 17th of March to 15th of May. Concentrations BTX were lower in the beginning of September to October campaign then their concentrations at the end of the campaign. Similarly, BTX concentrations were high in the beginning of the March to May campaign then their concentrations at the end of it. This pattern was observed not only in BTX concentrations, but also in the concentrations of most of the VOCs measured in this study. Part of this is due to variation of meteorological conditions, particularly the mixing height. In this study mixing height was calculated on an hourly basis using PCRAMMATE, which is pre-processor software for dispersion models. Monthly average mixing height was 950 m in September, 750 m in October, 700 m in

March and 950 m in May. Mixing height is directly related with dilution characteristics of the atmosphere and decreasing trends of atmospheric constituents with increasing mixing height is well-documented (Elbir et al., 2007; Kuntasal, 2005; Llop et al., 2010; Matysik et al., 2010). Increase in BTX concentrations from September to the end of October and decrease from March to May, is at least partly due to variations in the mixing height. Other factors contributing to this monthly pattern can be lower emissions from space heating in September and May, relative to emissions in October and March.

Figure 9   Monthly average BTX concentrations at Bursa atmosphere (see online version for colours)
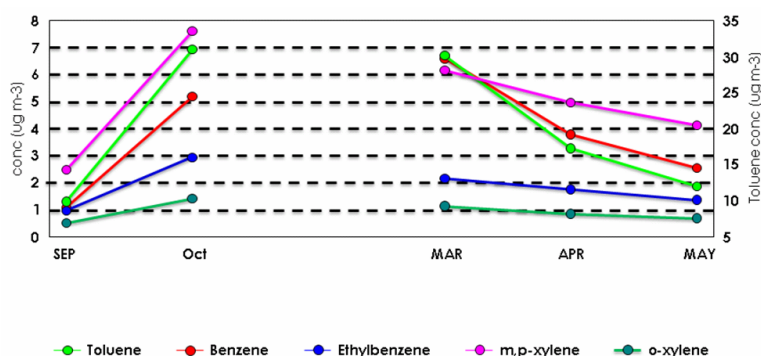
Binary correlation between BTX compounds can provide information on potential sources of these compounds affecting our sampling point. Scatter plots between measured BTX compounds are given in Table 3. All BTX compounds are strongly correlated with each other. Correlations between all compounds are statistically significant at 99% confidence level, in both spring and fall campaigns. Strong correlations between BTX compounds are frequently reported in literature and attributed to common traffic source for all of these compounds (Matysik et al., 2010; Murena, 2007; Pérez-Rial et al., 2009). TEX compounds are mostly originated from traffic, industrial processes, painting and industrial solvents (Lee et al., 2002; Ho et al., 2004; Qin et al., 2007; Hoque et al., 2008). However, benzene is mainly emitted from the traffic related sources namely exhaust, fuel evaporation and fuel losses (Rappenglück and Fabian, 1998). That is the reason of good correlations among TEX compounds and low correlation of benzene with TEX compounds. Moreover, a low R^2 values between benzene and toluene for both campaigns indicate that there were supplementary sources except than the traffic (Hoque et al., 2008). These sources could be industrial areas around the city centre, small commercial activities in city centre or motor vehicle service stations.

Bursa is a heavily industrial city. Therefore, there are too much complicated and mixed sources of measured BTEX compounds in Bursa atmosphere. However, strong correlations between all BTX compounds indicate that there is a dominating source which masks other industrial sources. This dominating source is traffic. This is confirmed with observed bimodal pattern in diurnal variations in concentrations of these elements. Industrial activities probably do affect measured BTX concentrations, but their contribution is masked by the overwhelming influence of traffic emissions. These minor contributions from non-traffic sources can probably be isolated using multivariate

statistical tools. However, source apportionment of BTX compounds will be discussed in another manuscript.

Table 3   Binary correlations between BTX compounds

Fall/spring	Toluene	Ethylbenzene	m,p-xylene	o-xylene
Benzene	0.74/0.70	0.77/0.67	0.82/0.72	0.72/0.72
Toluene	1	0.86/0.79	0.81/0.77	0.81/0.78
Ethylbenzene	1	1	0.96/0.98	0.94/0.96
m,p-xylene	1	1	1	0.97/0.96

4   Conclusions

Concentrations of benzene, toluene, ethylbenzene, m,p-xylene and o-xylene are measured, with hourly intervals, in two campaigns in the city of Bursa, which is one of the most heavily industrialised cities in Turkey. The first campaign, which is named as fall covered September and October 2005. The second campaign which is named as spring campaign, included March, April and May, 2006. Concentrations of BTX compounds were lower than corresponding concentrations reported in literature for the USA and Canada, but comparable to BTX concentrations measured in other Turkish cities. This is ascribed to lower traffic intensity in Turkey, compared to the number of cars on the roads of the USA and Canada.

Concentration of BTX compounds showed well defined short- and long-term variations. Episodic high concentrations that was observed in all BTX compounds was attributed to variations in meteorology, particularly wind direction and rainfall. Bimodal diurnal patterns observed for all of the BTX compounds was due to diurnal variations in motor vehicle emissions.

All BTX compounds are highly correlated with each other, indicating that traffic is the dominating source at our sampling location, even though sampling point was not very close to main traffic intensity in the city.

References

Badol, C., Locage, N., Leonardis, T. and Galloo, J.C. (2008) 'Using a source-receptor approach to characterise VOC behavior in a French urban area influenced by industrial emissions. Part I: study area description, data set acquisition and qualitative data analysis of the data set', *Science of the Total Environment*, Vol. 385, Nos. 2–3, pp.441–452.

Camel, V. and Caude, M. (1995) 'Trace enrichment methods for the determination of organic pollutants in ambient air', *Journal of Chromatography A*, Vol. 710, No. 1, pp.3–19.

Chou, C.C.K., Lee, C.T., Chen, W.N., Chang, S.Y., Chen, T.K., Lin, C.Y. and Chen, J.P. (2007) 'Lidar observations of the diurnal variations in the depth of urban mixing layer: a case study on the air quality deterioration in Taipei Taiwan', *Science of the Total Environment*, Vol. 374, No. 1, pp.156–166.

Demir, S., Saral, A., Ertürk, F., Kuzu, S.L., Goncaloğlu, B.I. and Demir, G. (2011) 'Effect of diurnal changes in VOC source strengths on performances of receptor models', *Environmental Science and Pollution Research International*, Vol. 19, No. 5, pp.1503–1514.

DMİ (2010) *Devlet Meteoroloji İşleri* [online] http://www.meteor.gov.tr/index.aspx#sfU (accessed 10 June 2010).

Durana, N., Navazo, M., Gómez, M.C., Alonso, L., García, J.A., Ilardia, J.L., Gangoiti, G. and Iza, J. (2006) 'Long term hourly measurement of 62 non-methane hydrocarbons in an urban area: main results and contribution of non-traffic sources', *Atmospheric Environment*, Vol. 40, No. 16, pp.2860–2872.

Ekpanyasku, C. (2010) 'Etiological investigation of unintentional solvent exposure among university hospital staffs', *Indian Journal of Occupational and Environmental Medicine*, Vol. 14, No. 3, pp.100–103.

Elbir, T., Cetin, B., Çetin, E., Bayram, A. and Odabası, M. (2007) 'Characterization of volatile organic compounds (VOCs) and their sources in the air of İzmir, Turkey', *Environment Monitoring Assessment*, Vol. 133, Nos. 1–3, pp.149–160.

Environ Yukon (2011) 'Protocol for the contaminated sites regulation under the environment AC. Protocol No. 5: petroleum hydrocarbon analytical methods and standards', Prepared pursuant to Part 6 – Administration, Section 21, *Contaminated Sites Regulation*, OIC 2002/171.

EPA (2005) *Peer Review of the Chemical Mass Balance Model (EPA-CMB8.2) and Documentation*, The KEVRIC Company Inc., Durham, NC, Under EPA Requisition No. U2C761.

EPA (2007) Federal Registration, Part 4, 40 CFR, Parts 51 and 59, National Volatile Organic Compound Emission Standards for Aerosol Coatings, Proposed Rule.

Fernandez, V.V., Lopez, M.P., Muniategu, S., Prada, R.D., Fernandez, F.E. and Tomas, X. (2004) 'C1 to C9 volatile organic compound measurements in urban air', *Science of the Total Environment*, Vols. 334–335, pp.167–176.

Guo, H., Wang, T., Blake, D.R., Simpson, I.J., Kwok, Y.H. and Li, Y.S. (2006) 'Regional and local contributions to ambient nonmethane volatile organic compounds at a polluted rural/coastal site in Pearl River Delta, China', *Atmospheric Environment*, Vol. 40, No. 13, pp.2345–2359.

Harrison, R.M. (2001) *Pollution, Causes, Effects and Control*, 4th ed., pp.249–250, The Royal Society of Chemistry, Cambridge.

Ho, K.F., Lee, S.C., Guo, H. and Tsai, W.Y. (2004) 'Seasonal and diurnal variations of volatile organic compounds (VOCs) in the atmosphere of Hong Kong', *Science of the Total Environment*, Vol. 322, Nos. 1–3, pp.155–166.

Hoque, R.R., Khillare, P.S., Agarwal, T., Shridhar, V. and Balachandran, S. (2008) 'Spatial and temporal variation of BTEX in the urban atmosphere of Delhi, India', *The Science of the Total Environment*, Vol. 392, No. 1, pp.30–40.

Kottek, M., Grieser, J., Beck, C., Rudolf, B. and Rubel, F. (2006) 'World map of the Köppen-Geiger climate classification updated', *Meteorologische Zeitschrift*, Vol. 15, No. 3, pp.259–263.

Kuntasal, Ö.O. (2005) *Temporal Variations and Sources of Organic Pollutants in Two Urban Atmospheres: Ankara and Ottowa*, Unpublished PhD thesis, Ankara.

Lee, S.C., Chiu, M.Y., Ho, K.F., Zou, S.C. and Wang, X. (2002) 'Volatile organic compounds (VOCs) in urban atmosphere of Hong Kong', *Chemosphere*, Vol. 48, No. 3, pp.375–382.

Llop, S., Ballester, F., Aguilera, I., Estarlich, M., Fernandez, O., Patier, R., Sunyer, J., Esplugues, A. and Iniguez, C. (2010) 'Outdoor, indoor and personal distribution of BTEX in pregnant women from two areas in Spain – preliminary results from the INMA project', *Atmospheric Pollution Research*, Vol. 1, No. 3, pp.147–154.

Lü, H., Cai, Q.Y., Wen, S., Chi, Y., Guo, S., Sheng, G., Fu, J. and Katsoyiannis, A. (2010) 'Carbonyl compounds and BTEX in the special rooms of hospital in Guangzhou, China', *Journal of Hazardous Materials*, Vol. 15, Nos. 1–3, pp.673–679.

Matysik, S., Ramadan, A.B. and Schlink, U. (2010) 'Spatial and temporal variation of outdoor and indoor exposure of volatile organic compounds in Greater Cairo', *Atmospheric Pollution Research*, Vol. 1, No. 2, pp.94–101.

Mohan, S. and Ethirajan, R. (2012) 'Assessment of hazardous volatile organic compounds (VOC) in a residential area abutting a large petrochemical complex', *Journal of Tropical Forestry and Environment*, Vol. 2, No. 2, pp.48–59.

Murena, F. (2007) 'Air quality nearby road traffic tunnel portals: BTEX monitoring', *Journal of Environmental Sciences*, Vol. 19, No. 5, pp.578–583.

Nath, S. and Patil, R.S. (2006) 'Prediction of air pollution concentration using an in situ real time mixing height model', *Atmospheric Environment*, Vol. 40, No. 20, pp.3816–3822.

Olumayede, E.G. and Okuo, J.M. (2012) 'Distribution, temporal and diurnal behaviors of total volatile organic compounds over the urban atmosphere of Southwestern Nigeria', *Journal of Environmental Science and Engineering*, Vol. A1, pp.785–796.

Öztürk, M.Z. (2010) 'Comparative climate of Uludağ (Zirve) and Bursa meteorology stations', *Turkish Geography Magazine*, Vol. 55, pp.13–24.

Parra, M.A., González, L., Elustondo, D., Garrigó, J., Bermejo, R. and Santamaría, J.M. (2006) 'Spatial and temporal trends of volatile organic compounds (VOC) in a rural area of northern Spain', *The Science of the Total Environment*, Vol. 370, No. 1, pp.157–167.

Pérez-Rial, D., López-Mahía, P., Muniategui-Lorenzo, S. and Prada-Rodríguez, D. (2009) 'Temporal distribution, behaviour and reactivities of BTEX compounds in a suburban Atlantic area during a year', *Journal of Environmental Monitoring*, Vol. 11, No. 6, pp.1216–1225.

Pierce, C.H., Dills, R.L., Lewandowski, T.A., Morgan, M.S., Wessels, M.A., Shen, D.D. and Kalman, D.A. (1997) 'Estimation of background exposure to toluene using a physiologically-based kinetic model', *Journal of Occupational Health*, Vol. 39, pp.130–137.

Qin, Y., Walk, T., Gary, R., Yao, X. and Elles, S. (2007) 'C2-C10 nonmathane hydrocarbons measured in Dallas, USA-seasonal trends and diurnal characteristics', *Atmospheric Environment*, Vol. 41, No. 28, pp.6018–6032.

Rappenglück, B. and Fabian, P. (1998) 'A study of BTEX-ratios in the urban area of Munich/Germany using rapid gas chromatography', *Environmental Science and Pollution Research*, Vol. 5, No. 28, pp.65–70.

Roukos, J., Plaisance, H., Leonardis, T., Bates, M. and Locoge, N. (2009) 'Development and validation of an automated monitoring system for oxygenated volatile organic compounds and nitrile compounds in ambient air', *Journal of Chromatography A*, Vol. 1216, No. 49, pp.8642–8651.

Skov, H., Hansen, A.B., Lorenzen, G., Andersen, H.V., Lostrom, P. and Christensen, C.S. (2001) 'Benzene exposure and the effect of traffic pollution in Copenhagen, Denmark', *Atmospheric Environment*, Vol. 35, No. 14, pp.2463–2471.

Song, Y., Dai, W., Shao, M., Liu, Y., Lu, S., Kuster, W. and Golden, P. (2008) 'Comparison of receptor models for source apportionment of volatile organic compounds in Beijing, China', *Environmental Pollution*, Vol. 156, No. 1, pp.174–183.

Sun, L., Guiying, L., Shungang, W. and Taicheng, A. (2010) 'Mechanistic study and mutagenicity assessment of intermediates in photocatalytic degradation of gaseous toluene', *Chemosphere*, Vol. 78, No. 3, pp.313–318.

USEPA (1997) *Compendium Method TO 15 – Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS)*, Center for Environmental Research Information Office of Research and Development, US Environmental Protection Agency Cincinnati, OH.

Velasco, E., Lamb, B., Westberg, H., Allwine, E., Sosa, G., Arriaga-Colina, J.L. and Jobson, B.T. et al. (2007) 'Distribution, magnitudes, reactivities, ratios and diurnal patterns of volatile organic compounds in the Valley of Mexico during the MCMA 2002 and 2003 field campaigns', *Atmospheric Chemistry and Physics*, Vol. 7, pp.329–353.

Velasco, E., Pressley, S., Grivicke, R., Allwine, E., Coons, T., Foster, W., Jobson, T., Westberg, H., Ramos, R., Hernández, F., Molina, L.T. and Lamb, B. (2009) 'Eddy covariance flux measurements of pollutant gases in Urban Mexico City', *Atmospheric Chemistry and Physics Discussions*, Vol. 9, No. 2, pp.7991–8034.

Whaysner, J., Reddy, M.V., Ross, P.M., Mohan, M. and Lax, E.A. (2004) 'Genotoxicity of benzene and its metabolites', *Mutation Research/Reviews in Mutation Research*, Vol. 66, No. 2, pp.99–130.

Yuval, A.Z. and Broday, D.M. (2008) 'Revealing source signatures in ambient BTEX concentrations', *Environmental Pollution*, Vol. 156, No. 2, pp.553–562.