TEMPORAL VARIATIONS OF BTEX COMPOUNDS IN BURSA/TURKEY ATMOSPHERE

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Abstract — Ambient concentrations of C2-C12 volatile organic compounds (VOCs) were hourly measured in Bursa which is the fourth largest city of Turkey. Two measurement campaigns were performed between September 14-November 6, 2005 and March 17 - May 10, 2006. A total 1667 chromatograms were generated during the study and 51 VOCs were determined in each chromatogram. However, only BTEX compounds were examined in this study.

In this study, BTEX concentrations increased from 05:00 am in the morning. The high concentration peaks were observed at 9:00-11:00 am. In the afternoon probably due to high mixing layer height, good dilution was occurred and lower BTEX concentrations were observed and peaks were delayed to 3 pm. Until the evening rush hour traffic, lower values were monitored. That is to say, diurnal pattern of the BTEX compounds were followed the traffic rush hours.

In the present study, correlations and ratios among the BTEX compounds were also investigated. High correlations observed for the BTEX suggest a common source. However, for benzene at the first campaign, other sources were found effective, apart from the traffic. Still, in the second campaign, benzene emissions were found consistent with the vehicular emissions.

Keywords — Air pollution, BTEX, GC-FID, VOCs

1 INTRODUCTION

2 Volatile Organic Compounds (VOCs) are organic compounds having a vapor pressure grated than 0.1 torr at 25 °C and 1 atm.

VOCs have different physical and chemical behaviors. Pure hydrocarbons containing carbon and hydrogen elements such as alkanes, alkenes, alkynes and aromatics are important VOCs. As VOCs are released to environment, they are likely to be distributed or to evaporate fairly rapidly into the atmosphere. VOCs are emitted from various sources into the atmosphere. These sources are combustion plants, vehicles, furnaces, industrial production processes and biological processes [1].

In urban areas, nearly 60% of the Non methane VOCs are BTEX group namely Benzene, Toluene, Ethylbenzene and Xylene and this group can be used for the determination of pollution from traffic [2]. VOCs are cause many serious environmental problems. They have adverse effects on living organisms and benzene is known also as a genotoxic carcinogen compound.

Objective of this study is to find out temporal variation of the BTEX concentrations in Bursa atmosphere. For this reason, two field campaigns were carried out for the measurement of VOCs in Bursa atmosphere. These campaigns were performed in the two seasons, namely autumn (September to November) and spring (March to May).

Online GC-FID coupled with Unity Air Server System was used for the measurements. Measurements were conducted hourly and one chromatogram was generated at every hour. Fairly large data sets that were generated in this study will enable to determine possible variation of pollutants in Bursa atmosphere.

2 MATERIAL AND METHODS

During the study, ambient concentrations of C6-C12 VOCs were hourly measured in Bursa atmosphere and total 1667 chromatograms were generated during the study. As a result of these sampling campaigns 51 VOCs were determined in each chromatogram.

GC-FID analysis were performed by Agilent Model 6890 GC equipped with 2 FID detectors and coupled to a Unity model thermal desorption and a Markes Air Server sampling system. Hourly measurements were performed and for each measurement 450 ml sample was pumped from the air. DB-1 and HP-Al/S columns were used. GC was calibrated using calibration gas mixture which includes 148 VOCs and obtained from Environment Canada. The GC program which was used in the present study is given below;

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Carrier gas: N_2
Inlet temperature: 300 °C
Detector temperatures: 300 °C
Temperature program: 40 °C hold for 10 min, 10 °C/min ramp to 195 °C and hold 10 min.

2 RESULTS AND DISCUSSION

During the study, toluene (23.81±43.7 µg m^{-3}) has the highest concentration among the BTEX compounds. Benzene concentration was found to be in the range 0.12 to 40.12 µg m^{-3}, toluene concentration 2.1 to 949 µg m^{-3}, ethylbenzene 0.15 to 79 µg m^{-3}, m,p-xylene 0.13 to 226 µg m^{-3} and o-xylene 0.1 to 24 µg m^{-3}. As median values of VOCs were compared, similar values were found, however as analysis of variance of the compounds (ANOVA) measured at each campaign investigated, except benzene a statistically significant ($p<0.10$) at 95% confidence level variation were observed between the compounds.

As the time series of the BTEX compounds are examined (Figure 1), a significant temporal variation was observed for each compound. For example, low concentrations were recorded at the second campaign probably due to increase in photochemical degradation.

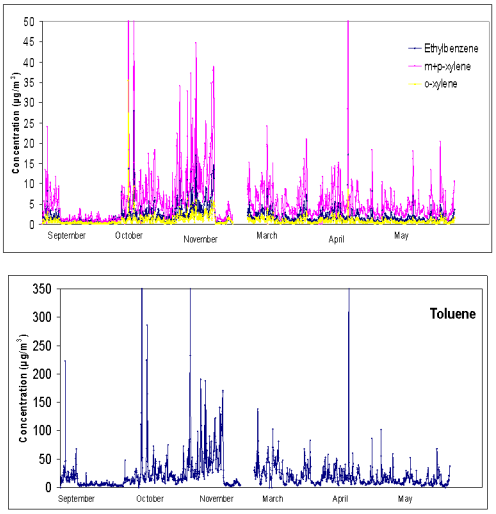

Figure 1. Time series of the BTEX concentrations for both campaign periods

The diurnal variation of the aromatics is affected from many factors such as traffic density, meteorological conditions and rush hours [3]. Mainly double peaks are observed in the diurnal profiles of the pollutants because of traffic [4]. In addition to the traffic originated emissions, evaporative sources are also very important marker for the determination of the diurnal profile characteristics of the VOCs. Especially in the afternoon, due to high temperatures, evaporative emissions show an increasing trend during the working hours between 09:00 am and 06:00 pm [3].

In the present study, BTEX concentrations started to gradual increase from 6 o'clock to 10 o'clock. The BTEX concentrations seem to increase again after 14:00. In the afternoon, probably due to high mixing layer height, good dilution and high solar intensity lower BTEX concentrations were observed, while peaks were delayed. After 19:00, BTEX emissions were also increased in the evening rush hours. Therefore, it can be said that the diurnal pattern of the compounds followed the traffic rush hours. The average diurnal variations of the BTEX compounds are shown in the Figure 2.

Diurnal variations of the BTEX ratios were also investigated in the study (Figure 3). In the literature, a wide range X/E ratio is given belong to different studies; however the general range is given between 2 and 3 [5]. As can be seen in Figure 4 and Figure 5, the ratio of the X/E was found nearly constant for this study and its range was found to be in the range 2.5 to 2.8. This constant ratio shows a common source that is traffic [6].

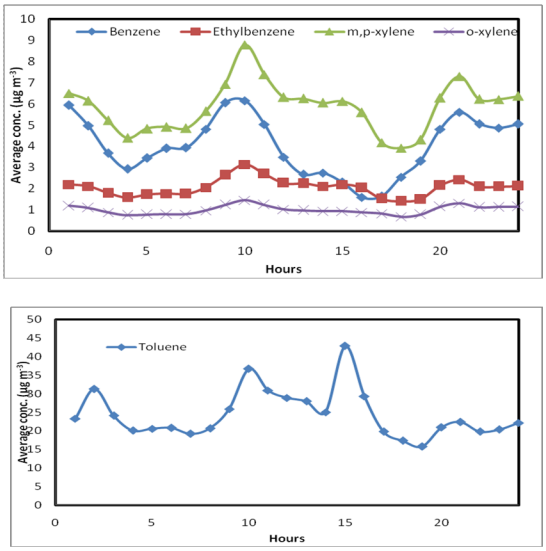

Figure 2. Average diurnal patterns of the BTEX concentrations

When the ratio of the B/E was investigated, two small increases were observed in the morning and in the evening rush hours, because both compounds are mainly originated from the traffic. Ethylbenzene may also be emitted from the solvent usage [7]. Moreover, the photochemical activity of the ethylbenzene is higher than the benzene [8].

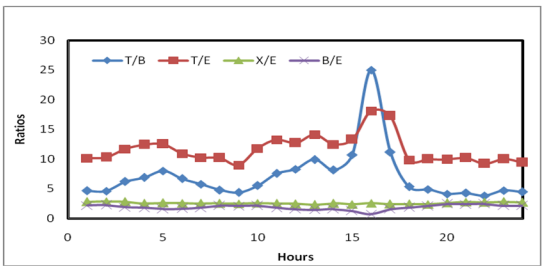

Figure 3. Diurnal variation of the BTEX ratios

Toluene may be originated from solvent emissions via evaporation in addition to the traffic. However, benzene is mainly emitted from the traffic related sources namely exhaust, fuel evaporation and fuel losses [7]. The increase in the toluene to benzene (T/B) and toluene to ethylbenzene (T/E) ratio during the 15:00-18:00 can be explained by the contribution of the evaporative sources as compared to traffic related emissions [6], [7], [9].

In the present study Pearson's correlation (2-tailed, $p < 0.01$) of the concentration of the BTEX compounds were also investigated for both campaigns (Table 1). Among TEX compounds, good correlations were obtained however, for benzene low correlations were obtained as compared to TEX compounds, probably due to other sources of VOCs. Moreover, the worst correlations were found between benzene and toluene. Probably, as traffic is the main source of the benzene, other sources of the toluene such as solvent usage, industrial activities, and evaporative sources can cause this kind of low correlation for both campaigns [2]. Especially for the second campaign for most of the compounds low correlations were obtained as compared to first campaign, other sources than the traffic in the second campaign might have caused this kind of low correlations.

Table 1. Correlation coefficients for BTEX

Comp.	Tol.	E.Ben.	m,p-xyl.	o-xyl.
Ben.	0.53 (0.46)*	0.64 (0.67)	0.62 (0.62)	0.71 (0.72)
Tol.	-	0.87 (0.82)	0.86 (0.83)	0.83 (0.81)
E.Ben.	-	-	0.98 (0.98)	0.96 (0.96)
m,p-xyl.	-	-	-	0.98 (0.96)

*Parenthesis indicates second campaign

3 CONCLUSION

Although similar median concentrations were observed, time series and analysis of variance results showed that the BTEX concentrations for two campaigns were different except benzene.

Diurnal pattern of the compounds followed the traffic rush hours.

High correlations were observed for TEX compounds indicate that a common source. However for benzene lower correlations indicates some additional sources aside from vehicular inputs.

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