Levels and sources of BTEX in ambient air of Ahvaz metropolitan city

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Abstract The benzene, toluene, ethylbenzene, and xylene (BTEX) compounds are categorized as volatile organic compounds (VOCs) that may contribute to the formation of ground-level ozone and photochemical smog, which can cause damage to plants and materials as well as pose human health concerns. BTEX compounds are considered harmful to aquatic organisms. Benzene, toluene, ethylbenzene, and xylenes can enter the environment during manufacture or use of these substances or products containing them. Due to the high volatility of BTEX compounds, emissions are expected to occur principally to air by industries and transportation. Ambient concentrations of BTEX were measured by means of active sampling at 12 sampling points in Ahvaz, capital city of Khuzestan province, from July to September 2012 and

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January to March 2013. BTEX were analyzed by chemical desorption followed by gas chromatography/flame ionization detector (GC-FID). Mean concentrations of benzene, toluene, ethylbenzene, xylenes, and BTEX were 1.78, 5.19, 0.51, 1.13, and 8.61 μ g m⁻³, respectively, and found to be highly correlated. The results of this study showed distinct seasonal and spatial variability in atmospheric BTEX concentrations at sampling sites. Their spatial distribution showed high differences between high-traffic and residential areas and also pointed to traffic as the main emission source of these compounds. The lowest levels of BTEX occurred during summer due to increases in solar radiation and photochemical reactions. Mean concentrations of benzene did not exceed the European limits at any of the monitored points. Based on BTEX levels, distribution maps were depicted to help urban air pollution authorities understand hotspots, spatial variations, future layout of industries, and their possible displacements for mitigation of BTEX levels.

Keywords BTEX \cdot Spatial variation \cdot Seasonal variation \cdot Photochemical reactions \cdot Ahvaz

Introduction

In recent decades, we are faced with increasing energy consumption in the world due to increasing population and fossil fuel consumption, promotion of industries, and enhancement in social welfare. The byproduct of this trend is producing air pollutants which can have adverse effects such as global warming, ozone depletion, acid rain, and photochemical smog.

Organic compounds produced due to anthropogenic activities into the atmosphere are very important air pollutants which were recognized 50 years ago in Los Angeles' smog by Haagen-Smit studies (Derwent 1995). Volatile organic compounds (VOCs), as the main group of hydrocarbons in the atmosphere, play a significant role in physico-chemical processes of the troposphere, since they contribute significantly to the formation of ozone and other photochemical oxidants (Kalabokas et al. 2001).

Some VOC effects were recognized so far including their contribution to stratospheric ozone depletion, carcinogenic and toxic human health effects, and their role in the enhancement of global greenhouse effects (Cetin et al. 2003).

The most typical component of volatile organic compounds pollution in air is BTEX which consist of benzene, toluene, ethylbenzene, and xylene (Chattopadhyay et al. 1997; Srivastava et al. 2005a, b). Polycyclic aromatic hydrocarbons with lower vapor pressure mostly exist in a solid phase, and monoaromatics such as benzene, toluene, ethylbenzene, and xylene (BTEX) exist in a gaseous phase.

BTEX present in urban atmosphere result from motor vehicle exhaust and a number of industrial activities such as petrochemical process, storage, distribution, paint, solvent, and combustion processes.

In urban areas, BTEX compounds constitute up to 60 % of non-methane VOCs (Lee et al. 2002); among these VOCs, benzene is a significant representative of aromatic hydrocarbons and has been a high-priority urban air pollutant for assessment (Brocco et al. 1997; Coursimault et al. 1995; Pfeffer et al. 1995).

Benzene is a carcinogen, and toluene strongly affects the nervous system (TOXNET 2000). Recently, special considerations have been paid to benzene pollution due to its high toxicity. It is also known as a myelotoxic and leukemiainducing compound. It is proven that the concentrations of airborne benzene related to an excess lifetime risk of leukemia of 10^{-4} , 10^{-5} , and 10^{-6} are 17, 1.7, and 0.17 µg m⁻³, respectively (WHO 2000).

However, a limit for ambient air benzene concentrations has been announced in many countries. The European Commission (EC) guideline value for the annual average benzene concentration in Europe was 5 μ g m⁻³ in 2000, then decreased on 1 January 2006 and every 12 months thereafter by 1 μ g m⁻³ to reach zero by 1 January 2010. However, up to now, this goal has not been achieved (Lan and Binh 2012). In Asian countries such as Japan, India, Korea, Nepal, Thailand, and Vietnam, the recommended annual thresholds for ambient air benzene are 3, 5, 5, 20, 1.7, and 10 μ g m⁻³, respectively (CAI-Asia 2009).

Therefore, benzene has been added to the compulsory limit list of Directive 2000/69/EC because of its health effects (European Community 2000). The negative effects of benzene are stated on the US EPA website (EPA 2012).

Attentiveness to the trace analysis of VOCs and BTEX in ambient air has grown considerably due to the important roles of these compounds in atmospheric photochemistry and their negative impacts on human health. Several papers have been lpublished, and the ambient levels of these compounds in the urban and rural atmosphere have been widely investigated all over the world. For example, in EU and USA, monitoring of these compounds has been legislated and their air quality standards established. Furthermore, there are some studies which investigated the important role of VOCs in producing organic aerosol in Los Angeles (Duong et al. 2011; Wonaschütz et al. 2011; Hersey et al. 2013).

Some studies suggesting that common sources of VOCs in the ambient air are vehicular emissions since VOCs in vehicle exhaust are present in fixed ratios (Pankow et al. 2003; Ho et al. 2004; Parra et al. 2006; Khoder 2007; Bruno et al. 2008; Hoque et al. 2008; Miller et al. 2009, 2010).

The atmospheric concentrations of BTEX and carbonyls were measured simultaneously in summers of Beijing from year 2008 to 2010 (Zhang et al. 2012). In another study, multi-season, multi-year concentrations, and correlations amongst the BTEX group of VOCs in an urbanized industrial city have been done; and in this study, benzene, toluene, ethylbenzene, (m + p)-xylene, and *o*-xylene were measured using 3M #3500 organic vapor samples (Miller et al. 2012).

Toluene to benzene (T/B) and (m + p)-xylenes to ethylbenzene ((m + p)-X/E) ratios have been also investigated. T/B ratio has been used as an indicator of emission sources in North America (Miller et al. 2010, 2011) and internationally (Hansen and Palmgren 1996; Khoder 2007; Hoque et al. 2008; Buczynska et al. 2009). The values of toluene to benzene ratios in these studies were 1.5 to 4.0 in urban areas impacted by mobile sources. The (m + p)-X/E ratio has been also used as an indicator of photochemical age (Zhang et al. 2008). The amount of (m + p)-X/E ratio was approximately 3.6 in urban areas regardless of geographic location (Monod et al. 2001).

In this study, the concentrations of BTEX compounds in Ahvaz were measured in two seasons. The sampling method was active using pump.

Ahvaz with latitude 31' 32, longitude 48' 68 and with a population of more than one million is located in the southwest of Iran and is the capital city of Khuzestan province. Ahvaz has experienced many environmental problems such as old infrastructure, deficiencies in wastewater collection systems, increasing salinity in water distribution network, as well as air pollution. Recently, dust storms over southwestern of Iran have added an anthropogenic source of air pollution to this city.

According to the vast usage of BTEX compounds and their effects on human health, sampling, and measurement of these pollutants are crucial. Moreover, this city has many industries especially petroleum industries, and the number of motor vehicles in this city are high. It is also worthy to say that the measurement of these compounds has not been done in Ahvaz.

Experimental section

Field measurement site

In this study, according to EN 14662:2005 standard (Directive 1998), the city was categorized into four areas with varied local activities including (1) residential area (urban background), (2) industrial area, (3) high-density traffic area (road side), and (4) entrances and exits of the city (rural background); then 12 locations of these different areas were selected.

The sampling locations are shown in the map of Ahvaz (Fig. 1). S1, S3, S10, and S11 are in residential areas, and traffic flows at these locations are nearly low. S2 and S8 are in industrial areas, and the air quality at these locations is influenced by the adjacent industrial areas. S5, S6, S7, and S12 are high-density traffic areas. S7 is a commercial area with good amount of traffic moment and S5 is near a gas station. S4 and S9 are located at the entrance and exit of the city, respectively. These two locations are far from industrial areas and with very low traffic flow.

Sampling and analysis

In this study, for determination and comparison BTEX concentrations in different seasons, samplings were done in two seasons. BTEX were sampled from July to September 2012 and January to March 2013. These two periods are representative of hot and cold periods of the year in Ahvaz, respectively. Sampling was carried out in the height of 1.5-2 m above the ground level by active sampling method using a hand-operated pump (SKC 224-44MTX). The air samples at each of the 12 sampling sites were collected by the pump at a flow rate of 200 ml min⁻¹ for 8 h, and ambient air was drawn through charcoal sorbent tubes. The glass tube was 7-cm long, 6-mm OD, and 4-mm ID, with flame-sealed ends and contained two sections of activated coconut shell charcoal (front=100 mg, back=50 mg) separated by a 2-mm urethane foam plug.

Six samples were collected from each sampling site (three samples for hot and three samples for cold periods of the year). Therefore, in this study 72 samples were collected. At the end of each sampling period, the sorbent tube was capped with plastic cap and packed securely in 4 °C for shipment. Sample preparation was done according to this trend: (a) each section of sorbent tube (front and back sections) was placed in separate 2 ml vials, (b) 1 ml CS_2 (as eluent) was added to each vial, and (c) sample was allowed to stand at least 30–45 min in ultrasonic bath for agitation and then it was injected into the chromatographic column.

The samples were transported to the laboratory and analyzed by gas chromatography–flame ionization detector (GC-FID) technique, and they were analyzed as soon as possible or kept in the refrigerator during storage and analyzed the day after the sampling.

Separation and detection were done in a 7890N GC-FID (Agilent Technologies, Palo Alto, USA), using a HP5-MS capillary column (30 m, 0.25 mm, 0.25 μ m) and 99.999 %



Fig. 1 Sampling points in Ahvaz

pure helium gas as the carrier at a flow rate of 1 ml min⁻¹. The injection volume is 1 µl with 5:1 split. The injection and detector temperatures were 250 and 300 °C, respectively. The oven temperature of GC was programmed for 40 °C and held for 6 min, raised to 70 °C at a rate of 4 °C min⁻¹ and held for 1 min, then raised to 100 °C at a rate of 10 °C min⁻¹ and held for 1 min. The calibration standards were prepared by diluting the stock standard of benzene, toluene, ethylbenzene, and xylene with CS2; then, the working standards in parts per billion levels were prepared from the standard concentrations (six working standards from below the LOD to ten times the LOO). Benzene, toluene, ethylbenzene, and xylene recovery ratios were 92± 3.5 %, 95±2.3 %, 95±2.4 %, and 90±2.2 %, respectively. Eight samples (10 % of the samples) were collected as blank samples, and the concentrations of BTEX in the blank tube were below detection. The method detection limit (MDL) for the benzene, toluene, ethylbenzene, and xylene were 0.3, 0.1, 0.1, and 0.07 μ g m⁻³, respectively.

Statistical analysis

SPSS software and Microsoft Excel were used for statistical analysis. Analysis of variance (ANOVA) was done for identification of statistically significant comparisons and least significant difference (LSD) calculations at an alpha level of 0.05 (α =0.05). Also, Spearman's correlation was used for identification of the coefficient among BTEX species.

Results and discussion

BTEX levels

The mean concentrations of BTEX compounds are presented in Table 1. Also, a statistical summary of the data on BTEX levels in Ahvaz from July to September 2012 and January to March 2013(a total of 72 sets of measurements) is shown in Table 1.

The results clearly indicate that toluene had the highest concentrations (annual mean among all sites and two seasons= $5.19 \ \mu g \ m^{-3}$), followed by benzene ($1.78 \ \mu g \ m^{-3}$) and xylene ($1.13 \ \mu g \ m^{-3}$). Ethylbenzene ($0.51 \ \mu g \ m^{-3}$) was present at a lower concentration. The annual mean of total BTEX was 8.61 $\ \mu g \ m^{-3}$. Among BTEX, toluene has reported as having the highest concentrations in urban areas in several other studies (such as Yamamoto et al. 2000; Ho et al. 2004; Srivastava et al. 2005b; Parra et al. 2006; Hoque et al. 2008; Johnson et al. 2010).

The concentration levels observed in this study are comparable to those observed in UK (Derwent et al. 2000), in Germany (Schneider et al. 2001), in Texas (Smith et al. 2007), and in Detroit, Michigan (Johnson et al. 2010), although there were some differences in the mean concentrations of BTEX in these studies. These differences can be attributed to the particular characteristics of the studied cities, sampling points, sampling periods, and main city activities as well as differences associated with vehicles, such as vehicle production quality and fuel composition (Gee and Sollars 1998).

Smith et al. (2007) reported the highest concentration of toluene (2.27 μ g m⁻³), followed by benzene (2.04 μ g m⁻³), (*m* + *p*)-xylene (1.42 μ g m⁻³), *o*-xylene (0.52 μ g m⁻³), and ethylbenzene (0.51 μ g m⁻³).

The rank order observed in this study was similar to that reported (Guo et al. 2007; Parra et al. 2006; Smith et al. 2007; Hoque et al. 2008) with toluene being the highest, followed by benzene, (m + p)-xylene, *o*-xylene, and ethylbenzene.

The annual mean concentration of benzene in ambient air according to Directive 2000/69/EC must not exceed 5 μ g m⁻³. In this study, the mean values of benzene in all sampling points were always below this limit. Moreover, the highest levels of benzene were registered in points S5 and S8 which were 3.79 and 4.47 μ g m⁻³, respectively.

Toluene levels are not regulated by European legislation, but WHO establishes a guideline value of 260 μ g m⁻³ as a weekly average for the protection of human health. In this case, the level remains much above the measured levels of toluene in this study.

Temporal variability of BTEX

Figure 2 illustrates the variability of BTEX mean concentrations of the 12 monitored points over the two sampling seasons. The results of one-way ANOVA showed that there was a statistically significant difference between two sampling periods for all these compounds.

The lowest BTEX levels related to summer (September 2012) with a mean concentration of 7.05 μ g m⁻³. On the other hand, the highest levels of BTEX compounds were measured in winter (February 2013), with a concentration of 9.90 μ g m⁻³. VOC concentrations were generally lower in spring and summer than in winter and autumn, as found in many other studies (Batterman et al. 2002; Kourtidis et al. 2002). Pankow et al. (2003) observed higher benzene and toluene concentrations in the winter throughout the USA. The concentrations of BTEX can be affected by several factors. In winter they reach a maximum level due to higher atmospheric stability and a minimum level in summer, when atmospheric dispersion is more significant. Because of more sunlight and higher temperatures, which produce higher chemical removal reaction rates, the removal of BTEX by OH radicals in summer is faster than in winter (Ho et al. 2004).

For each BTEX compounds alone, this temporal variability was also observed (Fig. 2). The lowest levels were registered in summer, when an incredible loss of these compounds by photochemical degradation was to be expected.

Table 1Mean concentrations $(\mu g m^{-3})$ of benzene, toluene,ethylbenzene, and xylenes for 12points

Sampling point	Benzene	Toluene	Ethylbenzene	Xylene	BTEX
S1	1.27	2.17	0.27	1.02	4.73
S2	1.33	10.46	0.32	1.52	13.62
S3	1.60	2.56	0.20	0.99	5.36
S4	0.18	0.35	0.08	0.09	0.70
S5	4.47	8.94	1.00	1.23	15.64
S6	2.74	5.49	0.70	1.33	10.26
S7	3.79	8.86	1.40	2.41	16.46
S8	1.50	11.87	0.54	1.62	15.53
S9	0.22	0.56	0.12	0.23	1.14
S10	0.66	3.30	0.25	0.92	5.13
S11	0.50	0.98	0.22	0.57	2.27
S12	3.12	6.74	1.07	1.58	12.51
Mean	1.78	5.19	0.51	1.13	8.61
(SD)	1.43	4.10	0.43	0.64	6.02
Median	1.42	4.40	0.30	1.13	7.81
Min	0.18	0.35	0.08	0.09	0.70
Max	4.47	11.87	1.40	2.41	16.46
Ν	72	72	72	72	72
Mean of residential area	1.01	2.25	0.24	0.88	4.37
Mean of industrial area	1.42	11.17	0.43	1.57	14.58
Mean of high-density traffic area	3.53	7.51	1.04	1.64	13.72
Mean of entrances and exits of the city	0.20	0.46	0.1	0.16	0.92

Although significant decreases in benzene and toluene concentrations based on their relatively slow reaction rates should not be expected, photochemical reactions in summer could decrease the concentrations of ethylbenzene and xy-lenes since their higher reactivity causes their early degradation (Upmanis et al. 2001; Hellén et al. 2002).

The meteorology in Ahvaz shows an explicit summer and winter characteristics. In winter the temperature decreases to

 $5 \,^{\circ}$ C and in summer rises even to $50 \,^{\circ}$ C. In the winter months, the calm meteorological conditions, temperature inversion and low mixing heights, and also the high stability of the atmosphere restrict the dilution process of the pollutant. Thus, in the winter months, the BTEX generally show a higher level of concentration.

In contrast, the summer months in Ahvaz show an unstable atmosphere with more insolation. These conditions help in the



Fig. 2 Temporal variation of BTEX and its species concentrations ($\mu g \ m^{-3}$)



Fig. 3 Distribution maps of the concentrations ($\mu g m^{-3}$) of a benzene, b toluene, c ethylbenzene, d xylene, and e BTEX in Ahvaz

photolysis of species like ozone and formation of more OH radical, which play an important role in the atmospheric degradation process of the aromatic VOCs. In the present study, clear seasonal profiles were observed for BTEX and they were almost similar at all sampling points.

Spatial distributions of BTEX

Distribution maps were drawn to show the spatial distribution of benzene, toluene, ethylbenzene, xylenes, and BTEX in ambient air of Ahvaz in both sampling periods. These maps show large spatial variations of the pollutants within the different parts of the city (Fig. 3). According to mean concentrations of BTEX for the each sampling points (Table 1) and spatial distribution (Fig. 4), the highest levels of BTEX were registered in points S5, S6, S7, and S12, close to roads with high-density traffic and S2 and S8, next to industrial zones. Sampling points S4 and S9 showed an opposite behavior, since these points were located far from sources of pollution such as roads and industries.

In this study, the benzene concentrations in the trafficked road were 3.5 to 9 times higher than in urban background (residential area). These results are comparable to those obtained in a number of European cities, where levels of benzene at hot spots were 3 to 5 times higher than the urban background levels (Hansen and Palmgren 1996).

Benzene concentrations decrease rapidly in relation to the distance from the source (high-density traffic areas), as also reported in (Thorsson and Eliasson 2006). This trend is also observed for other BTEX compounds emitted from traffic such as toluene, ethylbenzene, and xylenes. As shown in Fig. 3, toluene concentrations in downtown as well as points S2 and S8 were high, which shows that industries in points S2 and S8 produce significant amount of toluene.

BTEX ratios and correlations

The possible sources of BTEX can be revealed by correlation analysis (Wang et al. 2002; Christensen et al. 1999; Na and Kim 2001; Brocco et al. 1997). In the present study, Spearman's correlation (Table 2, two-tailed) of the concentrations of BTEX for all sampling points was evaluated. A strong

Table 2 Spearman's correlation coefficients for the studied compounds

	Benzene	Toluene	Ethylbenzene	Xylene	BTEX
Benzene	1.000				
Toluene	0.716	1.000			
Ethylbenzene	0.932	0.793	1.000		
Xylene	0.792	0.888	0.876	1.000	
BTEX	0.853	0.953	0.906	0.938	1.000

correlation was observed among the species, which indicates that the primary source of origin for these pollutants is similar.

The ratios between BTEX species have been widely used as an indicator to provide information about the different emission sources of these pollutants in the environment (Khoder 2007; Guo et al. 2007; Kerbachi et al. 2006).

The concentrations of relatively stable BTEX species (benzene and toluene, with atmospheric lifetimes of 12.5 and 2.0 days. respectively) gradually increase during daylight time due to accumulation. However, ethylbenzene and xylene concentrations, which are highly reactive in comparison with benzene and toluene, usually decrease in daylight time due to photochemical reactions (Prinn et al. 1987). In this study, toluene/benzene (T/B), xylene/benzene (X/B), and xylene/ethylbenzene(X/EB) ratios were investigated. T/B ratio approaching a value of 1 indicates traffic-originated emission sources, and the value increases with the closeness of the pollution source (Gelencsér et al. 1997). The mean of T/B ratio was 3.25 and as shown in Table 3: this ratio was observed to be high at industrial locations (>7). The highest T/B ratio was observed at points S8, S2, and S10 which were 7.91, 7.86, and 5, respectively. The high T/B values in these points indicated that the sources other than vehicle exhaust, such as evaporation of solvents from factories and emissions from other stationary sources like gas stations, could make noticeable contribution to atmospheric BTEX.

At all sampling points, low X/B ratios were observed (0.28 to 1.39), which imply aging of the air mass and the effects of photochemical reactions. The X/EB values were between 1.13 and 4.95. The T/B, X/B, and X/EB values obtained in this study are comparable to those reported ranges observed in

Table 3 Toluene/ben-zene, zene, xylene/ethylbenzene and xylene/ethylbenzene ratios at different sampling points pling points					
	Sampling points	T/B	X/B	X/EB	
	S1	1.71	0.80	3.78	
	S2	7.86	1.14	4.75	
	S3	1.60	0.62	4.95	
	S4	1.94	0.50	1.13	
	S5	2.00	0.28	1.23	
	S6	2.00	0.49	1.90	
	S7	2.34	0.64	1.72	
	S 8	7.91	1.08	3.00	
	S9	2.55	1.05	1.92	
	S10	5.00	1.39	3.68	
	S11	1.96	1.14	2.59	
	S12	2.16	0.51	1.48	
	Mean	3.25	0.80	2.68	
	Min	1.60	0.28	1.13	
	Max	7.91	1.39	4.95	
	N	72	72	72	





China (Liu et al. 2000), in Greece (Kalabokas et al. 2001), and in Rome (Gariazzo et al. 2005).

In present study, the T/B, X/B, and X/EB ratios increase in the cold period of the year but decrease in the warm period (Fig. 4). The reason for this differentiation might be related to the difference of benzene and toluene photochemical reactivity or photochemical ozone creating potential (POcP). If the POcP of ethylene is identified as 100, then the POcP of benzene, toluene, ethylbenzene, *o*-xylene, and (m + p)-xylene are 20, 55, 65, 105, and 90, respectively (Ciccioli et al. 1993). Because of high insolation periods during summer, toluene, ethylbenzene, and xylenes photodestruct and react with other atmospheric constituents much faster than benzene and as a result, these compounds are less abundant in relation to benzene.

Conclusions

This study measured BTEX concentrations and correlations in two seasons. The results of this study showed distinct seasonal and spatial variability in atmospheric BTEX concentrations at sampling sites. The concentrations and rank order of the BTEX species were in agreement with previously reported studies in other urban cities of the world. Seasonal value comparisons revealed that there were significant differences between BTEX concentrations in winter and summer. Seasonal trends in concentration values were observed with winter high and summer low for benzene, toluene, ethylbenzene, and xylenes, implying that photochemical conversion of BTEX species in Ahvaz was dominant in summer.

Strong correlations were observed between the BTEX species, suggesting that these pollutants originated from the same sources in the Ahvaz area. Using distribution maps of the concentrations generated across the study area, we were able to distinguish that the high-traffic areas and those adjacent to industrial areas (S2 and S8) experienced higher BTEX levels and concentrations decreased rapidly in relation to the distance from the sources.

Among the BTEX species, high concentrations of toluene were observed at industrial locations. In the present study, low concentrations of BTEX were measured at the residential areas. The highest and lowest concentrations of these pollutants were registered at high-traffic sampling points and entrance and exit of the city, respectively.

T/B ratios were observed to be higher in winter than summer and suggest that the main sources for BTEX in two seasons were attributed to vehicle emissions, and sources other than vehicle emission also made great contribution to atmospheric BTEX due to relatively high T/B ratios in Ahvaz.

The spatial variability of T/B ratios demonstrates to some areas being dominated by additional contributing sources as well as traffic sources. Areas of the high or low T/B values were stable over the seasons, suggesting that the T/B ratios could be useful to distinguish the industrial source impacts over and above the traffic signal. At industrial districts, T/B ratios were observed to be high, and low X/B ratios were observed at all the locations which reveal that photochemical reactions were active during daytime.

The X/EB ratios indicate a relatively homogenous photochemical age across the sampling points. Several differences, for example, in X/EB ratio analysis and spatial variability, were seen between the roadside and residential monitoring, suggesting that roadside monitors are more representative of fresh mobile emissions.

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References

- Batterman SA, Peng C-Y, Braun J (2002) Levels and composition of volatile organic compounds on commuting routes in Detroit, Michigan. Atmos Environ 36(39):6015–6030
- Brocco D, Fratarcangeli R, Lepore L, Petricca M, Ventrone I (1997) Determination of aromatic hydrocarbons in urban air of Rome. Atmos Environ 31(4):557–566

- Bruno P, Caselli M, de Gennaro G, Scolletta L, Trizio L, Tutino M (2008) Assessment of the impact produced by the traffic source on VOC level in the urban area of Canosa di Puglia (Italy). Water Air Soil Pollut 193(1–4):37–50
- Buczynska AJ, Krata A, Stranger M, Locateli Godoi AF, Kontozova-Deutsch V, Bencs L, Naveau I, Roekens E, Van Grieken R (2009) Atmospheric BTEX-concentrations in an area with intensive street traffic. Atmos Environ 43(2):311–318
- CAI-Asia (2009) (Clean Air Initiative for Asian Cities Centre). Ambient air quality standards in Asia. survey report. http://cleanairinitiative. org/portal/system/files/AQ_Standards_Report_Draft_2_Dec_ FINAL.pdf
- Cetin E, Odabasi M, Seyfioglu R (2003) Ambient volatile organic compound (VOC) concentrations around a petrochemical complex and a petroleum refinery. Sci Total Environ 312(1):103–112
- Chattopadhyay G, Samanta G, Chatterjee S, Chakraborti D (1997) Determination of benzene, toluene and xylene in ambient air of Calcutta for three years during winter. Environ Technol 18(2):211–218
- Christensen C, Skov H, Palmgren F (1999) C5 to C8 non-methane hydrocarbon measurements in Copenhagen: concentrations, sources and emission estimates. Sci Total Environ 236(1):163–171
- Ciccioli P, Bloemen HT, Burn J (1993) Volatile organic compounds in the environment. Blackie, London, pp 92–174
- Coursimault A, Donati J, Viellard H (1995) La pollution automobile due aux hydrocarbures aromatiques monocycliques a Paris. Sci Total Environ 169(1):17–23
- Derwent RG (1995) Sources, distributions, and fates of VOCs in the atmosphere. Issues Environ Sci Technol 4:1–16
- Derwent R, Davies T, Delaney M, Dollard G, Field R, Dumitrean P, Nason P, Jones B, Pepler S (2000) Analysis and interpretation of the continuous hourly monitoring data for 26 C2-C8 hydrocarbons at 12 United Kingdom sites during 1996. Atmos Environ 34(2):297–312
- Directive C (1998) Council directive on ambient air quality assessment and management working group on benzene http://ec.europa.eu/ environment/air/quality/legislation/assessment.htm
- Duong HT, Sorooshian A, Craven JS, Hersey SP, Metcalf AR, Zhang X, Weber RJ, Jonsson H, Flagan RC, Seinfeld JH (2011) Water-soluble organic aerosol in the Los Angeles Basin and outflow regions: airborne and ground measurements during the 2010 CalNex field campaign. J Geophys Res Atmos (1984–2012) 116 (D22)
- EPA U (2012) Benzene. http://www.epa.gov/ttn/atw/hlthef/benzene.html
- European Community (2000) Directive 2000/69/EC. Off J Eur Commun 13.12.2000. L 313/12
- Gariazzo C, Pelliccioni A, Di Filippo P, Sallusti F, Cecinato A (2005) Monitoring and analysis of volatile organic compounds around an oil refinery. Water Air Soil Pollut 167(1–4):17–38
- Gee IL, Sollars CJ (1998) Ambient air levels of volatile organic compounds in Latin American and Asian cities. Chemosphere 36(11):2497–2506
- Gelencsér A, Siszler K, Hlavay J (1997) Toluene-benzene concentration ratio as a tool for characterizing the distance from vehicular emission sources. Environ Sci Technol 31(10):2869–2872
- Guo H, So K, Simpson I, Barletta B, Meinardi S, Blake D (2007) C1-C8 volatile organic compounds in the atmosphere of Hong Kong: overview of atmospheric processing and source apportionment. Atmos Environ 41(7):1456–1472
- Hansen AB, Palmgren F (1996) VOC air pollutants in Copenhagen. Sci Total Environ 189:451–457
- Hellén H, Hakola H, Laurila T, Hiltunen V, Koskentalo T (2002) Aromatic hydrocarbon and methyl tert-butyl ether measurements in ambient air of Helsinki (Finland) using diffusive samplers. Sci Total Environ 298(1):55–64
- Hersey SP, Craven JS, Metcalf AR, Lin J, Lathem T, Suski KJ, Cahill JF, Duong HT, Sorooshian A, Jonsson HH (2013) Composition and hygroscopicity of the Los Angeles aerosol: CalNex. J Geophys Res Atmos 118(7):3016–3036

- Ho K, Lee S, Guo H, Tsai W (2004) Seasonal and diurnal variations of volatile organic compounds (VOCs) in the atmosphere of Hong Kong. Sci Total Environ 322(1):155–166
- Hoque RR, Khillare P, Agarwal T, Shridhar V, Balachandran S (2008) Spatial and temporal variation of BTEX in the urban atmosphere of Delhi, India. Sci Total Environ 392(1):30–40
- Johnson MM, Williams R, Fan Z, Lin L, Hudgens E, Gallagher J, Vette A, Neas L, Özkaynak H (2010) Participant-based monitoring of indoor and outdoor nitrogen dioxide, volatile organic compounds, and polycyclic aromatic hydrocarbons among MICA-Air households. Atmos Environ 44(38):4927–4936
- Kalabokas P, Hatzianestis J, Bartzis J, Papagiannakopoulos P (2001) Atmospheric concentrations of saturated and aromatic hydrocarbons around a Greek oil refinery. Atmos Environ 35(14):2545–2555
- Kerbachi R, Boughedaoui M, Bounoua L, Keddam M (2006) Ambient air pollution by aromatic hydrocarbons in Algiers. Atmos Environ 40(21):3995–4003
- Khoder M (2007) Ambient levels of volatile organic compounds in the atmosphere of Greater Cairo. Atmos Environ 41(3): 554–566
- Kourtidis KA, Ziomas I, Zerefos C, Kosmidis E, Symeonidis P, Christophilopoulos E, Karathanassis S, Mploutsos A (2002) Benzene, toluene, ozone, NO2 and SO2 measurements in an urban street canyon in Thessaloniki, Greece. Atmos Environ 36(34):5355– 5364. doi:10.1016/S1352-2310(02)00580-0
- Lan TTN, Binh NTT (2012) Daily roadside BTEX concentrations in East Asia measured by the Lanwatsu, Radiello and Ultra I SKS passive samplers. Sci Total Environ 441(0):248–257. doi:10.1016/j. scitotenv.2012.08.086
- Lee S, Chiu M, Ho K, Zou S, Wang X (2002) Volatile organic compounds (VOCs) in urban atmosphere of Hong Kong. Chemosphere 48(3): 375–382
- Liu C, Xu Z, Du Y, Guo H (2000) Analyses of volatile organic compounds concentrations and variation trends in the air of Changchun, the northeast of China. Atmos Environ 34(26):4459–4466
- Miller L, Xu X, Luginaah I (2009) Spatial variability of volatile organic compound concentrations in Sarnia, Ontario, Canada. J Toxic Environ Health A 72(9):610–624
- Miller L, Lemke LD, Xu X, Molaroni SM, You H, Wheeler AJ, Booza J, Grgicak-Mannion A, Krajenta R, Graniero P (2010) Intra-urban correlation and spatial variability of air toxics across an international airshed in Detroit, Michigan (USA) and Windsor, Ontario (Canada). Atmos Environ 44(9):1162–1174
- Miller L, Xu X, Wheeler A, Atari DO, Grgicak-Mannion A, Luginaah I (2011) Spatial variability and application of ratios between BTEX in two Canadian cities. Sci World J 11:2536–2549
- Miller L, Xu X, Grgicak-Mannion A, Brook J, Wheeler A (2012) Multiseason, multi-year concentrations and correlations amongst the BTEX group of VOCs in an urbanized industrial city. Atmos Environ 61:305–315
- Monod A, Sive BC, Avino P, Chen T, Blake DR, Sherwood Rowland F (2001) Monoaromatic compounds in ambient air of various cities: a focus on correlations between the xylenes and ethylbenzene. Atmos Environ 35(1):135–149
- Na K, Kim YP (2001) Seasonal characteristics of ambient volatile organic compounds in Seoul, Korea. Atmos Environ 35(15): 2603–2614
- Pankow JF, Luo W, Bender DA, Isabelle LM, Hollingsworth JS, Chen C, Asher WE, Zogorski JS (2003) Concentrations and co-occurrence correlations of 88 volatile organic compounds (VOCs) in the ambient air of 13 semi-rural to urban locations in the United States. Atmos Environ 37(36):5023–5046
- Parra M, González L, Elustondo D, Garrigó J, Bermejo R, Santamaría J (2006) Spatial and temporal trends of volatile organic compounds (VOC) in a rural area of northern Spain. Sci Total Environ 370(1): 157–167

- Pfeffer H-U, Friesel J, Elbers G, Beier R, Ellermann K (1995) Air pollution monitoring in street canyons in North Rhine-Westphalia, Germany. Sci Total Environ 169(1):7–15
- Prinn R, Cunnold D, Rasmussen R, Simmonds P, Alyea F, Crawford A, Fraser P, Rosen R (1987) Atmospheric trends in methylchloroform and the global average for the hydroxyl radical. Science 238(4829): 945–950
- Schneider P, Gebefügi I, Richter K, Wölke G, Schnelle J, Wichmann H, Heinrich J (2001) Indoor and outdoor BTX levels in German cities. Sci Total Environ 267(1):41–51
- Smith LA, Stock TH, Chung KC, Mukerjee S, Liao XL, Stallings C, Afshar M (2007) Spatial analysis of volatile organic compounds from a community-based air toxics monitoring network in Deer Park, Texas, USA. Environ Monit Assess 128(1-3):369–379
- Srivastava A, Joseph A, Patil S, More A, Dixit R, Prakash M (2005a) Air toxics in ambient air of Delhi. Atmos Environ 39(1):59–71
- Srivastava A, Sengupta B, Dutta S (2005b) Source apportionment of ambient VOCs in Delhi City. Sci Total Environ 343(1):207–220
- Thorsson S, Eliasson I (2006) Passive and active sampling of benzene in different urban environments in Gothenburg, Sweden. Water Air Soil Pollut 173(1–4):39–56
- TOXNET (2000) Hazardous substances data bank (internet ed.). National Library of Medicine. Retrieved from http://toxnet.nlm.nih.gov
- Upmanis H, Eliasson I, Andersson-Sköld Y (2001) Case studies of the spatial variation of benzene and toluene concentrations

in parks and adjacent built-up areas. Water Air Soil Pollut 129(1-4):61-81

- Wang X-M, Sheng G-Y, Fu J-M, Chan C-Y, Lee S-C, Chan LY, Wang Z-S (2002) Urban roadside aromatic hydrocarbons in three cities of the Pearl River Delta, People's Republic of China. Atmos Environ 36(33):5141–5148
- WHO (2000) Benzene. Air quality guidelines for Europe. 2nd ed. Copenhagen: World Health Organisation Regional Office for Europe; http://www.EURO.who.int/data/assets/pdf_file/0005/ 74732/E71922.pdf
- Wonaschütz A, Hersey S, Sorooshian A, Craven J, Metcalf A, Flagan R, Seinfeld J (2011) Impact of a large wildfire on water-soluble organic aerosol in a major urban area: the 2009 Station Fire in Los Angeles County. Atmos Chem Phys 11(16):8257–8270
- Yamamoto N, Okayasu H, Murayama S, Mori S, Hunahashi K, Suzuki K (2000) Measurement of volatile organic compounds in the urban atmosphere of Yokohama, Japan, by an automated gas chromatographic system. Atmos Environ 34(26):4441–4446
- Zhang J, Wang T, Chameides W, Cardelino C, Blake D, Streets D (2008) Source characteristics of volatile organic compounds during high ozone episodes in Hong Kong, Southern China. Atmos Chem Phys 8(16): 4983–4996
- Zhang Y, Mu Y, Liang P, Xu Z, Liu J, Zhang H, Wang X, Gao J, Wang S, Chai F, Mellouki A (2012) Atmospheric BTEX and carbonyls during summer seasons of 2008–2010 in Beijing. Atmos Environ 59(0):186– 191. doi:10.1016/j.atmosenv.2012.06.030